# ACTA CHIMICA

## ACADEMIAE SCIENTIARUM HUNGARICAE

ADIUVANTIBUS

M. T. BECK, R. BOGNÁR, V. BRUCKNER,
GY. HARDY, K. LEMPERT, F. MÁRTA,
K. POLINSZKY, E. PUNGOR,
G. SCHAY, Z. G. SZABÓ, P. TÉTÉNYI

REDIGUNT

B. LENGYEL et GY. DEÁK

TOMUS 98 FASCICULUS 1

AKADÉMIAI KIADÓ, BUDAPEST

1978

ACTA CHIM. ACAD. SCI. HUNG. ACASA2 98 (1) 1–139 (1978)

# ACTA CHIMICA

## A MAGYAR TUDOMÁNYOS AKADÉMIA KÉMIAI TUDOMÁNYOK OSZTÁLYÁNAK IDEGEN NYELVŰ KÖZLEMÉNYEI


FŐSZERKESZTŐ

LENGYEL BÉLA

SZERKESZTŐ

DEÁK GYULA

TECHNIKAI SZERKESZTŐ

HARASZTHY-PAPP MELINDA

SZERKESZTŐ BIZOTTSÁG

BECK T. MIHÁLY, BOGNÁR REZSŐ, BRUCKNER GYŐZŐ, HARDY GYULA, LEMPERT KÁROLY, MÁRTA FERENC, POLINSZKY KÁROLY, PUNGOR ERNŐ, SCHAY GÉZA, SZABÓ ZOLTÁN, TÉTÉNYI PÁL



Acta Chimica is a journal for the publication of papers on all aspects of chemistry in English, German, French and Russian.

Acta Chimica is published in 4 volumes per year. Each volume consists of 4 issues of varying size.

Manuscripts should be sent to

*Acta Chimica*
*H-1521 Budapest, Hungary*

Correspondence with the editors should be sent to the same address. Manuscripts are not returned to the authors.

Subscription: $ 36.00 per volume.

Hungarian subscribers should order from Akadémiai Kiadó, 1363 Budapest, P.O. Box 24. Account No. 215 11488.

Orders from other countries are to be sent to "Kultura" Foreign Trading Company (H-1389 Budapest 62, P.O. Box 149. Account No. 218 10990) or its representatives abroad.

# ACTA CHIMICA

## ACADEMIAE SCIENTIARUM HUNGARICAE

ADIUVANTIBUS

M. T. BECK, R. BOGNÁR, V. BRUCKNER,
GY. HARDY, K. LEMPERT, F. MÁRTA,
K. POLINSZKY, E. PUNGOR,
G. SCHAY, Z. G. SZABÓ, P. TÉTÉNYI

REDIGUNT

B. LENGYEL et GY. DEÁK

TOMUS 98

AKADÉMIAI KIADÓ, BUDAPEST

1978

# ACTA CHIMICA

TOMUS 98

Fasciculus 1: 1978
Fasciculus 2: 1978
Fasciculus 3: 1978
Fasciculus 4: 1978

## INDEX

ABDOU, S. s. SAKLA, A. B.
ABD EL REHIM, S. S. s. AZZAM, A. M.
AMBRUS, G. s. BARTA, I.
ANTUS, S., L. FARKAS, Á. GOTTSEGEN, NÓGRÁDI, M., PFLIEGEL, T.: Dihydrochalcone Type Sweetening Agents, I. Structure-Taste Relationships ..... 225
ANTUS, S., FARKAS, L., GOTTSEGEN, Á., NÓGRÁDI, M., STRELINSKY, J., PFLIEGEL, T.: Dihydrochalcone Type Sweetening Agents, II. The Synthesis of Some Dihydrochalcones ..... 231
AZZAM, A. M., ABD EL REHIM, S. S., BOCTOR, W. H.: Cathodic Behaviour of the Lead Dioxide Electrode in Sulfuric Acid Solution ..... 255
BAKÓ, P. s. TŐKE, L.
BARTA, I., AMBRUS, G., HORVÁTH, GY., SÓTI, M., SOHÁR, P.: Heterocyclic Analogues of Prostaglandins. Thiazoles, II. ..... 463
BARSOUM, B. N. s. SAKLA, A. B.
BENISKA, J., STAUDNER, E., KYSELA, G.: Initiator Combinations for Polymerization (in Russian) ..... 194
BÉRCES, T. s. NAMETKIN, N. S.
BOCTOR, W. H. s. AZZAM, A. M.
BOGNÁR, R. s. JÁSZBERÉNYI, J. Cs.
BOGNÁR, R. s. HERCZEG, P.
BOGNÁR, R. s. KEREKES, P.
BORDA, J. s. SZABÓ, V.
CHOCKALTINGAM, K. s. NATARAJAN, A.
DATTA, E., SENGUPTA, B. K.: Ionic Potential of Moderately Highly Concentrated Aqueous Solution of Strong Electrolytes ..... 421
DEÁK, GY. s. ZÁRA-KACZIÁN, E.
DINYA, Z., KISS Á. I., PONGOR, G.: Quantum Chemical Study on the Conformational Properties of Chalcone and Its Simple Model Compound ..... 37
DOBOLYI-FEJÉRDY, H. s. SZABÓ, Z. K.
FARKAS, E. R. s. JÁSZBERÉNYI, J. Cs.
FARKAS, L. s. ANTUS, S.
FARKAS, L. s. SZÉKELY, K.
FENICHEL, L. s. TŐKE, L.
FILO, O., MATHERNY, M.: Elimination of Spectrochemical Matrix Effects, Following of the Line Analogy and Determination of the Detection Limits of Trace Elements in Silicate Rocks (in German) ..... 13
FRISS, J. s. SCHÖN, I.
GAÁL J. s. HALMOS, P.
GALINOS, A. G. s. KAMINARIS, D. M.
GÁNTI, T.: Chemical Systems and Supersystems, III. Models of Selfreproducing Chemical Supersystems the Chemotons ..... 265
GOTTSEGEN, Á. s. ANTUS, S.
GUNDA, E. T. s. JÁSZBERÉNYI, J. Cs.
HALMOS, P., GAÁL, J., INCZÉDY, J.: Investigations on the Outer-Sphere Complexes of Tris-(ethylene-diamine)-cobalt(III) and Hexamine-cobalt(III) Cations Formed with Orthophosphate and Pyrophosphate Anions ..... 141
HALÁSZ, D. s. NAMETKIN, N. S.

HANKOVSZKY, O., HIDEG, K., TIGYI, J.: Nitroxides, II. 1-oxyl-2,2,5,5-tetramethylpyrroline-3-carboxylic Acid Derivatives ..... 339
HERCZEGH, P., BOGNÁR, R.: Synthesis of 2-amino-3-thio-2-deoxy-D-mannopyranose Pentaacetate ..... 321
HIDEG, K. s. HANKOVSZKY, O.
HORÁNYI, G. s. INZELT, G.
HORÁNYI, S. s. SZETEY, E.
HORÁNYI, G., INZELT, G., SZETEY, Z.: Electrochemical Behaviour of Ethylene Glycol and Its Oxidation Derivatives on a Platinum Electrode, II. Study of the Oxidation of Glyoxal and Glyoxylic Acid ..... 49
HORVÁTH, GY. s. BARTA, I.
HOSZTAFI, S. JÁSZBERÉNYI, J. CS.
INCZÉDY, J. s. HALMOS, P.
INCZÉDY, J. s. PAPP, E.
INCZÉDY, J. s. PUCHONY, Z.
INZELT, G., HORÁNYI, G.: Electrochemical Behaviour of Ethylene Glycol and its Oxidation Products on a Platinum Electrode, III. Effect of Chemisorption on the Kinetics of Oxidation of Glyoxal and Glyoxalic Acid ..... 403
INZELT, G. s. HORÁNYI, G.
INZELT, G. s. SZETEY, E.
JANCSÓ, G., VAN HOOK, V. A.: On the Interpretation of Precise Data on Vapor Pressures of Molecular Isotopic Isomers ..... 183
JÁSZBERÉNYI, J. CS., FARKAS, E. R., GUNDA, E. T., TAMÁS, J., MÁK, M., HOSZTAFI, S., SZILÁGYI, L., BOGNÁR, R.: Cycloaddition Reactions of Cephalosporin Compounds, III. 1,3-Dipolar Cycloadditions of Cephalosporin and Diazoalkanes ..... 103
KALINENKO, R. S. s. NAMETKIN, N. S.
KAMINARIS, D. M., GALINOS, A. G.: Preparation and Study of Pentafluorothiophenol Derivatives of In(III), Tl(III) and Rh(III) ..... 293
KARUNANITHI, S. s. RAMASWAMY, K.
KEREKES, P., MAKLEIT, S., BOGNÁR, R.: Synthesis of Alkaloids Using Reissert Compounds, II. A new Synthesis of (±)-reticuline, (Preliminary Communication) ..... 491
KISS, Á. I. s. DINYA, Z.
KISS, L., NÁNÁSI, P.: Synthesis of Phenyl 4-deoxy-β-D-glucopyranoside ..... 349
KISS, L., LIPTÁK, A., NÁNÁSI, P.: Quinovose Methyl Ethers. Synthesis of 2-O-Methyl, 3-O-methyl, and 4-O-methyl Ethers of Phenyl-β-D-quinovoside ..... 353
KISFALUDY, L. s. SCHÖN, I.
KÖRMENDY, K.: Aminophthalazinone Derivatives, III. The Reaction of Chlorophthalazinone with Primary Alkyl-, Cycloalkyl- and Aralkylamines. Study of the Steric Effect, I. ..... 303
KYSELA, G. s. BENISKA, J.
LAKATOS-SZABÓ, J.: Separation and Identification of Natural Porphyrins in Hungarian Crude Oils ..... 1
LALLAN MISHRA, s. H. N. PANDEY
LÁSZTITY, A., NÉMETH, M.: Comparison of Solvent Uptake and Ion Exchange Properties of Diethylaminoethylcellulose (De-Cellulose) and of Benzoilated Diethylaminoethylcellulose (BD-cellulose) in Methanol–Water–Hydrochloric Acid Mixtures ... 285
LATZEL, J.: An Improved Apparatus for the Microcatalytic or Pulse Technique (in German) 29
LÁZÁR, J., MÓD, L., VINKLER, E.: Synthetic Uses of Millon's Reagent, I. Synthesis of *o*-Nitrosophenols by Means of Millon's Reagent ..... 327
LÁZÁR, J., MÓD, L., VINKLER, E.: Studies on the Course of the Millon Reaction, II. ..... 335
LIPTÁK, A. s. KISS, L.
LISZI, J.: Static Dielectric Properties of Polar Liquids ..... 395
LISZI, J.: Cohesion Energy of a Liquid Due to Permanent Dipoles ..... 93
LOCHMANN, R. s. WELLER, TH.
MAKLEIT, S. s. KEREKES, P.
MÁK, M. s. JÁSZBERÉNYI, J. CS.
MALLÁT, T., PETRÓ, J., SCHÄFFER, M.: Electrochemical Study of Carbon-Supported Palladium-Copper Catalysts ..... 167
MATHERNY, M. s. FILO, O.
MIKA, J. s. SZABÓ, K.
MILLNER, T.: On the Role of Chemical Factors in the Drawing of Dotted Tungsten Wires (in German) ..... 199
MÓD, L. s. LÁZÁR, J.

Mollov, N. M., Venkov, A. P.: Internal α-Aminoalkylation Leading to 1,4-dihydro-3(2*H*)-Isoquinolinones ..... 315
Nametkin, N. S., Kalinenko, R. A., Shevelkova, L. V., Zalotai, L., Halász, D., Bérces, T., Márta, F.: Mechanism of the Pyrolysis of Propane and *n*-Butane at Low (about 800 k) and High (about 1100 K) Temperatures ..... 375
Nánási, P. s. Kiss, L.
Natarajan, A., Chockaltingam, K.: Molecular Constants of $ONF_3$ ..... 205
Németh, M. s. Lásztity, A.
Nógrádi, M. s. Antus, S.
Nógrádi, M. s. Székely, K.
Ötvös, L. s. Szammer, J.
Pandey, H. N., Lallan Mishra, Ram, V. J.: Metal Chelates with Ethylmalondihydrazide 77
Papp, E., Inczédy, J.: Investigation on the Distribution of 4-(2-pyridilazo)-resorcinol(PAR) in Aqueous Solution–Chloroform and Aqueous Solution–Chloroform Solution of Quaternary Ammonium Chloride Two-Phase Systems ..... 429
Petneházy, I., Szakál, Gy., Rusz, K., Tőke, L.: Kinetics of the Perkow Reaction ..... 447
Petró, J. s. Mallát, T.
Pfliegel, T. s. Antus, S.
Pongor, G. s. Dinya, Z.
Puchony, Z., Inczédy, J.: Investigations on Mercury(II)-PAN Complexes. Indirect Photometric Determination of Chloride Ion ..... 439
Ram, V. J. s. Pandey, H. N.
Ramanamurti, M. V., Qayum, A., Singh, R. K.: Specific Adsorption of Iodate Ions at the $Hg/KIO_3(aq)$ Interface At 25 °C ..... 261
Ramaswamy, K., Karunanithi, S.: Force Field Study of Chloroform by Parametric Method ..... 167
Recensiones ..... 133, 251, 361, 495
Riad, B. Y. s. Sakla, A. B.
Rusz, K. s. Petneházy, I.
Sakla, A. B., Riad, B. Y., Abdou, S., Barsoum, B. N.: Further Data Relevant to the Physical and Chemical Properties of Diazosulfides ..... 479
Sengupta, B. K. s. Datta, E.
Shevelkova, L. V. s. Nametkin, N. S.
Singh, H. B., Tandon, J. P.: Boron Complexes of Bifunctional Tridentate Schiff Bases 81
Singh, R. K. s. Ramanamurti, M. V.
Sohár, P. s. Barta, I.
Sóti, M. s. Barta, I.
Standner, E. s. Beniska, J.
Strelinsky, J. s. Antus, A.
Schäffer, M. s. Mallát, T.
Schön, I., Friss, J., Kisfaludy, L.: Side Reactions During the Removal of Protecting Groups of N-(Protected Aminoacyl) Urea Derivatives ..... 215
Szabó, K., Sziráki, L., Mika, J.: Effect of Aliphatic Alcohols on the Hydrogen Overvoltage on Dropping Gallium Electrodes ..... 67
Szabó, Z. L., Dobolyi-Fejérdy, H.: Some Chemical Reactions of the Electrode Gap and Their Role in Spectrochemical Analysis, XXXI. Behaviour of Metal Oxides in the Arc in an Argon Flow. Role of Burning Tine and Current of the Arc with RW O Auxiliary Electrodes ..... 147
Szabó, Z. L., Dobolyi-Fejérdy, H.: Some Chemical Reactions of the Electrode Gap and their Role in Spectrochemical Analysis, XXXII. Behaviour of Metal Oxides in the Arc in an Argon Flow. Role of the Metal Oxide to Carbon Powder Ratio with RW O Auxiliary Electrode ..... 157
Szabó, V., Borda, J., Végh, V.: Cleavage of the Heterocyclic Ring of Isoflavonoids by Nucleophillic Reagents, VII. Reactions of Isoflavone and its 4-thione Derivative with Hydrazine and its Derivatives ..... 457
Szakál, Gy. s. Petneházy, I.
Szammer, J., Ötvös, L.: Thermal Transcarboxylation Reactions, XII. Irreversibility of the Thermal Decarboxylation of Alkali Benzoates ..... 211
Székely, K., Vermes, B., Farkas, L., Nógrádi, M.: Synthesis of Some Natural Methylated Quercetin Glycosides ..... 241
Szebényi, I., Széchy, G.: Aromatization of *n*-Nonane and *n*-Decane Over a Platinum-Rhenium Catalyst ..... 115
Széchy, G. s. Szebényi, I.

Szejtli, J. s. Tőke, L.
Szetey, E., Inzelt, G., Horányi, G.: Photometric Determination of Oxalic Acid as Iron(III) Oxalate Complex in the Presence of Ethylene Glycol, Glyoxalic Acid, Glycolic Acid and Glyoxal ..... 367
Szetey, Z. s. Horányi, G.
Szilágyi, L. s. Jászberényi, J. Cs.
Sziráki, L. s. Szabó, K.
Tamás, J. s. Jászberényi, J. Cs.
Tandon, J. P. s. Singh, H. B.
Tigyi, J. s. Hankovszky, O.
Tőke, L. s. Petneházy, I.
Tőke, L., Fenichel, L., Bakó, P., Szejtli, J.: Crown Ethers Incorporating Sugar Units, I. (Preliminary Communication) ..... 357
Van Hook, V. A. s. Jancsó, G.
Végh, B. s. Szabó, V.
Venkov, A. P. s. Mollov, N. M.
Vermes, B. s. Székely, K.
Vinkler, E. s. Lázár, J.
Weller, Th., Lochmann, R.: Theoretical Investigations of Barriers to Inversion ..... 297
Zalotai, L. s. Nametkin, N. S.
Zára-Kaczián, E., Deák, Gy.: The Reaction of 2-ethoxycarbonyl-1-phenyl-1,4-dihydro-3(2H)-isoquinolinone with Ammonia Yielding N-2-(carbamoylmethyl) benzhydryl ethylurethane (Short communication) ..... 247
Qayum, A. s. Ramanamurti, M. V.

*Acta Chimica Academiae Scientiarum Hungaricae, Tomus 98 (1), pp. 1—11 (1978)*

# SEPARATION AND IDENTIFICATION OF NATURAL PORPHYRINS IN HUNGARIAN CRUDE OILS

J. LAKATOS-SZABÓ

*(Petroleum Engineering Research Laboratory of the Hungarian Academy of Sciences, Miskolc-University City)*

Received July 1, 1977

The study of the porphyrin content of characteristic Hungarian crude oils is closely related to the geochemical classification of liquid hydrocarbons occurring in the Pannonian basin. Laboratory investigations include the separation of porphyrins from petroleum, their quantitative determination and structural identification.

Experimental results show that the petroleum samples investigated contain exclusively nickel and vanadyl porphyrins at very different concentrations (1—127 ppm). The petroleum sample from Nagylengyel has the highest porphyrin content (127 ppm), while the porphyrin content of the Hungarian, so-called light oils is relatively low (1—10 ppm). Porphyrins isolated comprise both etio and phyllo types, however, the presence of chlorines or of metal complexes other than those mentioned above could not be detected in the Hungarian crude oils.

## Introduction

Of the geochemical trace compounds, the degradation products of chlorophyll and hemin are of outstanding importance [1, 2]. Porphyrins to be found at present in crude oils and bitumina are to be considered as stable endproducts or partially decomposed intermediates of the pigments, which have been an important part of the initial organic sediment. These compounds, though in different concentrations, maintained their original tetrapyrrol ring structure during thousands of years of biogenesis or diagenesis.

On the basis of the quality and quantity of porphyrins isolated from petroleum, it can be established with high probability, whether the hydrocarbon has predominantly plant or animal origin, and the decomposition process resulting the endproduct can be reconstructed [3, 4]. Moreover, certain conclusions can be drawn on those environmental conditions under which the organic sediment has been accumulated or transformed [5].

In addition to their geochemical role, porphyrins may be brought into connection with production and processing problems. As natural surface active agents they may influence the properties of petroleum film on rock surfaces (wettability), the formation of rigid films on water-oil interface, and the interfacial tension [6, 7]. Moreover, it should be mentioned that an important part of vanadium and nickel, acting as catalyst poisons in petroleum processing, is also bound to porphyrins [8].

Even if in a small concentration, through these factors petroporphyrins may play a decisive role in the displacement of petroleum by water, and their concentration in petroleum cannot be considered as indifferent from the aspect of the processing and quality of petroleum products.

## Experimental

The main aspect in the selection of the crude oils to be investigated was to choose characteristic Hungarian oils having different chemical compositions and physical properties from occurrences of different geological age and from different geochemical environments.

The formation, where the crude oils derived from, the age of the reservoires, the average molecular weight of the oils, their asphaltene content and their elemental analysis data are collected in Tables I and II.

**Table I**

*Formation of the crude oils and age of the reservoirs*

| Oil field | Symbol of the well | Age of the reservoir |
|---|---|---|
| Algyő | Algyő-1 | Lower Pannonian |
| | Algyő-3 | Lower Pannonian |
| Ásotthalom | Ás-20 | Lower Pannonian |
| Barabásszeg | Ba-17 | Mesozoic |
| Budafa | B (average) | Lower Pannonian |
| Demjén-Dél (-South) | De-D (average) | Oligocene |
| Demjén-Észak (-North) | De-É-50 | Oligocene |
| Lovászi | L-143 | Lower Pannonian |
| Mezőkeresztes | Me-54 | Oligocene |
| Nagylengyel | N1—187 | Mesozoic |
| | N1—296 | Mesozoic |
| Ortaháza | Or-29 | Lower Pannonian |
| | Or-31 | Mesozoic |
| Pusztaföldvár | Pf-53 | Lower Pannonian |
| Szank | Szk-71 | Tortonian |

Porphyrins contained in the oils were identified on the basis of their spectra in the ultraviolet and visible regions. Spectra were recorded with a Perkin—Elmer 402 spectrophotometer.

The absolute limit of detection of metal porphyrin complexes on the basis of the Soret band at about 400 nm is $1.6 \times 10^{-8}$ mol for vanadium complexes, and $3.0 \times 10^{-8}$ mol for nickel complexes in solutions of 5 g $dm^{-3}$ concentration and 1.0 cm cells, generally used during the measurements.

For the qualitative and quantitative spectrophotometric determinations, as well as for the separation techniques, hematoporphyrin, made by Fluka AG, and Ni(II) and VO(II) porphyrins synthesized from it was used as model compounds.

The metal content was determined spectrographically by the rotating electrode technique. Spectra were recorded with a Zeiss Q 24 quartz spectrograph. The method [9] permits in small samples (0.1—0.2 g) the quantitative determination of metals present at 1—10 ppm concentrations with a relative error of 4—6%.

**Table II**

*Average molecular weight, asphaltene content and elemental composition of the crude oils*

| Symbol | Average mol. wt. | Asphaltene content, wt.% | Composition | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | C | H | N | S | V | Ni |
| | | | wt.% | | | | ppm | |
| Algyő-1 | 309 | 4.1 | 84.8 | 14.2 | <0.05 | 0.2 | <1 | 8 |
| Algyő-3 | 276 | 3.9 | 85.0 | 13.9 | <0.05 | 0.1 | <1 | 6 |
| Ás-20 | 365 | | 85.0 | 13.9 | <0.05 | 0.1 | <1 | <2 |
| Ba-17 | 538 | 11.4 | 83.9 | 12.1 | <0.05 | | | |
| B | 270 | 1.8 | 85.1 | 13.5 | <0.05 | 0.1 | <1 | <2 |
| De-D | 307 | 2.1 | 85.1 | 14.1 | <0.05 | 0.1 | <1 | 16 |
| De-É-50 | 503 | 2.7 | 84.8 | 13.9 | 0.1 | | | |
| L-143 | 228 | 1.8 | 85.1 | 13.9 | <0.05 | 0.1 | <1 | <2 |
| Me-54 | 316 | 5.4 | 85.0 | 13.7 | <0.05 | | | |
| Nl—187 | 430 | 11.7 | 83.8 | 11.3 | 0.3 | 3.2 | 92 | 6 |
| Nl—296 | 466 | 12.4 | 82.9 | 10.9 | 0.3 | 4.2 | 101 | 8 |
| Or-29 | 259 | 3.0 | 84.6 | 14.0 | <0.05 | 0.5 | 12 | 9 |
| Or-31 | 306 | 3.1 | 85.0 | 13.8 | <0.05 | 0.3 | 4 | 10 |
| Pf-53 | 399 | 7.3 | 85.2 | 13.2 | <0.05 | 0.3 | <1 | <2 |
| Sz-71 | 299 | 6.8 | 85.1 | 13.8 | <0.05 | 0.2 | <1 | 20 |

The average molecular weight of crude oils and hydrocarbon fractions was determined by a Hewlett—Packard 302 vapour pressure osmometer. The error of the molecular weights measurement is $\pm$ 2% [10].

A Hewlett–Packard 185B semi-automatic CHN analyzer was used for elemental analysis, and the error of measurements being $\pm$0.3%.

For the determination of average molecular weights, *n*-triacontane of gas-chromatographic purity was used as calibrating compound, while for CHN analysis NBS acetanilide and cystine. Solvents used for the recording of the absorption spectra were pyridine and benzene, for the determination of the average molecular weight, benzene of highest analytical purity was employed.

For liquid extraction and for the column chromatographic separation of the hydrocarbons, benzene, acetonitrile and cyclohexane of analytical purity were used, while column packings were silicagel (0.05—2.0 mm Merck) and Sephadex LH 20 (25—100 $\mu$, Pharmacia Fine Chemicals products).

In case of demetallization of porphyrins, metallic lithium and anhydrous ethylenediamine (purum) were used.

## Results and discussion

### *Separation of porphyrins from crude oils*

The low concentration of porphyrins in petroleum does not make possible their direct qualitative and quantitative determination, so that they must be enriched. The separation methods used most often and with the best results are based on the specific extraction and adsorption properties of metalloporphyrins.

To achieve optimal separation, we have examined the applicability to Hungarian crude oils of methods reported in the literature as standard procedures [11]. To select the appropriate method, the sharpness of separation, porphyrin yield and the basic experimental conditions of the separation processes have been studied. In view of the fact that hydrocarbons are involved, a further aspect to be considered was that the separation system should permit group separation to a certain degree (asphaltenes, resins, saturated and unsaturated hydrocarbons).

The petroleum samples investigated were processed in the separation system elaborated by BERTI *et al.* [12] and developed further by us (Fig. 1).

Without a detailed evaluation of the single separation processes, the most important results can be summarized as follows:

a) For the isolation of porphyrins present in the Hungarian crude oils, the separation system consisting of extraction with acetonitrile, iso-octane deasphaltization, partition and adsorption column chromatography and gel chromatography was found to be satisfactory from every aspect.

b) Acetonitrile, as extracting, partitioning phase and eluting agent proved to be selective for petroporphyrins.

c) The porphyrin content of the hydrocarbon fractions obtained at the end of the separation procedure is sufficient and permits subsequent demetallization of the complexes and the absorption spectrophotometric determination of their characteristic structure.

Table III shows the porphyrin content of the hydrocarbone fractions obtained in the separation of petroleum sample N1—187 and the separation factors characteristic of the single operations.

**Table III**

*Porphyrin content of the fractions obtained in the separation of petroleum sample N1—187 and the separation factors*

| Separating operation | Petroleum fraction | | Separation factor |
|---|---|---|---|
| | Denomination | Porphyrin content mol kg$^{-1}$ | |
| | petroleum | $2.3\times10^{-4}$ | |
| Extraction | extract | $3.9\times10^{-4}$ | 1.7 |
| Deasphaltization | iso-octane-soluble | $2.8\times10^{-4}$ | 1.2 |
| | iso-octane-asphaltene | $28.0\times10^{-4}$ | 12.2 |
| Column chromatography | iso-octane elute | $1.6\times10^{-4}$ | 0.7 |
| | acetonitrille elute | $21.3\times10^{-4}$ | 9.3 |
| | cyclohexane elute | $27.6\times10^{-4}$ | 12.0 |
| | acetonitrile elute | $120.8\times10^{-4}$ | 52.5 |
| Gel chromatography | dimethyl formamide elute | $360.6\times10^{-4}$ | 156.8 |

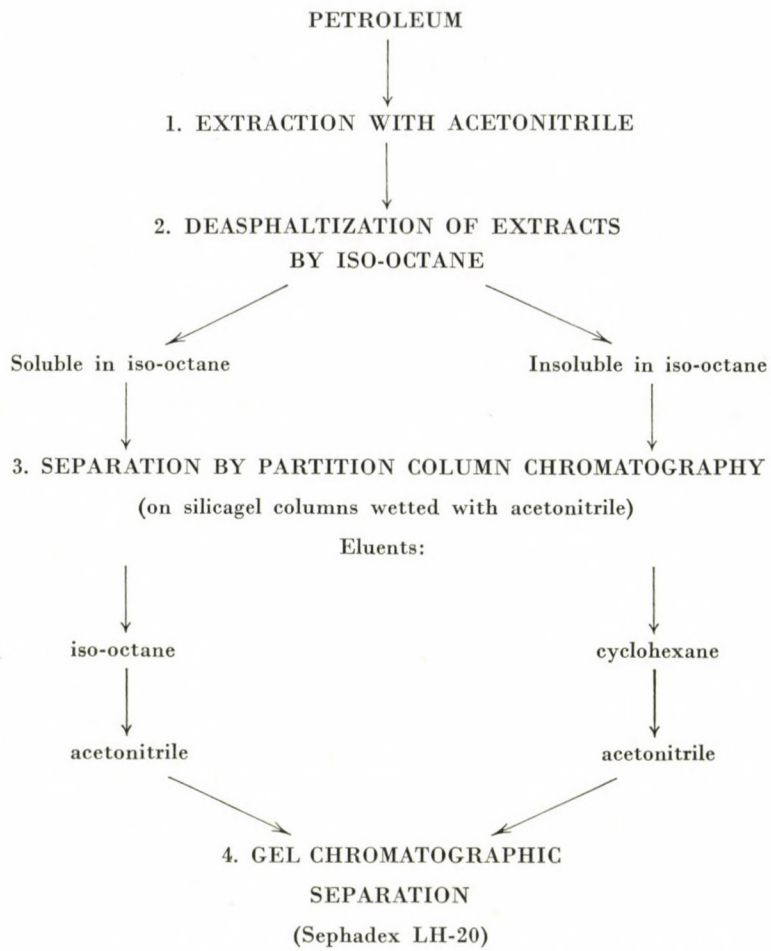



*Fig. 1.* Separation system used for the recovery of porphyrins

During separation, hydrocarbon fractions became gradually enriched in metalloporphyrins. The last operation, namely the gel chromatography, is particularly efficient because the original porphyrin content of the crude oil being increased 100—170-fold, depending on the samples. Thus, the separation of crude oil sample N1—187 resulted a hydrocarbon fraction with a porphyrin content of 2.1 wt.%.

### *Qualitative and quantitative determination of metalloporphyrins isolated from the crude oils*

Porphyrins of various types, in accordance with their structure, have a relatively simple and very characteristic spectrum in the visible region. Thus, the spectra of complexes formed with divalent metals consist of two bands

($\alpha$, $\beta$), and their position depending mainly on the nature and perturbation effect of the metal coordinated in the porphyrin ring [14, 15]. On the other hand, free porphyrins reveal in the same region a quadruple band system, in which the position of the peaks and the order of the peak heights depend on the nature of the peripheral groups.

The absorption spectra for all hydrocarbon fractions obtained in the separation system have been recorded in the 190—800 nm region. Figures 2 and 3 show by way of an example the characteristic spectra of petroleum samples N1—296, Or-29, Ás-20 and De-D.

The spectra of porphyrins detectable in Hungarian crudes exhibit without exception a double band system in the visible region. It can be unequivocally established on the basis of the wavelength values of the maxima

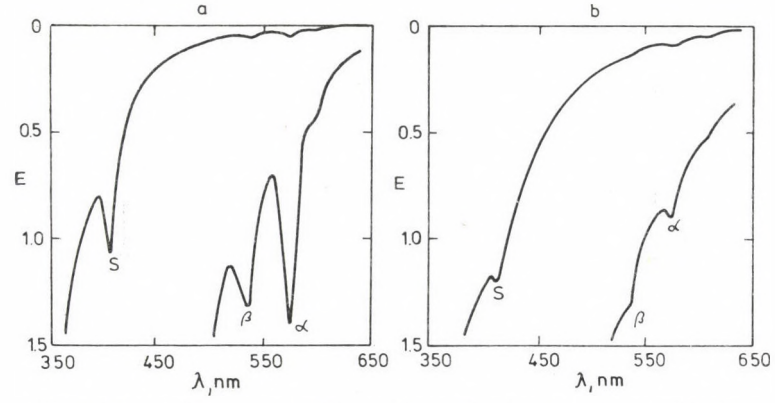



*Fig. 2.* Absorption spectra of metalloporphyrins found in crude oils N1—296 (a) and Or-29 (b)

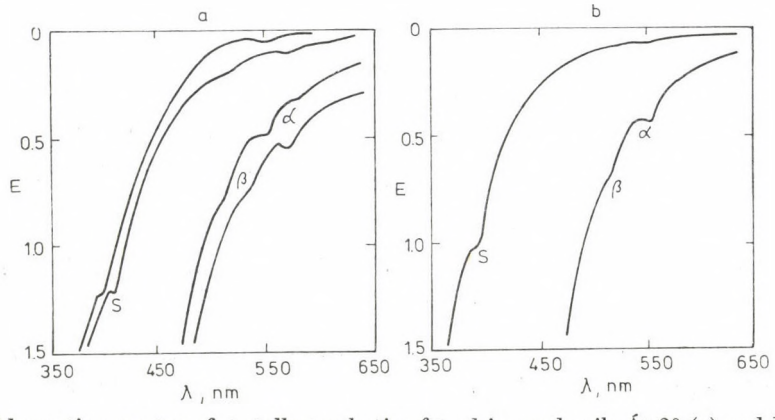



*Fig. 3.* Absorption spectra of metalloporphyrins found in crude oils Ás-20 (a) and De—D (b)

of the bands and their intensity ratios that only metalloporphyrins are present in the crude oils investigated. In the spectra, the intensity of the $\alpha$ band is always higher, indicating the presence of a stable complex.

Table IV summarizes the wavelength values of the $\alpha$ bands of metalloporphyrins detected in the crude oils studied, and the nature of the metal coordinated in the complexes.

**Table IV**

*Characteristic data of metalloporphyrins present in the crude oils*

| Symbol of petroleum | Wavelength of the $\alpha$ band maximum (nm) | | Coordinated metal |
|---|---|---|---|
| Algyő-1 | 555 | 574 | Ni, V |
| Algyő-3 | 555 | 574 | Ni, V |
| Ás-20 | 555 | 573 | Ni, V |
| Ba-17 | | 572 | V |
| B | 554 | 573 | Ni, V |
| De-D | 554 | | Ni |
| De-É-50 | 554 | | Ni |
| L-143 | 555 | | Ni |
| Me-54 | 554 | | Ni |
| N1—187 | | 573 | V |
| N1—296 | | 573 | V |
| Or-29 | | 573 | V |
| Or-31 | | 572 | V |
| Pf-53 | 555 | 573 | Ni, V |
| Szk-71 | 555 | 574 | Ni, V |

In most of the crude oils investigated (primarily V in samples of mesozoic origin, and Ni in samples of oligocene origin) only the complex of a single metal, either that of vanadium or that of nickel is present. However, in some of the petroleum samples both complexes can be detected, in a form of distribution that nickel complexes become enriched mainly in the part soluble in iso-octane, while vanadyl complexes are bound mainly to the iso-octane asphaltenes. Summarizing the results, it can be stated that:

a) The crude oils contain exclusively stable vanadyl and nickelporphyrins. Complexes formed with other metals or free porphyrins could not be detected.

b) The crudes from Nagylengyel, Ortaháza and Barabásszeg contain only vanadyl complexes, those from Demjén, Lovászi and Mezőkeresztes only nickel complexes. In the other Hungarian crudes, both vanadyl and nickel complexes are present.

The quantity of metal complexes has been determined on the basis of the peak heights of the $\alpha$ bands relative to the standard and in knowledge of the molar absorbances (Table V). The porphyrin content of the crudes and their hydrocarbon fractions has been obtained in units of mol $kg^{-1}$.

To give the porphyrin content in ppm units, the molecular weight, the spectral type and the structure of the porphyrins detected must be known. For this purpose, metalloporphyrins must demetallized, *i.e.* converted into

**Table V**

*Wavelengths of the absorption maxima of synthetic Ni(II) and VO(II) complexes and their molar absorbences*

| Band | Wavelength (nm) | | Molar absorbence | |
|---|---|---|---|---|
| | Ni(II) | VO(II) | Ni(II) | VO(II) |
| | complexes | | complexes | |
| Soret | 400 | 402 | $1.65\times10^5$ | $3.10\times10^5$ |
| $\alpha$ | 556 | 572 | $2.55\times10^4$ | $2.91\times10^4$ |
| $\beta$ | 518 | 535 | $8.70\times10^3$ | $9.87\times10^3$ |

free porphyrins. The decomposition of the complexes requires caution, and can be carried out only in a mild medium. Otherwise, simultaneously with demetallization, the tetrapyrrol ring structure is also easily destroyed.

After trying several methods, porphyrin complexes were decomposed in an alkaline medium with lithium exchange [16]. The process takes place according to the following reaction scheme:

$$MP + 2Li^+ \rightleftharpoons Li_2P + M^{2+}$$

$$Li_2P + 2H_2O = 2LiOH + PH_2$$

The lithium complex obtained in the first step is easily decomposed by water, and free porphyrin, free of metal, can be recovered.

Owing to stability problems, demetallization cannot be carried out on each porphyrin-enriched hydrocarbon fraction obtained from petroleum. Of the spectra of free porphyrins obtained, those characteristic of N1—296 are shown in Fig. 4 as an example.

The spectral type of the isolated and demetallized porphyrins has been determined on the basis of their spectra, and is summarized in Table VI for four petroleum samples.

The etio type of porphyrins in crude oil corresponds to etioporphyrin III, the phyllo type to $\gamma$-phylloporphyrin XV [17], so that their molecular weights have been used for quantitative determination. Results of quantitative determinations are listed in Table VII.

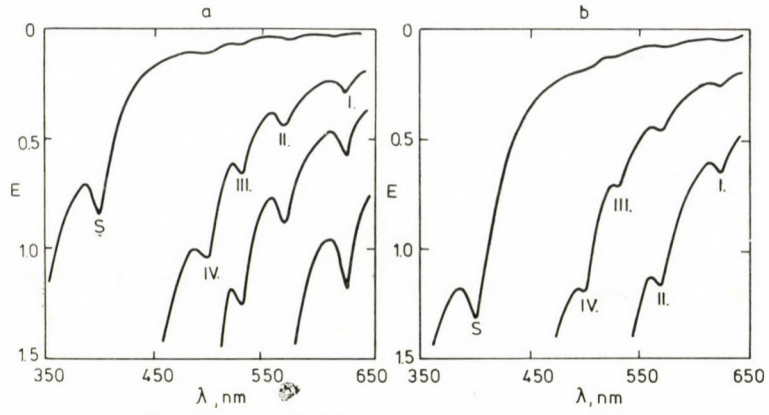



*Fig. 4.* Absorption spectra of demetallized free porphyrins separated from crude oil sample N1—296 iso-octane (a), iso-octane asphaltene (b)

It will be noted from the data in Table VII that:

a) the only petroleum samples from Nagylengyel contain more than 100 ppm porphyrin;

b) the sample De-É-50 has a porphyrin content close to 100 ppm;

c) the samples Ás-20, De-D, Me-54 and Or-29 have 10—20 ppm porphyrin, and

d) the other Hungarian crude oils have less than 10 ppm porphyrin.

In the petroleum samples from Demjén deoxophylloerythroetioporphyrin (DPEP) has been unequivocally identified. Characteristic of this type is that it contains besides the four pyrrole rings a fifth isocyclic ring. This structure suggests plant origin, and is indicative of the fact that the degradation of chloropyll was blocked under the low pressure and temperature conditions of the reservoir.

**Table VI**

*Order of the peak heights of absorption bands measured for demetallized petroporphyrins and the corresponding spectral types*

| Petroleum fraction | | Order of peak height | Spectral type |
|---|---|---|---|
| Ás-20 | iso-octane soluble | IV > III > II > I | etio |
| De-D | iso-otane soluble | IV > I > II > III | DPEP |
| | iso-octane asphaltene | IV > I > II > III | DPEP |
| N1—296 | iso-octane soluble | IV > III > II > I | etio |
| | iso-octane asphaltene | IV > II > III > I | phyllo |
| Or-29 | iso-octane soluble | IV > III > II > I | etio |
| | iso-octane asphaltene | IV > II > III > I | phyllo |

**Table VII**

*Porphyrin content of characteristic Hungarian crude oils*

| Symbol | Porphyrin content ppm |
|---|---|
| Algyő-1 | 6.5 |
| Algyő-3 | 5.4 |
| Ás-20 | 11.3 |
| B | 9.7 |
| Ba-17 | 8.2 |
| De-D | 16.9 |
| De-É-50 | 94.0 |
| L-143 | 1.4 |
| Me-54 | 10.4 |
| N1—187 | 127.4 |
| N1—296 | 124.4 |
| Or-29 | 10.5 |
| Or-31 | 5.6 |
| Pf-53 | 5.1 |
| Szk-71 | 2.0 |

The porphyrin content of the crudes from Nagylengyel and Ortaháza is completely identical with respect to both the coordinated metal and the structure. In the iso-octane soluble fractions of these samples porphyrins of the etio type, in the iso-octane asphaltenes porphyrins of the phyllo type have been identified. This fact indicates a common origin, though in other respects there are great differences between the two petroleums and in spite of the closeness of the two reservoirs. It is of interest that in the sample of Barabásszeg originating from the neighbourhood of these two petroleum samples similarly only vanadium complex was found.

Qualitative and quantitative results are in good agreement with general experiences reported in the literature [14, 17]. Indeed, the porphyrin content of the Hungarian petroleum samples also varies within wide limits (1—127 ppm). Only metalloporphyrins could be identified, in which the coordinated metal is nickel or vanadium. Free porphyrins, chlorines and the presence of other than the metals mentioned above, could not be detected. Of the petroleum samples investigated, that from Nagylengyel has the highest asphaltene content, and at the same time, the highest prophyrin content. Moreover these crudes are the richest in sulfur, contain exclusively vanadyl complexes, which also supports the relationship between sulfur and porphyrin contents [18].

## REFERENCES

[1] TREIBS, A.: Ann. Chem., 103 (1934)
[2] THOMAS, D. W., BLUMER, M.: Geochim. Cosmochim. Acta, 1147 (1964)
[3] DODD, C. G., MOORE, J. W., DENEKAS, M. O.: Ind. Eng. Chem., **44,** 2585 (1952)
[4] DUNNING, H. N., RABON, N. A.: Ind. Eng. Chem., **48,** 951 (1956)
[5] VALLENTYNE, J. R.: Fossil Pigments, in Comparative Biochemistry of Photoreactive systems, Ed. M. B. Alien. Academic Press, New York 1960
[6] DUNNING, H. N., MOORE, J. W., DENEKAS, M. O.: Ind. Eng. Chem., **45,** 1759 (1953)
[7] BAKER, E. G.: Bull. AAPG, **46,** 76 (1962)
[8] O. I. MILNER: Analysis of Petroleum for Trace Elements. Pergamon Press, New York 1963
[9] LAKATOS, I.: Kőolaj és Földgáz, **106,** 115 (1973)
[10] LAKATOS-SZABÓ, J., LAKATOS, I.: Acta Chim. (Budapest), **80,** 237 (1974)
[11] LAKATOS, I., LAKATOS-SZABÓ, J., WAGNER, O.: Kőolaj és Földgáz, **105,** 184 (1972)
[12] BERTI, V., ILARDI, A. M., NUZZI, M.: 7th World Petroleum Congress, Paper V. 149. Mexico City 1967
[13] LAKATOS-SZABÓ, J.: Thesis, University of Chemical Industries Veszprém, Veszprém 1975
[14] HODGSON, G. W., BAKER, B. L., PEAKE, E.: Geochemistry of Porphyrins, in Fundamental Aspects of Petroleum Geochemistry, Eds. B. Nagy and U. Colombo. Elsevier Publ. Co., New York 1967
[15] FALK, J. E.: Porphyrins and Metalloporphyrins. Elsevier Publ. Co., Amsterdam 1964
[16] EISNER, U., HARDING, M. C. J.: J. Chem. Soc., **1964,** 4089
[17] BAKER, E. W.: Porphyrins, in Organic Chemistry, Eds G. Eglinton and M. T. I. Murphy. Springer Verlag, New York 1969
[18] RADCSENKO, O. A.: Dokl. Akad. Nauk SSSR, **182,** 193 (1968)

Julianna LAKATOS-SZABÓ H-3515 Miskolc. Egyetemváros.

*Acta Chimica Academiae Scientiarum Hungaricae, Tomus 98 (1), pp. 13—28 (1978)*

# ELIMINIERUNG DER SPEKTROCHEMISCHEN MATRIXEFFEKTE, VERFOLGUNG DER LINIENHOMOLOGIE UND FESTLEGUNG DER NACHWEISGRENZEN DER SPURENELEMENTE IN SILIKATGESTEINEN*

O. Filo und M. Matherny

*(Lehrstuhl für Chemie der Hüttenmännischen Fakultät der Technischen Hochschule in Košice)*

Eingegangen am 3. Februar, 1977

Die ausgearbeitete, neue analytische Methode zur Bestimmung von Spurenelementen in Silikatgesteinen durch Anwendung eines Wechselstromabreißbogens ermöglicht die Analyse saurer Granite und Granodiorite, intermediärer Gesteine und auch basischer Basalte mittels einheitlicher Eichkurven. Diese Ergebnisse wurden erhalten, indem die Matrixeffekte sukzessiv durch Bestimmung der optimalen Misch- und Verdünnungsverhältnisse ausgeschaltet wurden. Weiter wurde das Verhältnis der optimalen Vorbrenn- und Expositionszeiten anhand des Verlaufs der integralen Verdampfungskurven festgelegt. Die Optimalisierung der Auswahl der analytischen Linienpaare wurde mit Hilfe der kombinierten Korrelations-Regressionsanalyse durchgeführt, gleichzeitig wurden diese Ergebnisse den Werten der aufgestellten analytischen Eichgeraden gegegenübergestellt. Schließlich wurden diese als optimal befundenen analytischen Linienpaare auch zur Ermittlung der Genauigkeit der analytischen Methode herangezogen.

## 1. Einführung

Der Hauptvorteil der emissionsspektrochemischen Analyse besteht in der Möglichkeit der Durchführung von Mehrkomponentenbestimmungen. Diese Bestimmungen treten bei der Analyse von Spurenelementen im Silikatgesteinen, Bodenproben und ähnlichen Materialien immer mehr in der Vordergrund, u.zw. nicht nur aus ökonomischen Gründen, sondern auch wegen des guten Nachweisvermögens der spektrochemischen Methoden.

Die Leistungsgrenzen der spektrochemischen Analysen bei Mehrkomponenten-Bestimmungen sind jedoch von der Optimalisation der experimentellen Bedingungen abhängig. Diese kann aber für alle in Frage kommenden Elemente niemals vollkommen erfüllt werden, und deswegen stellt die Optimalisierung einen quasi durchschnittlichen Einfluß der experimentellen Bedingungen auf die Leistungsparameter der Methode dar.

Die Optimalisierung besteht aus einer Reihe von Teilprozeduren, wobei der erste aber auch entscheidenste Schritt die Eliminierung der Matrixeffekte

* Vorgetragen auf der Sitzung des Arbeitskreises für Spektrochemie der Ungarischen Akademie der Wissenschaften in Eger, Mai 1975.

ist [1], da diese systematische analytische Fehler hervorrufen können. Im Zusammenhang mit dieser Prozedur ist es nicht nur vom Standpunkt der Eliminierung der Matrixeffekte, sondern auch im Interesse der Erreichung von günstigsten Nachweisgrenzen wichtig, die Verdampfungsprozesse auf ein quasi einheitliches Niveau zu bringen. Der Verlauf der analytischen Eichgeraden muß linear sein, da nach KAISER [2] nur in diesem Falle eine zuverlässige Berechnung der Werte der Nachweisgrenzen möglich ist. Alle Leistungsparameter der analytischen Methoden (Korrelation, Regression u.s.w.) müssen für eine im voraus definierte, minimale relative Genauigkeit der Konzentrationsbestimmung erreicht werden. Dieser Grenzwert wurde im konkreten Fall mit $\pm 20\%$ festgelegt.

## 2. Allgemeiner und rechnerischer Teil

Bei der experimentellen Ausarbeitung einer analytischen Methode müssen der Reihe nach die folgenden Untersuchungen und Optimalisationsschritte durchgeführt werden. Erstens müssen die Matrixeffekte, unter Anwendung spektrochemisch aktiver Beimischungen, eliminiert werden [1]. Für diesen Optimalisierungsschritt, bei dem das optimale Mischverhältnis nach HOLDT's Vorschlag [3] durch die $\Delta Y_V$-Temperaturindexmethode festgelegt wird, wurde eine statistische Testmethode entwickelt [4—7]. Weiter müssen die Verdampfungsprozesse anhand der integralen Bezugskurven [8] untersucht werden, wobei bei der experimentellen Untersuchung die Empfehlungen von FLÓRIÁN [9] berücksichtig wurden. Aufgrund dieser Resultate wurde auch die optimale Expositionszeit bestimmt. Bei der Auswahl der optimalen analytischen Linienpaare wurde die kombinierte Korrelation-Regressions-Methode [10—12] angewandt, wobei auch die Linienhomologie aufgrund der von PLŠKO [13] festgelegten Kriterien wiederum mit Hilfe einer Testprozedur [14, 15] überprüft wird. Die analytischen Eichfunktionen der einzelnen Spurenelemente, die für ein im voraus definiertes Konzentrationsintervall $\langle c_{X,\min}, c_{X,\max}\langle$ als linearverlaufende Eichgeraden interpretiert wurden [16], ermöglichten die gleichzeitige Ermittlung der Werte der Nachweisgrenzen $c_L$ sowie der Garantiegrenzen $c_G$ [17—19].

Für die obenerwähnten Rechenprozeduren sowie für die Anwendung der l-Transformation [20] wurde eine Reihe von neu ausgestellten Rechenprogrammen [21] angewandt.

## 3. Experimenteller Teil

Die allgemeinen Versuchsbedingungen, die die Resultate der Optimalisierungsprozeduren sind, sind in Tabelle I angegeben. Die veränderlichen Versuchsbedingungen sind in Tabelle II zusammengefaßt, und die zur Analyse herangezogenen Spektrallinien sind zusammen mit deren wichtigsten spektrochemischen Parametern (nach Literaturangabe [22]) in Tabelle III veranschaulicht.

**Tabelle I**

*Die allgemeinen experimentellen Versuchsbedingungen*

| | |
|---|---|
| Spektrograph | PGS-2, einfacher Durchgang, m = 2<br>D = 0,363. $10^{-6}$ |
| Spektralbereich | 270 nm bis 370 nm |
| Abbildungsart | dreilinsig mit Zwischenabbildung |
| Spalbreite | 0,040 mm |
| Elektrodenmaterial | Graphit, VEB Elektrokarbon, Topolčany |
| Trägerelektrode | SU-304 |
| Gegenelektrode | SU-201 |
| Verdünnungsmittel | Graphitpulver SU-602 |
| Elektrodenabstand | 4,0 mm |
| Emulsionsart | ORWO, WU-3 |
| Entwickler | ORWO, F-43; 10 Min. bei 20 °C |
| Anregungsart | Wechselstrom-Abreißbogen |
| Anregungsquelle | Generator DG-1 |
| Dämpfungswiderstand | 250 $\Omega$ |
| Stromspannung | 220 V |
| Stromstärke | 5 bis 6 A |

Die gemessenen Schwärzungswerte S wurden entweder aufgrund der I-Transformation [20] in die I-Werte oder aber auch weiter in die relativen Intensitätswerte ($I = 10^{I}$) umgerechnet und in dieser Form zu den Rechenprozeduren herangezogen.

Für alle experimentellen Untersuchungen wurden zwei Reihen von Proben parallel angewandt (Tab. IV). Die erste Reihe wurde von typischen slowakischen Gesteinen: Quarzit [23], Granodiorit — Granit — Andesit — Basalt [24] so zusammengestellt, daß von stark saurem Quarzit über intermediäre Gesteine bis zu basischen Basalten alle bedeutenden Gesteinstypen vertreten waren. Die zweite Reihe war durch die drei Gesteinsstandards der ZGI-Berlin Granit — Basalt — Tonschiefer vertreten [25]. Schließlich wurde noch ein Modellmatrixgemisch aus spektralreinen Oxidverbindungen zusammengestellt, welches auch einigen Spurenelementen, wiederum in Oxidform (Ag, Cd, Co, Cr, Cu, Mn, Mo, Ni, Sc, Sn, Ti, V, W, Zn) im Konzentrationsinterwall von $10^{-1}\%$ bis $5 \cdot 10^{-4}\%$ enthielt. Diese Modellmatrix mit abgestuften Konzentrationen der Spurenelemente wurde nicht nur für die Aufstellung der analytischen Eichgeraden, sondern auch bei allen anderen Optimalisierungsschritten verwendet.

**Tabelle II**

*Veränderliche experimentelle Versuchsbedingungen*

| | |
|---|---|
| Vorbrennzeit | 10 s mit Ausnahme der Fahrspektrogramme |
| Expositionszeit | a) bei der Aufnahme der Verdampfungskurven mittels des Fahrspektrogrammverfahrens 10 s<br>b) bei allen anderen Untersuchungen 60 s |
| Abbildungsblende | a) 5,0 mm<br>b) 3,2 mm |

Die spektrochemischen Matrixeffekte wurden an folgenden Mischverhältnis-Serien untersucht: für die erste Versuchsreihe wurden nur Mischungen von Probe und Graphitpulver eingesetzt. Für die zweite und dritte Versuchsreihe wurde zu den Mischungen der ersten Reihe 1 Teil bzw. 2 Teile Bariumkarbonat zugegeben, da die günstige Auswirkung dieser Beimischung schon früher bestätigt wurde [26—28]. Zu diesen Grundmischungen wurden noch 0,3% $V_2O_3$ beigemengt und die Proben so gebrannt. Der Verlauf der $\Delta Y_V$-Werte in Abhängigkeit vom Verdünnungsgrad ist in den Abbildungen 1 bis 4 dargestellt.

Bei der Verfolgung der Verdampfungsprozesse wurden drei Silikatgesteinstypen (Granodiorit — Andesit — Basalt) sowie das synthetische Modellmatrixgemisch im Verhältnis 6 : 2 : 2 mit Graphit und Bariumkarbonat angewendet. Bei diesen Experimenten wurden immer 5 Elektroden gebrannt, und die Endresultate wurden entsprechend FLÓRIÁN's Vorschlag [9] ausgewertet. Die typischen Versuchsergebnisse sind in den Abbildungen 5 bis 7 graphisch dargestellt.

Die Endergebnisse der Optimalisation, der Auswahl der analytischen Linienpaare sowie der Homologieprüfungen sind in Tabelle V zusammengefaßt. Bei diesen Experimenten wurde mit einer 0,02%-igen PdO-Beimengung gearbeitet, da die Pd-Linien als Bezugslinien notwendig waren. Da die Untersuchungen des Matrixeffektes bestätigt haben, daß das Mischverhältnis 6 : 2 : 2 ausreichend ist, wurde auch bei der Homologiebestimmungen mit diesem Mischverhältnis gearbeitet. Selbstverständlich wurden für die Homologiebestimmung die $B_X$- und $B_R$-Parameter der Eichgeraden der analytischen sowie der Bezugslinien getrennt bestimmt. Diese Ergebnisse sind in Tabelle VI enthalten.

Schließlich wurde mit der optimalisierten analytischen Methode einige Spurenelementgehalte der international anerkannten Standards G-1, W-1 und T-1 [32, 36] sowie des Standards ZGI [35] bestimmt und den entsprechenden Festwerten gegenübergestellt (Tab. VII).

## 4. Diskussion

Die chemische Zusammensetzung der angewandten Gesteine und der synthetischen Modelmatrix (Tab. IV) erlaubt die Proben aufgrund der prägnanten Abänderung einiger Hauptelemente von zwei Standpunkten aus zu beurteilen. Die Summe der Oxide der Alkalimetalle und das Verhältnis von CaO zu MgO beeinflussen entscheidend die Plasmatemperatur und den Elektrodendruck. Die Ionisationsenergien von Ca und Mg unterschieden sich um etwa $10^2$ kJ · $M^{-1}$ was sich schon mäßiger auf die Plasmatemperatur und den Elektrodendruck auswirkt, aber ihre mineralischen Verbindungen in Silikatgesteinen weisen bedeutend unterschiedliche Zersetzungstemperaturen auf, was eine bedeutende Rolle bei den Matrixeffekten spielt [6, 27].

### 4.1. *Beseitigung der Matrixeffekte*

Die ausschließliche Graphitaugabe [26] hat bei den untersuchten ZGI-Standardproben (Abb. 1) schon bei einem Graphit/Matrix-Verhältnis von 3:7 zur Eliminierung der Matrixeffekte im Falle von Granit und Basalt geführt. Bei der Tonschiefer-Matrix, die bedeutende Unterschiede im kristallchemischen Charakter aufweist, wurde auch für das Mischverhältnis von 9:1 keine allgemeine Eliminierung der Matrixeffekte erreicht. Man darf nicht vergessen, daß beim Tonschiefer Hellglimmer, Chlorit und teilweise Quarz; beim Granit dagegen Plagioklas, Kalifeldspat und Quarz bzw. beim Basalt

**Tabelle III**

*Verwendete Spektrallinien*

| Element | Wellenlänge [nm] | Intensität im Cu-Bogen | Ionisationspotential [kJ · mole$^{-1}$] | Anregungspotential [kJ · mole$^{-1}$] |
|---|---|---|---|---|
| A. Linien der thermometrischen V-Elemente | | | | |
| V II | 310,23 | 400 | 650,3 | 418,8 |
| V I | 318,54 | 500 | 650,3 | 382,1 |
| B. Linien der analytischen Elemente | | | | |
| Cd I | 326,11 | 32 | 867,5 | 366,7 |
| Cd I | 346,62 | 250 | 867,5 | 711,1 |
| Co I | 340,92 | 280 | 758,4 | 400,4 |
| Co I | 345,35 | 1300 | 758,4 | 387,9 |
| Cr I | 301,52 | 90 | 652,3 | 489,2 |
| Cr I | 302,16 | 360 | 652,3 | 495,0 |
| Mn I | 322,81 | 160 | 716,92 | 575,1 |
| Mn I | 323,68 | 130 | 716,92 | 577,0 |
| Mo I | 313,26 | 1800 | 685,1 | 382,1 |
| Mo I | 317,03 | 1100 | 685,1 | 377,3 |
| Ni I | 305,08 | 280 | 736,2 | 394,6 |
| Ni I | 344,63 | 440 | 736,2 | 357,0 |
| Sc I | 326,99 | 400 | 631,0 | 365,7 |
| Sc I | 327,36 | 500 | 631,0 | 367,6 |
| Sn I | 283,99 | 1400 | 708,2 | 461,2 |
| Sn I | 317,50 | 550 | 708,2 | 417,8 |
| Ti I | 295,61 | 150 | 658,1 | 409,1 |
| Ti I | 337,14 | 360 | 658,1 | 358,9 |
| V I | 318,34 | 420 | 650,3 | 377,3 |
| V I | 318,40 | 700 | 650,3 | 380,2 |
| W I | 289,46 | 190 | 770,0 | 446,7 |
| W I | 294,70 | 300 | 770,0 | 491,0 |
| Zn I | 334,50 | 140 | 906,0 | 750,7 |
| Zn I | 334,56 | 30 | 906,0 | 750,7 |
| C. Bezugslinien | | | | |
| Pd I | 302,79 | 130 | 803,8 | 487,3 |
| Pd I | 346,08 | 850 | 803,8 | 424,6 |

Bewirkung:
Der Umrechnungsfaktor [37] für (SI-Einheiten)
1 kJ · $M^{-1} = 0{,}01036$ [eV].

**Tabelle IV**

*Chemische Zusammensetzung der Modellmatritzen*

| Komponente | Matrix | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
| $SiO_2$ | 73,30 | 49,42 | 60,11 | 95,54 | 60,80 | 54,94 | 47,71 | 72,53 | 60,00 |
| $Al_2O_3$ | 13,68 | 16,68 | 20,89 | 2,32 | 14,79 | 18,81 | 16,58 | 12,57 | 16,00 |
| $Fe_2O_3$ | 0,78 | 1,64 | 0,97 | 0,57 | 5,70 | 2,70 | 4,29 | 2,73 | 7,00 |
| FeO | 1,23 | 7,31 | 5,40 | — | 0,60 | 3,40 | 6,76 | 0,70 | — |
| MnO | 0,04 | 0,15 | 0,06 | — | 0,12 | 0,07 | 0,16 | 0,04 | — |
| $TiO_2$ | 0,22 | 1,45 | 0,91 | 0,06 | 0,53 | 1,18 | 2,05 | 0,58 | — |
| $P_2O_5$ | 0,06 | 0,10 | 0,09 | — | 0,93 | 0,40 | 0,57 | 0,08 | — |
| MgO | 0,40 | 7,46 | 1,95 | 1,00 | 2,50 | 2,50 | 5,72 | 1,59 | 4,00 |
| CaO | 1,10 | 6,49 | 0,39 | 0,31 | 5,22 | 7,42 | 9,45 | 1,10 | 6,00 |
| $Na_2O$ | 3,75 | 4,60 | 1,28 | — | 4,05 | 4,04 | 3,12 | 2,34 | 7,00 |
| $K_2O$ | 4,67 | 0,19 | 3,80 | 0,19 | 2,00 | 2,36 | 2,20 | 4,49 | — |
| $+H_2O$ | 0,35 | 3,63 | 3,76 | 0,20 | 0,40 | 1,55 | 0,89 | 0,05 | — |
| $-H_2O$ | 0,25 | 1,35 | 0,11 | 0,03 | 2,90 | 0,28 | 0,21 | 1,73 | — |

Bemerkung:

Matrix 1 bis 3: Gesteinsstandarde aus ZGI, Berlin (1 — Granit, 2 — Basalt, 3 — Tonschiefer)

Matrix 4 bis 8: Slowakische Gesteinsproben (5 — Granodiorit aus Banská Hodruša, 4 — Quarzit aus Sklenné Teplice, 6 — Andesit aus Banská Hodruša, 7 — Basalt aus Ochtinná, 8 — saurer Granodiorit aus Zlatá Idka)

Matrix 9: Synthetische Modellmatrix mit 1% Spurenelementgehalt.

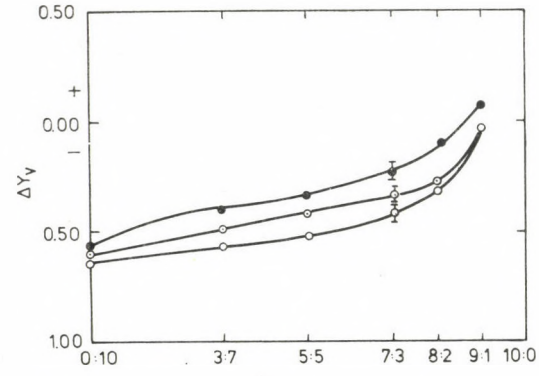



*Abb. 1.* Verlauf der $\Delta Y_V$-Indexwerte in Abhängigkeit vom Mischverhältnis Graphit zu Matrix, ZGI-Standarde: ● Tonschiefer-Matrix, ○ Granit-Matrix, ⊙ Basalt-Matrix

**Tabelle V**

*Testprüfungen der Parameter von Streudiagrammen*

| Analytische Linienpaar | Testergebnisse | | | |
|---|---|---|---|---|
| | $t_{r=0}$ | $t_{sY_X=sY_R}$ | $t_{wX=w_w}$ | $t_{s\Delta Y<sY_X}$ |
| Cd 326,11 / Pd 302,79 | — | + | + | + |
| Co 345,35 / Pd 346,08 | — | + | — | + |
| Cr 301,52 / Pd 302,79 | — | + | + | + |
| Mn 322,81 / Pd 346,08 | + | | | |
| Mo 313,26 / Pd 346,08 | — | + | + | + |
| Ni 305,08 / Pd 346,08 | — | + | — | + |
| Sc 327,36 / Pd 346,08 | — | + | — | + |
| Sn 317,50 / Pd 346,08 | + | | | |
| Ti 337,14 / Pd 346,08 | — | + | + | + |
| V 318,40 / Pd 346,08 | — | + | + | + |
| W 294,70 / Pd 302,79 | — | + | + | + |
| Zn 334,56 / Pd 302,79 | — | + | + | + |

Albit, Hornblende und Pyroxene die mineralische Hauptkomponenten [25] darstellen. Eine Zugabe von 1 Teil Bariumkarbonat zu diesen Mischungen [27] hatte sofort eine günstige Wirkung, aber die vollkommene Eliminierung der Matrixeffekte [28] wurde nur bei 2 Teile Bariumkarbonat enthaltenden Mischungen erreicht (Abb. 2). Die Mischverhältnisse mit 2 Teilen Bariumkarbonat, wobei die Graphitzugabe eigentlich bis auf 2 Teile vermindert und die Zugabe der analysierenden Matrix auf 7 Teile gesteigert werden kann, sind nicht nur wegen der Eliminierung der Matrixeffekte, sondern auch für die Verbesserung des Nachweisvermögens der Spurenelemente außerordentlich wichtig.

Die Untersuchungen von typischen slowakischen Gesteinsproben [23, 24] haben gezeigt, daß die Untersuchungen in unverdünntem Zustand ausgenommen, die Matrixeffekte bei der ausschließlich Graphitzugabe für alle Mischverhältnisse signifikant identisch sind (Abb. 3). Für die Basalte konnte

**Tabelle VI**

*Parameter- und Testwerte der optimalen analytischen Eichgeraden*

| Analytische Linienpaar | Parameter- und Testwerte | | | | |
|---|---|---|---|---|---|
| | $R$[%] | ${}^{t}B_X=1$ | $c_L \cdot 10^4$ [%] | $c_G \cdot 10^4$ [%] | ${}^{s}c_{X,r}$[%] |
| Cd 326,11 / Pd 302,79 | 93,2 | + | 10,0 | 13,0 | ±22,5 |
| Co 345,35 / Pd 346,08 | 92,6 | + | 11,0 | 14,0 | ±9,3 |
| Cr 302,16 / Pd 302,79 | 97,6 | — | 12,0 | 17,0 | ±16,5 |
| Mo 313,26 / Pd 302,79 | 85,8 | — | 1,1 | 2,0 | ±39,4 |
| Ni 305,08 / Pd 346,08 | 97,7 | — | 11,0 | 12,0 | ±19,0 |
| Sc 327,36 / Pd 346,08 | 91,3 | + | 69,0 | 76,0 | ±28,8 |
| Sn 317,50 / Pd 346,08 | 94,8 | + | 5,8 | 6,5 | ±21,0 |
| Ti 337,14 / Pd 346,08 | 94,9 | — | 9,3 | 13,0 | ±21,2 |
| V 318,40 / Pd 346,08 | 97,9 | + | 6,6 | 7,8 | ±17,6 |
| W 294,70 / Pd 302,79 | 80,3 | — | 330,0 | 440,0 | ±49,6 |
| Zn 334,50 / Pd 302,79 | 94,6 | — | 57,0±8,0 | 75,0±9,0 | ±24,7 |

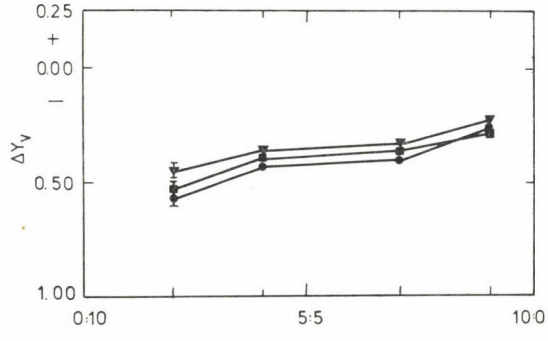



*Abb. 2.* Verlauf der $\Delta Y_V$-Indexwerte in Abhängigkeit vom Mischverhältnis Graphit zu Matrix mit 2 Teilen Bariumkarbonat, ZGI-Standarde: ■ Tonschiefer-Matrix, ● Granit-Matrix, ▼ Basalt-Matrix

**Tabelle VII**

*Vergleich der analytischen Konzentrationswerte $c_{X,i} \pm s_{c_{X,i}}$ mit den „wahren" $c_0$-Werten für sechs internationale Standardprobe*

| Element | Literaturangaben | ZGI — Standarde | | | USGS — Standarde | | MRT — Standard |
|---|---|---|---|---|---|---|---|
| | | G | B | T | G-1 | W-1 | T-1 |
| Co | Eigene Angabe | 11,9 ± 1,5 | 37,3 ± 3,7 | 23,0 ± 6,2 | (9,0) | 44,3 | 24, ± 2,2 |
| | Lit. Ang. [34] | 1,9 | 30,0 | 16,0 | 2,0 | 53,0 | 11,26 |
| | „WW" | 4,3 | 31,8 | 16,1 | 2,4 | 50,0 | 13,0 |
| Cr | Eigene Angaben | (8,4 ± 1,3) | 117,0 ± 24,0 | 76,2 ± 22,2 | (8,3) | 120,0 | 22,3 ± 2,6 |
| | Lit. Ang. [34] | 12,0 | 135,0 | 98,6 | 17,0 | 125,0 | 22,5 |
| | „WW" | 7,9 | 111,7 | 63,0 | 22,0 | 120,0 | 24,0 |
| Mo | Eigene Angabe | 3,9 ± 1,2 | 3,8 ± 2,1 | 5,0 ± 2,1 | 4,5 | 7,6 | 3,7 ± 0,3 |
| | Lit. Ang. [34] | <3 | <5 | <3 | 7,4 | <5 | <3 |
| | „WW" | 1,0 | 1,0 | 2,0 | 7,0 | 0,5 | 2,5 |
| Ni | Eigene Angabe | — | 62,2 ± 13,3 | 44,3 ± 13,3 | — | 69,2 | 16,2 |
| | Lit. Ang. [34] | 5,9 | 61,0 | 37,1 | 1,2 | 76,0 | 12,2 |
| | „WW" | 8,2 | 53,0 | 38,5 | 1,0 – 2,0 | 78,0 | 13,0 |
| Sc | Eigene Angabe | — | 117,0 ± 42,0 | 74,1 | — | 143,0 | 97,5 |
| | Lit. Ang. [34] | 4,5 | 35,0 | 15,6 | 3,6 | 44,4 | 14,6 |
| | „WW" | 5,0 | 30,3 | 16,6 | 3,0 | 34,0 | 14,5 |
| Sn | Eigene Angabe | 5,8 ± 0,7 | 6,5 | 9,9 ± 1,9 | (5,4) | 10,8 | 48,2 ± 6,3 |
| | Lit. Ang. [34] | 6,5 | 1,9 | 7,7 | 5,0 | 2,9 | 53,0 |
| | „WW" | 4,5 | 2,0 | 8,0 | 4,0 | 3,0 | 43,0 |
| V | Eigene Angabe | 11,8 ± 1,1 | 157,0 ± 41,0 | 73,5 ± 14,5 | 103,0 | 161,0 | 69,5 ± 15,1 |
| | Lit. Ang. [34] | 23,0 | 34,7 | 36,0 | 35,0 | 250,0 | 86,6 |
| | „WW" | 40,0 | — | — | 37,0 | 240,0 | 96,0 |
| Zn | Eigene Angabe | 118,0 ± 53,0 | 88,6 ± 27,8 | 108,0 ± 17,0 | (35,3) | 207,0 | 146,0 ± 36,0 |
| | Lit. Ang. [34] | 48,0 | 90,0 | 98,0 | 46,0 | 82,0 | 123,0 |
| | „WW" | 46,0 | 103,0 | 102,0 | 45,0 | 82,0 | 190,0 |

Bemerkungen:

G — Granodiorit-Matrix, B — Basalt-Matrix, T — Tonschiefer-Matrix; G-1, W-1 USGS — Standarde [32]; T — 1 MRT — Standard [36].

Die Konzentrationsangaben $c_{X,i} \pm s_{cX\,i}$ sowie die Standardabweichungen sind in ppm-Einheiten angegeben. Die Standardabweichungen wurden nur für die Proben ermittelt, von denen mindestens drei Parallelmessungen durführbar waren.

„WW" sog. wahre Konzentrationswerte laut Literaturangaben [32, 35, 36].

Angaben in Klammern () sind kleiner als der festgelegte Wert der Nachweisgrenze.

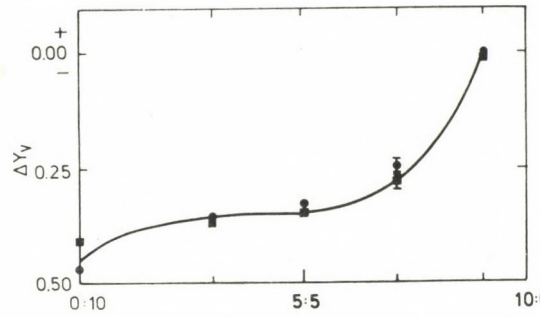



*Abb. 3.* Verlauf der $\Delta Y_V$-Indexwerte in Abhängigkeit vom Mischverhältnis Graphit zu Matrix mit 1 Teil Bariumkarbonat, slowakische Gesteinsproben: ● Andesit-Matrix, ▼ Granit-Matrix

die Eliminierung der Matrixeffekte nur für das Verdünnungsverhältnis von 1:9 erreicht werden. Der Verlauf der $\Delta Y_V$-Indexwerte für die hochsauren Quarzite verläuft oberhalb der $\Delta Y_V$-Werte der sauren Granodiorite und pyroxenischen Andesite. Aber auch für das extrem hohe Verdünnungsverhältnis von 1:99 ist die erwünschte signifikante Vereinheitlichung noch nicht erreicht. Die Anwendung von weiteren spektrochemisch aktiven Beimischungen [27] hat die Lage verbessert. Bei den Beimischungen von 1 Teil Bariumkarbonat zu den oben angegebenen Grundmischungen wurde für die intermediären Gesteine und auch für saure Granite und Granodiorite bei allen Mischverhältnissen eine signifikante Vereinheitlichung der $\Delta Y_V$-Werte erreicht. Die $\Delta Y_V$-Werte der basischen Basalte zeigen dagegen nur für das hohe Mischverhältnis von 1 Teil Probe zu 9 Teilen Graphit und 1 Teil Bariumkarbonat die erwünschte signifikante Übereinstimmung mit den $\Delta Y_V$-Werten der anderen Matrizen. Leider weichen die $\Delta Y_V$-Werte der Quarzite so weit von allen anderen $\Delta Y_V$-Werten ab, daß es überflüssig war, diese graphisch in Abbildung 3 darzustellen. Schließlich hat die Zugabe von 2 Teilen Bariumkarbonat zu allen Matrix-Graphit-Mischungen (Abb. 4) noch ergeben daß die Mischverhältnisse von

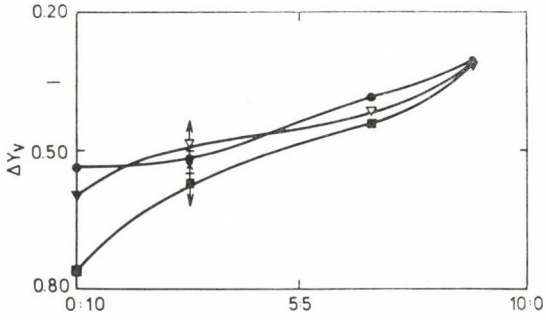



*Abb. 4.* Verlauf der $\Delta Y_V$-Indexwerte in Abhängigkeit vom Mischverhältnis Graphit zu Matrix mit 2 Teilen Bariumkarbonat, slowakische Gesteinsproben: ● Andesit-Matrix, ▼ Granodiorit-Matrix, ■ Basalt-Matrix

Probe zu Graphitpulver und Bariumkarbonat in dem breiten Mischverhältnis-Intervall von 8:2:2 bis 3:7:2 die Eliminierung der Matrixeffekte, mit Ausnahme der von hochsauren Quarziten, ausreichend gewährleisten [27, 28].

### 4.2. *Verfolgung der Verdampfungseigenschaften*

Bei der Verfolgung der Verdampfungseigenschaften wurde erhöhte Aufmerksamkeit den drei typisch unterschiedlichen Matrizen Granodiorit (G), Andesit (A) und Basalt (B) sowie der synthetischen Modellmatrix (SM) gewidmet. Die Unterschiedlichkeiten sind in den Abbildungen 5 (V/Pd-Linienpaar) und 6 (Zn/Pd-Linienpaar) veranschaulicht. Vanadin wurde als typisches Beispiel für schwerflüchtige Elemente und Zink für leichtflüchtige Elemente gewählt. Aus diesen zwei graphischen Darstellungen der integralen Beziehungskurven ist ersichtlich, daß mit Ausnahme des Verlaufes der Zn/Pd-Kurve der SM-Matrix alle Abhängigkeiten im Rahmen der Meßfehler linear sind. Der Verlauf der Beziehungskurven der schwerflüchtigen Elemente (Abb. 5) wird vom Charakter der Matrix teilweise beeinflußt. Die Intensitätszunahmen sind beim Granodiorit und Andesit signifikant größer als die Intensitätszunahmen der Basaltmatrizen, hauptsächlich im zweiten Teil der Exposition. Das Verhalten der SM-Matrizen im zweiten Teil der Exposition ist ziemlich unregelmäßig. Diese Unterschiede lassen die Vermutung aufkommen, daß trotz der erfolgreichen Eliminierung der Matrixeffekte die Spurenelemente bei der thermischen Zersetzung teilweise unterschiedlich freigesetzt werden. Da aber

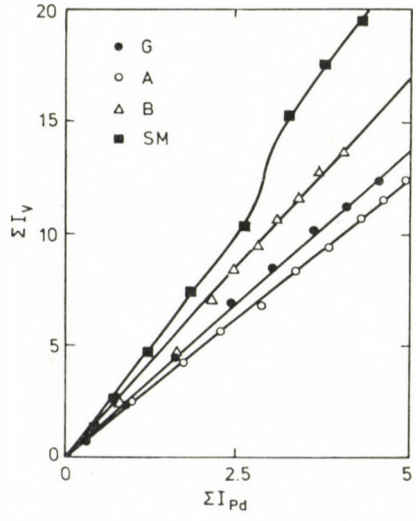



*Abb. 5.* Integrale Verdampfungskurven der analytischen Linienpaare V 318,34/Pd 302,79 in unterschiedlichen Matrizen, ● Granodiorit-Matrix, ○ Andesit-Matrix, ▽ Basalt-Matrix, ■ synthetische Modellmatrix SM

diese Prozesse die Verdampfung des beigemengten PdO im gleichen Maße beeinflussen, führen diese Unterschiede nicht zu einem systematischen Fehler. Bei der Verfolgung der Verdampfung von leichtflüchtigen Elemente (Abb. 6) sieht die Lage noch günstiger aus. Die Kurven für saueren Granodiorit und intermediären Andesit überlagern sich innerhalb der Meßfehler, und teilweise trifft dies auch für die Kurven für die Basalt- und SM-Matrix zu. Die Differenz zwischen den beiden genannten Gruppen wird wiederum durch die proportionale Veränderung der Verdampfung des analytischen und des Bezugselementes kompensiert.

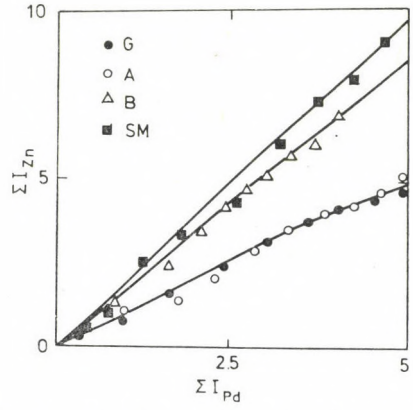



*Abb. 6.* Integrale Verdampfungskurven der analytischen Linienpaare Zn 334,50/Pd 302, 79 in unterschiedlichen Matrizen, ● Granodiorit-Matrix, ○ Andesit-Matrix, ▽ Basalt-Matrix, ■ synthetische Modellmatrix

Hier sei noch erwähnt, daß die integralen Beziehungskurven für einige spektro- und thermochemisch sich unterschiedlich verhaltende Elemente in einer SM-Matrix (Abb. 7) deutliche Unterschiede aufgewiesen haben. Am regelmäßigsten verdampfen die schwerflüchtigen Elemente, wie Sn (und z.B. auch Co, Cr, Ni, Ti); die leichtflüchtigen Elemente, wie z.B. Cd, aber auch Ag und Cu, zeigen neben dem unregelmäßigeren Verlauf auch eine bedeutende Senkung der Verdampfung nach einer Exposition von etwa 40 bis 60 Sekunden. Schließlich sind einige Elemente, wie z.B. W, wegen ihrer schwächeren Linienintensitäten durch flachverlaufende Kurven repräsentiert, die die Auswertung des Verdampfungscharakters nur begrenzt erlauben.

Im ganzen genommen haben für die Expositionszeit von 60 Sekunden alle integralen Beziehungskurven eine annehmbare Proportionalität für die Verdampfung der analytischen Elemente und des Pd-Bezugselements bestätigt, so daß diese Wahl gerechtfertigt ist.

### 4.3. *Beurteilung und Optimalisierung der analytischen Linienpaare*

Die Beurteilung und Optimalisierung der optimalen analytischen Linienpaare wurde aufgrund der folgenden Sequenz und Resultate der Testprüfungen ausgeführt: die Prüfung der Übereinstimmung der Werte der Korrelationskoeffizienten mit Null muß abgelehnt werden, die Prüfung der Übereinstimmung der Standardabweichungswerte $s_{Y_X}$ mit den $s_{Y_R}$ muß Signifikanz ergeben und die Standardabweichungswerte $s_{\Delta Y}$ und $s_{Y_X}$ müssen entweder gleich sein oder aber die Prüfung muß die Hypothese $s_{\Delta Y} < s_{Y_X}$ bestätigen. Die Prüfung der Übereinstimmung der Werte $w_X$ und $w_R$ spielt eigentlich nur bei der Bestimmung der idealen Homologie eine gewisse Rolle [15].

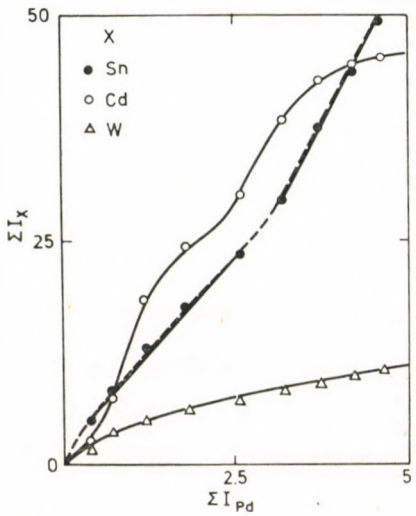



*Abb. 7.* Integrale Verdampfungskurven von drei analytischen Linienpaaren in der syntetischen Modellmatrix SM, ● Sn 284,00/Pd 302,79, ○ Cd 326,11/Pd 302,79, ▽ *W* 294,70/Pd 302,79

In Tabelle V angeführten Ergebnisse zeigen, daß es möglich war, in den meisten Fällen ein gut korrelierendes Linienpaar zu finden. Die angegebenen Werte wurden aufgrund der ermittelten Korrelation und Standardabweichung $s_{\Delta Y}$ ausgewählt. Ausnahmen bilden die Mn/Pd- und Sn/Pd-Linienpaare, wo bereits die erste Testprüfung, die Prüfung des Korrelationskoeffizienten die Signifikanzgrenze erreichte. Diese ungünstigen Parameter wurden jedoch ausschließlich durch schwärzungsmeßtechnische Faktoren [29, 30] hervorgerufen. Bei Schwärzungswerten der analytischen Linie oberhalb 1,50 S und unterhalb 0,35 ist nähmlich die Aussage der kombinierten Korrelations-Regressionsanalyse sehr fraglich [29]. Bei den anderen Linienpaaren wurde eine geringere Zahl von ausreichenden Fällen gefunden, dies ist aber bei den Multielementanalysen eine allgemein anerkannte Tatsache, da für alle Elemente

und Linien nicht alle Anregungsparameter im gleichen Maß optimalisiert werden können.

Die weiteren Experimente haben gezeigt, daß auch für die Mn- und Sn-Linien eine annehmbare Korrelation erreicht werden kann.

### 4.4. *Verlauf der analytischen Eichgeraden und die statistische Bewertung deren Parameter*

Zuerst wurden die analytischen Eichgeraden für alle potentiell möglichen Kombinationen der analytischen Linien und der zwei Pd-Bezugslinien experimentell ermittelt und die endgültigen Kombinationen aus dieser Matrix der Teilergebnisse ausgewählt. Die Tabelle VI faßt nur die endgültigen optimalisierten Ergebnisse samt der ermittelten Werten der Nachgeweisgrenzen und Garantiegrenzen zusammen, deren Ermittlung [31] durch Aufstellung der analytischen Eichgeraden erfolgt. Zwischen den analytischen Linienpaaren der Tabelle V und VI kann man gewisse Unterschiede feststellen, die davon kommen, daß nicht unbedingt durch Streudiagramme optimalisierte analytische Linienpaare optimalverlaufende analytische Eichgeraden sichern. Meistens findet man eine gute Übereinstimmung. Wenn bei der Aufstellung der analytischen Eichgeraden ein anderes Linienpaar des gleichen Elementes ausgewählt wird, so liegen die Werte der Streudiagrammparameter dieses Linienpaares fast so hoch wie die Werte des optimal befundenen Linienpaares.

Die optimalisierten analytischen Eichgeraden weisen mindestens 80%-ige Bestimmtheitsmaßwerte, auf die Richtungstangenten sind entweder signifikant gleich 1, oder aber sie erreichen den Wert 0,80. Für W und teilweise auch für Sc wurden ziemlich ungünstige Nachweisgrenzwerte gefunden, bei anderen lag diese Grenze bei $10^{-3}$% bis $5.10^{-4}$%. Mit Ausnahme von Mo und W lag der $s_{c_{X,r}}$-Wert, der eigentlich auch die relative Präzision der Eichung darstellt, unterhalb $\pm 25$%, was für die Spurenelementebestimmung noch annehmbar ist. Schließlich soll noch bemerkt werden, daß Mn in Silikatgesteinen kein Spurenelement darstellt, und deshalb wurde in der letzten Phase der Ausarbeitung der Methode von dessen Bestimmung abgesehen. Weiter wurde auch die Möglichkeit der Ag- und Cu-Bestimmung verfolgt, aber die zur Verfügung stehenden Chemikalien, aus denen die Modellmatrix zusammengestellt wurde, war so weit mit Ag und Cu verunreinigt, daß es unmöglich war, diese Elemente zu bestimmen.

### 4.5. *Prüfung der Richtigkeit der ausgearbeiteten analytischen Methode*

Wie im allgemeinen anerkannt wird, ist die Prüfung der Richtigkeit einer analytischen Methode, das heißt die Übereinstimmung der ermittelten Konzentrationswerte $c_X$ mit den „wahren Werten" $c_0$ [32, 35, 36] eine offene

Frage, da gerade die Bestimmung der sog. wahren Werte („WW") prinzipiell auch durch Streuung der Werte der experimentellen Bestimmung sowie durch evtl. systematische Fehler belastet sein können.

In der emissionsspectrochemischen Praxis wurde diese Frage umgegangen, indem man die „spektrochemischen natürlichen Standarde" in die Praxis einführte [32—34]. Diese wurden von mehreren anerkannten Laboratorien analysiert, u.zw. auch auf den Spurenelementegehalt, und die „wahren" Konzentrationswerte wurden nach einem komplizierten Verfahren [33, 35] erhalten.

Die Standarde G-1 (Granitmatrix), W-1 (Basaltmatrix) und T-1 (Tonalitmatrix) sowie die ZGI-Standards wurden auch mit der neu ausgearbeiten Methode analysiert und in Tabelle VII sind diese erhaltenen Werte den empfohlenen „wahren" Werten gegebenübergestellt.

Im allgemeinen wurden, hauptsächlich wenn man die konkreten Standardabweichungswerte $s_{c_{X,i}}$ in Betracht zieht, gut übereinstimmende Werte erhalten (Tab. VII). Dieses Ergebnis erlaubt die Feststellung, daß die neuentwickelte Methode solche analytischen Angaben liefert, die frei von systematischen Fehlern sind. Die Bestimmung von Sc stellt jedoch eine Ausnahme dar, da die Konzentrationswerte, die mit der neuentwickelten Methode erhalten wurden, im allgemeinen um den Faktor 3 höher als die sog. wahren Werte [33, 35, 36] liegen. Höchstwahrscheinlich wurde diese Verschiebung der Konzentrationswerte für Sc durch die Verunreinigungen im Puffer verursacht.

## LITERATUR


[1] Matherny, M.: Chem. Anal. (Warszawa), **11,** 1053 (1966)
[2] Kaiser, H.: Z. Anal. Chem., **216,** 80 (1966)
[3] Holdt, G.: Appl. Spectry. **16,** 96 (1962)
[4] Matherny, M.: Chem. Anal. (Warszawa), **21,** 339 (1976)
[5] Flórián, K.: Kémiai Közlemények, **48,** 167 (1977)
[6] Matherny, M.: Chem. Anal. (Warszawa), **21,** 1053 (1976)
[7] Flórián, K., Matherny, M.: Sborník ved. prác VST, Košice, **1977,** tv, 2
[8] Plško, E.: Chem. Zvesti, **18,** 830 (1964)
[9] Flórián, K.: Chem. Zvesti, **28,** 306 (1974)
[10] Keddy, R. J., Strasheim, A.: Appl. Spectry., **12,** 29 (1958)
[11] Holdt, G., Strasheim, A.: Appl. Spectry., **14,** 64 (1960)
[12] Holdt, G.: Emissionsspektroskopie, Akademie Verlag, Berlin 1964, S. 63
[13] Plško, E.: Collection Czech. Chem. Commun., **30,** 1246 (1965)
[14] Matherny, M.: Chem. Zvesti, **24,** 112 (1970)
[15] Matherny, M.: Spectroscopy Letters, **6,** 711 (1973)
[16] Flórián, K., Lavrin, A., Matherny, M.: Chem. Zvesti, **27,** 623 (1973)
[17] Matherny, M.: Chem. Zvesti, **24,** 121 (1970)
[18] Matherny, M.: Proceedings XIV. Coll. Spectrosc. Internat., Heidelberg 1971, Vol. II., S. 19
[19] Matherny, M.: Z. Anal. Chem., **271,** 101 (1974)
[20] Török, T., Zimmer, K.: Quantitative Evaluation of Spectrograms by Means of I-Transformation, Akadémiai Kiadó, Budapest 1972
[21] Matherny, M.: Kémiai Közlemények, **48,** 183 (1977)
[22] Meggers, W. F., Corliss, Ch. H., Scribner, B. F.: Tables of Spectral-Line Intensities, NBS Monograph No. 53, 1961

[23] JARKOVSKÝ, J.: Geol. práce, Zošit 36, S. 106 (1954)
[24] BELEŠOVÁ, O., DÁVIDOVÁ, Š., MATHERNY, M.: Acta Rer. Natur. Nat. Mus. Slov., **IX**, 11 (1963)
[25] GRASSMANN, H.: Z. angew. Geol., **12**, 368 (1966)
[26] FILO, O., LAVRIN, A., MATHERNY, M.: Acta. Geol.-Geograph. Univ. Commenianae, Geologica No. 15, S. 219 (1968)
[27] FILO, O., MATHERNY, M., RYBÁROVÁ, Ž.: Proceedings XIV. Coll. Spectrosc. Internat., Debrecen 1967, S. 955
[28] FILO, O., MATHERNY, M.: Nichtveröffentlichte Angaben
[29] MATHERNY, M.: Spectroscopy Letters, **9**, 113 (1976)
[30] FLÓRIÁN, K.: Kémiai Közlemények, im Druck
[31] KAISER, H.: Optik, **21**, 309 (1964)
[32] FLEISCHER, M.: Geochim. Cosmochim. Acta **31**, 65 (1965)
[33] FLANAGAN, F. J.: Geochim. Cosmochim. Acta, **33**, 81 (1969)
[34] HUBER-SCHAUSBERGER, I., JANDA, I., DOLEZAL, P., SCHROLL, E.: Tschermaks Mineral. Petrogr. Mitt., **14**, 195 (1970)
[35] SCHINDLER, R.: Z. angew. Geol., **12**, 188 (1966)
[36] THOMAS, W. K. L., KEMPE, D. R. C.: Rep. Geol. Survey, Tanganyika, Suppl. No. 1, 1 (1963)
[37] HUHEEY, J. E.: Inorganic Chemistry — SI Units Edition, Harper and Row, New York 1975

Ondrej FILO—Mikuláš MATHERNY

Lehrstuhl für Chemie der Hüttenmännischen Fakultät der Technischen Hochschule in Košice
Švermova 9,
04385 Košice

*Acta Chimica Academiae Scientiarum Hungaricae, Tomus 98 (1), pp. 29—36 (1978)*

# EINE APPARATIVE ERWEITERUNG DER MIKROKATALYTISCHEN ODER PULS-TECHNIK

J. LATZEL

*(Institut für Physikalische Chemie der TU-Wien)*

Eingegangen am 13. April, 1977, in umbearbeiteter Form am 5. Oktober, 1977

Ein adaptierter Gaschromatograph gestattet nicht nur eine Erweiterung der klassischen Puls-Technik durch neuere gaschromatographische Techniken, sondern auch die Durchführung von Temperaturprogrammierter Desorption (TPD), sowie von Vergiftungsexperimenten.

Für die Untersuchung heterogen katalysierter Reaktionen sind mehrere Methoden bekannt. Die erstmals von KOKES [1] beschriebene mikrokatalytische Technik besteht darin, daß eine kleine Menge Reaktant mit einer Injektionsspritze in einen kontinuierlichen Trägergasstrom eingebracht wird. Der Puls passiert das Katalysatorbett, setzt sich um, und die entstehenden Produkte werden in einen Gaschromatographen gespült und analysiert. Nähere Details finden sich u.a. bei ZOIDL [7], ANDREV [6] und DORAISWAMY [2]. Theoretische Überlegungen wurden von HATTORI [3] angestellt.

Das gelegentliche Auftreten komplexer Reaktionsgemische, sowie der Wunsch, aus den Versuchen möglichst viel Information zu erhalten, hat zur Entwicklung der hier beschriebenen Apparatur geführt. Neben der klassischen Pulstechnik mit 1 Säule können damit eine Reihe anderer Trenn- und Untersuchungstechniken angewandt werden.

## Die Apparatur

Als Gaschromatograph dient ein VARIAN Aerograph 1520, ausgerüstet mit WLD und FID, für jeden Detektor ist ein Schreiber vorhanden. Ein HAAKE KT-32 Kryostat erlaubt Trennbedingungen bei Temperaturen unterhalb der Raumtemperatur (Abb. 1). Zwei Säulen kommen in verschiedenen Kombinationen zur Anwendung (Abb. 2a, 2b).

Der Katalysator (Pulverform) befindet sich in einem Quarzrohr (Länge ca. 300 mm, Innendurchmesser 6 mm) zwischen zwei Quarzwollstopfen. Der Reaktor-Ofen besteht aus einem Keramikrohr mit Heizdrahtwicklung und Thermoelement. Zum raschen Abkühlen ist er in ein Aluminiumgehäuse montiert, durch das kalte Luft geblasen werden kann.

## Zweidimensionale Gaschromatographie

Eine beliebte Testreaktion für Katalysatoren ist die Eliminierungsreaktion

$$2\text{-BuOH} \rightarrow H_2O + \text{Butene}$$

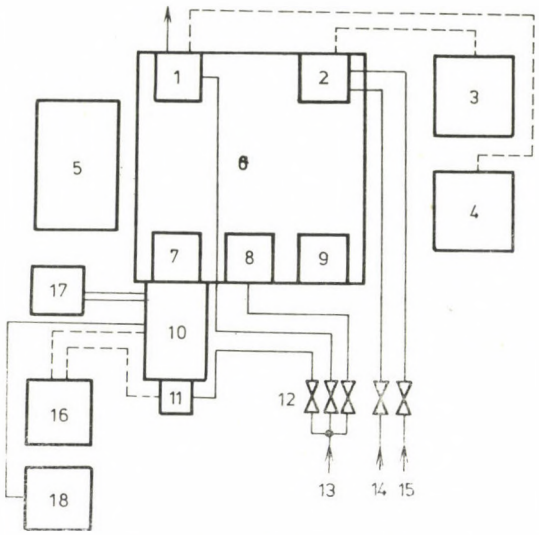



*Abb. 1.* Aufbau der Mehrzweck-Pulsapparatur (Die verschiedenen Kombinationen von Trennsäulen mögen Abb. 2a und 2b entnommen werden): 1 Wärmeleitfähigkeitsdetektor (WLD); 2 Flammenionisationsdetektor (FID); 3 Schreiber 2 für FID; 4 Schreiber 1 für WLD; 5 Kryostat, HAAKE KT-32; 6 Säulenofen des Gaschromatographen, VARIAN Aerograph 1520; 7 Einspritzblock A; 8 Einspritzblock B; 9 Einspritzblock C; 10 Reaktorofen; 11 heizbarer Einspritzteil; 12 Regelventil der Gasversorgung; 13 He-Versorgung für Reaktor, WLD-Referenz und Einspritzblock B; 14 $H_2$-Versorgung für FID; 15 Luft-Versorgung für FID; 16 Temperaturmeßgerät für Reaktor und Einspritzteil; 17 Gebläse für Kühlluft; 18 Elektronische Temperatursteuerung für Reaktorofen; 19 Detektorauslaß (WLD)

Den Katalytiker interessiert hierbei nicht nur die Menge an umgesetztem Reaktant, sondern auch die Verteilung der vier isomeren Butene. Bei mikrokatalytischen Techniken in früheren Arbeiten [7—9] wurde so verfahren, daß zunächst der Umsatz (Menge an entstandenem Buten, bezogen auf eingesetzte Butanolmenge) bestimmt wurde, in einem Parallelversuch die Produktverteilung (Zusammensetzung des Butenisomerengemisches). Die chromatographische Trenntechnik wurde im 2. Fall so ausgelegt, daß nur die Butene getrennt und angezeigt wurden. Butanol und $H_2O$ blieben auf der Säule adsorbiert.

Gegenüber früheren Arbeiten [7—9] kann mit der beschriebenen Apparatur (Abb. 2a) der Umsatz und die Produktverteilung von einunddemselben Puls mittels zweidimensionaler Auftrennung ermittelt werden. Die Reaktionsprodukte ($H_2O$, Butene) werden in Säule $S_1$ aufgetrennt, vom WLD angezeigt und mit Schreiber 1 registriert.

Das unaufgetrennte Butengemisch (1. Peak im Chromatogramm) kann auf Säule $S_2$ wie folgt analysiert werden: Der Buten-Peak hat eine Basisbreite von etwa 20 Sekunden. Während dieser Zeit liegt das Butengemisch am Auslaß des Detektors (WLD) vor (Pkt. 19 in Abb. 1). Unter Beobachtung des Schreibersignals wird durch langsames gleichmäßiges Aufziehen einer 1 ml

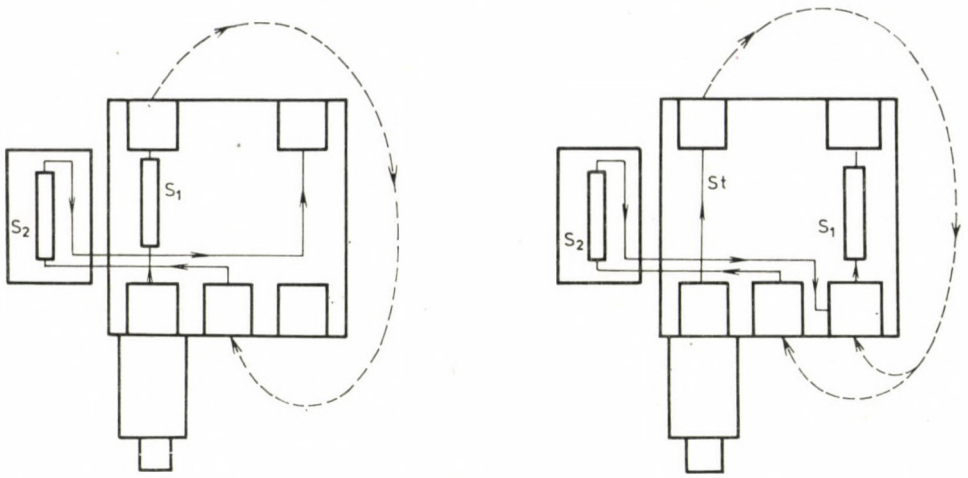



*Abb. 2a, Abb. 2b.* Schalten der Trennsäulen für verschiedene Untersuchungstechniken mit der Mehrzweckpulsapparatur (nach Abb. 1)
Durchführung der Analyse siehe Text. a) zweidimensionale Gaschromatographie; b) Serienschaltung zweier Säulen: $S_1$ 15% Carbowax 1500 auf Chromosorb W, 60—80 mesh, 1/8" Stahlsäule, 1 m lang, 75—100 °C, 40 ml/min Helium; $S_2$ 20% Propylencarbonat auf Chromosorb P—AW, 60—80 mesh, 1/8" Stahlsäule, 8 m lang, 0 °C, 40 ml/min Helium; St 1/16" Stahlkapillare; 1 Eingabe des Reaktions-Ausgangsstoffes (siehe Abb. 1); 2 Abnahme des Gemisches am Detektorauslaß (siehe Abb. 1)

Gasspritze das Gemisch gesammelt und anschließend in Einspritzblock Bl (Abb. 1, Abb. 2a) eingemessen. Die Auftrennung der Butene erfolgt auf Säule $S_2$, welche die entsprechenden Trenneigenschaften aufweisen muß. Das aus dem Detektor WLD während der Probennahme austretende Gemisch ist soweit homogen, daß es sich als belanglos erwiesen hat, ob die aufsteigende Flanke, das Peakmaximum oder die absteigende Peakflanke mit der Probenspritze abgenommen worden ist. Um ausreichende Mengen zu erhalten, ist es jedoch günstig, möglichst den gesamten Peak aufzunehmen. Infolge der Verdünnung bei der Probennahme um 1—2 Zehnerpotenzen erweist sich die Empfindlichkeit des FID als vorteilhaft. Die Reproduzierbarkeit blieb in allen Fällen in dem von früheren Meßmethoden [7—9] bekannten Rahmen (5—10%ige Schwankungen, abhängig vom verwendeten Katalysator).

Ein Umsatz-Chromatogramm (Trennung von Butenen als Summenpeak, 2-Butanol und $H_2O$) dauert etwa 4 Minuten. Bei überlappendem Einspritzen der Butene (Produktverteilung), die eine $t_R$ zwischen 4 und 7 Minuten haben, kann in kurzer Zeit eine hohe Zahl von Pulsen durchgebracht werden. Treten außer den Butenen noch andere $C_1$—$C_4$-(Crack-) Produkte auf, können diese mit der gleichen Technik auf Säule $S_2$ getrennt werden. Überlappendes Einspritzen in Säule $S_2$ ist dann wegen Peaks mit $t_R < 4$ Min. nicht in dem Ausmaß wie vorher möglich. (Der Methanpeak tritt nach 2′ 30″ auf.)

### Crackreaktion von sec-Butylbenzol

Bei dieser Reaktion entstehen aus sec-Butylbenzol Benzol, diverse substituierte Benzole, sowie $C_1$—$C_4$-Kohlenwasserstoffe. Da Aromaten und Aliphaten mit einundderselben Säule nur unbefriedigend getrennt werden können, behilft man sich hier mit einer Serienschaltung zweier Säulen (Abb. 2b). Substanzen, die in Einspritzblock B eingegeben werden, werden durch Säule $S_2$ und $S_1$ hindurchgespült. In C eingemessene Gemische gelangen nur durch $S_1$ hindurch (→ Peaks Nr. 1—6 in Abb. 3), Säule $S_1$ kann aber die leichter flüchtigen Komponenten ($C_1$—$C_4$-Kohlenwasserstoffe) nicht auftrennen. Sie treten als 1. Peak auf (Peak 1 in Abb. 3 = Summe aller $C_1$—$C_4$-Kohlenwasserstoffe). Bei dieser in Abb. 2b illustrierten Methode wird nun das aus dem Reaktor ausströmende Gas in einer Spritze gesammelt, ein Teil des Spritzeninhaltes in Einspritzblock B, der Rest unmittelbar darauf in Einspritzblock C eingemessen. Das Teilungsverhältnis richtet sich nach den gewünschten Peakhöhen der beiden Chromatogrammabschnitte.*

Die erste von Säule $S_2$ aufgetrennte und ohne weitere Trennung Säule $S_2$ passierende Substanz (hier Methan) erreicht nach 3′ 36″ den Detektor. Diese 3 1/2 Minuten reichen aber aus, daß das zur gleichen Zeit in C eingemessene Gemisch auf Säule $S_1$, so gut es diese vermag, getrennt wird (siehe oben). Auf diese Weise kann das komplexe Gemisch wie mit 2 getrennten Gaschromatographen analysiert werden. Das resultierende Chromatogramm, welches eigentlich aus zwei Chromatogrammen besteht, ist in Abb 3 zu sehen. Bei der Berechnung der prozentuellen Zusammensetzung des Reaktionsgemisches ist zu beachten, daß alle von Säule $S_2$ getrennten Produkte als Summe den 1. Peak aus Säule $S_1$ ergeben müssen (= Summe aller aliphatischen KW).

Mit der beschriebenen Anordnung (Abb. 2b) ist es möglich, nicht nur die Zusammensetzung des Reaktionsgemisches, sondern auch die Pulsform am Ausgang des Reaktors (WLD-Signal) zu analysieren. Dies kann besonders für Untersuchungen von Adsorptions- und Diffusionsphänomenen im Katalysatorbett von Interesse sein [4]. Obendrein sei bemerkt, daß es zum Unterschied zur Methode nach Abb. 2a, wo bloß ein Peak bestehend aus unaufgetrennten Butenen abgenommen wird, hier nicht unwesentlich ist, ob während der aufsteigenden oder der absteigenden Flanke des WLD-Signals die Probe gezogen wird. Während man in der aufsteigenden Peakflanke vorwiegend leichtflüchtige Substanzen findet, überwiegen im Tailing langsamer vom Katalysator abgegebene Substanzen, also vor allem schwerflüchtige Produkte, bzw. Stoffe mit intensiver Katalysatorwechselwirkung. Das alles gehört bereits zum Informationsgehalt der Untersuchungsmethode.

Der Nachteil der Methode liegt allerdings darin, daß die für die Trennung der aliphatischen Kohlenwasserstoffe bestimmte Säule $S_2$ mit der Zeit von

* Das im Spritzenvolumen befindliche Gemisch ist soweit homogen, daß beide Säulen dieselbe Gaszusammensetzung eingemessen erhalten.

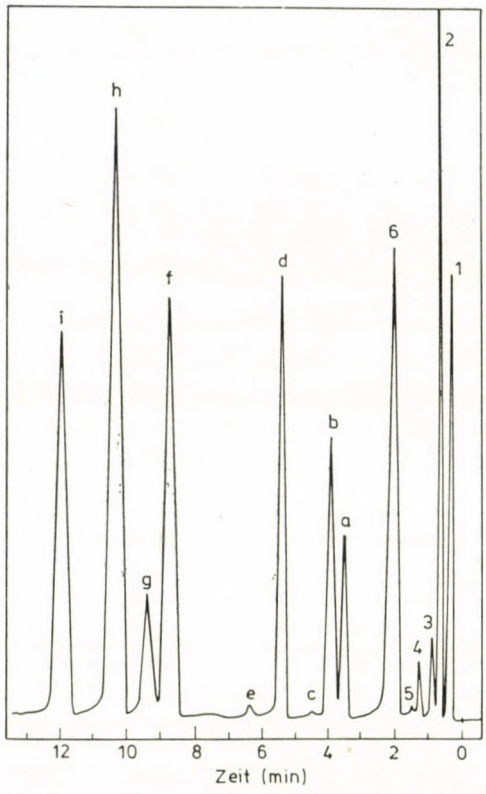



*Abb. 3.* Trennung eines bei der Crackung von *sec.*-Butylbenzol anfallenden Gemisches mittels Serienschaltung zweier Trennsäulen nach Abb. 2b

1 Summenpeak der $C_1$—$C_4$-Kohlenwasserstoffe
2 Benzol
3 Toluol
4 Äthylbenzol
5 Cumol
6 sec.-Butylbenzol

} von Säule $S_1$ aufgetrennt

a Methan
b Äthan
c Propan
d Propen + *i*-Butan
e *n*-Butan
f 1-Buten
g *iso*-Buten
h *trans*-Buten
i *cis*-Buten

} von Säule $S_2$ aufgetrennt

ebenfalls im eingegebenen Gemisch enthaltenen aromatischen Kohlenwasserstoffe durch Kondensation verunreinigt wird. Hier kann durch gelegentliches Ausheizen über Nacht Abhilfe geschaffen werden, was allerdings bekanntermaßen die Lebensdauer der Säule verkürzt. Mit der in Abb. 2b verwendeten Anordnung wurde nach etwa einem Monat Betriebszeit keine störende Änderung der Trennleistung bemerkt.

Mit der beschriebenen Serienschaltung kann auch die Eliminierungsreaktion durchgeführt werden (Säule $S_2$ trennt Butanol, Buten und $H_2O$). Die Methode wird man jedoch nur dann der zweidimensionalen Gaschromatographie vorziehen, wenn man direkt den vom Katalysator abgegebenen Substanzstrom (Pulsform) beobachten will oder Proben von verschiedenen Stellen des Pulses (Maximum, Tailing) entnehmen will (z.B. „Vergiftungen", Abb. 4).

## Temperaturprogrammierte Desorption (TPD)

Erwärmt man ein Adsorptionssystem, so findet Desorption statt. Die Temperatur, bei der dies eintritt, ist ein Maß für die Festigkeit der Bindung zwischen Adsorbens und Adsorptiv. Die desorbierenden Substanzen werden von einem Trägergas mitgeführt und in einem geeigneten Detektor quantitativ bestimmt. Die erhaltenen Desorptionsspektren können Aufschluß geben über die Heterogenität von Katalysatoroberflächen [10, 11].

Zur Durchführung solcher TPD-Messungen wird der Reaktor über 1/16″ Stahlkapillaren mit den beiden Detektoren verbunden. WLD und FID erhalten den Substanzstrom entweder hintereinander (Serienschaltung) oder über ein den Detektorempfindlichkeiten angepaßtes Splitsystem. Zunächst werden etwa bei Raumtemperatur einige Mikroliter des Adsorptivs über das Katalysatorbett geschickt. Danach werden die adsorbierten Substanzen durch (annähernd lineare) Temperaturerhöhung des Reaktorofens desorbiert und vom He-Strom in WLD und FID gespült. Die Aufheizrate beträgt dabei ca. 10° C/Min. (abhängig von Adsorptionssystem und Problemstellung). Die Kombination der beiden Detektoren erlaubt eine gewisse Selektion der desorbierenden, bzw. der aus während des Desorptionsvorganges stattfindenden Reaktionen entstandenen Gase und Dämpfe, vor allem die Unterscheidung von $H_2O$ und $CO_2$ von organischen Adsorptiven.

## Vergiftung von Katalysatoren

Dazu dient die Apparatur nach Abb. 2b. Der Katalysator wird durch mehrere aufgegebene Pulse mit einem geeigneten Adsorptiv belegt („Vergiftung"). Durch die Zahl der Pulse läßt sich die Bedeckung variieren, durch die Adsorptionstemperatur oft auch die Art der Adsorption (das Adsorptionszentrum). Nach Durchführung einer Test-Reaktion (Pulstechnik) kann das Katalysatorgift entfernt (temperaturprogrammierte Desorption), und die Reaktion abermals durchgeführt werden. Die Bauweise des Reaktorofens erlaubt ein rasches Aufheizen und Abkühlen (Kühlluft wird durch den Isoliermantel geblasen), was bei diesen Versuchen besonders wichtig ist. Adsorption und Desorption des Katalysatorgiftes, sowie die Form des aufgegebenen Pulses sind mit dem WLD verfolgbar.

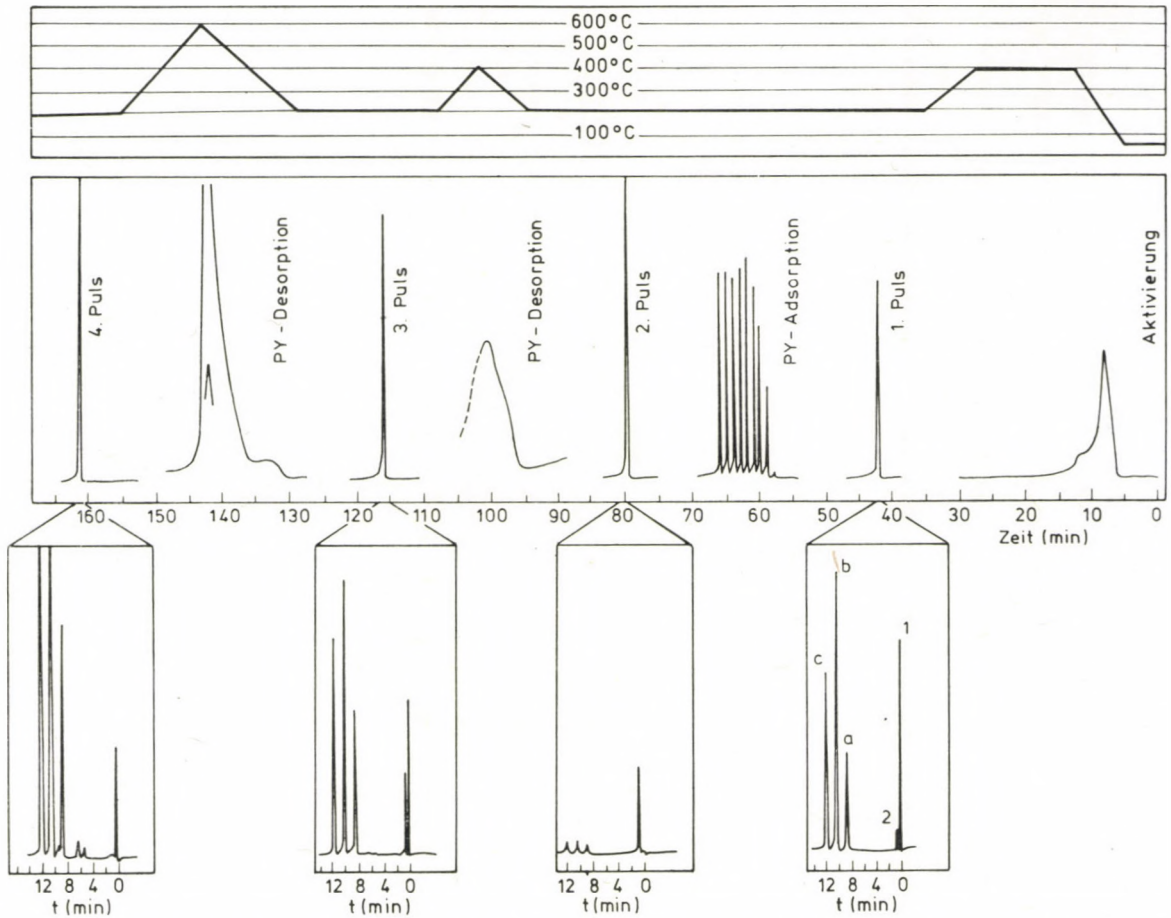



*Abb. 4.* Verlauf eines Vergiftungsversuches (Beschreibung im Text). Dehydratisierung von 2-Butanol an NiX-Zeolith

1 Summe der Butene } von Säule $S_1$ aufgetrennt
2 2-Butanol }

a 1-Buten
b *trans*-Buten } von Säule $S_2$ aufgetrennt
c *cis*-Buten }

Durch die gewählte Anordnung (Abb. 2b) gelangt das „Gift" nie in hohen Konzentrationen in das gaschromatographische System (Säulen $S_1+S_2$), wodurch eine „Vergiftung" der Trennsäule ausgeschlossen ist.

Abb. 4 zeigt die für einen derartigen Versuch typischen Schreibersignale: Der obere Streifen zeigt die jeweils im Reaktor herrschende Temperatur, der mittlere Streifen gibt das WLD-Signal wieder (= Substanzkonzentrationen am Reaktorausgang, siehe Abb. 2b), der unterste Streifen das FID-Signal, also die Analysen der nach dem 1., 2., 3. und 4. Puls am WLD austretenden Substanzgemische.

Die untersuchte Probe, 25 mg NiX-Zeolith, wurde zunächst bei 400 °C aktiviert („Aktivierung"), wobei das desorbierende $H_2O$ mittels WLD (siehe Abb. 2b) registriert wurde. Nach Abkühlung auf Reaktionstemperatur (200 °C) wurde der „1. Puls" (1 $\mu$l 2-Butanol) eingegeben. Als Testreaktion diente die Dehydratisierung des 2-Butanols. Das WLD-Signal zeigt das den Reaktor als schlanker Peak verlassende Reaktionsgemisch. Dieses wurde zwecks Analyse, wie weiter vorne beschrieben (Abb. 2b), mittels Gasspritze gesammelt und in Säulen $S_2$ und $S_1$ aufgeteilt (s. Abb. 2b). Aus dem FID-Signal (unterster Streifen in Abb. 4) ist nun die Gemischzusammensetzung analog Abb. 3 entnehmbar:

Peak 1 ist die Summe der leichtflüchtigen Komponenten (3-Butene), Peak 2 das nicht umgesetzte 2-Butanol. 2-Butanol wurde fast vollkommen umgesetzt. Die gleichzeitig auf Säule $S_2$ (Abb. 2b) getrennten Butene (a = 1-Buten, b = *trans*-Buten, c = *cis*-Buten) findet man im Anschluß daran.

Danach wurde der Katalysator bei 200 °C durch 10 mal 1 $\mu$l Pyridin belegt („PY-Adsorption"). Der Test mit 1 $\mu$l 2-Butanol („2. Puls") zeigte nahezu keine Aktivität des vergifteten Katalysators (im FID-Signal nur nicht umgesetztes 2-Butanol, = Substanz 2 in Abb. 4). Nach Desorption des Pyridins bei 400 °C („PY-Desorption") wurde die Probe wieder teilweise aktiv („3. Puls"), nach „PY-Desorption" bis zu 600 °C war die alte Aktivität hergestellt („4. Puls").

## LITERATUR

[1] Kokes, J. et al.: J. Amer. Chem. Soc. **77,** 5860 (1955)
[2] Doraiswamy, L. K., Tajbl, D. G.: Cat. Rev. 10 (2), 177 (1974)
[3] Hattori, T., Murakami, Y.: J. Catalysis **10,** 114 (1968)
[4] Cremer, E.: Mh. Chem., **92,** 112 (1961)
[5] Kladnig, W.: Chromatographia **6,** 243 (1973)
[6] Andreu, P.: Hewlett Packard, Analytical Instrument Division, Technical paper No. 42 (1967)
[7] Zoidl, Z.: Diplomarbeit an der TU Wien, 1972
[8] Villalba, S., Noller, H.: Z. phys. Chem. N. F. **90,** 113 (1974)
[9] Thomke, K., Noller, H.: V. Katalyse-Kongreß, paper No. 84
[10] Cvetanovic, R. J., Amenomiya, Y.: Cat. Rev. **6,** 21 (1972)
[11] Cvetanovic, R. J., Amenomiya, Y.: Adv. Catalysis, **17,** 103 (1967)

J. Latzel, Institut für Physik. Chemie d. Techn. Universität, A-1060 Wien.

*Acta Chimica Academiae Scientiarum Hungaricae, Tomus 98 (1), pp. 37—48 (1978)*

# QUANTUM CHEMICAL STUDY ON THE CONFORMATIONAL PROPERTIES OF CHALCONE AND ITS SIMPLE MODEL COMPOUND

Z. DINYA, Á. I. KISS* and G. PONGOR**

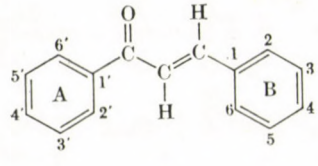
*(Department of Organic Chemistry, Kossuth Lajos University, Debrecen, * Department of Physical Chemistry, Technical University Budapest, and ** Chinoin Pharmaceutical and Chemical Works, Ltd., Budapest)*

Received July 15, 1977

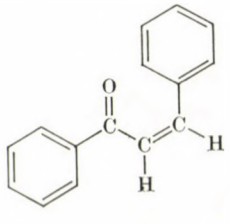
Conformational analysis by semi-empirical quantum chemical methods was carried out on some $\alpha$, $\beta$-unsaturated carbonyl compounds. Extended Hückel and CNDO/2 calculations on chalcone and on a simple model ketone reproduced well the experimental stability order, showing the *E-s-cis* form to be the most stable. The potential energy curve of the *s-cis-s-trans* rotational isomerization in the *E* form is correctly given by the PCILO method contrary to the CNDO/2 results. Calculations on acrolein demonstrate the reliability of PCILO results. A discussion of the calculated height of the rotational barrier in comparison with the experimental data is given.

## 1. Introduction

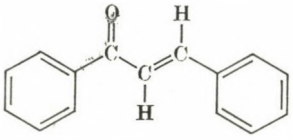
Chalcone (benzalacetophenone) may be regarded as the simplest parent compound of flavonoids, a group of natural products of great interest. The ethylenic group of the characteristic $\alpha, \beta$-unsaturated carbonyl system of chalcone is under normal conditions in the *trans* (*E*) form (**I**); the *cis* (*Z*) isomer (**II**) can be produced by photoisomerization from the *E* form [1]. By condensation of acetophenones with aromatic aldehydes *trans*(*E*)-chalcone (**I**) is always formed [2]. The geometry and stereochemistry of *E*-chalcone (**I**), and its derivatives substituted in ring A and B have been extensively studied by dipole moment [3—6], infrared [4, 7—15] NMR [16] and X-ray [17—23]



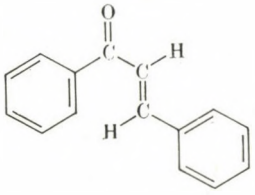

I




II



**Ia** *E-s-cis*

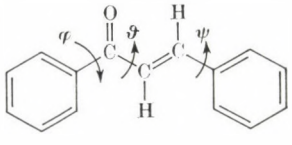


**Ib** *E-s-trans*

measurements. The experimental results demonstrate that in the solid state *E*-chalcone is present in the nearly planar *s-cis* (**Ia**) form; in solution, on the other hand, an *s-cis* (**Ia**) $\rightleftharpoons$ *s-trans* (**Ib**) conformational equilibrium exists.

Under normal conditions the *s-cis* conformer (**Ia**) is favoured. According to infrared spectroscopic measurements, the proportion of the *s-cis* form in $CCl_4$ solution is $\sim 70\%$ [14]; on the basis of NMR measurements $\sim 83\%$ is reported [16], i.e. the *s-cis* form is more stable. Of the *E*-chalcones, neither the *s-cis*, nor the *s-trans* conformer is completely planar [5, 18, 23, 24]; in the *s-cis* form (**Ia**) $\vartheta$ is between 10° and 30°, $\varphi$ and $\psi$ being 4—20° (**III**). It seems the stereochemical data of the *Z*-chalcone have not yet been published.

As extension of our earlier work [14, 25—27] dealing with the spectroscopic investigation of chalcones, we investigated the *s-cis*, *s-trans* conformational properties of *E*- and *Z*-chalcone by semiempirical quantum chemical methods. Besides chalcone a simple model compound (**V**), as well as acrolein was studied in order to obtain information on the rotational isomerism of $\alpha,\beta$-unsaturated carbonyl compounds by different quantum chemical approximations (for a review, see e.g. [28]). Calculations of this kind were reported for smaller molecules by semiempirical [29—34, 43—56], as well as by *ab initio* methods [57—60]. Concerning flavonoids only the CNDO/S results by GROUILLER *et al.* [32] are available for the planar *s-cis* and *s-trans* forms of 2'-hydroxychalcone.



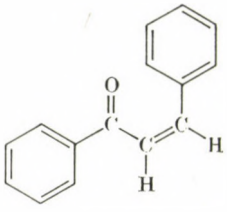
**III**

$A \neq \varphi \neq \psi \neq 0$

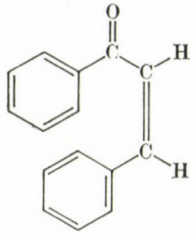
## 2. Calculations

### 2.1. *Model*

In the calculations for chalcone, four planar conformers (**Ia**, **Ib**, **IIa** and **IIb**) may be considered, further the non-planar forms arising from the variation of the rotational angle $\vartheta$, $\varphi$ and $\psi$ being 0°.



**IIa** *Z-s-cis*



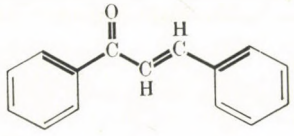
**IIb** *Z-s-trans*

An inspection of the Dreiding models of *Z*-chalcone show that the existence of the *Z-s-trans* (**IIb**) form can be excluded because of the great proximity of the aromatic rings; therefore only three planar conformers (**Ia**, **Ib** and **IIa**) should be considered. The CNDO/2 [35] and EH [36] methods are applied for the calculations of the chalcone isomers. Chalcone cannot be unambiguously treated by the PCILO method [37] because the calculations using different Kekulé structures of unsymmetrically substituted aromatic rings do not produce the same results [38]. In order to have comparable CNDO/2, EH and PCILO results, a simplified model compound was required: we omitted the benzene rings of chalcone and replaced them by ethylenic linkages (**IV**); *i.e.* 1-vinyl 1-buta-dienyl ketone (**V**) (called "model ketone") was used. The four planar forms (**Va**—**d**) as well as the rotamers obtained by change in $\vartheta$ were involved into the calculations on the model ketone.

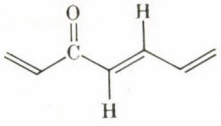
### 2.2. *Methods*

The bond distances [18] used in the computations are given in Table I. All bond angles in the planar molecules are taken as 120°.

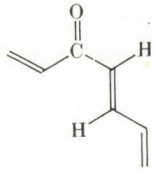
To the CNDO/2 calculations the original program and parametrization was used [35]. The EH method [36] was used in its original form with starting parameters given in Table II. The PCILO method [41] was applied in the form modified by KLÖPPER, WELLER and KÖHLER [42], using CNDO/2 parametrization.



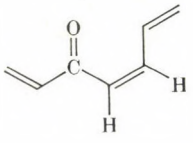
IV



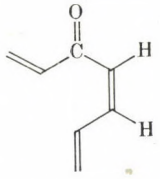
Va *E-s-cis*



Vb *E-s-trans*



Vc *Z-s-cis*



Vd *Z-s-trans*

## 3. Results

### 3.1. *Planar forms*

The first aim of our calculations was to study the stability of the planar conformers of chalcone. The EH and CNDO/2 calculations reproduce the experimentally established order: *E-s-cis*, *E-s-trans*, *Z-s-cis*. A satisfactory qualitative agreement is attained, exact numerical results, however, cannot be expected. The *s-cis*, *s-trans* total-energy difference (isomerization energy) of the *E* forms is some kcal/mole, the EH value being higher than the CNDO/2 result.

**Table I**

*Bond distances used in the calculations*

| Bond* | Bond length (Å) |
|---|---|
| C = O | 1.204 |
| C = C(e) | 1.330 |
| C = C(a) | 1.397 |
| C(O) — C(e) | 1.479 |
| C(O) — C(a) | 1.500 |
| C(e) — C(a) | 1.465 |
| C—H | 1.08 |

*e: ethylenic, a: aromatic carbon atom

**Table II**

*Starting parameters of the Extended Hückel calculations*

| Atom ($\mu$) | $\zeta\mu$* | $I\mu$ (eV)** |
|---|---|---|
| H | 1.0 | 1*s* : 13.6 |
| C | 1.625 | 2*s* : 21.01<br>2*p* : 11.27 |
| O | 2.275 | 2*s* : 36.07<br>2*p* : 18.53 |

* Slater exponent [39].
** Valence state ionization potential [40].

All the four planar forms of the model ketone were calculated by the EH and CNDO/2 methods; the total energies are presented in Table III. The calculated stability order corresponds to the experimental order for chalcone. The CNDO/2 total-energy difference between the *E-s-cis* and *E-s-trans* forms is 1.7 kcal/mole, that between the *E-s-trans* and *Z-s-cis* forms is 1.5 kcal/mole. The latter value seems to be too low. The energy difference of the two *Z* forms is more than 200 kcal/mole, pointing correctly to the instability of the *Z-s-trans* conformer. The EH energy differences are too high: 6.3, 24.0, and 111.3 kcal/mole, respectively; their ratios are, however, reasonable.

It can be stated that the model ketone adequately represents the conformational properties of chalcone. For this reason, the further detailed computations (with the PCILO method, and as a function of the rotational angle $\vartheta$) were performed for the model ketone.

**Table III**

*Total energies (in kcal/mole*) of the planar forms of the model ketone*

| Form | EH | CNDO/2 |
|---|---|---|
| *E-s-cis* | —17983.438 | —46291.378 |
| *E-s-trans* | —17977.186 | —46289.686 |
| *Z-s-cis* | —17953.225 | —46288.173 |
| *Z-s-trans* | —17841.905 | —46073.942 |

*The conversion factors used:

1 a. u. = 627.104 kcal/mole
1 eV = 23.0454 kcal/mole

The PCILO zeroth-order total energy $E_0$, and the total energies obtained after second- and third-order perturbation correction ($E_2$, and $E_3$, respectively) for the three more probable conformers of the model ketone are given in Table IV. The computation for the *Z-s-trans* form did not converge. It can be seen

**Table IV**

*PCILO total energies (in kcal/mole) of the model ketone*

| Form | $E_0$ | $E_2$ | $E_3$ |
|---|---|---|---|
| *E-s-cis* | −46071.550 | −46535.578 | −46470.799 |
| *E-s-trans* | −46069.447 | −46534.918 | −46470.977 |
| *Z-s-cis* | −46060.737 | −46533.880 | −46465.861 |
| *Z-s-trans* | No convergence was attained | | |

that $E_0$ is the lowest for the *E-s-cis* form; the stability order is identical with the above calculated as well as with the experimental order. Inclusion of the second-order perturbation does not alter the stability order, only the energy separation of the most stable conformer decreases. Third-order perturbation does change the stability order: the *E-s-trans* form becomes the most stable. The energy difference of the two *E* forms is less than 0.2 kcal/mole, which means that the PCILO method produces nearly identical energy for the most stable two conformers.

A formal explanation of the change in the stability order may be given by examination of the components of the third-order correction. The delocalization interaction terms are much smaller for the *E-s-cis* than for the *E-s-trans* form, the bond correlation terms are, however, larger. The latter terms cause a total third-order correction larger for the *E-s-cis* form involving a greater destabilization.

### 3.2. *Investigation of the rotational isomerism of the trans (E) forms*

The EH calculations were performed for the *E*-chalcone as a function of the rotational angle $\vartheta$, varied between 0° and 180°. The value $\vartheta = 0°$ represents the *s-cis* form. The total energy as a function of $\vartheta$ is shown in Fig. 1. Only one minimum at $\vartheta = 60°$ and a very high maximum at 180° is obtained; this result does not agree with the experimental facts.

The CNDO/2 and PCILO calculations for different $\vartheta$ values were carried out with the model ketone; the potential energy curves are shown in Fig. 2.

The CNDO/2 method produces a single minimum at 60° just as the EH calculation. The PCILO result is, on the other hand, qualitatively correct,

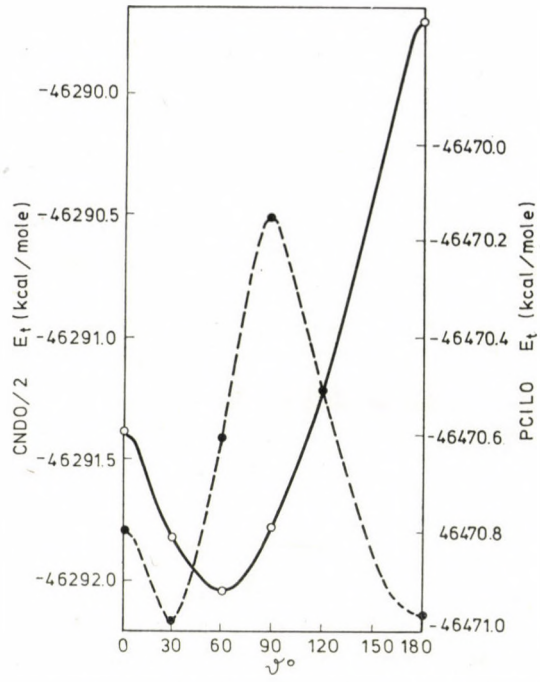



*Fig. 1.* Extended Hückel conformational energy curve for *E*-chalcone

the potential energy curve has two minima, the lower at $\vartheta = 30°$, and a somewhat higher at 180°, the maximum being at 90° (Fig. 2). The energy difference of the two minima (isomerization energy) is rather small (0.2 kcal/mole) the height of the rotational barrier being about 0.8 kcal/mole.

## 4. Discussion

In order to judge the realiability of the results obtained it seemed worth-wile to survey the experimental and theoretical data on simple vinyl and carbonyl derivatives, and to find a correlation between the characteristics of the potential energy curve and the essential structural elements of the molecules. Only double-minimum potential curves will be considered.

According to recent investigations, the CNDO/2 method fails to give correct results for the stable conformation of molecules where the bond representing the rotational axis is delocalized [43]. The CNDO and INDO calculations for the simplest alkyl-aldehydes (acetaldehyde, propionaldehyde) could not correctly reproduce the experimental potential curve; the PCILO calculation, however, produces qualitatively correct results [41]. The same was observed with thioacetaldehyde [44]. The height of the rotational barrier of PCILO

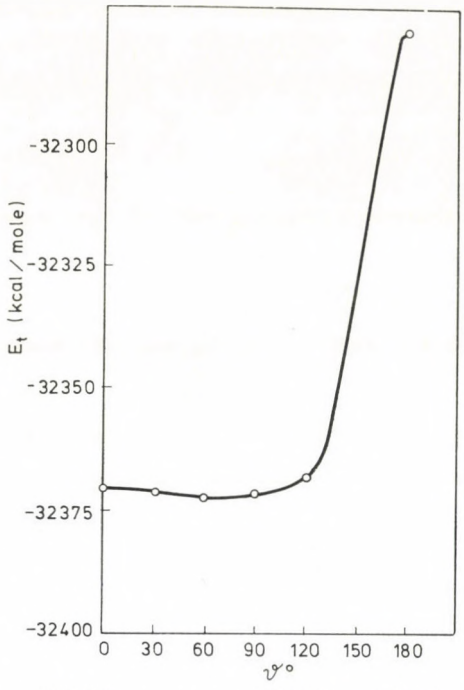



*Fig. 2.* ——— CNDO/2, — — — PCILO curve for the model ketone

calculations agrees better with experiment than that of CNDO. All calculated heights are lower than the experimental ones.

For simple conjugated molecules (butadiene, glyoxal) the CNDO/2 calculations give an energy minimum at 60° and 90°, respectively [45], the PCILO result is, however, again correct, the *trans* planar form ($\vartheta = 180°$) is obtained as the most stable one [46, 47], and a second minimum is observed at $\vartheta = 30°$. The energy difference between these two conformers is 1.5 kcal/mole and the barrier is 2.5 kcal/mole [46, 47]. The corresponding PCILO results for glyoxal are 0.7 and 1.75 kcal/mole, the two minima are at $\vartheta = 180°$ and 0° [46]. All these values are lower than the experimental ones (Table V). The calculated values for the model ketone are lower than those for the simple conjugated molecules.

In order to have reliable check to our results, it seemed worth to perform some calculations on acrolein, the simplest unsaturated carbonyl compound. It is believed that acrolein has not yet been calculated by the PCILO method. Recently COURTIEU *et al.* [52] reported NMR results for the isomerization energy and height of rotational barrier of acrolein. The isomerization energy of acrolein falls between those of butadiene and glyoxal (Table V). A CNDO/2 calculation optimized to the C=C—C angle [53] showed the *trans* isomer to be more stable by 4.79 kcal/mole than the *cis* form. Our CNDO/2 calculation

**Table V**

*Experimental and calculated (by PCILO method) isomerization energies and rotational barriers of some simple conjugated systems*

| Molecule | Experimental | | | | Calculated | | |
|---|---|---|---|---|---|---|---|
| | $\Delta E$ | $E_{rot}$ | Method | Ref. | $\Delta E$ | $E_{rot}$ | Ref. |
| | (kcal/mole) (State) | | | | (kcal/mole) | | |
| Butadiene | 2.3 | 4.9 | UV, IR (V) | [48] | 1.5 | 2.5 | [46] |
| | 2.1 | | UV (V) | [50] | 1.5 | 2.5 | [47] |
| Acrolein | 2.14 | 7.15 | ultrason. (L) | [49] | 0.8 | 2.2 | this paper |
| | 2.8 | 5.0 | NMR (L) | [52] | | | |
| Glyoxal | 3.2 | — | UV (V) | [51] | 0.7 | 1.75 | [46] |
| Crotonaldehyde | 1.92 | 7.41 | ultrason. (L) | [49] | | | |
| Cinnamaldehyde | 1.51 | 7.01 | ultrason. (L) | [49] | | | |
| Model ketone | — | — | | | 0.2 | 0.8 | this paper |

(original version) gave similarly wrong results for acrolein as for butadiene: the potential minimum is at 60°. The isomerization energy and the height of the barrier is lower for acrolein.

The PCILO calculation gives again good qualitative results: a sharper and deeper minimum appears at 180°, and a flatter and higher one at 0° (Fig. 3). The *s-cis–s-trans* energy difference and the height of barrier are here also smaller than the experimental values (Table V). The PCILO energy values are higher for acrolein than for the model ketone. The PCILO calculations fail to reproduce, however, the experimental order of energies for the series butadiene, acrolein, glyoxal.

The height of barrier is primarily determined by the strength of the twisted bond, and by the size and electronic symmetry of the twisted molecular fragment. The larger the bond strength, the size of the group and the deviation from spherical symmetry in the electronic structure, the higher is the rotational barrier. The increase of barrier in acrolein with respect to butadiene may probably be attributed to the latter effect. The opposite trend of the calculated and experimental barrier in the series butadiene, acrolein, glyoxal suggest that the influence of electronic repulsion of the twisted groups on the barrier is not correctly involved into the semi-empirical methods used.

It can be stated that an increase in conjugation increases the height of barrier around the twisted C–C bond in unsaturated carbonyl derivatives [61]. Some evidence seems to be appropriate. Methyl groups increase the strength of the twisted C–C bond thereby increasing the barrier. DODZIUK [54] obtained, by a classical approximation, for methyl-substituted unsaturated ketones, higher isomerization energy and height of barrier compared with the parent compound, in accordance with the experimental results. A good evidence for

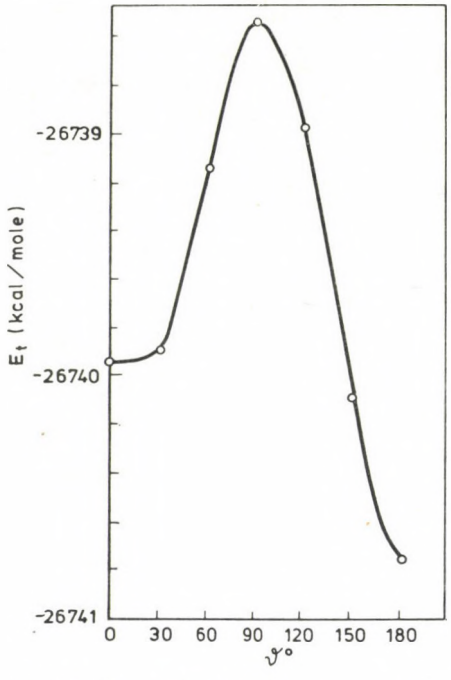



*Fig. 3.* PCILO conformational energy curve of acrolein

the effect of conjugation is the decrease of the height of the barrier (above the higher minimum) in acrolein as compared with, cinnamaldehyde [49] (Table V). Molecular acoustical investigation [62] of methylacroleins and methylcinnamaldehydes showed the strength of the twisted C–C bond to be the dominating factor in determining the height of the barrier.

In molecules having the carbonyl group attached to two unsaturated groups, the conjugation decreases, which can be demonstrated, *e.g.*, by the infrared spectra [55]. Thus, for the model ketone a decrease of the height of the barrier is expected as compared with acrolein. The PCILO calculation really produces the expected changes (Table V). Some remarks are still appropriate.

The PCILO method tends to give smaller height of the barrier than the experimental value. The reproduction of the experimental order, *i.e.* a higher value for acrolein than for butadiene, is expected, but a continuous decrease is observed. The difference between the calculated values of butadiene and acrolein is essentially smaller than between those of acrolein and the model ketone. Despite the incorrect trend, the larger decrease in the latter case may be attributed to the decrease of conjugation.

The heights of the barriers are larger than the energy differences of the isomers, thus the calculated values of the former are more accurate. The same

behaviour of the two quantities justifies the reliability of the calculated isomerization energy of the model ketone, though it is in the magnitude of error of the PCILO method. Because of the small energy difference of the model ketone isomers, the stability of the *E-s-cis* form cannot be proved by the PCILO calculation. This conclusion may be drawn only from the identical trend of all the computations presented.

It can be concluded that the PCILO method gives acceptable results. Its applicability to conformational calculations may be justified by a comparison with PANCER's recently published CNDO/2 results [56]. Let us recall that RANDHAWA [53] obtained qualitatively good CNDO/2 energies by optimizing one bond angle. PERAHIA and PULLMAN [46], on the other hand, concluded that introduction of CI did not improve the conformational CNDO/2 calculation. PANCIR [56] stated from CNDO/2 calculation on glyoxal that CI and geometry optimization were both needed for getting good results. The PCILO method does involve CI, thus it can be expected that PCILO results are equivalent to PANCIR's improved CNDO/2 results which seem to be justified by our calculations.

## REFERENCES


[1] LUTZ, R. L., JORDAN, R. H.: J. Am. Chem. Soc. **72,** 4090 (1950)
[2] GEISSMAN, T. A. (editor): The Chemistry of Flavonoid Compounds, p. 153. Pergamon Press, Oxford, 1962
[3] BRAMLEY, R., LE FEVRE, R. J. W.: J. Chem. Soc. **1962,** 56
[4] TSUKERMAN, S. V., SUROV, Y. N., LAVRUSHIN, V. F.: Zh. Obshch. Khim. **38,** 524 (1967)
[5] MAURET, M. P., MERMILLOD-BLARDET, D., MARONI, P.: Bull. Soc. Chim. France **1971,** 903
[6] GRUNFEST, H. G., KOLODASNI, Y. V., JANOVSKAJA, O. A., UMIRZAKOV, B., KUCEROV, V. F., VORONCOVA L. G.: Izv. Akad. Nauk SSSR, Ser. Khim. **1972,** 2662
[7] PERJESSY, A.: Chem. Zvesti **23,** 905 (1969)
[8] SILVER. N. L., BOYKIN, D. W.: J. Org. Chem. **35,** 759 (1970)
[9] TSUKERMAN, S. V., KUTULIA, L. A., SUROV, Y. N., PIVCENKO, N. S., LAVRUSHIN, V. F.: Zh. Obshch. Khim. **1970,** 1337
[10] DZURILLA, M., KRISTIAN, P., GYÖRYOVA, K.: Chem. Zvesti **24,** 207 (1970)
[11] WINECOFF, W. F., BOYKIN, D. W.: J. Org. Chem. **37,** 674 (1972)
[12] GROUILLER, A., THOMASSERY, P., PACHECO, H.: Bull. Soc. Chim. France **1973,** 3448
[13] SAVIN, V. I., KITAEV, Y. P.: Zh. Obshch. Khim. **1973,** 1101
[14] DINYA, Z., LITKEI, Gy.: Acta Chim. (Budapest) **75,** 161 (1973)
[15] SEGUIN, J. P., BEAUPÈRE, D., BAUER, P., UZAN, R.: Bull. Soc. Chim. France **1974,** 167
[16] MONTAUDO, G., LIBRANDO, V., CACCAMESE, S., MARAVIGNA, P.: J. Am. Chem. Soc. **95,** 6365 (1973)
[17] RABINOVICH, D., SCHMIDT, G. M. J.: J. Chem. Soc. B **1970,** 6
[18] RABINOVICH, D.: J. Chem. Soc. B **1970,** 11
[19] JUNG, A. E., SCHMIDT, G. M. J.: J. Chem. Soc. B **1970,** 1427
[20] RABINOVICH, D., SCHMIDT, G. M. J., SHAKKED, Z.: J. Chem. Soc. Perkin II **973,** 33
[21] OHKURA, K., KASHINO, S., HAISA, M.: Bull. Chem. Soc. Japan **46,** 627 (1973)
[22] RABINOVICH, D., SHAKKED, Z.: Acta Cryst. B, **30,** 2829 (1974)
[23] WARSHEL, A., HULER, E., RABINOVICH, D., SHAKKED, Z.: J. Mol. Struct. **23,** 175 (1974)
[24] CUSSAC, M., BOUCHERLE, A., PIERRE, J. L.: Bull. Soc. Chim. France **1974,** 1427
[25] DINYA, Z., BOGNÁR, R.: Acta Chim. (Budapest) **73,** 453 (1972)
[26] DINYA, Z., LITKEI, Gy., BOGNÁR, R., MÁTYÁS, Gy.: Acta Chim. (Budapest) **77,** 323 (1973)

[27] DINYA, Z., LITKEI, Gy., TAMÁS, J., CZIRA, G.: Acta Chim. (Budapest **84,** 181 (1975)
[28] GOLEBIEWSKI, A., PARCZEWSKI, A.: Chem. Rev. **74,** 519 (1974)
[29] HOFFMANN, R.: Tetrahedron Letters **1965,** 3819
[30] KATO, H., KONISHI, H., YAMABE, H., YONEZAWA, T.: Bull. Chem. Soc. Japan **40,** 2761 (1967)
[31] ELSON, J. H., KEMP, T. J., GREATOREX, D., JENKINS, H. D. B.: J. Chem. Soc. Faraday II **69,** 665 (1973)
[32] GROUILLER, A., THOMASSERY, P., PACHECO, H., DECORET, C., TINLAND, B.: Bull. Soc. Chim. France **1973,** 3454
[33] HOFMANN, H.-J., KÖHLER, H.-J., THIEROFF, K., UHLMANN, P.: J. Prakt. Chem. **316,** 659 (1974)
[34] HOFMANN, H.-J., VETTER, R.: Z. Chem. **12,** 427 (1972)
[35] POPLE, J. A., BEVERIDGE, D. L.: Approximate Molecular Orbital Theory, McGraw-Hill, New York 1970
[36] HOFFMANN, R.: J. Chem. Phys. **39,** 1397 (1963)
[37] DINER, S., MALRIEU, J. P., CLAVERIE, P.: Theor. Chim. Acta **13,** 1 (1969)
[38] KLÖPPER, D.: Personal communication
[39] SLATER, J. C.: Phys. Rev. **36,** 57 (1930)
[40] HINZE, J., JAFFÉ, H. H.: J. Am. Chem. Soc. **84,** 540 (1962)
[41] KÖHLER, H.-J., WELLER, T., KLÖPPER, D.: Z. Chem. **15,** 224 (1975)
[42] KLÖPPER, D., WELLER, T., KÖHLER, H.-J.: PCILO Program Description
[43] SIEIRO, C., GONZALES-DIAZ, P., SMEYERS, Y. G.: J. Mol. Struct. **24,** 345 (1975)
[44] WELLER, T., KLÖPPER, D., KÖHLER, H.-J.: Chem. Phys. Lett. **36,** 475 (1975)
[45] GROPEN, O., SEIP, H. M.: Chem. Phys. Lett. **11,** 445 (1971)
[46] PERAHIA, D., PULLMAN, A.: Chem. Phys. Lett. **19,** 73 (1973)
[47] WELLER, T., KLÖPPER, D.: Z. Chem. **14,** 493 (1974)
[48] ASTON, J. G., SZASZ, G., WOOLLEY, H. W., BRICKWEDDE, F. G.: J. Chem. Phys. **14,** 67 (1946)
[49] DEGROOT, M. S., LAMB, J.: Proc. Roy. Soc. (London), A, **242,** 36 (1957)
[50] LIPNICK, R. L., GARBISCH, E. W.: J. Am. Chem. Soc. **95,** 6700 (1971)
[51] CURRIE, G. N., RAMSAY, D. A.: Can. J. Phys. **49,** 317 (1971)
[52] COURTIEU, J., GOUNELLE, Y., GONORD, P., KAN, S. K.: Org. Magn. Resonance **6,** 151 (1974)
[53] RANDHAWA, H. S.: Z. Physik. Chem. (Frankfurt) **94,** 147 (1975)
[54] DODZIUK, H.: J. Mol. Struct. **20,** 317, 363 (1974)
[55] LUTSKII, A. E., GRANZHAN, V. A.: Ukr. Khim. Zh. **37,** 455 (1971)
[56] PANCIR, J.: Theor. Chim. Acta **40,** 81 (1975)
[57] RADOM, L., LATHAN, W. A., HEHRE, W. J., POPLE, J. A.: Aust. J. Chem. **25,** 1601 (1972)
[58] DEL BENE, J. E., WORTH, G. T., MARCHESE, F. T., CONRAD, M. E.: Theor. Chim. Acta **36,** 195 (1975)
[59] SKANCKE, P. N., SAEBO, S.: J. Mol. Struct. **28,** 279 (1975)
[60] DYKSTRA, C. E., SCHAEFER III, H. F.: J. Am. Chem. Soc. **97,** 7210 (1975)
[61] International Rotation in Molecules (Ed. W. J. ORVILLE-THOMAS), p. 317. Wiley, London 1974
[62] PETHRICK, R. A., WYN-JONES, E.: Trans. Faraday Soc. **66,** 2483 (1970)

Zoltán DINYA H-4010 Debrecen, Pf. 20.
Árpád KISS H-1111 Budapest, Budafoki út 8.
Gábor PONGOR H-1077 Budapest, Rottenbiller u. 26.

*Acta Chimica Academiae Scientiarum Hungaricae, Tomus 98 (1), pp. 49—66 (1978)*

# ELECTROCHEMICAL BEHAVIOUR OF ETHYLENE GLYCOL AND ITS OXIDATION DERIVATIVES ON A PLATINUM ELECTRODE, II

## STUDY OF THE OXIDATION OF GLYOXAL AND GLYOXYLIC ACID

G. HORÁNYI

*(Central Chemical Research Institute of the Hungarian Academy of Sciences, Budapest)*

G. INZELT and Z. SZETEY

*(Department of Physical Chemistry and Radiology Eötvös Loránd University, Budapest)*

Received 15 July 1977

A study was made of the electrochemical oxidation of glyoxal and glyoxylic acid on a platinized platinum electrode in acidic medium. The product composition was investigated as a function of the potential. It was found that, at not too high potentials (600—700 mV RHE), primarily oxalic acid is formed in both reactions.

A photometric procedure was elaborated for determination of oxalic acid. The occurrence of galvanostatic potential oscillations (known from the literature) was observed in the case of both reactions. A radioactive tracer technique was used to investigate the adsorption of $Cl^-$ in the presence of the two compounds, in order to study their chemisorption.

In a previous publication [1] we discussed questions connected with the reduction of glycolaldehyde, glyoxal and glyoxylic acid. It was found that in acidic medium these compounds can be reduced on a platinum electrode; in the study of their oxidation, therefore (and this must accordingly be taken into consideration in the frequently-employed anodic — cathodic regeneration, for example), even temporarily it is not advisable to attain potentials at which the reduction processes can occur, if it is wished to avoid the disturbing effects of the products of the reduction.

In the present publication we deal with questions of the oxidation of glyoxal and glyoxylic acid, the two compounds figuring in the reaction scheme assumed for the oxidation of ethylene glycol to oxalic acid or carbon dioxide.

## Experimental

Essentially the experimental method described previously [1] was used. The polarization measurements were made on an electrode with a geometrical surface area of 10 $cm^2$. In those studies where product analysis was also necessary the electrode used had a geometrical surface area of 100 $cm^2$. The roughness factor of the platinized platinum electrodes lay in the range 500—1000.

The previously-described [2] method and apparatus were employed in the tracer investigations. *M* $H_2SO_4$ and *M* $HClO_4$ solutions were used as supporting electrolyte. All of the potential values given in this paper refer to a one-atmosphere hydrogen electrode immersed

in the supporting electrolyte. For purposes of product analysis it was necessary to elaborate the most appropriate analytical method for determination of the quantity of oxalic acid formed. This will be returned to in more detail below. The carbon dioxide evolved during the oxidation was measured volumetrically.

## Oxidation products

Before a detailed study and analysis of the polarization curves to be observed in the presence of the compounds examined, it is necessary to clarify what reactions take place in the potential interval in question. The polarization curves of glyoxal, glyoxylic acid and oxalic acid, taken by means of a potentiostatic method, are presented in Fig. 1. Starting from 300—400 mV, these curves were recorded with a waiting period of 10—15 minutes at the individual potentials. Even in spite of these waiting times, it can not be stated

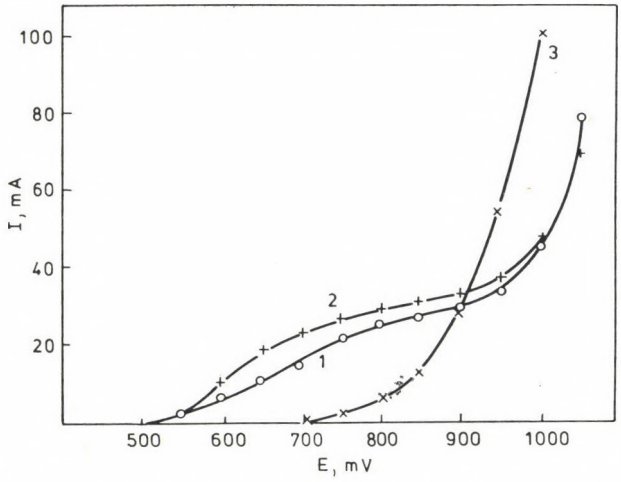
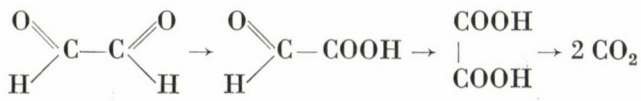



*Fig. 1.* Comparison of polarization curves of (1) glyoxylic acid, (2) glyoxal and (3) oxalic acid

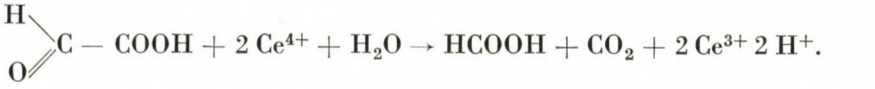
with certainty that the stationary state was fully established at every potential. During longer waiting periods the slow increase or decrease of the current can be observed, depending on the potential. We shall return later to the difficulties arising in the taking of the polarization curves. The curves depicted in the Figure thus primarily give a possibility only for the estimation-like comparison of the rates of the reactions with the various substances.

It is clear from the Figure that the rate of oxidation of oxalic acid is less than those of the other two substances in a fairly wide potential interval. At the same time, the behaviours of glyoxal and glyoxylic acid are very similar. To a first approximation it may be concluded from the polarization curves

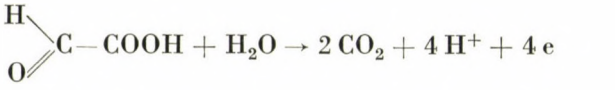
that, if the oxidation occurs in accordance with the reaction route



then at potentials more negative than 700 mV, at most oxalic acid may be formed from either glyoxal or glyoxylic acid; that is, the complete oxidation resulting in carbon dioxide can not play a significant role. In contrast, at higher potentials the formation of carbon dioxide comes increasingly into the foreground. It must be pointed out, however, that the scheme above is by no means to be taken for granted. For example, in homogeneous oxidation processes glyoxylic acid does not react with $Ce^{4+}$ in this way [3], but according to the equation



If such a reaction step were to take place in the case of the electrode process too, then, because of the oxidation of the formic acid, which is well known to be fast, the overall process



should be observed, but without oxalic acid as intermediate.

On the basis of the above, it is obvious that the need arises for a method whereby the oxalic acid formed in the course of the electrolysis can be determined quickly and with certainty in the presence of glyoxal and glyoxylic acid. There is a possibility for this if it is considered that oxalic acid forms a yellowish-green complex with $Fe^{3+}$, whereas in the cases of glyoxylic acid and glyoxal it is not necessary to reckon with the formation of coloured complexes. Hence, we have the possibility to determine the concentration of oxalic acid photometrically in samples taken from the electrolysis cell. Although the coloured complexes formed between $Fe^{3+}$ and $SO_4^{2-}$ in sulphuric acid medium do interfere, their effect can be eliminated by using a $Fe_2(SO_4)_3$ solution as comparison solution. Figure 2 shows the experimentally determined extinction values as a function of the concentration of oxalic acid, in the case of the addition of the same quantity of $Fe_2(SO_4)_3$ and a constant $H_2SO_4$ concentration. The comparison solution was $Fe_2(SO_4)_3$ solution of definite concentration. The concentrations of the solution samples examined were adjusted so that their oxalic acid concentrations should fall in the interval corresponding to the calibration curve in Fig. 2. The fact that the presence of a large excess of glyoxylic acid or glyoxal does not influence the determination of the oxalic

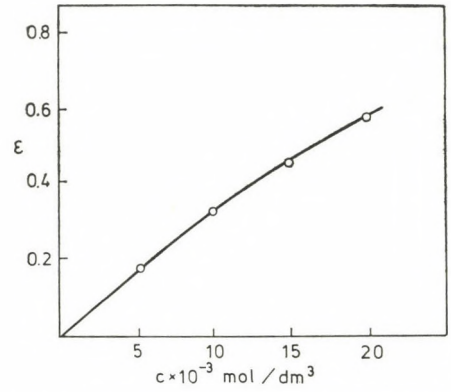



*Fig. 2.* Extinction values as a function of the oxalic acid concentration in a basic solution of $M$ $H_2SO_4$ in the case of a constant $Fe_2(SO_4)_3$ concentration, at 380 mm

acid concentration or the measured extinction, was confirmed in separate experiments. This is illustrated in Table I.

Overall, it may be stated that with this method the quantity of oxalic acid formed in the course of the electrolysis can be determined with an accuracy of a few per cent, and this appears to be sufficient for the revelation of the fundamental tendencies.

In the case of glyoxylic acid the products of electrolysis were studied at 650, 800, 1000 and 1050 mV. In general, no effort was made to attain the total transformation of the substance taken. Electrolysis was carried out up to a conversion of 5—80%.

As a result of electrolysis at 650 mV, primarily oxalic acid is formed. The current yield referred to oxalic acid moved around 95%. Even then the evolution of a small quantity of carbon dioxide can also be observed, but the charge devoted to total oxidation can be only a few per cent of the overall charge passing through the system.

**Table I**

| Additive | Basic electrolyte 1 $M$ $H_2SO_4$ | |
|---|---|---|
| | Oxalic acid $10^{-2}$ mole/dm³ | |
| | Added | Found |
| 0.1 mole/dm³ glyoxal | 1.0 | 1.0 |
| 0.1 mole/dm³ glyoxylic acid | 1.0 | 1.0 |
| 0.1 mole/dm³ glyoxal + 0.1 mole/dm³ glyoxylic acid | 1.0 | 1.0 |

At 1050 mV the situation is the opposite. An extremely intensive evolution of carbon dioxide can be observed. From measurement of the volume of gas liberated, it can be stated that even in the case of the conversion of 5% of the glyoxylic acid taken, 90—95% of the charge is devoted to total oxidation. Figure 3 depicts the volume of carbon dioxide evolved as a function of the charge passing through the system. For comparison, the dashed straight line is the plot that would be obtained if the charge in its entirety were devoted to the reaction supplying the carbon dioxide. The variations in the concentrations of oxalic acid and glyoxylic acid in the course of electrolyses at 800 and 1000 mV are illustrated in Fig. 4. (The variation in the glyoxylic acid concentration was calculated from the mass and charge balances.)

The results of the measurements at the four different potentials clearly suggest that the complete oxidation of glyoxylic acid does indeed proceed via the intermediate oxalic acid.

In the case of glyoxal the picture is somewhat more complicated than previously. At 650 mV the concentration of oxalic acid becomes increasingly higher as the electrolysis proceeds. After the conversion of 10—20% of the glyoxal initially, the current yield referred to oxalic acid already attains 50%. Figure 5 shows the current yield referred to oxalic acid as a function of the charge passing through the system. A slight extent of carbon dioxide evolution can also be observed, but the charge equivalent to this does not exceed 5% of the charge passing through the system in this case either. The variations in the glyoxylic acid and oxalic acid concentrations as the electrolysis progresses are illustrated in Fig. 6.

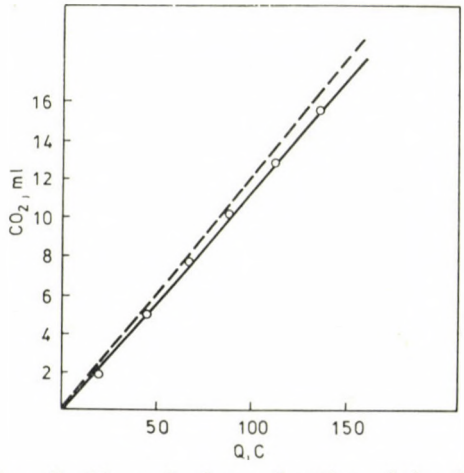



*Fig. 3.* Volume of carbon dioxide evolved as a function of the charge passed through the system, in the case of the oxidation of glyoxylic acid at 1050 mV. The full curve shows the experimentally determined values, and the dashed line the values calculated for 100% transformation

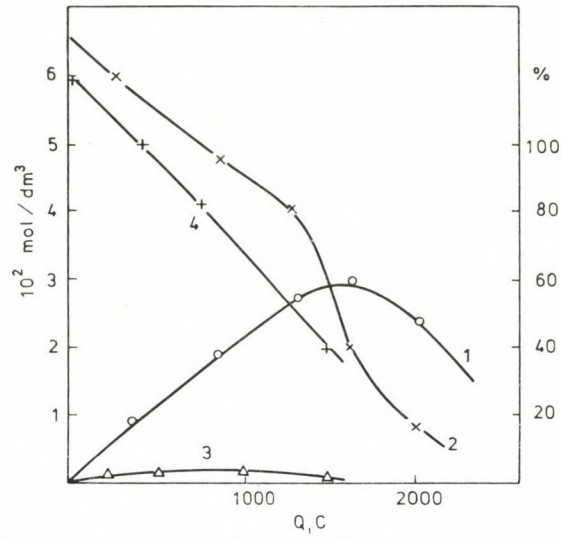



*Fig. 4.* Variation of the concentrations of oxalic acid and glyoxylic acid in the course of the electrolysis: (1) oxalic acid at 800 mV, (2) glyoxylic acid at 800 mV, (3) oxalic acid at 1000 mV, (4) glyoxylic acid at 1000 mV

From the charge balance and from what was said in connection with glyoxylic acid, it clearly follows that the oxalic acid can be formed only from the glyoxylic acid produced in the first step of the oxidation. The fact that, together with the glyoxylic acid, the oxalic acid appears very early, at the beginning of the electrolysis, is in agreement with the conclusion to be drawn from the polarization curves in Fig. 1, *i.e.* with the conclusion that the polarization properties of glyoxal and glyoxylic acid do not greatly differ.

For both glyoxal and glyoxylic acid it was seen that carbon dioxide too is formed, even at the lowest potentials we employed. However, it can by no means be considered that this carbon dioxide originates exclusively from the further oxidation of the oxalic acid formed, since the rate of oxidation of

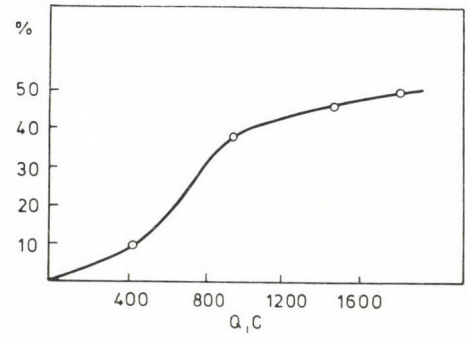



*Fig. 5.* Current yield referred to oxalic acid as a function of the progress of the electrolysis during oxidation of glyoxal

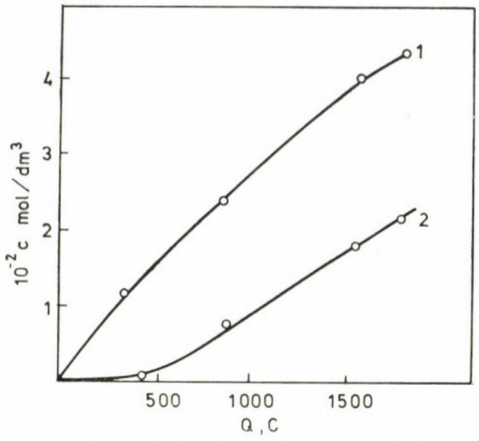
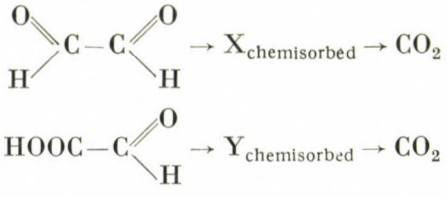



*Fig. 6.* Variation of concentration of (1) glyoxylic acid and (2) oxalic acid during oxidation of glyoxal as a function of the charge passed at 650 mV

oxalic acid at 650 mV is extremely small. It is known from the literature [4] that both compounds are strongly chemisorbed at potentials of 200—500 mV, and the products of chemisorption (dehydrogenated molecules, possibly ruptured at the C–C bond) can be removed by oxidation only at potentials more positive than 500 mV. Carbon dioxide is formed during the oxidation. We have no reason to assume that this chemisorption need not be reckoned with at the potentials we employed; indeed, it appears imperative to take it into consideration. Accordingly, besides the reaction pathway mentioned earlier, the reactions




also take place.

The products of chemisorption have been denoted by X and Y, for opinions in the literature are very divided as to their compositions. As was seen above, the rates of these reactions, *e.g.* at 650 mV, may be even one-two orders of magnitude lower than the rates of the reactions resulting in oxalic acid and glyoxylic acid.

However, the role of the oxidation processes taking place via chemisorption presumably become relatively significant when the rates of the reactions resulting in glyoxylic acid and oxalic acid are low, that is at potentials more negative than those considered so far. In such a case, however, the magnitude of the current flowing through the system is also small, and this makes the studies more difficult, as even with large electrodes long electrolysis times are

required to achieve an appreciable conversion. During electrolysis at 550 mV in the case of glyoxylic acid it did in fact emerge that the current yield referred to oxalic acid is substantially smaller than at 650 mV, and carbon dioxide formation can be observed then too. Accordingly, in the case of 10% conversion of the initial quantity of substance, the current yield referred to oxalic acid can be characterized by a curve passing through a maximum as a function of the potential, as is to be seen in Fig. 7.

From all this it emerges that there exists no potential interval in which exclusively only one reaction takes place, not even in the case of such a simple substance as glyoxylic acid. Since it is always necessary to reckon with chemisorption and with oxidation of the chemisorbed molecules, in the following we shall touch on some questions connected with the effect of chemisorption on the entire oxidation process.

## Effect of the chemisorbed layer on the oxidation processes

As is known from the literature [5], the chemisorption layer exerts an inhibitory effect on the oxidation reaction, since the chemisorbed molecules occupy the surface sites necessary for the oxidation.

If study of the oxidation is begun at potentials (*e.g.* 400 mV) where the chemisorption occurs, but the oxidation of the chemisorbed molecules does not yet proceed, practically no reaction at all can be observed after the chemisorption processes have taken place. As soon as potentials (550, 600 mV) are attained at which the oxidation of the chemisorbed molecules becomes appreciable, a slow increase of the current can be observed. At times the stationary state is not achieved after even 20—30 minutes, and this is in agreement with the fact that the oxidation of the chemisorbed molecules is still not too fast a process at 550—600 mV.

This behaviour of the chemisorbed layer can be well followed by a tracer technique, using some labelled anion, as described in a previous publication for the cases of methanol, formaldehyde and formic acid [6].

Figure 8 shows the potential-dependence of the adsorption of chloride ion in the presence of glyoxylic acid and glyoxal. It is seen that at potentials more negative than 500 mV the glyoxylic acid and the glyoxal completely displace chloride ion. Such an effect of the irreversibly chemisorbed organic substances is totally in accordance with expectations.

When the potential of the electrode is changed from 400 to 600 mV, for instance, the increase in the adsorption of chloride ion takes place only very slowly. In parallel with this, an increase can also be observed in the current, and thus in the rate of oxidation. The rates of the two processes following the switch-over are depicted in Fig. 9. As shown in Fig. 10, a linear correlation

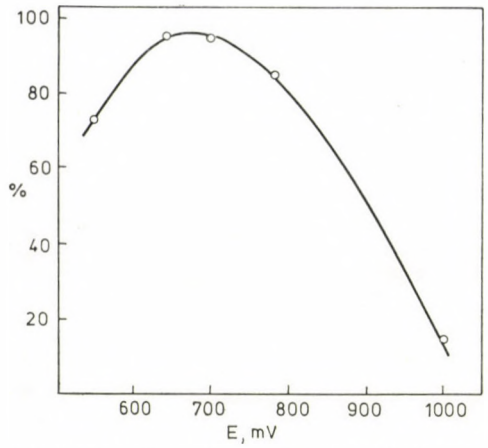



*Fig. 7.* Current yield referred to oxalic acid as a function of the potential in the case of the oxidation of glyoxylic acid, at a 10% conversion of the quantity of starting material

can be established between the magnitude of the current and the count rate, which is proportional to the adsorption of chloride ion.

The phenomena can be interpreted unambiguously in that chloride ion can be adsorbed only on those surface points where the oxidative desorption of the chemisorbed molecules has already occurred. The extent of adsorption of chloride ion is therefore proportional to the number of free surface sites. The same naturally refers to the rate of oxidation on the free surface points too. The linear connection between the count rate and the measured current arises in accordance with this. It follows from what has been said that in the polarization investigations it is by no means irrelevant which direction we set out from to record the polarization curves, or for how long we wait at the indi-

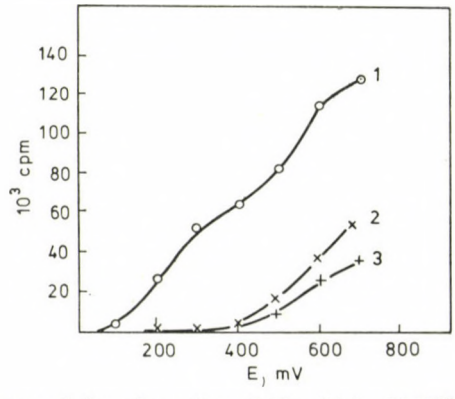



*Fig. 8.* Potential-dependence of the adsorption of $Cl^-$ (1) in *M* $HClO_4$ basic solution, (2) in the presence of glyoxal, and (3) in the presence of glyoxylic acid. $c_{HCl} = 5 \times 10^{-4}$ mole/dm$^3$, $c_{glyoxal} = 0.1$ mole/dm$^3$, $c_{glyoxylic\ acid} = 0.1$ mole/dm$^3$

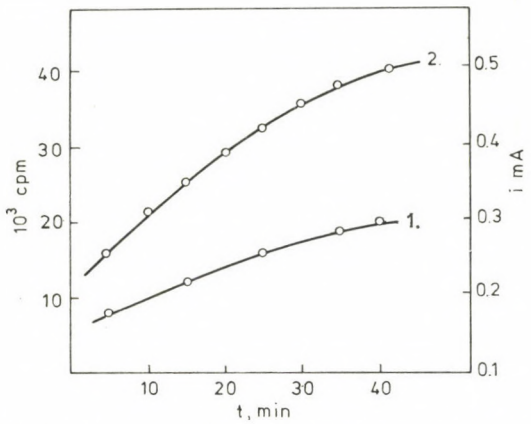



*Fig. 9.* Variation of (1) the current, and (2) the count rate proportional to the adsorption of $Cl^-$, as functions of time, in the presence of glyoxylic acid, at 600 mV

vidual potentials. To a certain extent it is questionable whether the stationary state can be attained with certainty at every potential of interest. At the same time, this also means thatthe frequently-employed potentio-dynamic methods can not be used to study the electrode process in this case either, as already observed in similar cases [7, 8].

## Polarization studies

It emerged from the foregoing that it is advisable to employ only stationary methods in the recording of the polarization curves. The use of galvanostatic study methods can not be considered in all cases, however, as potential oscillations occur in a certain current density interval, depending on the experimental conditions. This phenomenon is well known from the literature [9] in connection with the oxidation of other organic substances. Figures 11

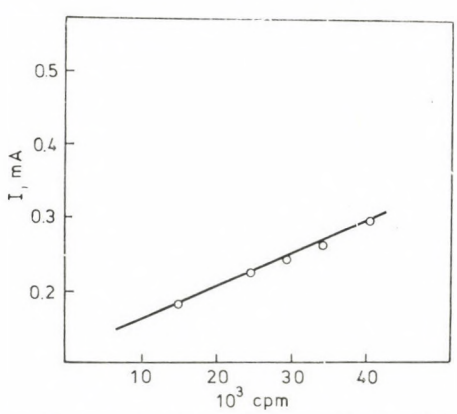



*Fig. 10.* Connection between the count rate and the magnitude of the current in the presence of glyoxylic acid, at 600 mV

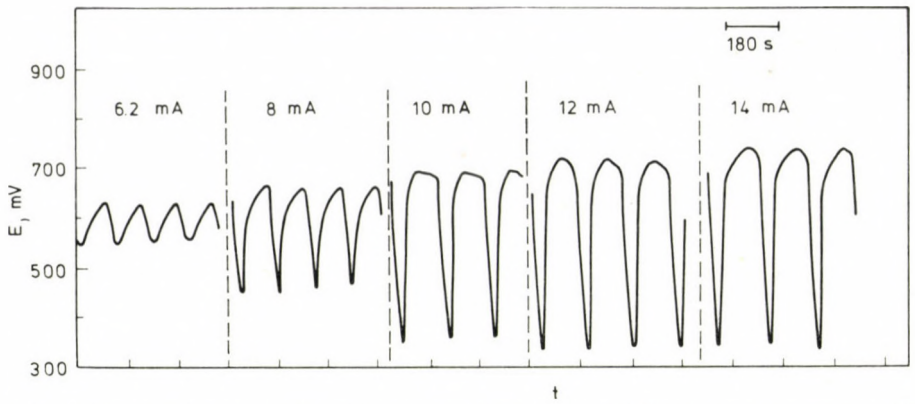



*Fig. 11.* Galvanostatic potential oscillations in the presence of glyoxylic acid. $c = 5.4 \times 10^{-2}$ mole/dm$^3$

and 12 present the observed potential oscillations in the cases of both glyoxylic acid and glyoxal. Just as for other organic compounds, in the event of a given concentration the potential oscillation occurs only in a certain current density interval, and the amplitude of the oscillation increases with increasing current density, but beyond a certain current density limit the potential varies only in the increasing direction.

In connection with the galvanostatic potential oscillations occurring for glyoxal and glyoxylic acid, it is noteworthy that, particularly at low currents, the potential oscillation of the electrode does not extend into the potential interval corresponding to oxygen adsorption. This means that the occurrence of the oscillation can scarcely be brought into correlation with the oxygen adsorption, which is in contrast with the conception widespread in the literature.

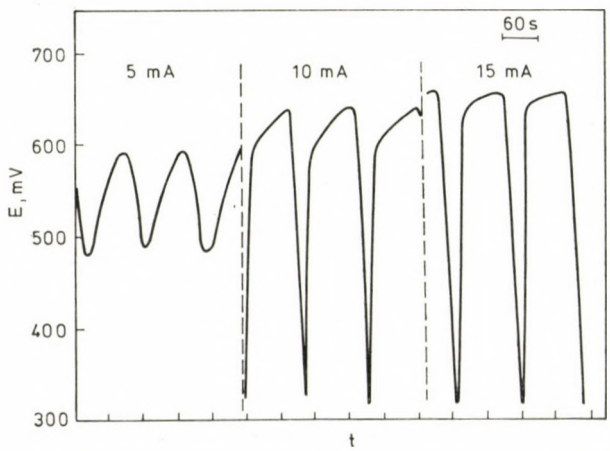



*Fig. 12.* Galvanostatic potential oscillation in the presence of glyoxal. $c = 0.1$ mole/dm$^3$

It appears much more probable that a role is played in the occurrence of the oscillation by the competition of the two reactions outlined above, the reaction resulting in oxalic acid and the oxidation proceeding via chemisorption. This assumption seems to be supported by the fact that the first occurrence of the oscillation can be observed at those potentials (500—600 mV) at which the oxidation of the chemisorbed molecules is already becoming appreciable.

In an earlier publication [10] we demonstrated that, in the event of the ensuring of the appropriate experimental conditions, the galvanostatic potential oscillations can also be attained as the oscillation of rest potentials, if some suitably selected redox system is added to the system containing the oxidizable organic substance in the case of an open circuit. Oscillation of the rest potential could be observed in numerous cases when $Ce^{4+}$ and $Fe^{3+}$ were used. A basic requirement was that there should not be a chemical reaction with an appreciable rate in the liquid phase between the ions and the organic compounds in question. In the cases of glyoxal and glyoxylic acid, the rates of the oxidation reactions with $Ce^{4+}$ in the aqueous phase are fairly high, and thus the oscillation of the rest potential could not be observed if a solution containing $Ce^{4+}$ was added to the system.

In contrast, the oscillation of the rest potential could be observed in a system containing glyoxal and $Fe^{3+}$, as illustrated in Fig. 13. In the potentiostatic polarization curve for the system (Fig. 14) it can be seen well that

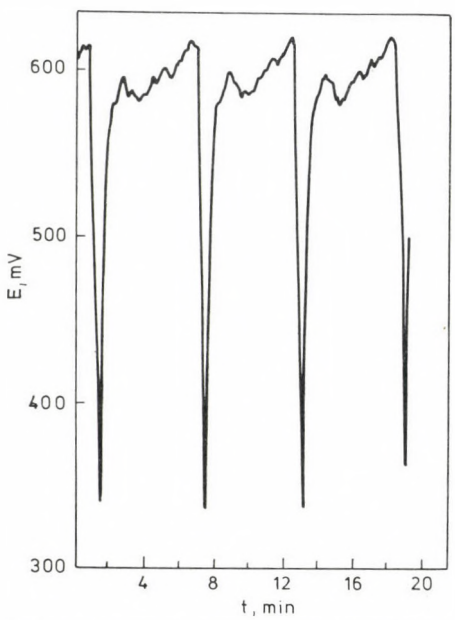



*Fig. 13.* Oscillation of the rest potential of the glyoxal–$Fe^{3+}$ system

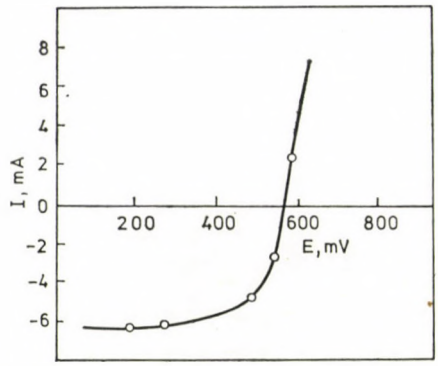



*Fig. 14.* Polarization curve recorded for the glyoxal–$Fe^{3+}$ system

the potential corresponding to the current $i = 0$ (*i.e.* the rest potential that would be observed if the oscillation did not occur) is at about 600 mV; that is, it lies fairly distant from those potentials for which it is necessary to reckon with the appreciable development of the oxide layer. It was seen above, however, that the chemisorption of glyoxal and the oxidation of the chemisorbed glyoxal influence the rate of oxidation to a significant extent at potentials around 600 mV. This observation too suggests that the competition of the chemisorption and the oxidation of the glyoxal plays a role in the occurrence of the galvanostatic potential oscillation. In addition, it is also obvious that the external circuit plays no part in the development of the galvanostatic potential oscillation, for if this were not the case then we could not observe the oscillation of the rest potential.

In the case of glyoxylic acid, the oscillation of the rest potential could not be induced, even with $Fe^{3+}$. The cause of this is probably that oxalic acid, the only product of the oxidation, forms a complex with $Fe^{3+}$, and this changes the electrochemical behaviour of the system (*e.g.* the redox potential and polarization properties of the $Fe^{3+}/Fe^{2+}$ system vary continuously with the extent of formation of the complex). Although oxalic acid is formed in the case of glyoxal too, primarily glyoxylic acid is produced at the beginning of the reaction, and the further oxidation of this (at least initially) does not interfere with the observation of the oscillation.

It follows from the above, therefore, that the analysis of the potentiostatic curves can provide information on the mechanisms of oxidation of glyoxal and glyoxylic acid, but attention was drawn earlier to the fact that, even after long waiting periods, it is not certain that stationary rates are measured in the range of chemisorption or on the oxidation of the chemisorbed material. Thus, prior to the recording of the polarization curves it is necessary to establish how long after the variation of the potential the reaction rate attains a constant, or practically constant value. These results are given in Fig. 15. For both

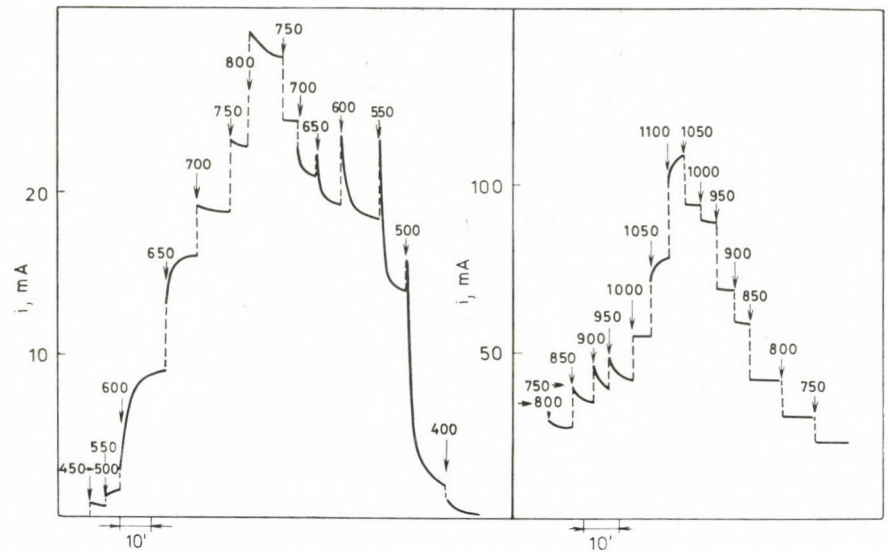



*Fig. 15.* (a) Study of establishment of the stationary state in the case of $1.6\times10^{-1}$ mole/dm$^3$ glyoxylic acid; (b) The same for $1.6\times10^{-1}$ mole/dm$^3$ glyoxal

glyoxylic acid and glyoxal, a slow but considerable increase of the current can be observed in the potential interval 550—650 mV, if we reach the lower limit of this potential range on proceeding from smaller potential values. In the interval 700—1050 mV the rate of the reaction either changes very little in time, or decreases, while from 1050 to 1200 mV a further increase in time can be observed. If the range 650—500 mV is approached from higher potentials,

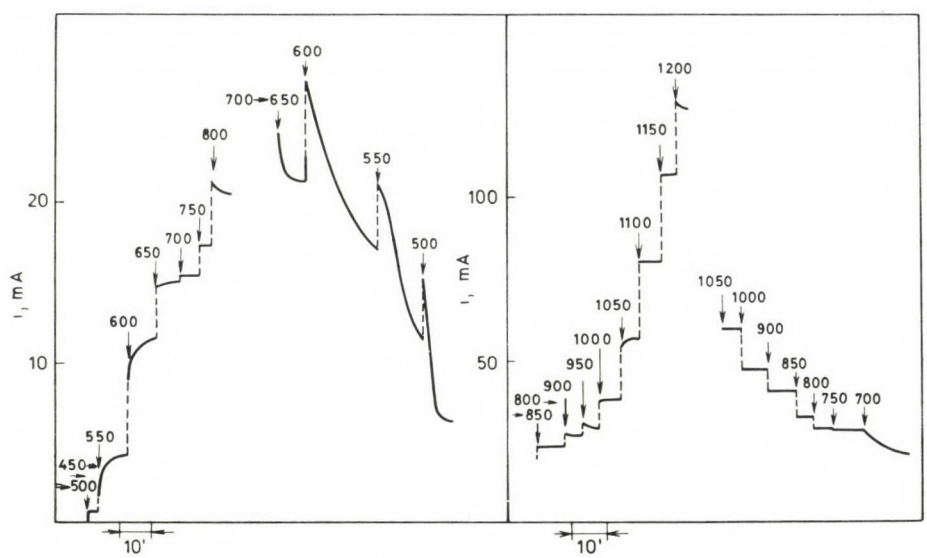



*Fig. 15.* (b)

characteristic behaviour can similarly be observed. On switching-over the current increases considerably; then, after relatively long waiting times (15—30 minutes) it decreases and attains constant values. Our observations indicate that in potentiostatic measurements a waiting period of at least 3—5 minutes is necessary in general after the switching-over to each new potential; this period increases to 15—20 minutes in the vicinity of 600 mV.

In the polarization curves of the two compounds examined (recorded by the above method) three characteristic stages can be distinguished, as shown in Fig. 16. In the potential intervals 600—700 mV and 800—900 mV the rate of the reaction varies to only a slight extent with the potential. Below 500 mV the rate of the oxidation becomes insignificant, while above 1000 mV the reaction accelerates. If the potentiostatic polarization curve is recorded from the direction of higher potentials and is then compared with that recorded in the opposite direction, hysteresis can be observed not only in the oxide range, but also in the potential interval corresponding to the oxidation of the chemisorbed species (Fig. 17).

We assume that the complicated polarization behaviour is connected with chemisorption, with oxidation of the chemisorbed product, and with transformations in the oxide layer. Attention must be drawn to the fact that in the case of these oxo compounds inhibition is not observed with the development of the oxide layer. For alcohols it is known [5] that the rate of reaction decreases considerably following the formation of the oxide layer, as illustrated

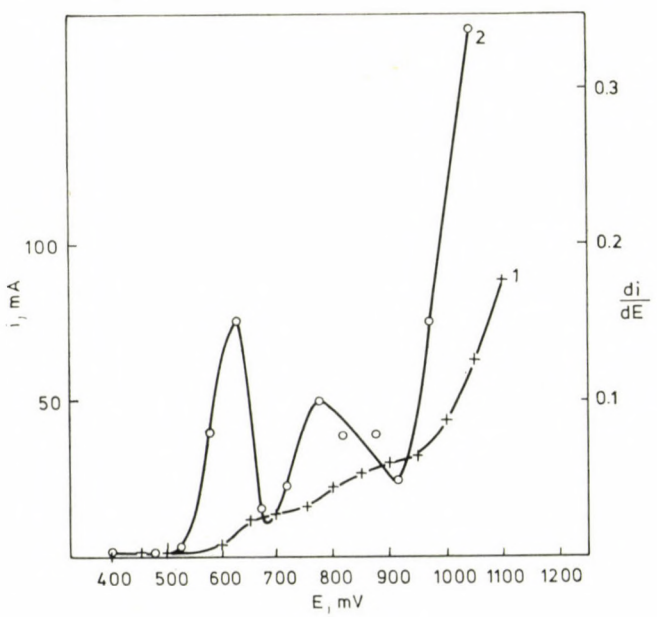



*Fig. 16.* (a)

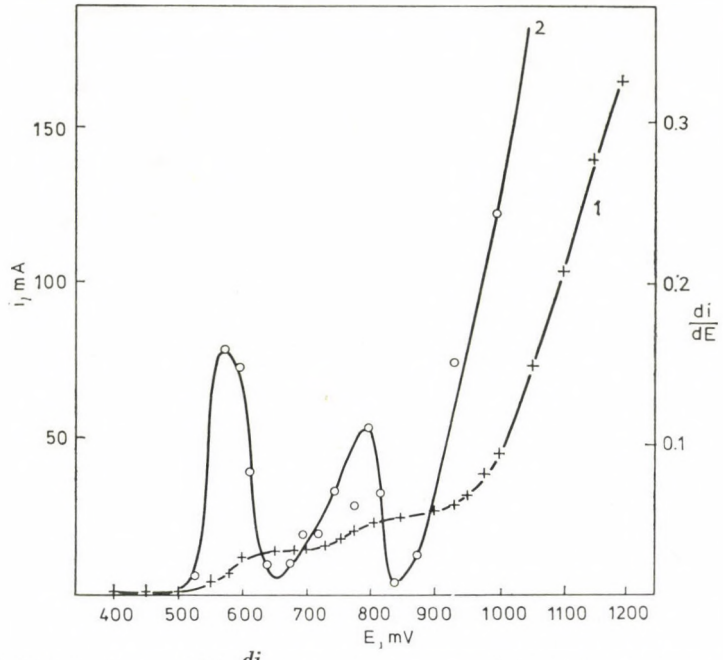



*Fig. 16.* (b) Polarization and (2) $\frac{di}{dE}$ curves in the case of (a) 0.16 mole/dm$^3$ glyoxylic acid, and (b) 0.32 mole/dm$^3$ glyoxal

in Fig. 18, where the potentiostatic polarization curves of glyoxylic acid, ethylene glycol and glycolic acid in this potential interval are compared.

It must also be noted that the polarization curves of glyoxal and glyoxylic acid do not change if the solution contains $HSO_4^-$ instead of $ClO_4^-$, *i.e.* they are independent of whether we work in sulphuric acid or perchloric acid solutions.

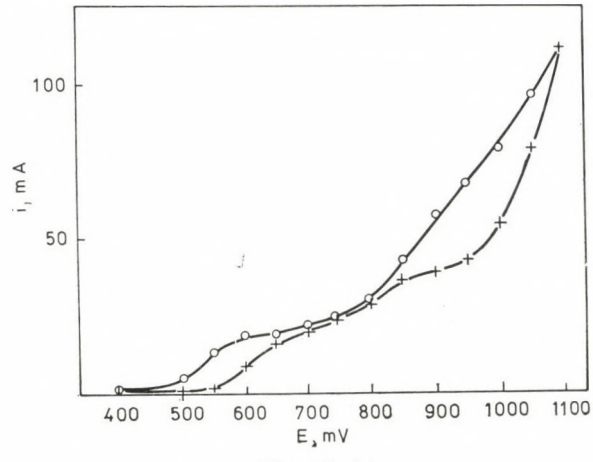



*Fig. 17.* (a)

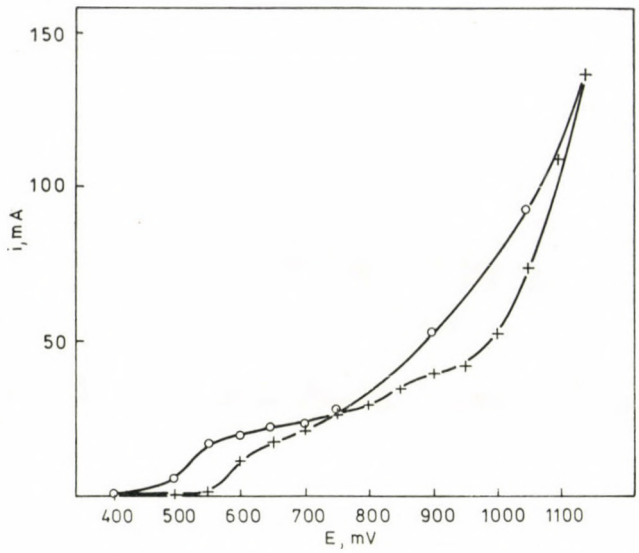



*Fig. 17.* (b) Hysteresis of the polarization curve in the case of (a) glyoxylic acid, and (b) glyoxal

Because of the complex nature of the polarization curves, it is necessary to carry out further investigations in order to elucidate the mechanism. We shall return to these measurements in a subsequent publication, and we shall attempt to outline the probable mechanisms of oxidation of glyoxal and glyoxylic acid.

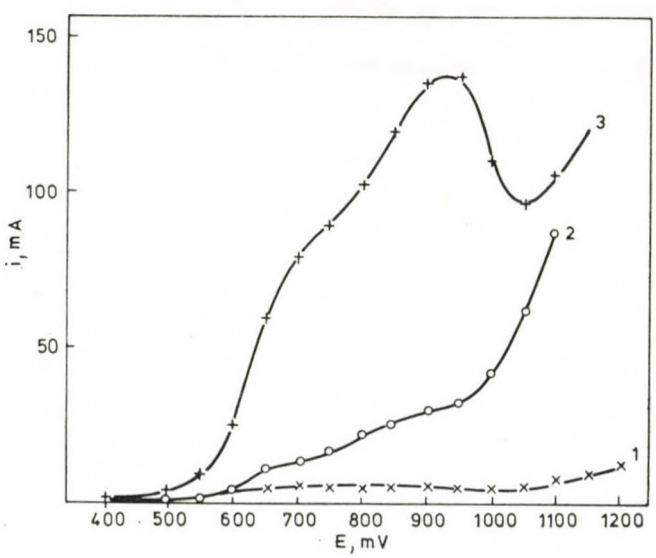



*Fig. 18.* Comparison of the polarization curves of (1) glycolic acid, (2) glyoxylic acid, and (3) ethylene glycol

## REFERENCES

[1] HORÁNYI, G., INZELT, G., SZETEY, Z.: Acta Chimica (Budapest), **97,** 313 (1978)
[2] HORÁNYI, G., SOLT, J., NAGY, F.: J. Electroanal. Chem. **31,** 87 (1971)
[3] PETZOLD, W.: Die Cerimetrie. Verlag Chemie, 1955
[4] DAMASKIN, B. B., PETRII, O. A., BATRAKOV, V. V.: Adsorbtsiya organyicheskikh soedinenii na elektrodakh, Izd. Nauka, Moscow, 1968
[5] BREITER, M. W.: Electrochemical Processes in Fuel Cells, Springer-Verlag, Berlin 1969
DELAHAY, P.: Double Layer and Electrode Kinetics. Wiley, New York 1965
BIANCHI, G., FORMARO, L., TRASATTI, S.: Chim. Ind. **50,** 26 (1968)
SIDHESWARAN, P.: J. Electrochem. Soc. India **24,** 81 (1975)
INDIRA, C. J., SIDHESWARAN, P.: Trans. Saest. **8,** 103 (1973)
SIDHESWARAN, P.: Ind. J. Chem. **12,** 1077 (1974)
[6] HORÁNYI, G., VÉRTES, G.: J. Electroanal. Chem. **51,** 417 (1974)
[7] VIJH, A. K.: Can. J. Chem. **48,** 197 (1970); **49,** 78 (1971)
[8] HORÁNYI, G., KŐNIG, P., TELCS, I.: Acta Chim. (Budapest) **72,** 165 (1972)
HORÁNYI, G., VÉRTES, G., KŐNIG, P.: Acta Chim. (Budapest) **72,** 179 (1972)
[9] WOJTOWICZ, J.: Oscillatory Behavior in Electrochemical Systems, Modern Aspects of Electrochemistry, No. 8, p. 47, Plenum Press, New York 1972
[10] HORÁNYI, G., INZELT, G., SZETEY, É.: Electroanal. Chem. **81,** 395 (1977)

György HORÁNYI
György INZELT } H-1025, Pusztaszeri u. 58—67.
Éva SZETEY H-1088 Budapest, Puskin u. 11—13.

*Acta Chimica Academiae Scientiarum Hungaricae, Tomus 98 (1), pp. 67—75 (1978)*

# EFFECT OF ALIPHATIC ALCOHOLS ON THE HYDROGEN OVERVOLTAGE ON DROPPING GALLIUM ELECTRODES

K. SZABÓ, L. SZIRÁKI and J. MIKA

*(Department of Physical Chemistry and Radiology, L. Eötvös University, Budapest)*

Received August 2, 1977

The effect of methanol, 1-propanol and 1-butanol on the rate of electrolytic hydrogen evolution has been investigated on a dropping gallium electrode. We have established that the rate of hydrogen evolution increases with increasing number of carbon atoms in the alcohol.

The results can be interpreted on the assumption that in the presence of alcohols the $ROHH^+$ ion is the proton donor, and with increasing adsorption heat of alcohols due to dispersion interactions, the activation energy of the hydrogen evolution reaction decreases.

We have found a correlation between the change in the rate of hydrogen evolution, lg $i$, and the mean polarizability of the alcohol, $\alpha_2$.

The hydrogen overvoltage on gallium electrodes was investigated previously in methanol and aqueous hydrochloric acid solutions [1, 2]. We have observed that upon changing the solvent from water to methanol the hydrogen overvoltage decreases. This can be explained, on the one hand, by the fact that methanol is adsorbed more strongly on gallium than water, and, on the other hand, by changes in the structure of the electric double layer. Consequently, the $\psi'$ potential (the electric potential in the double layer on the boundary between the Helmholtz layer and diffuse layer) is shifted into the negative direction.

A comparison of hydrogen overvoltage ($\eta$) values measured in various alcoholic acid solutions shows that, depending on the nature of the cathode metal, in methanol solutions the value is generally smaller, while in higher alcohols greater, than the value measured in aqueous solutions [3—5]. At the same time, in the case of Hg and Pt electrodes the overvoltage decreases in the sequence water $>$ methanol $>$ ethanol [3—6].

The variation of the hydrogen overvoltage upon going from water to methanol may be the result of several effects [7]. The variation of the zero charge potential, and the $\psi'$, are related to the change in the structure of the electrode-electrolyte boundary layer. With the variation of the adsorption heat of the solvent, the activation energy of the process may change. Depending on the nature of the solvent molecule adsorbed on the electrode surface, changes may occur in the binding energy of the adsorbed hydrogen ($W_{Me-H}$) and/or in the interaction between the hydrogen atom adsorbed on the electrode surface and the solvent molecule.

As a consequence of the adsorption of alcohol molecules, part of the electrode surface may be blocked, resulting in a decrease of the surface available for hydrogen evolution, which may lead to the increase of $\eta$.

At present there are not enough experimental data in the literature to decide which of the above factors predominates depending on the nature of the metal and alcohol. Therefore, for gathering further information, it is of interest to investigate the effect of some lower aliphatic alcohols on the hydrogen overvoltage measured on gallium electrodes.

According to the literature [8] and our own investigations, the hydrogen overvoltage, the capacity of the double layer on a stationary electrode is time-dependent in the presence of organic substances such as alcohols. The reason for this is that in acidic solutions the products of the reaction between alcohols and metallic gallium are adsorbed on the electrode, thereby contaminating the electrode surface.

In order to avoid contamination, we carried out the investigations on a dropping gallium electrode.

## Experimental

For the measurements we used the dropping gallium electrode described in Ref. [9]. The current *vs.* time curves for the given potentials were recorded on a PAR-170 device, and from these data we determined the mean current I. The current density can be calculated [10] as

$$i = (5/3)\frac{I}{S_{max}}$$

where $S_{max}$ is the maximal surface of the drop, which can be calculated from the drop weight and the density of gallium.

The drop weight at each potential was determined as an average of the accurate weight of 10—20 drops. The surface of one drop was about 0.1 $cm^2$. Lg $i$ *vs.* $\eta$ curves were constructed from $i$-$\eta$ pairs.

Measurements were carried out on a dropping gallium electrode of 99.9999% purity, at 32 °C in aqueous or aqueous-alcoholic 1 $M$ $HClO_4$ solutions saturated with hydrogen. For the preparation of the solutions analytical grade 70 wt.% $HClO_4$ (Germed), methanol, 1-propanol and 1-butanol (Reanal) were used.

The solutions to be investigated were prepared with bidistilled water. In order to purify them before measurement, the solutions were electrolyzed using a separate gallium cathode, with a current density of $1.5 \times 10^{-3}$ A/$cm^2$ for 14—16 hrs.

Figure 1 shows the lg $i$ *vs.* $\eta$ curves for 1 $M$ aqueous $HClO_4$ and for 1 $M$ $HClO_4$ + 0.84 $M$ alcohol solutions. It is to be seen that for the methanol-containing solution, the polarization curve is nearly parallel to the curve for the aqueous solution, whose slope is b = 0.095—0.199 V. For 1-propanol and 1-butanol, this parallelism is observable only at lower overvoltages, in the range of $\eta = -0.6 - 0.8$ V. At more negative overvoltages ($\eta < -0.8$ V), the slope of the polarization curve increases in the presence of propanol and butanol and at $\eta \approx -0.9$ V reaches and exceeds the overvoltage measured in aqueous solutions.

On comparison of the effect of the three alcohols, it can be seen that the rate of hydrogen evolution in the overvoltage range of $-0.6 - 0.8$ V increases in the sequence methanol < propanol < butanol, *i.e.* the greater the number of carbon atoms, the more the alcohols decrease the hydrogen overvoltage. This sequence changes, however, at more negative potentials $\eta < -0.8$ V.

The effect of thiourea on the hydrogen overvoltage was investigated in aqueous and aqueous — alcoholic solutions of $HClO_4$.

As is apparent from Fig. 2, thiourea increases the rate of the hydrogen evolution reaction. At a thiourea concentration of $10^{-3}$ $M$, the increase is the greatest in the case of the

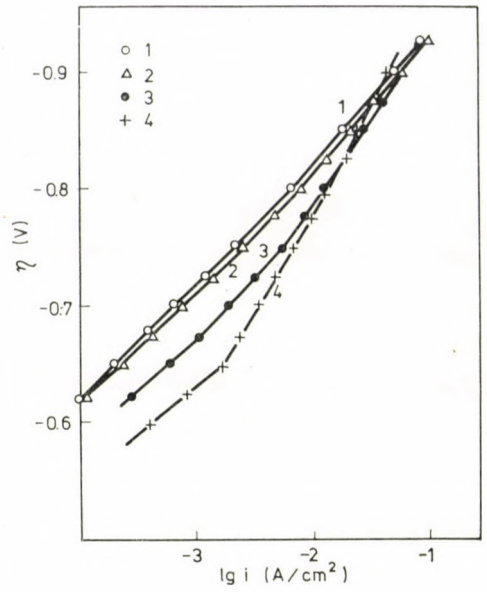



*Fig.* 1. $\eta$ *vs.* lg $i$ curves on the dropping gallium electrode: (1) 1 $M$ aqueous $HClO_4$ solution; (2) 1 $M$ aqueous $HClO_4$ solution + 0.84 $M$ methanol; (3) 1 $M$ aqueous $HClO_4$ solution + + 0.84 $M$ 1-propanol; (4) 1 $M$ auqeous $HClO_4$ solution + 0.84 $M$ 1-butanol

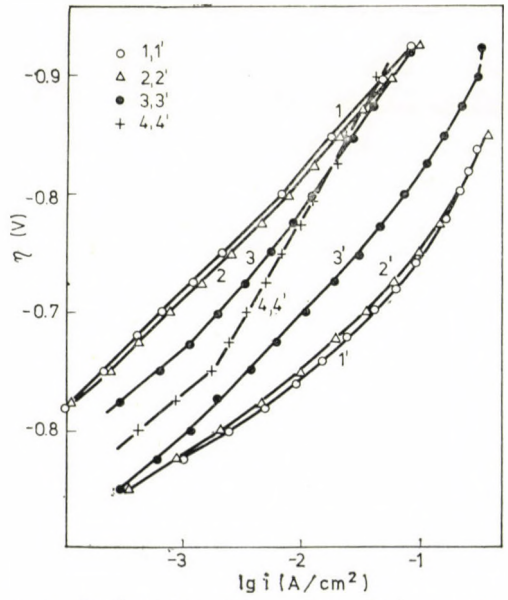



*Fig. 2.* $\eta$ *vs.* lg $i$ curves on the dropping gallium electrode (curves 1—4 the same as in Fig. 1) (1′) 1 $M$ $HClO_4$ + $10^{-3}$ $M$ aqueous $(NH_2)_2CS$; (2′) the same as 1′ + 0.84 methanol; (3′) the same as 1′ + 0.84 1-propanol; (4′) the same as 1′ + 0.84 1-butanol

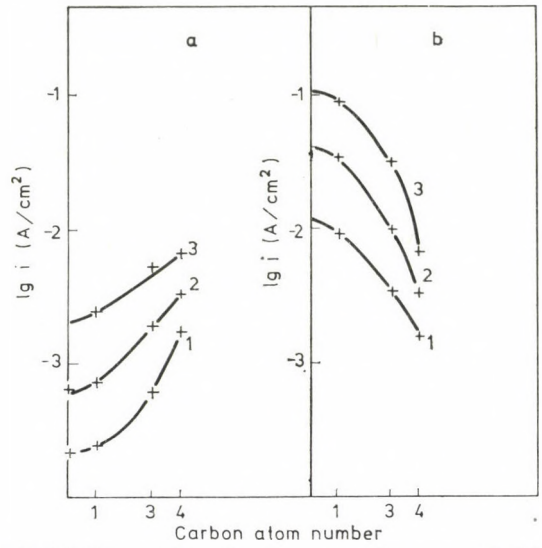



*Fig. 3.* Variation of lg $i$ with the number of carbon atoms ($\eta$ = const.): (a) 1 $M$ $HClO_4$ + 0.84 $M$ aqueous ROH; (b) 1 $M$ $HClO_4$ + 0.84 $M$ ROH + $10^{-3}$ $M$ $(NH_2)_2CS$. (1) $\eta = -0.65$ V, (2) $\eta = -0.70$ V, (3) $\eta = -0.75$ V

aqueous $HClO_4$ solution; in the presence of alcohols, the catalytic effect of thiourea diminishes in the sequence methanol > propanol > butanol. The rate of hydrogen evolution, plotted against the number of carbon atoms in the alcohol at $\eta$ = const. is shown in Fig. 3a, and the same in the presence of thiourea in Fig. 3b.

## Discussion

Figures 1 and 3a show that with increasing carbon atom number in alcohols, at $\eta$ = const. and $c_{alc.}$ = const., the rate of hydrogen evolution increases relative to the aqueous $HClO_4$ solution. It is also known for $C_1$—$C_6$, *n*-aliphatic, primary alcohols adsorbed from aqueous solutions on metal electrodes (Hg, Sn, Cd, Ga—In, Bi) that the free enthalpy of adsorption $\Delta G_a$ increases with increasing carbon atom number of the alcohol [11—15].

Consequently, the increase of the rate of hydrogen evolution with the carbon atom number can be attributed to the increase of the Ga–ROH interaction in the same direction.

The hypothesis that the interaction between the alcohols and gallium increases with increasing carbon atom number is supported by the experimental fact that the catalytic effect of thiourea is smaller for higher alcohols, because the displacement of the alcohol by thiourea from the gallium surface is less pronounced if the interaction between the alcohol and metal is stronger.

The free enthalpy of adsorption, $\Delta G_a$, for a given metal can be regarded as the measure of the variation of the interaction between the metal and

alcohol. To establish that the change in the rate of hydrogen evolution is a consequence of the change in the metal–alcohol interaction, it seems reasonable to examine on which parameters it is dependent.

According to BOCKRIS [16], the free enthalpy of adsorption is

$$\Delta G_a = \Delta G_1 - \Delta G_2 - \Delta G_3 \tag{1}$$

where $\Delta G_1$, $\Delta G_2$, $\Delta G_3$ refer to the ROH/Me, ROH/$H_2O$ and $H_2O$/Me interactions, respectively.

$\Delta G_3$ depends on the nature of the metal and is constant for a given metal; $\Delta G_2$ and $\Delta G_1$ — for a given metal — depend on the nature of the alcohol. Assuming physical adsorption, the latter quantity includes dispersion ($U_d$), image ($U_i$) and repulsion ($U_r$) interactions. As $U_i$ and $U_r$ are governed by metal–dipole and dipole–dipole interactions, and the dipole moments ($\mu$) of alcohols do not differ significantly (they vary between 1.60—1.68), on comparing the energy changes accompanying the adsorption of various alcohols, these terms can be neglected. Therefore, it may be assumed that the energetics of alcohol adsorption are mainly governed by dispersion interactions. The metal–adsorbate interaction ($U_d$) can be described [17] by the following relationship:

$$U_{d,1} = \frac{N\, mc^2 \alpha_1 \alpha_2}{\left(\frac{\alpha_1}{\varkappa_1} + \frac{\alpha_2}{\varkappa_2}\right) R^3} \tag{2}$$

where N — number of metal atoms in 1 $cm^3$,
R — distance between the center of the alcohol molecule and the metal surface,
m — mass of the electron,
c — velocity of light,
$\varkappa_1, \varkappa_2$ — diamagnetic susceptibilities, and
$\alpha_1, \alpha_2$ — electron polarizabilities of the metal and alcohol, respectively.

According to LONDON's theory, the dispersion interaction between two different molecules is proportional to the product of the electron polarizabilities of these molecules [18]; in our case

$$U_{d,2} \sim \alpha_{H_2O} \cdot \alpha_2 \tag{3}$$

(Relationship (3) is only qualitative, because the theory is only approximately applicable for a condensed system of polar molecules.)

Equation (2) seems to be very complicated, however, the calculation of $U_{d,1}$ for some metals and 1-butanol, yields nearly identical values: Hg/1-

butanol 2.6, Cd/1-butanol 2.51 and Zn/1-butanol 2.26 kcal/mol, which means that the metal–alcohol dispersion interaction for the above metals is nearly independent of the nature of the metal. (Values were used for $\varkappa_1$ and $\varkappa_2$ from [20], for $\alpha_1$ and $\alpha_2$ from [19] and for N and R from [21].) According to our assumption, the total energy of adsorption is composed of the dispersion energy and of the characteristic energy for the metal–$H_2O$ interaction, thus being equal to the corresponding change of enthalpy. By analogy to Eq. (1)

$$\Delta H_a \approx U_{d,1} - U_{d,2} - \Delta H_{Me-H_2O} \tag{4}$$

where, on the basis of Eqs (2) and (3),

$$U_{d,1} - U_{d,2} \sim \alpha_2 .$$

Assuming that the change in the $\Delta S$ values is negligible,

$$\Delta G_a \approx \Delta H_a$$

Eq. (1) may be written as

$$| \Delta G_a | \sim \alpha_2 - \Delta G_{Me-H_2O} \tag{5}$$

*i.e.* for a given metal $| \Delta G_a |$ increases with the mean electron polarizability of the alcohol. The correctness of Eq. (5) may be checked by using the $\Delta G_a$ values for various alcohols measured on Hg [11], Sn [12], Cd [13], Ga–In [14] and Bi [15] electrodes.

Figure 4 shows that it is qualitatively correct to assume that the metal–alcohol interaction is mainly due to dispersion forces, which are proportional to the electron polarizability of the alcohol. Figure 4 also shows that the

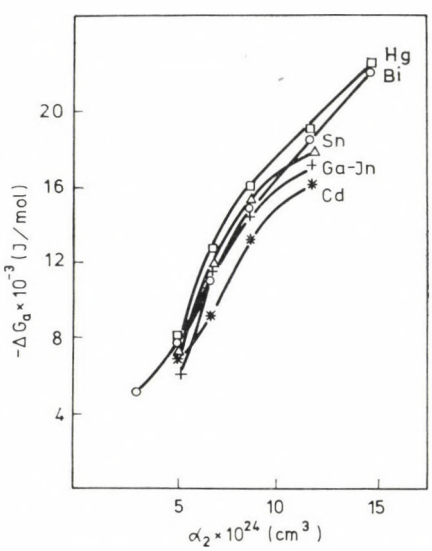



*Fig. 4. $\Delta G_a$ vs. $\alpha_2$ curves on various metals ($\alpha_2$ mean electron polarizability of the alcohol)*

measured $\Delta G_a$ *vs.* $\alpha_2$ curves are similar for various metals and that the $|\Delta G_a|$ values decrease from Hg to Cd in the interval of $\alpha_2 \approx (6-10)\times 10^{24}$ cm$^3$. Thus the $\Delta G_3$ characteristic of the metal–water interaction increases in the sequence Hg < Sn < Bi < Cd, which corresponds to the hydrophilic character of these metals [22].

The $\Delta G_a$ values for alcohol adsorption on gallium are not known, but, assuming similar $\Delta G_2$ *vs.* $\alpha_2$ curves for gallium and for the above metals and the Ga–In alloy, Eqs (4) and (5) can be used for describing the gallium–alcohol–water system. The relationship between the reaction rate and the gallium–alcohol interaction may be discussed in terms of the equation [23]

$$E_0 = \Delta H_H + \Delta H_S + RT \tag{6}$$

where it is assumed that the rate-determining step is

$$SH^+ + e \rightarrow H_a + S_a$$

and $E_0$ — activation energy,
$\Delta H_S$ — adsorption heat of S,
$\Delta H_H$ — adsorption heat of the H atom on the electrode surface.

(Equation (6) is strictly valid only for $\eta = 0$ and for a barrier-free process, but qualitative conclusions may be drawn in the present case, too.)

The rate-determining step in aqueous solutions is

$$H_3O^+ + e \rightarrow H_a + H_2O\,.$$

By analogy, we assume that in the presence of alcohols the rate-controlling step will be

$$ROHH^+ + e \rightarrow H_a + ROH\,.$$

Consequently, upon going from the $H_2O-H^+$ to the $H_2O-ROHH^+$ system, the change in the activation energy according to Eq. (6) ($\Delta H_H$ = const.) is

$$\Delta E \approx \Delta H_a$$

and, according Eq. (4),

$$\Delta H_a \sim \alpha_2\,.$$

The reaction rate at $\eta$ = const. is

$$\lg i = \lg A - \frac{E}{2{,}3\,RT}$$

and its change

$$\Delta \lg i \sim \Delta E \sim \alpha_2\,.$$

This means that if, according to our assumption, the increase in the rate of hydrogen evolution parallels the increase of the gallium–alcohol interaction and the latter is mainly controlled by the change in the dispersion energy, than lg $i$ should change monotonously with $\alpha_2$.

Figure 5 shows that the lg i *vs.* $\alpha_2$ curve is a straight line, confirming the assumed effect of alcohols on the rate of hydrogen evolution.

The lg $i$ *vs.* $\alpha_2$ correlation explains the experimental result (Fig. 3a) that the increase of lg $i$ is proportional to the number of carbon atoms in the alcohols, the latter being nearly proportional to $\alpha_2$.

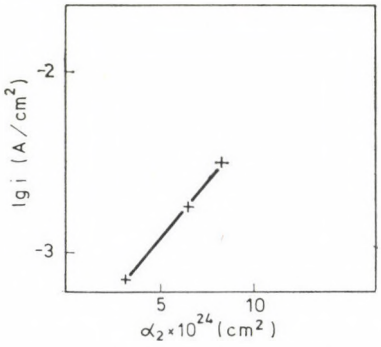



*Fig. 5.* lg $i$ *vs.* $\alpha_2$ curve (on the basis of data in Fig. 1, at $\eta = -0.70$ V)

To decide whether the mechanism found for gallium and the investigated alcohols is valid for other metals and alcohols, too, further experiments are needed. Probably, with higher alcohols, in addition to the variation of the adsorption heat, changes in the double layer structure and the surface blocking effect of the alcohol molecules should also be considered, so much the more because with increasing carbon atom number the proton-binding capability decreases, thus the proton-donor role of $ROHH^+$ becomes less important.

## REFERENCES

[1] Szabó, K., Vas, M.: Magy. Kém. Folyóirat, **77,** 40 (1971)
[2] Szabó K., Mika, J., Hangos, K.: Magy. Kém. Folyóirat, **80,** 569 (1974)
[3] Grigorev, V. P., Ekilik. G. N., Ekilik, V. V.: Khim. Khim. Tekhnol., **16,** 577 (1973)
[4] Ekilik, V. V., Grigorev, V. P., Ekilik, G. N.: Zashchita Metallov, **1,** 51 (1973)
[5] Bockris, J. O. M., Parsons, R.: Trans. Faraday Soc., **44,** 860 (1948)
[6] Lewina, S. D., Silberfar, V.: Physicochim., **4,** 275 (1936)
Novoselsky, B.: J. Phys. Chem. Soc. Russ., **11,** 369 (1938)
[7] Damaskin, V. B., Petrii, O. A.: Vvedenie v elektrokhimicheskuyu kinetiku, p. 229, Moskva 1975
[8] Bagotskaya, J. A., Durmanov, C.: Elektrokhimiya, **4,** 115, 1414 (1968); **5,** 1236 (1969)
[9] Szabó, K., Bagotskaya, I. A.: Zh. Fiz. Khim., **37,** 2581 (1963)
[10] Iofa, Z. A., Kolichev, A.: Zh. Fiz. Khim., **14,** 58 (1940)
[11] Damaskin, B. B., Survile, A. A., Ribalka, L. E.: Elektrokhimiya, **3,** 146 (1967)
[12] Grigorev, N.: Elektrokhimiya, **9,** 1842 (1973); **5,** 87 (1969)
[13] Ribalka, L. E., Damaskin, B. B., Leikis, D. I.: Elektrokhimiya, **11,** 9 (1975)

[14] GRIGOREV, N., KALUZHNAYA, A.: Elektrokhimiya, **10,** 1287 (1974)
[15] PULERITS, R., MOLDAI, M., PALM, V.: Elektrokhimiya, **10,** 482 (1975)
[16] BOCKRIS, J. O'M., BLONGREN, E., JESCH, C.: J. Phys. Chem., **65,** 2000 (1961)
[17] ANDERSEN, T. N., BOCKRIS, J. O'M.: Electrochim. Acta, **9,** 347 (1964)
[18] MOELWYN-HUGHES, E. A.: Physical Chemistry, 2nd ed., p. 339. Pergamon, London 1961
[19] LANDOLT—BÖRNSTEIN: Physicochemical Tables, VI. ed., Vol. I, p. 401, 1950
[20] LANDOLT—BÖRNSTEIN: Physicochemical Tables, VI. ed., Vol. II, p. 220, 1955
[21] MOELWYN-HUGHES, E. A.: Physical Chemistry, 2nd ed., p. 644. Pergamon, London 1961
[22] SALEM, R. R.: Zh. Fiz. Khim., **43,** 2876 (1969)
TRASATTI, S.: J. Electroanal. Chem., **65,** 815 (1975)
[23] KISHTALIK, L. I.: Zh. Fiz. Khim., **30,** 117 (1960)

Kálmán SZABÓ
József MIKA
Laura SZIRÁKI

H-1088 Budapest, Puskin u. 11—13.

*Acta Chimica Academiae Scientiarum Hungaricae, Tomus 98 (1), pp. 77—80 (1978)*

# METAL CHELATES WITH ETHYLMALONDIHYDRAZIDE

H. N. PANDEY, Lallan MISHRA and V. J. RAM

*(Department of Chemistry S.C. College, Ballia (U.P.) India)*

Received April 30, 1977
in revised form September 26, 1977

New complexes of ethylmalondihydrazide with Fe(III), Co(II), Ni(II), Cu(II) and Zn(II) are described. The complexes are characterized by spectral studies, elemental analyses and magnetic measurements. Some of the compounds are active as pesticides.

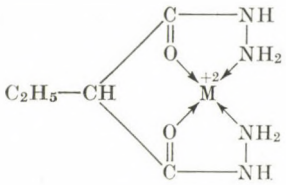
Metal complexes with hydrazides and their derivatives as anti-tubercular [1] agents have attracted special attention in recent years and prompted the investigation of new chelates, which might possess pronounced biological activity. Coordination compounds of monohydrazides and their derivatives with transition metal ions have been described [2—4], but little is known about the chelates of transition metal ions with dihydrazides. DUTTA *et al.* [5] have reported transition metal complexes with dihydrazides but have not studied the pesticidal activities of these compounds. It is expected that a repetition of the hydrazide group and introduction of a hydrophilic moiety into malondihydrazide may enhance the pesticidal activity. In this anticipation transition metal chelates with Fe(III), Co(II), Ni(II), Cu(II) and Zn(II) were prepared to evaluate their pesticidal activities. It is evident from the structure that the ligand has several possible donor groups.

There is some controversy [6] as to whether coordination involves the carbonyl and the amino group (**I**, **V**) or two carbonyl (**II**), two amino (**III**) or two imino groups (**IV**). Spectral studies of the complexes revealed that the ligand is tetradentate rather than bidentate as reported by earlier workers and the sites for coordination occurs via the carbonyl and amino groups. The structure of the complexes are discussed on the basis of spectral studies, elemental analyses and magnetic measurements.

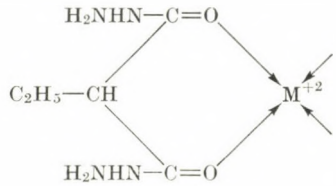
## Experimental

**Ethylmalondihydrazide (EMDH).** A mixture of diethylethylmalonate (0.1 mol) and hydrazine hydrate (100%, 0.21 mol) in 50 ml of ethanol was refluxed for 3 hrs. During this period, a white solid separated out which was cooled, filtered and washed with cold methanol. Finally, the crude product was crystallized from a water–ethanol mixture as reported by RAM [7]. Yield 85%, m.p. 160 °C.

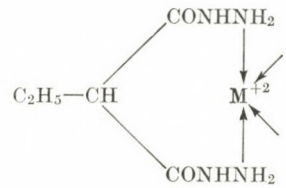
**Preparation of chelates.** All the complexes were prepared by heating a mixture of an equimolar solution of ligand and metal salt in distilled water, followed by addition of metha-



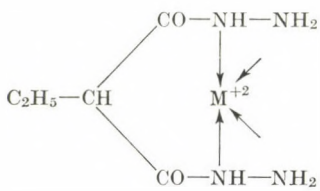
I



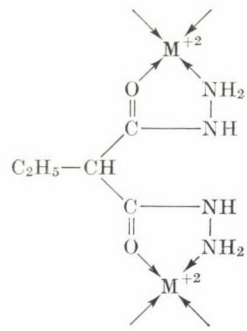
II



III



IV



V

nol. In the case of cobalt, the mixture was refluxed for 4 hrs and processed as usual. The m.p.'s of all complexes were above 300 °C.

**Apparatus and measurements.** IR spectra (KBr pellets) of the ligand and the complexes were recorded on a Perkin Elmer grating IR spectrophotometer, U.V. spectra were recorded in dilute HCl (lmg/100 m) using a Cary 15 spectrophotometer. Both IR and UV spectra were recorded at the Department of Chemistry, University of Konstanz, West Germany. Magnetic measurements on the complexes were performed by Faraday's technique at Banaras Hindu University, India.

**Analyses.** Nitrogen was analyzed by the microanalytical section of the chemistry Department, B.H.U., India. Metal ions were estimated by dissolving a known amount of the complex in concentrated nitric acid followed by evaporation to dryness, extraction with water and analysis for the metal ions [10]. Results of elemental analyses together with other relevant data are shown in Table I.

**Table I**

*Elemental analyses and magnetic measurements of the chelates of EMDH*

| Complex | Colour | N(%) | | Metal (%) | | Magnetic moment (B. M.) | $\lambda_{max}$ | (log $\varepsilon$) |
|---|---|---|---|---|---|---|---|---|
| | | Calcd. | Found | Calcd. | Found | | | |
| $NH_4FeL(SO_4)_2 \cdot 4H_2O$ | Brown | 14.0 | 13.98 | 11.2 | 10.8 | 5.6 | 222 | (4.29) |
| $CoL(NO_3)_2 \cdot 2H_2O$ | Pink | 22.17 | 22.23 | 15.5 | 14.67 | 3.7 | 204, 256 | (4.57) (3.87) |
| $NiLSO_4 \cdot 2H_2O$ | Blue | 15.9 | 15.81 | 16.7 | 16.1 | 2.9 | 204 | (3.57) |
| $CuLCl_2 \cdot 2H_2O$ | Green | 16.9 | 16.81 | 19.2 | 18.9 | 1.9 | 202 | (4.51) |
| $ZnLSO_4 \cdot 2H_2O$ | White | 15.6 | 15.4 | 18.2 | 18.9 | Diamagnetic. | 202 | (4.22) |

L = EMDH.

## Discussion

*IR spectra.* IR spectra of KBr-pelleted samples of both the hydrazide and its complexes were recorded in the range of 4000—200 $cm^{-1}$. The major IR bands and their assignments are shown in Table II. In EMDH the carbonyl

**Table II**

*IR spectra* of EMDH and its metal chelates*

| EMDH | Fe(III) Complex | Co(II) Complex | Ni(II) Complex | Cu(II) Complex | Zn(II) Complex | Bands assigment |
|---|---|---|---|---|---|---|
| $3280^{s}$, $3040^{s}$ | $3200^{w}$ | $3400-3200^{s}$ | $3260-3200^{b}$ | 3400<br>3220 | $3260-3200^{b}$ | $\nu$(NH, $NH_2$, OH) |
| 2960, 2940,<br>2880 | 2960,<br>2940 | 2960, 2880 | 2960, $2880^{w}$ | 2960<br>2880 | 2960, $2880^{w}$ | $\nu(CH_3)$ |
| $1650^{s}$ | $1610^{w}$ | $1550^{w}$ | $1650^{w}$ $1600^{w}$ | $1600^{w}$ | $1650^{w}$, $1600^{w}$ | $\nu(-C=O)$ |
| $1520^{s}$ | $1500^{w}$ | $1500^{w}$ | $1500^{w}$ | $1510^{w}$ | $1520^{w}$ | $\delta(NH_2)$ |
| 1460 | 1400 | $1380^{s}$ | $1360^{w}$ | 1420 | 1460 | $\delta$ assym. $CH_3$ |
| 1360, $1320^{s}$ | 1360<br>1320 | 1360 | 1320 | 1360 | 1320 | $\delta$ sym. $CH_3$ |
| 1280, 1230 | — | — | — | $1280^{w}$ | $1280^{w}$ | $\omega$ $NH_2$ |
| 1150, 1100 | 1110 | $1150-1110^{w}$ | $1100^{w}$ | $1180^{w}$ | 1100 | $\beta$ NH and $\tau NH_2$ |
| 1040, 1010<br>990 | 990 | 990 | $960^{b}$, $900^{w}$ | $990^{w}$ | 960, $900^{w}$ | $\gamma NH_2$ |
| 900, 800<br>— | $800^{w}$<br>600<br>440 | 800<br>610<br>440 | 800<br>590<br>480 | $830^{w}$<br>600<br>400 | $800^{b}$<br>600<br>$480^{w}$ | $\gamma$CH<br>$\nu$M—N<br>$\nu$M—O |

* $cm^{-1}$; $s$ = Strong; $w$ = Weak; $b$ = Broad.

oxygen atom and nitrogen atom of the primary amino group are expected to be the donor sites of the ligand. A comparative study of the spectra of EMDH [8] and its complexes [9] indicates that the hydrogen-bonded carbonyl band (1650 $cm^{-1}$) is shifted to lower wavenumbers and is reduced in intensity. This is caused by chelation with the metal ion via metal–oxygen bonds, which is also revealed at lower wavenumbers (400 $cm^{-1}$). This excludes structures **III** and **IV** for the complexes. Other vibrations in the amino group range (3200 $cm^{-1}$) do not clearly indicate its participation in the coordination. There is overlapping with the OH vibrations of water and NH of the secondary amide group.

$\delta$ $NH_2$ at 1520 $cm^{-1}$, $\beta$ $NH_2$ at 1150 $cm^{-1}$ and the $\gamma$ $NH_2$ at $\sim$1000 $cm^{-1}$ are shifted to lower values in some cases due to breaking of the hydrogen bond and formation of metal–nitrogen bonds, which is further confirmed by the

presence of a band at $\sim$600 $cm^{-1}$. From these assignments and repeated observations one can conclude that the coordination of the ligand to the central ion takes place through the $-NH_2$ as well as $>C=O$ groups, which excludes structure **II** and contradicts the results reported by DUTTA *et al.* [5]. Elemental analyses also exclude the possibility of polymeric structure **V**.

*UV Spectra.* Ligand and chelates both show a similar spectral pattern. The spectra are not informative enough for any structural conclusions. The UV data are presented in Table I.

*Magnetic measurements.* The magnetic moments of the complexes (Table I) indicate a high-spin octahedral geometry ($sp^3d^2$ hybridization). However, in the case of the Ni(II) complex, the experimental magnetic moment (3.10 B.M.) is higher than the calculated value (2.83 B.M.) which may be due to spin-orbit coupling in the complex. In the case of Fe(III), a lower magnetic moment is observed, which indicates a slight deviation from the regular octahedral geometry.

*Pesticidal activity.* All the complexes were screened by Diamond Shamrock Corporation, U.S.A., for their insecticidal, viruscidal, bactericidal and fungicidal activities at different concentrations but only the zinc and copper complexes demonstrated a marginal fungicidal activity against *Rhizoctonia solani* and *Pythium* at 64 ppm concentration. The pesticidal activity was evaluated by a combination of foliage spray and soil drench methods.

*

The authors wish to thank Prof. R. P. RASTOGI, Head, Chemistry Department, University of Gorakhpur, for his inspiration, and college authorities for providing the necessary facilities.

## REFERENCES

[1] SACCONI, L.: J. Am. Chem. Soc., **74,** 4503 (1952)
[2] ISSA, R. M., EL-SHAZLY, M. F., ISKANDER, M. F.: Z. Anorg. Chem., **354,** 90 (1967)
[3] SHMANKO, P. I., BUTSKO, S. S.: Zhr. Neorg. Khim., **20,** 438 (1975)
[4] SHAMILISHVILI, P. I. et al.: Zh. Neorg. Khim. **20,** 3003 (1975)
[5] DUTTA AHMED, A. et al.: J. Inorg. Nucl. Chem. **28,** 2951 (1966)
[6] DUTTA AHMED, A., RAY COUDHARY, N.: J. Inorg. Nucl. Chem., **31,** 2545 (1969)
[7] RAM, V. J.: (Unpublished result)
[8] MASHIMA, N.: Bull. Chem. Soc. Japan, **35,** 2020 (1962)
[9] EL-SHAZLY, M. F.: M. Sc. Thesis, Alexandria University, Egypt, U.A.R. (1966)
[10] VOGEL, A. I.: Quantitative Inorganic Analysis. Pp. 496, 523, 526, 528, 532 (1961)

H. N. PANDEY
Lallan MISHRA
V. J. RAM

Department of Chemistry, S. C. College,
Ballia (U.P.), India.

*Acta Chimica Academiae Scientiarum Hungaricae, Tomus 98 (1), pp. 81—91 (1978)*

# BORON COMPLEXES OF BIFUNCTIONAL TRIDENTATE SCHIFF BASES

H. B. SINGH and J. P. TANDON

*(Department of Chemistry, University of Rajasthan, Jaipur, India)*

Received May 26, 1977
In revised form October 14, 1977

Tetracoordinated $B(OC_2H_5)$ (SB) and B(SB) (SBH) [where $SB^{2-}$ and $SBH^-$ represent the anions of the corresponding Schiff base, $SBH_2$] type of boron Schiff base derivatives have been synthesized by the reactions of boron ethoxide with bifunctional tridentate Schiff bases having the donor system, HO⌢N⌢OH and of the genera formula, $CH_3COCHC(CH_3)NHXOH$ [where $X = -C_6H_4-$, $-CH_2CH_2-$ and $-CH_2CH-CH_3$] in high yield and in a state of sufficient purity. These have been found to be monomeric in boiling benzene and their infrared and proton magnetic resonance spectra have been recorded. The conductance measurements in DMF show these derivatives to be non-electrolytes.

## Introduction

Complexes containing boron–nitrogen bond have been found to be useful biologically [1, 2] as well as industrially [3]. These have been synthesized by the reactions of boric acid with triethanolamine [4, 5, 6], tri-*n*-propanolamine [7] or triisopropanolamine [8] in common organic solvents. Further, the synthesis of monosubstituted triethanolamine borates and the so-called monosubstituted triethanolamine borates and the so-called monosubstituted triptychboroxazolidines have also been reported [9]. However, sufficient attention does not seem to have been given to synthesize boron Schiff base derivatives, although some addition products of boron halides with the Schiff bases have been reported [10, 11]. Earlier, from these laboratories, a variety of aluminium and gallium derivatives of Schiff bases have been described [12—15].

It was, therefore, considered of interest to study the reactions of alkoxyboranes with azomethines and during the course of present investigations several new boron Schiff base derivatives have been synthesized by the reactions of boron ethoxide with bifunctional tridentate Schiff bases obtained by the condensation of 2,4-pentanedione with 2-aminophenol, 2-hydroxyethylamine or 2-hydroxy-*n*-propylamine. The results of these studies are discussed in the present paper.

## Experimental

All-glass apparatus fitted with quickfit interchangeable joints was used and the reactions were carried out under strictly anhydrous conditions. The fractionations were made on a column packed with Raschig rings and fitted to a ratiohead with condenser.

### Materials

Boron ethoxide was prepared by refluxing boric acid (S. Merck) with absolute alcohol in benzene (B.D.H.) and removing water azeotropically [16]. It was distilled before use and analyzed.

| | | | |
|---|---|---|---|
| $B(OC_2H_5)_3$: | B 7.44, | $OC_2H_5$ | 91.95% |
| Calcd.: | B 7.41, | $OC_2H_5$ | 92.59% |

Benzene (B.D.H.) was first refluxed over sodium wire for several hours and finally distilled azeotropically with ethanol. Dimethylformamide was kept over sodium carbonate (anhydrous) for two days, decanted and then distilled. It was redistilled under vacuum (55 °C/35 mm).

### Preparation of Schiff bases

(i) 4-(2-Hydroxyphenyl)amino-3-pentene-2-one ($C_{11}H_{13}NO_2$):

2,4-Pentanedione (12.4 g) and 2-aminophenol (13.5 g) were dissolved in absolute alcohol and the solution was heated on a water bath for 2—3 hrs. On cooling, yellow, needles were obtained, which were purified by recrystallisation (m.p. 189—90 °C).

| | | | |
|---|---|---|---|
| Calcd. | C 69.10, | H 6.85, | N 7.32% |
| Found: | C 69.94, | H 6.72, | N 7.26% |

(ii) 4-(2-Hydroxyethyl)amino-3-pentene-2-one ($C_7H_{13}NO_2$):

2,4-Pentanedione (14.3 g) and 2-hydroxyethylamine (8.7 g) were taken up in benzene and refluxed for 8—9 hrs. The water was then azeotropically removed with benzene and the product distilled at 113—115 °C/0.2 mm.

| | | | |
|---|---|---|---|
| Calcd. | C 58.72, | H 9.15, | N 9.79% |
| Found: | C 58.19, | H 9.23, | N 9.81% |

(iii) 4-(2-Hydroxy-*n*-propyl)amino-3-pentene-2-one ($C_8H_{15}NO_2$):

This was prepared similarly by refluxing 2,4-pentanedione (12.6 g) and 2-hydroxy-*n*-propylamine (9.5 g) in benzene. The product was distilled at 111—112 °C/0.3 mm

| | | | |
|---|---|---|---|
| Calcd. | C 61.12, | H 9.63, | N 8.90% |
| Found: | C 60.95, | H 9.77, | N 8.74% |

### Synthesis of boron Schiff base derivatives

Boron ethoxide (1.13—1.97 g) was dissolved in dry benzene (60—75 ml) and the calculated amount of the Schiff base was added. The contents were refluxed over a fractionating column and the ethanol liberated in the reaction was removed azeotropically with benzene. The progress of the reaction was followed by the estimation of the ethanol in the azeotrope. The solvent was removed and the product dried under vacuum. The details of these reactions as well as the resulting products are summarized in Table I.

### Exchange reactions of ethoxyboron Schiff base derivatives

*t*-Butylalcohol (excess, 3.2—4.6 g) was mixed with the solution of the ethoxy boron Schiff base derivative (1.66—2.02 g) in presence of dry benzene (100—120 ml). The solution was refluxed under a fractionating column and the azeotrope collected slowly, till the distillate attained a constant temperature of 80 °C. The resulting compounds were dried under reduced pressure. Table II contains the details about these reactions and the resulting products.

### Analytical methods and physical measurements

Boron in boron ethoxide was estimated by hydrolyzing a weighed sample and titrating the boric acid so produced against standard sodium hydroxide solution in the presence of mannitol using phenolphthalein as an indicator. In case of boron Schiff base complexes, the weighed sample was treated with methanol containing 2—3 drops of concentrated sulphuric acid in a distilling flask and the contents were distilled over a fractionating column. The

**Table I**

*Reactions of boron ethoxide with Schiff bases*

| Reactants | | Mole ratio | Refluxing time (hours) | Product and characteristics | Ethanol in the azeotrope (g) Found (Calcd.) | Analysis % | | Molecular weight Found (Calcd.) |
|---|---|---|---|---|---|---|---|---|
| $B(OC_2H_5)_3$ (g) | Schiff base (g) | | | | | B | N | |
| | | | | | | Found (Calcd.) | Found (Calcd.) | |
| 1.30 | $C_{11}H_{13}NO_2$ 1.70 | 1:1 | 6 | $B(OC_2H_5)(C_{11}H_{11}NO_2)$ Canary yellow solid, soluble in benzene | 0.79 (0.82) | 4.36 (4.41) | 5.73 (5.71) | 236 (245) |
| 1.15 | $C_{11}H_{13}NO_2$ 3.02 | 1:2 | 11 | $B(C_{11}H_{11}NO_2)(C_{11}H_{12}NO_2)$ Yellow solid, soluble in benzene | 0.95 (1.09) | 2.74 (2.77) | 7.08 (7.17) | 372 (390) |
| 1.97 | $C_7H_{13}NO_2$ 1.93 | 1:1 | 10 | $B(OC_2H_5)(C_7H_{11}NO_2)$ Reddish yellow semisolid, soluble in benzene | 1.22 (1.25) | 5.42 (5.49) | 6.98 (7.11) | 185 (197) |
| 1.15 | $C_7H_{13}NO_2$ 2.25 | 1:2 | 15 | $B(C_7H_{11}NO_2)(C_7H_{12}NO_2)$ Reddish brown semisolid, soluble in benzene | 1.02 (1.09) | 3.62 (3.68) | 9.40 (9.52) | 286 (294) |
| 1.41 | $C_8H_{15}NO_2$ 2.04 | 1:1 | 11 | $B(OC_2H_5)(C_8H_{13}NO_2)$ Reddish yellow semisolid, soluble in benzene | 0.84 (0.89) | 5.06 (5.13) | 6.68 (6.63) | 205 (211) |
| 1.13 | $C_8H_{15}NO_2$ 2.44 | 1:2 | 23 | $B(C_8H_{13}NO_2)(C_8H_{14}NO_2)$ Reddish yellow semisolid, soluble in benzene | 1.00 (1.04) | 3.29 (3.36) | 8.59 (8.69) | 318 (322) |

**Table II**

*Exchange reactions of ethoxy schiff base derivatives of boron with t-butylalcohol*

| Compound (g) | *t*-Butyl-alcohol (in excess) (g) | Product and characteristics | Ethanol in the azeotrope Found (Calcd.) (g) | Analysis (%) | | Molecular weight Found (Cacld.) |
|---|---|---|---|---|---|---|
| | | | | B Found (Calcd.) | N Found (Calcd.) | |
| $B(OC_2H_5)(C_{11}H_{11}NO_2)$ 1.66 | 3.2 | $B(O\text{-}t\text{-}C_4H_9)(C_{11}H_{11}NO_2)$ yellow solid, soluble in benzene | 0.31 (0.35) | 3.88 (3.96) | 5.12 (5.13) | 265 (273) |
| $B(OC_2H_5)(C_7H_{11}NO_2)$ 2.02 | 4.3 | $B(O\text{-}t\text{-}C_4H_9)(C_7H_{11}NO_2)$ reddish yellow semisolid, soluble in benzene | 0.42 (0.47) | 4.80 (4.81) | 6.13 (6.22) | 218 (225) |
| $B(OC_2H_5)(C_8H_{13}NO_2)$ 1.98 | 4.6 | $B(O\text{-}t\text{-}C_4H_9)(C_8H_{13}NO_2)$ reddish yellow semisolid, soluble in benzene | 0.35 (0.43) | 4.45 (4.53) | 5.82 (5.86) | 232 (239) |

methylborate so produced was collected into a receiver flask containing distilled water. The boric acid so produced was then titrated as described above.

Nitrogen was estimated by Kjeldahl's method and the ethanol liberated in the reactions was estimated oxidimetrically [17]. Infrared spectra were recorded on a Perkin—Elmer model 337 Infrared Spectrophotometer in the region, 4000—400 $cm^{-1}$ using KBr optics.

Proton magnetic resonance spectra were recorded on a Perkin—Elmer RB-12 Spectrometer using TMS as internal reference. Molar conductance measurements were made in dimethylformamide at $35 \pm 1$ °C using a conductivity bridge type 235 (ANU VIDYUT, ROORKEE) with the cell having a cell constant of 0.78 $cm^{-1}$.

## Results and discussion

In general, the reactions of boron ethoxide with the above mentioned Schiff bases in 1:1 and 1:2 molar ratios may be represented by the following equations:

$$B(OC_2H_5)_3 + SBH_2 \rightarrow B(OC_2H_5)(SB) + 2C_2H_5OH$$

$$B(OC_2H_5)_3 + 2SBH_2 \rightarrow B(SB)(SBH) + 3C_2H_5OH$$

[where $SB^{2-}$ and $SBH^{-}$ are the anions of the azomethine $SBH_2$].

However, 2:3 molar reactions yielded a mixture of 1:1 and 1:2 derivatives and in the case of 4-(2-hydroxyphenyl)amino-3-pentene-2-one; the 1:1 derivative could be isolated in the pure form by crystallization from the benzene–hexane mixture.

To show the labile nature of the ethoxy group, the 1:1 derivatives were subjected to exchange reactions with *t*-butylalcohol and these may be represented as follows:

$$B(OC_2H_5)(SB) \xrightarrow[(excess)]{C_4H_9^tOH} B(O\text{-}t\text{-}C_4H_9)(SB) + C_2H_5OH$$

[where $SB^{2-}$ is the anion of the azometine, $SBH_2$].

All the above derivatives have been obtained as coloured, non-volatile solids or semisolids. The ebullioscopic determinations of the molecular weights in boiling benzene show them to be monomers indicating thereby stable tetracoordinated environment for the central boron atom.

## Infrared spectra

A comparison of the characteristic infrared absorption bands of the Schiff bases or boron ethoxide with those of the corresponding derivatives reveals the following salient points:

(i) In the spectra of Schiff bases, bands in the 3400—3200 $cm^{-1}$ region may be assigned to the intermolecular (O—H . . . O) or intramolecular

(O—H . . . N) hydrogen bonded NH or OH as reported earlier also in the case of 4-(methyl)amino-3-pentene-2-one and 4-anilino-3-pentene-2-one [18]. These bands disappear in the boron-Schiff base derivatives showing the chelation of boron through the functional groups. However, in 1:2 products the same bands appear as one of the NH/OH group remains uncoordinated.

(ii) A band of strong intensity is observed in the 1610—1600 $cm^{-1}$ region in the spectra of Schiff bases and this may be assigned to $\nu$ C=N overlapping with hydrogen bonded $\nu$ C=O. However, in the boron derivatives, this is slightly shifted to the higher frequency side and this indicates probably the coordination of boron to nitrogen [11] as well as to oxygen.

(iii) The band at $\sim$1332 $cm^{-1}$ in the spectra of boron ethoxide may be ascribed to $\nu$ B—O asym [19]. This, however, disappears from its original position in the spectra of the boron Schiff base derivatives and it may be due to the strong coordinate bond being formed between boron and nitrogen resulting in the lowering of the double bond character of B–O bond initially present in boron ethoxide [20].

## Proton magnetic resonance spectra

The proton magnetic resonance spectra of 4-(2-hydroxyphenyl)amino-3-pentene-2-one (**I**) and its 1:1 (**II**) and 1:2 (**III**) derivatives have been recorded in $CDCl_3$ and are shown in Figs 1, 2 and 3. The chemical shift values ($\delta$) for different protons are given in Table III. The following points, which support the suggested structures, are worth mentioning:

(i) The proton magnetic resonance spectra, however, show preference for the ketamine structure over other equilibrium forms for 4-(2-hydroxyphenyl)amino-3-pentene-2-one as well as for the Schiff bases derived by the condensation of $\beta$-diketones with alkyl or aryl amines or diamines [21—24] as reported earlier.

(ii) The bonding of the phenolic oxygen of the ligand moiety in compounds (**I**) and (**II**) is suggested by the disappearance of the OH proton signal which is observed at 7.10 $\delta$ in the ligand.

(iii) The 12.12 $\delta$ peak due to hydrogen bonded NH proton of the ligand disappears in the compound (**I**) indicating its chelating nature. However, in compound (**II**), this peak is observed and thus in one of the ligand moieties the NH . . . O type of hydrogen bridging remains intact.

(iv) In compound (**I**), the methine and one of the methyl proton (levelled by c in the structure given in the Table III) signals are shifted downfield leaving behind another methyl proton (labelled by d in the structure in the same Table) signal almost unaltered. This shows that boron acquires stable tetracoordinated environment as a result of donation of lone pair of electrons from nitrogen. This is further supported by the proton magnetic resonance

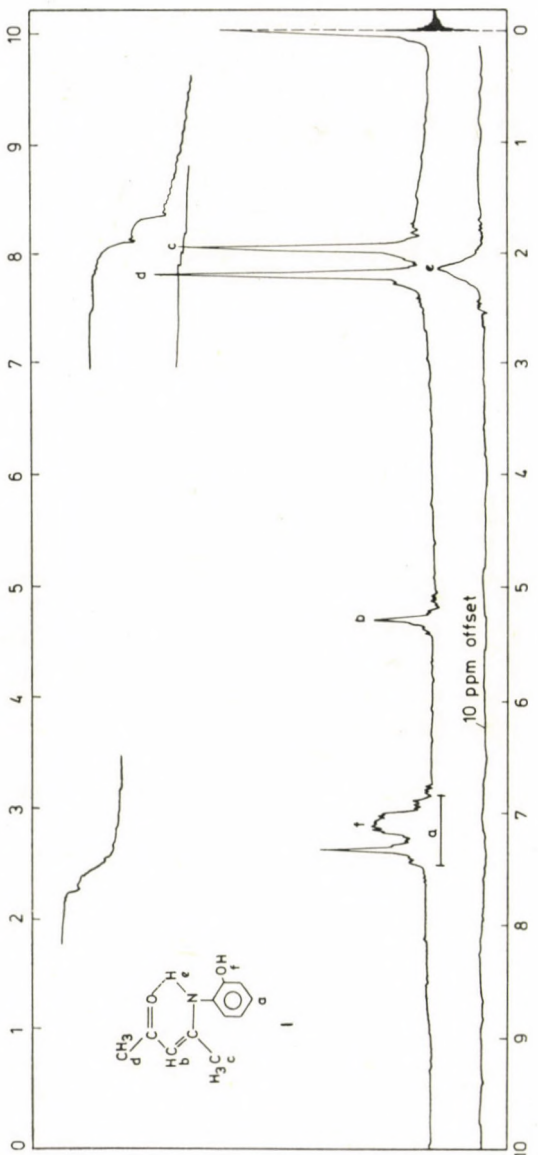



*Fig. 1*

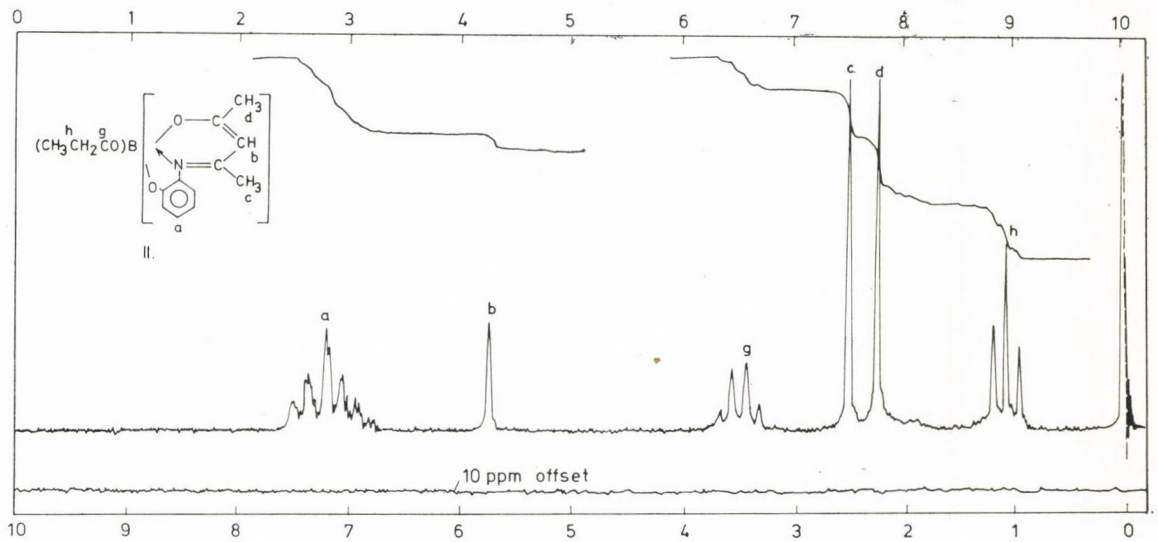

0 1 2 3 4 5 6 7 8 9 10
h g
(CH3CH2CO)B
II.
a
b
g
c
d
h
10 ppm offset
10 9 8 7 6 5 4 3 2 1 0

*Fig. 2*

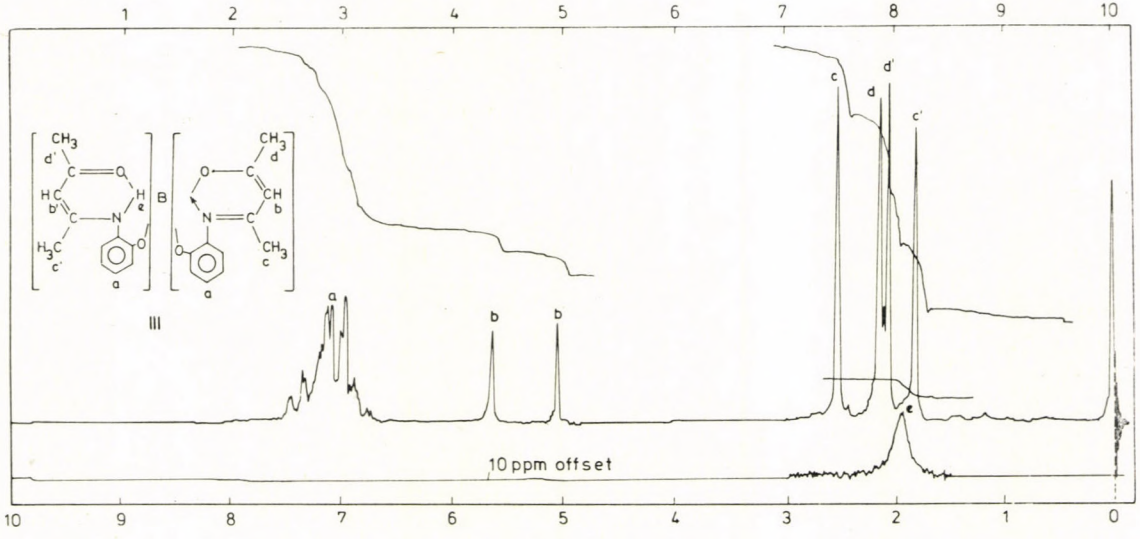
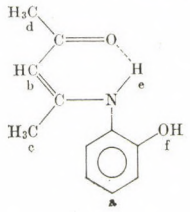
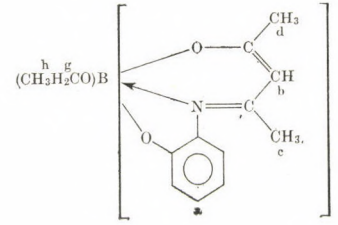
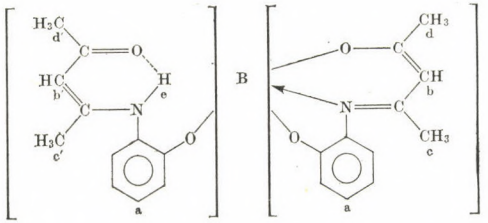



*Fig. 3*

**Table III**

*Proton resonance data for Schiff base and its boron derivatives in δ (p.p.m.) relative to tetramethylsilane*

| Compound | a | b (b′) | c, d (c′), (d′) | e | f | g | h |
|---|---|---|---|---|---|---|---|
| I  | 6.84—7.50* | 5.28 | 1.94, 2.18 | 12.12 | 7.10 | — | — |
| II  | 6.70—7.56* | 5.73 | 2.51, 2.23 | — | — | 3.52** | 1.14*** |
| III  | 6.70—7.52* | 5.64 (5.05) | 2.50, 2.13 (1.82, 2.07) | 11.96 | — | — | — |

* complex multiplet, ** quartet. *** triplet

spectrum of compound (**II**) as in that case, two signals for methine and four signals for methyl protons are observed. One set of these signals for methine and methyl protons is observed at almost the same position as in the spectrum of compound (**I**) and thus indicating the tridentate behaviour of one of the ligand moieties. However, another set of methine and methyl protons is observed at the same position as in the spectra of ligand itself and this corresponds to the monodentate behaviour of the second ligand moiety.

### Conductance measurements

Very low molar conductance values for the boron Schiff base derivatives in dimethylformamide show their non-electrolytic nature.

*

We are thankful to the Head of the Chemistry Department, for providing laboratory facilities. The financial assistance to one of us (H.B.S.) by UGC, New Delhi is also gratefully acknowledged.

## REFERENCES

[1] Sowa, F. J.: U.S. 2,655.524 Oct. 13 (1953)
C.A. **48,** 13 710 (1954)
[2] Sowa, F. J.: U.S. 2,626 212 Jan. 20 (1953)
C.A. **47,** 6086 (1953)
[3] Brown, H. C.: (To ethyl crop) U.S. 2,330 167 No. 11 (1958)
C.A. **53,** 9060 (1959)
[4] Rajahn, C. A.: Ger. 582, 149 (1933)
C.A. **27,** 5153 (1933)
[5] Brown, H. C., Fletcher, E. A.: J. Amer. Chem. Soc., **73,** 2808 (1951)
[6] Hein, F., Buckhardt, R.: Z. Anorg. Allg. Chem., **268,** 159 (1952)
[7] Groszos, J., Day, N. E.: (to American Cyanamid Co.)
U.S. 2,942 021 June 21 (1960)
C.A. **54,** 24 396d (1960)
[8] Steinberg, H., Hunter, D. L.: J. Amer. Chem. Soc., **82,** 853 (1960)
[9] Schleppnik, A. A., Gutsche, C. D.: J. Org. Chem., **25,** 1378 (1960)
[10] Niedenzu, K., Miller, C. D., Nahm, F. C.: Tetrahedron Letters, **28,** 2441 (1970)
[11] Samuel, B., Smaith, R., Summerford, C., Wade, K.: J. Chem. Soc., A, **1970,** 2019
[12] Prasad, R. N., Tandon, J. P.: J. Inorg. Nucl. Chem., **36,** 1473 (1974)
[13] Prasad, R. N., Tandon, J. P.: Z. Naturforsch., **28,** 63 (1973)
[14] Prasad, R. N., Tandon, J. P.: J. Less-Common Metals, **37,** 141 (1974)
[15] Prasad, R. N., Tandon, J. P.: J. Inorg. Nucl. Chem., **37,** 35 (1975)
[16] Lippincott, S. B.: U.S. Pat., 2,642 453 (1953, to Standard Oil Developments Co.)
[17] Bradley, D. C., Halim, F. M., Abdel, Warlow: J. Chem. Soc., 3450 (1950)
[18] Henry, F. H., Jr, James, P. C., Richard, M. A.: J. Amer. Chem. Soc., **80,** 1100 (1958)
[19] George, P. D., Ladd, J. R.: J. Amer. Chem. Soc., **77,** 1900 (1955)
[20] Bellamy, L. J., Gerrard, W., Lappert, M. F., Williams, R. J.: J. Chem. Soc., 2412 (1958)
[21] Everett, G. W., Jr., Holm, R. H.: J. Amer. Chem. Soc., **87,** 2117 (1965)
[22] Brown, N. M. D., Nonhebel, D. C.: Tetrahedron, **24,** 5655 (1968)
[23] Dudek, G. O., Holm, R. H.: J. Amer. Chem. Soc., **84,** 2691 (1962)
[24] Dudek, G. O., Holm, R. H.: J. Amer. Chem. Soc., **83,** 2099 (1961)

H. B. Singh
J. P. Tandon
University of Rajasthan, Jaipur-302004, India

*Acta Chimica Academiae Scientiarum Hungaricae, Tomus 98 (1), pp. 93—102 (1978)*

# COHESION ENERGY OF A LIQUID DUE TO PERMANENT DIPOLES

J. LISZI

*(Department of Physical Chemistry, University of Chemical Industries, Veszprém)*

Received February 1, 1977*

The contribution of permanent dipoles to the cohesion energy ($W$) of a liquid was investigated. $W$ was calculated using four different dielectric models. A comparison with thermodynamic data shows that $W$ is mainly determined by the interaction of the polar molecule with its nearest neighbours. $W$ can be described by a dielectric model which takes this interaction into consideration. Such a model consists of a point dipole in a cavity surrounded by a spherical layer embedded in an infinite continuous dielectric with a relative permittivity different from that of the layer. It is pointed out that the relative permittivity of the layer is lower than that of the bulk of the liquid.

## Introduction

The properties of liquids are principally determined by the intermolecular forces acting between a molecule and its nearest neighbours [1]. In this sense the nearest neighbouring molecules have an important role. The interaction of a molecule with its closest neighbours is different from that with more distant molecules.

One of the methods for the description of dipolar interactions uses the ONSAGER reaction field [2]. In the ONSAGER theory the polar molecule is treated as a point dipole at the center of a spherical cavity of molecular dimensions in a continuous medium of static permittivity $\varepsilon_0$. The reaction field R is set up in the cavity by the polarization which the dipole induces in its surroundings. The dipolar interactions are taken into consideration by the interaction between the central dipole, and the reaction field. As the nearest neighbours of a polar molecule have a special role from the viewpoint of intermolecular forces, the homogeneous medium of the ONSAGER theory must be replaced by a heterogeneous one. The heterogeneous medium takes into account that in the interaction the closest neighbours behave differently from the molecules of the bulk. In the simplest model of this kind the polar molecule is treated as a point dipole at the center of a spherical cavity of radius $a$ and static permittivity $\varepsilon_i = 1$. The cavity is surrounded by a spherical layer of thickness $(b-a)$ and static permittivity $\varepsilon_l$, immersed in the bulk of the liquid

* English text received: December 6, 1977.

of static permittivity $\varepsilon_0$. The layer and the bulk are considered as continuous media. On the molecular level the layer consists of the nearest neighbours of the polar molecule. The difference between $\varepsilon_0$ and $\varepsilon_l$ is caused by the non-homogeneous polarization which the dipole induces in its surrounding. The central molecule and the local layer together give the polarization of the bulk and this holds true for every molecule of the liquid.

In an earlier paper it has been shown [3] that the reaction field strength of the heterogeneous model may differ considerably from that of the ONSAGER model. The present work investigates the extent of the difference between $\varepsilon_0$ and $\varepsilon_l$ *via* concrete examples.

The dipolar part of the cohesion energy ($W$) has been determined from four different dielectric models. Two of these take into consideration the special role of the nearest neighbours, using the concentric dielectric continua mentioned above. The cohesion energies calculated from the dielectric models are compared with $W$ derived from thermodynamic data. This comparison may give answers to the following three questions:

1. Which is the dielectric model that gives $W$ in agreement with the thermodynamic data?

2. What is the ratio of $\varepsilon_l$ and $\varepsilon_0$ in the case of concentric dielectric continua?

3. What percentage of $W$ originates from the interaction between the central molecule and the layer?

## Method

If special interactions (*e.g.* H-bonding) are absent and the effect of higher electric moments (*e.g.* quadrupole moment) is negligible, the cohesion energy in polar liquids consists of two parts, viz.

1. energy due to Van der Waals forces,
2. energy due to dipole–dipole interactions.

If the permanent dipole moment of the molecule is zero, all the interaction energy is due to Van der Waals forces. Image two liquids consisting of identical molecules with the only exception that the molecules of the first liquid have a permanent dipole moment, whereas those of the second liquid have not. The difference between their cohesion energy provides the dipolar part of $W$ for the polar liquid.

There are no such liquid pairs, however, it is a good approximation if one compares the cohesion energy of a polar liquid with that of its isomorphic hydrocarbon.

Liquids at their normal boiling points are in corresponding states [4]. The difference between the cohesion energy of a polar liquid and that of its isomorphic hydrocarbon at their normal boiling points can be considered as the dipolar part of $W$.

In the calculations the internal energy change of vaporization is used. Neglecting the volume of the liquid relative to the volume of the gas and applying BOYLE's law to the gas, one can find the change in the internal energy from

$$\Delta U = \Delta H - RT_b , \tag{1}$$

where $\Delta H$ is the heat of vaporization, $R$ is the gas constant and $T_b$ is the normal boiling point.

In Table 1 the change in internal energy at the normal boiling point is given for six polar liquids and for their isomorphic hydrocarbons. In the last column the differences be-

tween the internal energies are given

$$-W_t = \Delta U_{\text{pol.}} - \Delta U_{\text{nonpol.}} \tag{2}$$

$W_l$ is the contribution of permanent dipoles to the cohesion energy of the polar liquid at the normal boiling point.

Thus the procedure to be followed is to calculate values of $W$ from dielectric data using four different dielectric models and to compare them with the $W_l$ derived from thermodynamic data. In the case of concentric dielectric continua, the $\varepsilon_0/\varepsilon_l$ value that yields the correct $W_l$ is considered as satisfactory.

**Table I**

*Comparison of the internal energy change of vaporization for some polar compounds with that of an isomorphic hydrocarbon*

| Compound | $\Delta U_{\text{pol.}}$ (kcal mol$^{-1}$) | Isomorphic hydrocarbon | $\Delta U_{\text{nonpol}}$ (kcal mol$^{-1}$) | $W_l$ (kcal mol$^{-1}$) |
|---|---|---|---|---|
| Acetonitrile | 6.80 [5] | Propyne | 4.75* | −2.05 |
| Propanone | 6.61 [6] | 2-Methylpropene | 4.80 [6] | −1.81 |
| Butanone | 6.74 [6] | 2-Methylbutane-1 | 5.50 [6] | −1.24 |
| Nitromethane | 6.25 [6] | Ethane | 3.10 [6] | −3.15 |
| Nitrobenzene | 9.08 [6] | Toluene | 7.20 [6] | −1.88 |
| *o*-Nitrotoluene | 9.31 [6] | *o*-Xylene | 8.00 [6] | −1.31 |

* Calculated from Eq. (1) using data of Ref [5].

The hydrocarbons in Table I (except ethane) are not quite nonpolar compounds. All of them have permanent dipole moments of a few tenths of a Debye. However, the small permanent dipole moment and the low static permittivity (thus the small reaction field factor) result in a very low value of $W$. This is negligible as compared with the other part of the cohesion energy. For example the permanent dipole moment of toluene is 0.37 D [4]. If one supposes that at the normal boiling point, $\varepsilon_0 = 2$, then from Eq. (8), $W_A = -8 \times 10^{-3}$ kcal mol$^{-1}$. This is negligible compared with $\Delta U$ nonpol $= -7.20$ kcal mol$^{-1}$.

## Calculation of W from dielectric data

In the absence of an external electric field, the average field at the permanent dipole of a molecule is the reaction field **R**. The work required to surround a permanent dipole $\mu$ with dielectric is given by

$$W = -\frac{1}{2}\boldsymbol{\mu}\mathbf{R} \tag{3}$$

$W$ is the contribution of the permanent dipole to the cohesion energy of the liquid. The reaction field strength is proportional to the permanent dipole moment:

$$\mathbf{R} = f\boldsymbol{\mu} \tag{4}$$

where $f$ is the reaction field factor. Thus for 1 mol of a system of identical molecules, the part of the cohesion energy due to the permanent dipoles is given by

$$W = -\frac{1}{2} N_A f \mu^2 , \tag{5}$$

where $N_A$ is Avogadro's number. Considering that $N_A$ is a constant and $\mu$ is an experimental datum, the value of $W$ given by Eq. (5) depends on the model used for the determination of the reaction field factor.

## The dielectric models

*Model A (ONSAGER's model)*

The polar molecule is treated as a point dipole at the center of a spherical cavity of radius $a$. The cavity is surrounded by a continuous, homogeneous medium of static permittivity $\varepsilon_0$. The reaction field factor is given by

$$f_A = \frac{1}{a^3} \frac{2(\varepsilon_0 - 1)}{2\varepsilon_0 + 1} . \tag{6}$$

The radius of the cavity is defined by

$$\frac{4\pi}{3} N_A a^3 = V , \tag{7}$$

where $V$ is the molar volume of the liquid. The dipolar part of the cohesion energy ($W_A$) from Eqs (5), (6) and (7) is

$$W_A = -\frac{4\pi N_A^2}{3V} \frac{\varepsilon_0 - 1}{2\varepsilon_0 + 1} \mu^2 . \tag{8}$$

*Model B (BÖTTCHER's model)*

The polar molecule is treated as a polarizable point dipole at the center of a spherical cavity of radius $a$. The cavity is surrounded by a continuous, homogeneous medium of static permittivity $\varepsilon_0$. The reaction field factor is given by

$$f_B = \frac{f_A}{1 - \alpha f_A} , \tag{9}$$

where $f_A$ is the reaction field factor corresponding to model $A$ and $\alpha$ is the molecular polarizability

$$\alpha = \frac{n^2 - 1}{n^2 + 2} \frac{3V}{4\pi N_A}, \tag{10}$$

where $n$ is the internal refractivity. The cohesion energy of the liquid due to the permanent dipoles according to model $B$ is given by

$$W_B = -\frac{4\pi N_A^2}{3V} \frac{(\varepsilon_0 - 1)(n^2 + 2)}{3(2\varepsilon_0 + n^2)} \mu^2. \tag{11}$$

If the molecule is non-polarizable ($\alpha = 0$, *i.e.* $n^2 = 1$), then Eq. (11) simplifies into Eq. (8).

*Model C*

The polar molecule is treated as a non-polarizable point dipole at the center of a spherical cavity of radius $a$. The cavity is surrounded by a spherical layer of thickness $(b-a)$ and static permittivity $\varepsilon_l$, immersed in the bulk of the liquid of static permittivity $\varepsilon_0$. $\varepsilon_0$ is the measurable relative permittivity of the liquid. The cohesion energy of the liquid due to the permanent dipoles is

$$W_c = -\frac{1}{2} N_A f_c \mu^2 \tag{12}$$

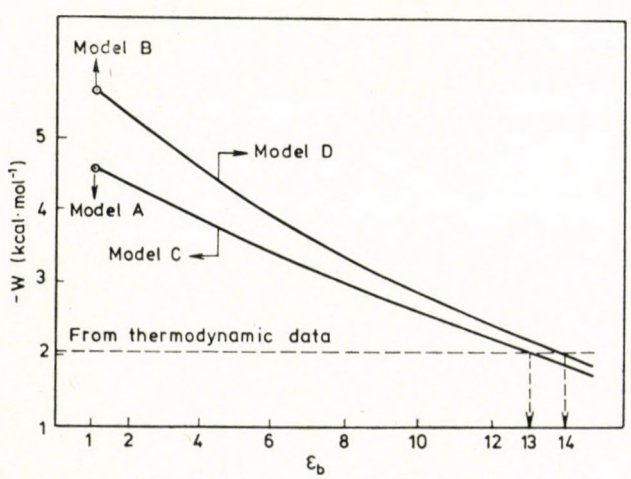



*Fig. 1.* Dipolar part of the cohesion energy of acetonitrile as a function of $\varepsilon_b$. $B$,

where the reaction field factor is given by [3]

$$f_c = \frac{2(\varepsilon'_a - 1)}{(2\varepsilon'_a + 1)a^3} + \frac{2(\varepsilon_b - 1)}{(2\varepsilon_b + 1)b^3}\left[1 - \frac{1 - \varepsilon'_a}{2\varepsilon'_a + 1}\right] \tag{13}$$

$$\varepsilon_b = \varepsilon_0/\varepsilon_l \tag{14}$$

$$\varepsilon'_a = \varepsilon_l\left[1 + \frac{2(1 - \varepsilon_l)(1 - \varepsilon_b)}{2\varepsilon_b + 1}\frac{a^3}{b^3}\right]^{-1}. \tag{15}$$

The radius of the cavity is given by Eq. (7). Considering that the liquid consists of identical molecules, $b = 3a$.

The difference in relative permittivities between the layer and the bulk ($\varepsilon_l \neq \varepsilon_0$) shows that the interaction between a molecule and its nearest neighbours is different from that with more distant molecules. A stronger interaction with the closest neighbours provides a greater difference between $\varepsilon_l$ and $\varepsilon_0$.

On the basis of this model the percentage of $W$ originating from the interaction between the central molecule and the layer can be estimated. The first member of Eq. (13),

$$f_{c1} = \frac{2(\varepsilon'_a - 1)}{(2\varepsilon'_a + 1)a^3} \tag{16}$$

is principally determined by the interaction between the dipole and the spherical layer. The second term,

$$f_{c2} = \frac{2(\varepsilon_b - 1)}{(2\varepsilon_b + 1)b^3}\left[1 - \frac{1 - \varepsilon'_a}{2\varepsilon'_a + 1}\right] \tag{17}$$

mostly depends on the interaction between the dipole and the bulk of the liquid. Substituting $f_c$ for $f_{c1}$ in Eq. (12), one obtains that part of $W$ which originates from the interaction between the dipole and the spherical layer ($W_{c1}$). Substituting $f_{c2}$ for $f_c$ in Eq. (12), one obtains that part of $W$ which is due to the interaction between the dipole and the bulk of the liquid ($W_{c2}$). This is not without interest if one considers the spherical layer as the nearest neighbours of the polar molecule.

If $\varepsilon_0 = \varepsilon_l$, $\varepsilon_b = 1$, then $\varepsilon'_a = \varepsilon_0$ and model $C$ simplifies into model $A$.

*Model D*

Model $D$ uses concentric dielectric continua like model $C$ but the dipole is considered to be polarizable.

$$W_D = -\frac{1}{2} N_A f_D \mu^2 \tag{18}$$

where

$$f_D = \frac{f_c}{1 - \alpha f_c} \tag{19}$$

This model is the most realistic one, taking into consideration the special role of the closest neighbours and the polarizability of the dipole. If $\varepsilon_b = 1$, then model $D$ is identical with model $B$. If $\alpha = 0$, then model $D$ simplifies into model $C$. If $\varepsilon_b = 1$ and $\alpha = 0$, then model $D$ is the same as model $A$.

## Results and discussion

The data needed for the calculations were taken BÖTTCHER's book [6] after the measurements of Grimm and Patrick [7]. The properties of the liquids at the normal boiling point are given in Table II.

**Table II**

*Properties of liquids at the normal boiling point*

| Compound | $T_b$(K) | $\varrho$(g cm$^{-3}$) | $M$(g mol$^{-1}$) | $\varepsilon_0$ | $n_D^2$ | $\mu$(D) |
|---|---|---|---|---|---|---|
| Acetonitrile | 355 | 0.72 | 41.1 | 26.2 | 1.76 | 3.9 |
| Propanone | 329 | 0.75 | 58.1 | 17.68 | 1.76 | 2.9 |
| Butanone | 353 | 0.73 | 72.1 | 14.48 | 1.83 | 2.8 |
| Nitromethane | 374 | 1.03 | 61.0 | 27.75 | 1.80 | 3.5 |
| Nitrobenzene | 384 | 1.01 | 123.1 | 15.61 | 2.12 | 4.2 |
| o-Nitrotoluene | 495 | 0.96 | 137.1 | 11.82 | 2.10 | 3.6 |

In Table, $\varrho$ is the density and $n_D$ is the refractivity referring to the sodium $D$ line. In the calculations, $n_D$ was used instead of the internal refractivity, however, this is not a rough approximation [8].

The results calculated from Eqs (8) (model $A$) and (11) (model $B$) are given in Table III. For comparison, the cohesion energies originating from thermodynamic data ($W_t$) are given in the last column.

The data in Table III show that:

1. Model $B$, taking into consideration the polarizability of the dipole, provides higher values of $W$ than does model $A$. (A similar tendency can be observed on comparing models $C$ and $D$.)

2. With the exception of toluene, the cohesion energies calculated from dielectric data are higher than $W_t$. This indicates that the special role of the nearest neighbours cannot be neglected.

**Table III**

*Cohesion energies due to the permanent dipole moments according to models A and B as well as from thermodynamic data*

| Compound | $W_A$ (kcal $mol_{1-1}$) | $W_B$ (kcal $mol_{-1}$) | $W_t$ (kcal $mol_{-1}$) |
|---|---|---|---|
| Acetonitrile | −4.55 | −5.65 | −2.05 |
| Propanone | −1.81 | −2.22 | −1.81 |
| Butanone | −1.30 | −1.61 | −1.24 |
| Nitromethane | −3.65 | −4.45 | −3.15 |
| Nitrobenzene | −2.26 | −3.17 | −1.88 |
| *o*-Nitrotoluene | −1.45 | −1.90 | −1.31 |

Models *C* and *D* based on concentric dielectric continua, take into account the non-homogeneous polarization which the dipole induces in its surrounding. Considering that $\varepsilon_l$ is not a measurable datum, $\varepsilon_0/\varepsilon_l = \varepsilon_b$ was used as a parameter in the calculations. $W_c$ and $W_D$ were determined as a function of $\varepsilon_b$. That value of $\varepsilon_b$ was accepted which provided a $W$ equal to $W_t$. Figure 1 shows that

1. $W_D$ is always greater then $W_c$, because model *C* neglects the polarizability of the dipole.

2. Both $W_c$ and $W_D$ decrease with increasing $\varepsilon_b$. The curves start from $W_c(\varepsilon_b = 1) = W_A = -4.55$ kcal $mol^{-1}$ and $W_D(\varepsilon_b = 1) = W_B - 5.65$ kcal $mol^{-1}$, their extreme points are at $\varepsilon_b = \varepsilon_0/n^2 = 26.2/1.76 \simeq 14.9$.

3. $W_c$ at $\varepsilon_b = 13$ and $W_D$ at $\varepsilon_b = 14$ are equal to $W_t = -2.05$ kcal $mol^{-1}$.

The same procedure was applied for the other compounds, too. The results are given in Table IV. If $\varepsilon_b = \varepsilon_{bc}$, then $W_c = W_t$. If $\varepsilon_b = \varepsilon_{bD}$, then $W_D = W_t$.

**Table IV**

*Decrease of the relative permittivity in the spherical layer as compared with that of the bulk of the liquid*

| Compound | $\varepsilon_{bc}$ | $\varepsilon_{bD}$ |
|---|---|---|
| Acetonitrile | 13 | 14 |
| Propanone | 1 | 3 |
| Butanone | 1.5 | 3 |
| Nitromethane | 3 | 6 |
| Nitrobenzene | 3.5 | 5 |
| *o*-Nitrotoluene | 2.5 | 3.5 |

The data show that:

1. Models *C* and *D*, based on concentric dielectric continua, reproduce the cohesion energy due to permanent dipoles in agreement with the thermodynamic experience.

2. As a consequence of intermolecular forces, the static relative permittivity of the spherical layer is smaller than that of the bulk of the liquid. Presumably, this decrease is greater if the polar molecule is smaller and its permanent dipole moment is greater. (It should be mentioned that in the hydrate layer the ions reduce the static permittivity of water to 1/20—1/25 of the bulk permittivity. However, it is probable that $\varepsilon_l$ cannot be smaller then the square of the internal refractivity.)

Practically both models *C* and *D* are suitable for the calculation of the cohesion energy due to dipolar interactions. Theoretically, model *D* has an advantage over model *C*, because it takes into account the polarizability of the dipole.

Model *C* clearly shows that the reaction field factor (and thus the dipolar part of the cohesion energy too) consists of two parts. The first is determined by the interaction between the dipole and the spherical layer, the second originates from that between the dipole and the bulk of the liquid. Using model *C*, the ratio of these parts was determined. In Table V $(W_{c1}-W_{c2})\,100/W_{c1}=\eta\%$ is given for the compounds investigated. $\eta$ is the per cent contribution of the interaction between the dipole and the layer to the value of $W$.

According to Table V, the interaction between the dipole and the layer plays a role of decisive importance in producing $W$. The cohesion energy, and probably the other properties of polar liquids, too, are essentially determined by the interaction of the molecule with its nearest neighbours.

**Table V**

*Per cent contribution of the interaction between the dipole and the layer to the value of W*

| Compound | $\eta$(%) |
|---|---|
| Acetonitrile | 90 |
| Propanone | — |
| Butanone | 98 |
| Nitromethane | 96 |
| Nitrobenzene | 96 |
| *o*-Nitrotoluene | 96 |

## REFERENCES

[1] GUGGENHEIM, E. A.: Mixtures. Calderon Press, Oxford 1952
[2] ONSAGER, L.: J. Amer. Chem. Soc., **58,** 1486 (1936)
[3] LISZI, J., MÉSZÁROS, L.: Magy. Kém. Folyóirat, **82,** 546 (1976)
[4] BRETSNAIDER, S.: Svoistva gazov i zhidkostei Moskva 1966
[5] REID, R. C., SHERWOOD, T. K.: The Properties of Gases and Liquids. McGraw-Hill, 1966
[6] BÖTTCHER, C. J. F.: Theory of Electric Polarization (Revised by O. C. VAN BELLE, P. BORDEWIJK, A. RIP) Vol. 1 Elsevier, 1973
[7] GRIMM, F. V., PATRICK, W. A.: J. Amer. Chem. Soc., **45,** 2794 (1923)
[8] HILL, N. E., VAUGHAN, W. E., PRICE, A. H., DAVIES, M.: Dielectric Properties and Molecular Behaviour, Van Nostrand Reinhold, London 1969

János LISZI H-8201 Veszprém.

*Acta Chimica Academiae Scientiarum Hungaricae, Tomus 98 (1), pp. 103–113 (1978)*

# CYCLOADDITION REACTIONS OF CEPHALOSPORIN COMPOUNDS, III*

## 1,3-DIPOLAR CYCLOADDITIONS OF CEPHALOSPORINS AND DIAZOALKANES

J. Cs. JÁSZBERÉNYI, E. R. FARKAS, E. T. GUNDA, J. TAMÁS**, M. MÁK,**
S. HOSZTAFI, L. SZILÁGYI and R. BOGNÁR

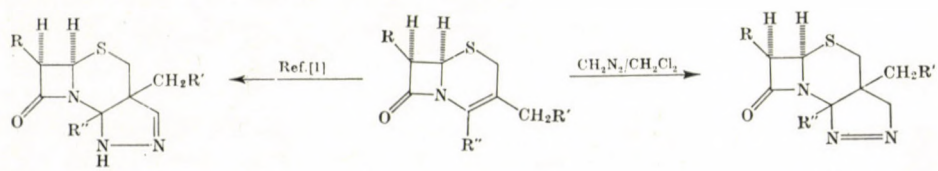
*(Institute of Organic Chemistry, Kossuth Lajos University, Debrecen, and **Central Research Institute of Chemistry, Budapest)*

Received March 5, 1976

Diazoalkanes add to 3-cephems and oxidized derivatives of 3-cephems to giv 1-pyrazolinocephams as primary products in neutral solvents. Although higher diazo alkanes react with the double bond of 3-cephems, no additions occurs in the case o diazoalkanes substituted with alkoxycarbonyl or aryl groups, because of the reduced reactivity of these 1,3-dipoles and the low reactivity of the 3-cephem dipolarophile. Diazomethane gives cycloadducts with 3-, but not with 2-cephems. The structures of the new pyrazolinocephams are discussed.

## Introduction

Cycloaddition of diazomethane to 3-cephems was described several years ago [1], but not other additions were reported because of the unreactive double bond. Bromine and other electrophilic reagents do not add to the double bond [2]. Cycloaddition of diazomethane to the double bond is of synthetic importance [3]. Further investigations [4, 5] showed the possibility of obtaining 1- and 2-pyrazolines, as well as different paths to prepare cycloadducts of diazomethane and 3-cephems of a higher oxidation state at position 1 [6]. The orientation of 1,3-dipolar cycloaddition in the case of alkenes and different 1,3-dipoles has been investigated by experimental methods [7] and also by CNDO/2 calculations [8]. In our previous work [4] we studied the regioselectivity of the cycloaddition to the double bond of 3-cephems, which is influenced by the lone-pair electrons of the lactam nitrogen and the $\pi$ and $p$ orbitals of the ester carbonyl at position 4. The orientation might be affected by the various oxidation states of sulfur at position 1.




3 1 2

* Part II: ref. [4].

**a**: $R'' = -H$ **d**: $R'' = -COOH$

**b**: $R'' = -COOCH_2C_6H_4\text{-}pNO_2$ **e**: $R'' = -COOCH_3$

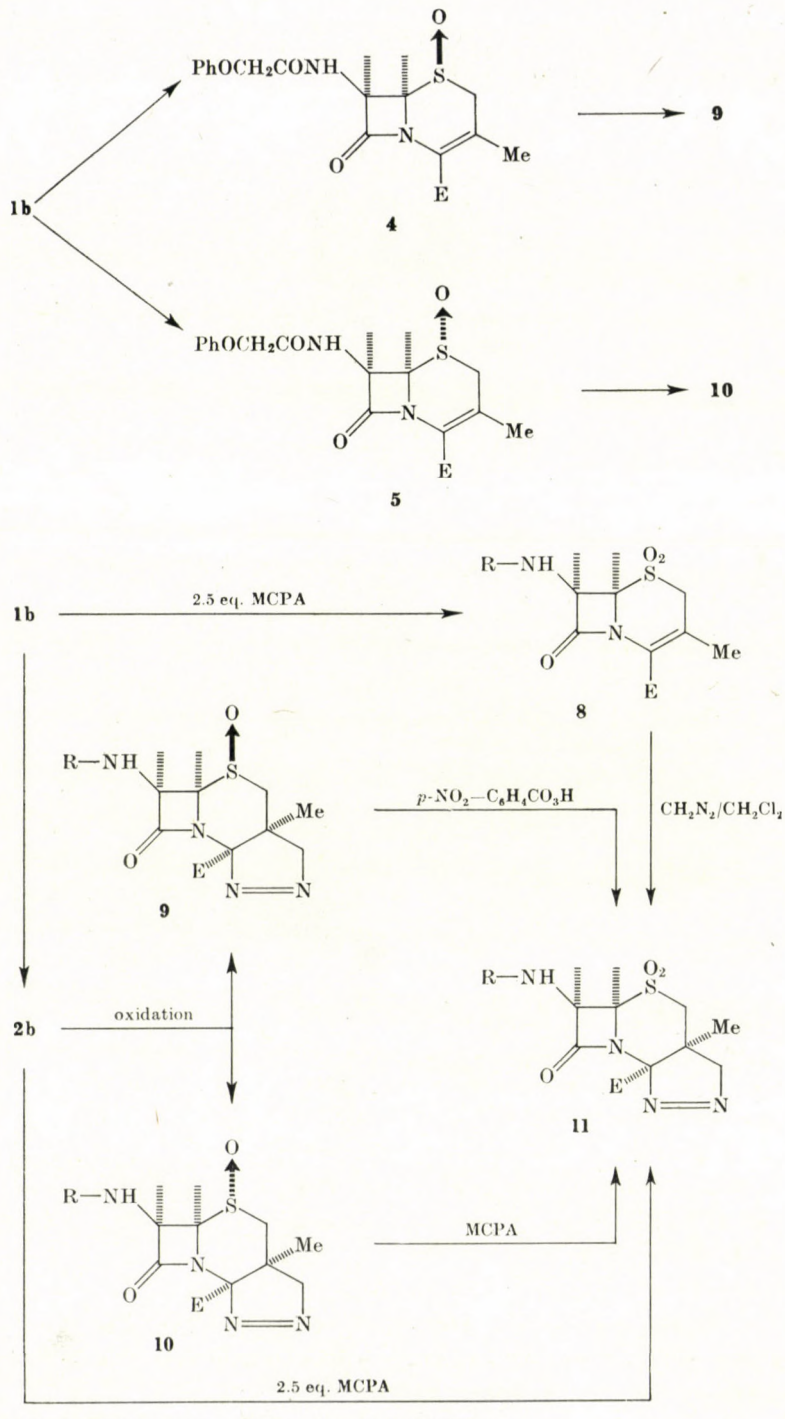
**c**: $R'' = -COOCH_2CCl_3$ **f**: $R'' = -COOCHPh_2$

In the present work we also studied the effect caused by replacement of the hydrogens of the diazomethane dipole by various substituents.

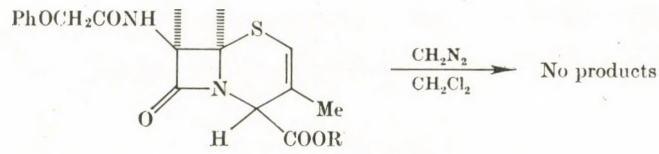
1-Pyrazolines were isolated when the cycloadditions were carried out in neutral solvents dichloromethane, chloroform, ether. Nevertheless, the same orientation of the cycloaddition was observed as previously [1]. These data, and the previously described unreactivity [4] of the decarboxylated compound **1a** [23a], suggest that the electronic influence of the lactam lone-pair electrons and the $\pi$ and $p$ electrons of the ester carbonyl is superior to the $d\pi$—$p\pi$ through-space conjugation between the cephem double bond and the sulfur 3d orbitals. Although this orientation is in accordance with that observed in the cycloaddition of diazoalkanes and acrylic acid derivatives [9, 10], it is noteworthy that in the case of allyl sulfides [11] and allyl sulfones [12] homoallylic $d\pi$—$p\pi$ conjugation was found to be determinant in 1,3-dipolar cycloaddition with diazomethane; only one (the $\gamma$ [23b]) adduct was formed in these reactions. Surprisingly, the cycloadducts obtained from the reactions of 2*H*-thiopyran-1,1-dioxide [13] and 5-phenyl-2*H*-thiopyran-1,1-dioxide [14] with diazomethane do not show this through-space conjugation, *i.e.* the orientation is the same as in the case of the cephem sulfone **8** [5]. Cycloaddition of diazomethane to the double bond of cephem sulfone **8** gives rise to the same compound, **11**, as obtained from the cycloaddition reaction of 3-cephems, followed by an oxidation process to **11** directly, or through the corresponding (S) or (R) sulfoxides (**9** and **10**).

Having prepared the corresponding (S) and (R) sulfoxides of **1b** (compounds **4** and **5**, respectively), we attempted to prepare compounds **9** and **10** in order to investigate the effect of the sulfoxide group on the course of the cycloaddition of diazomethane.

The activating influence of the sulfur hetero atom of 2-cephems in the cycloaddition with diazomethane was also studied. In the reaction of vinyl sulfides with diazomethane the activating effect of the sulfur was found to be determinant by $d\pi$—$p\pi$ interaction [11], since the compounds show $\beta$-orientation [23c], and no $\alpha$-adduct formation was observed. However, no reaction could be detected when compounds **6a**—**e** were treated with diazomethane for a week in dichloromethane-ether solution. This fact is probably connected with electronic and steric effects caused by the isomerization of the double bond.




E = $-COOCH_2C_6H_4$-*p*-$NO_2$; R = $PhOCH_2CO-$




**6a—e**

2-cephems may be regarded as both vinyl sulfides and derivatives of α-aminovinylacetic acid esters. The complete unreactivity observed in the attempted reaction of 2-cephems with diazomethane shows that the resonance structure **7** is not formed, although this structure led to the exclusive formation of the β-adduct when phenyl vinyl sulfide was treated with diazomethane [11].




**7**

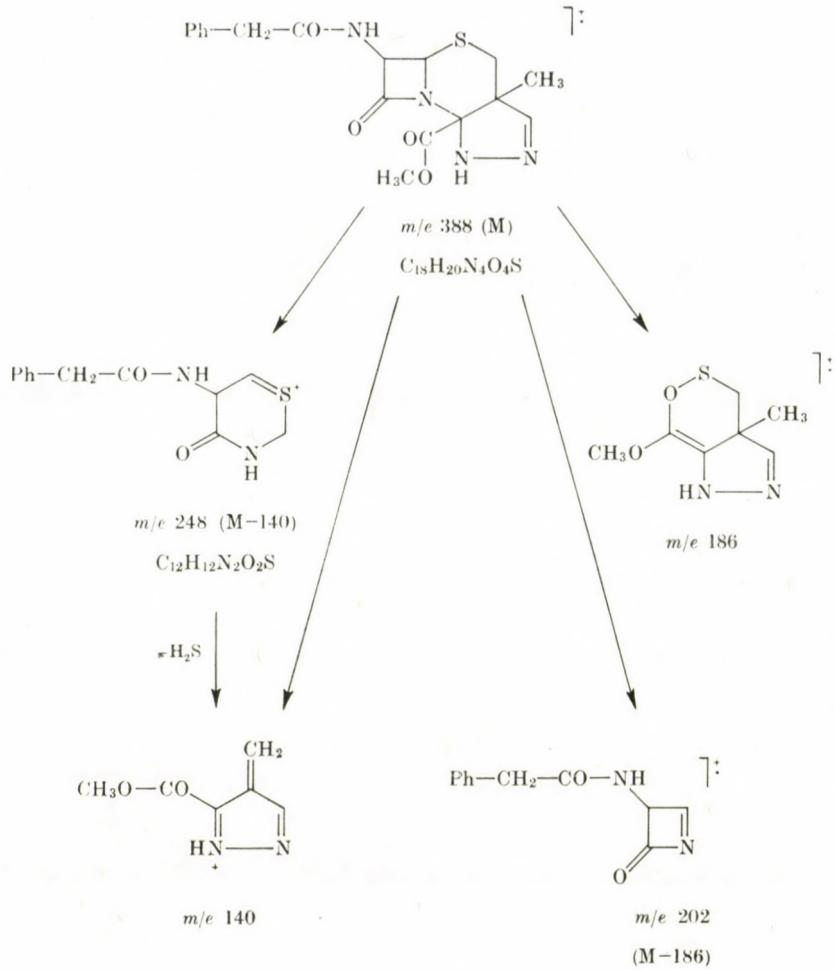
In accordance with literature data [7], replacement of the hydrogens of the diazo compound by carbonyl substituents reduces the reactivity of the diazo compound in cycloaddition reactions. In this case unreactivity is already observed when the first ethoxycarbonyl group is introduced into diazomethane (Table I).

**Table I**

*Rates of addition of substituted diazoalkanes to the double bond of 3-cephems*

| Diazo compound | Temperature | Reaction rate |
|---|---|---|
| Diazomethane | room temp. | slow (one week) |
| Diphenyldiazomethane [23d] | up to 100 °C | no addition |
| Ethyl diazoacetate | up to 100 °C | no addition |
| Diethyl diazomalonate | up to 100 °C | no addition |
| Diazoethane [23e] | room temp. | very slow (weeks) |

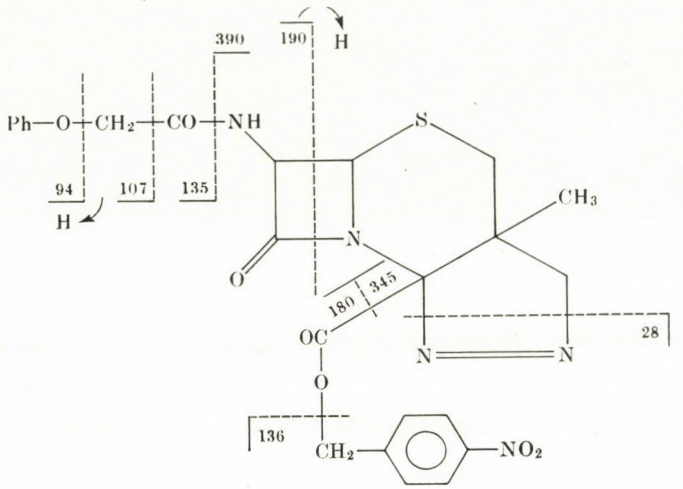
Reaction of **1c** with diazomethane-DMF gave a mixture of two compounds, **3b** and **3c**. The compounds were separated by column chromatography on silicagel, using benzene-ethyl acetate as the developing solvent. The 2-pyrazolinocepham structures of **3b** and **3c** were verified by their mass spectra. Compound **3b** gave a peak at 388 (M for $C_{18}H_{20}N_4O_4S$), and both of these 2-pyrazolinocephams show a fragmentation pattern not characteristic of cephalosporins [15], but consistent with the structures suggested for **3b** and **3c**.




1-pyrazolinocephams show a significant loss of nitrogen, as characteristic of 1-pyrazolines [16], and undergo a fragmentation of the cephalosporin type [15].

Attempts to initiate the prototropic rearrangement of 1-pyrazolinocephams to the corresponding 2-pyrazolino derivatives proved to be unsuccesful [20] in acidic media, but it was possible when using organic bases (**2b** rearranged to **3b** while standing in dichloromethane in the presence of triethylamine).

The PMR results offer additional support for the assumption that the dipolarophilic attack takes place on the $\beta$-face. Thus, this step involves the formation of compounds having the general view shown in Fig. 1. The importance of electronic effects in determining the direction of cycloaddition has




**2b**

been discussed in detail previously. Its alteration, together with the new conformation of the tetrahydrothiazine ring, serves as an ample source for the data to be discussed.

The cephem dihydrothiazine ring has been the subject of a recent review [22], although only a brief description of data of interest can be found. As to the 2-$CH_2$ protons, for purposes of comparison their chemical shifts in **12** and **13** are shown in Table II.

On oxidation, the protons in question of **12**, despite the different substituents at C-3 and 4, reflect the same general pattern. Clearly, this effect in **12** shows that its conformation as regards the relative orientations of the 2$\alpha$- and 2$\beta$-protons and the sulfoxide bond, can adopt a flattered chair-like structure similar to that of **13**. It is rather suprising that both in the sulfide and $\alpha$-sulfoxide of **12** the 2$\alpha$- and 2$\beta$-protons exhibit the same shift.

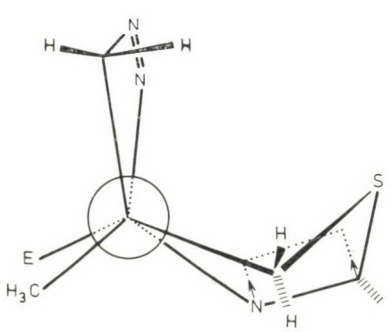
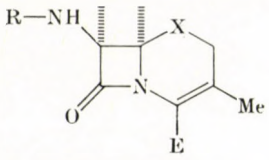
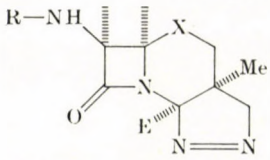


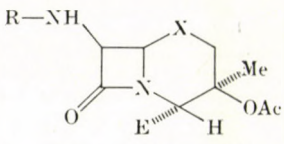

*Fig. 1*



11



12



13

**11, 12**: E = $-COOCH_2C_6H_4$-*p*-$NO_2$

R = $PhOCH_2CO-$

**13**: E = $-CONH$-*t*-Bu

R = $PhOCH_2CO-$

**a**: X = $>S$

**b**: X = $>S\dashrightarrow O$

**c**: X = $>S\rightarrow O$

**d**: X = $>SO_2$

The signals of the $CH_2$-protons of the pyrazoline moiety appear at about 5 ppm, as shown in Table III. The diamagnetic anisoropy caused by the α-sulfoxide bond has only a small influence on these protons and the result is only a slight upfield shift. Because of the spatial proximity of the β-sulfoxide bond and the 'inner' $CH_2$ proton, a marked downfield shift can be observed: δ 4.69 ppm for **12b** and δ 5.48 ppm for **12c**.

One further point of interest regarding the pyrazolino protons in sulfone **12**d is the coincidence of their PMR shifts as a result of diamagnetic anisotropy caused by the sulfone group.

**Table II**

*Chemical shifts of the 2-$CH_2$ protons in* 11, 12 *and* 13.

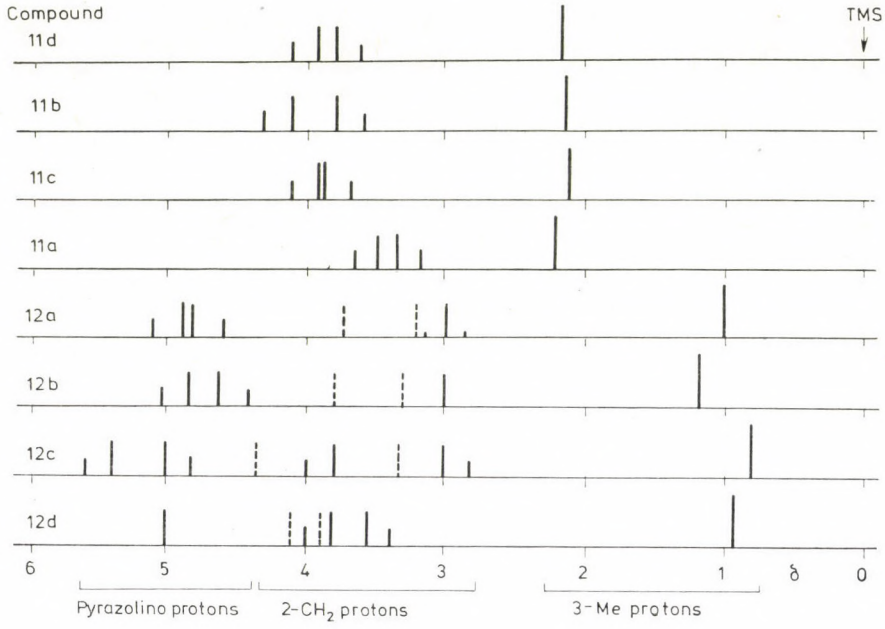
| Compound | 11 | 12 | 13** |
|---|---|---|---|
| **a** | 3.55* | 2.94 | 3.75 |
| | 3.25 | | 3.20 |
| **b** | 3.69 | 3.05 | 3.30 |
| | 4.23 | | 3.80 |
| **c** | 3.98 | 2.93 | 3.35 |
| | 3.67 | 3.87 | 4.33 |
| **d** | 4.06 | 3.90 | 4.07 |
| | 3.72 | 3.58 | 3.90 |

* All data (δ, TMS) were obtained in DMSO-$d_6$, with this exception ($CDCl_3$).

** Ref. [21].

**Table III**

*Pattern of characteristic protons of compounds 11 and 12. Dotted lines are signals of the 2-$CH_2$ group of the corresponding compound 13*




## Experimental

Melting points were determined on a Kofler hot-stage apparatus. The absorbent for TLC was silica gel G (Reanal), activated at 105—110 °C for 2 hrs before use. UV spectra were determined on a Unicam SP 800 UV-visible instrument, IR spectra on a Unicam SP 200G infrared spectrophotometer using KBr pellets. Mass spectra were obtained on a A.E.I. MS 902 instrument (70 eV, 170—200 °C) and $^1$H—NMR spectra on a JEOL-Minimar instrument (operating at 100 MHz), using $CDCl_3$ or DMSO-$d_6$ as solvents and TMS or HMDS as standards.

### Preparation of 2b (R = $PhOCH_2CONH$-, R′ = —H)

To a solution of *p*-nitrobenzyl-7-phenoxyacetamido-3-methyl-3-cephem-4-carboxylate (2 g) in $CH_2Cl_2$ (40 ml), freshly prepared etheral diazomethane (30 ml) was added (1 mmole/ml). The reaction mixture was allowed to stand at room temperature for a week, meanwhile some fresh diazomethane solution was added. The crystalline product which deposited was filtered off and washed successively with ether to obtain 635 mg of pale yellow crystals (m.p. 185.5—186.5 °C, d.). On careful concentration in vacuum the mother liquor gave an oil, which solidified on trituration with ether yielding a second crop (931 mg, m.p. 185.5 °C d.).

$C_{24}H_{23}N_5O_7S$.
Calcd. N 13.4; S 6.1.
Found N 13.0; S 6.2%.

UV: $\lambda_{max}$ (in dioxane) 326 nm ($\epsilon = 400$).
MS: 525 ($M^+$), 497 ($M^+ - 28$).
IR (KBr): 1780, 1690, 1530, 1356 $cm^{-1}$.
Similarly were obtained **2c** and **2e**.

### Preparation of 4 (E = —$COOCH_2C_6H_4$—*p*—$NO_2$)

This compound was prepared by MCPA oxidation of **1b** according to KAISER *et al.* [24] m.p. 181—182 °C.

$C_{23}H_{21}N_3O_8S$ (499.5.)
Calcd. C 55.3; H 4.21; S 6.41.
Found C 55.3; H 4.16; S 6.30%.
IR (KBr): 1790, 1676, 1521, 1220, 1052 $cm^{-1}$.

### Preparation of 5 (E = —$COOCH_2C_6H_4$—*p*—$NO_2$)

Compound **1b** (2 g) was dissolved in a minimal amount of $CH_2Cl_2$ and N,N-dichlorourethane (0.7 g) was added in one portion at ambient temperature. The mixture was allowed to stand with occasional shaking for 5 min, then it was washed with 10% $NaHCO_3$ solution, water, dil. HCl and water. The dried solution ($Na_2SO_4$) was evaporated to half of its volume. After cooling the separated **5** was filtered off to obtain 1.7 g (82.3%) of colourless needles (m.p. 189—191 °C).

$C_{23}H_{21}N_3O_8S$ (499.5).
Calcd. N 8.42; S 7.41.
Found N 8.40; S 6.36%.
MS: 499.49 ($M^+$).
IR (KBr): 1791, 1678, 1518, 1226, 1050 $cm^{-1}$.

### Preparation of 8 (R = $C_6H_5OCH_2CO$—, E = —$COOCH_2C_6H_4$—*p*—$NO_2$)

Compound **1b** (1.9 g) was dissolved in $CH_2Cl_2$ (20 ml) and the solution was treated dropwise with MCPA (85%, 2.2 g) dissolved in the same solvent (40 ml). After the addition had been completed, the mixture was gently refluxed for 90 min. and then thoroughly washed three times with 15 ml of 10% $NaHCO_3$ solution. After drying and evaporation 1.5 g (74%) of **8** was obtained as an oil which solidified on trituration with benzene–petroleum ether (m.p. 172—175 °C).
MS: 515 ($M^+$) for $C_{23}H_{21}N_3O_9S$.
IR: (KBr): 1810, 1708, 1530, 1230, 1112, 1065 $cm^{-1}$.

### Oxidation of 2b

To a cooled solution of **2b** (2.8 g) in $CH_2Cl_2$ (100 ml), a solution of 80% MCPA (1.42 g) in $CH_2Cl_2$ (32 ml) was added by drops during 1 hr. The mixture was stirred for an additional hour. The concentrated solution was chromatographed on 100 g of activated silicagel using benzene–ethyl acetate 1 : 1 mixture as the eluent and collecting 10 ml fractions. Fractions No. 4—10 contained 0.17 g of **11** m.p. 208—209 °C which proved to be identical with the compounds obtained from **2b**, **8**, **9**, or **10**.

Elution was continued using a mixture of benzene–ethyl acetate 1 : 4. Fractions No. 20—30 were combined and evaporated to 2 ml. Crystals of **9** were collected and recrystallized from $CH_2Cl_2$–petroleum ether 0.46 g; m.p. 186—187.5 °C. From the mother liquor a further 0.13 g was obtained.

IR (KBr): 1776, 1530, 1240, 1060 $cm^{-1}$.
MS: 541 ($M^+$), 513 ($M^+ - 28$).

From fractions No. 32—110, 394 mg of **10** was obtained by the same work-up; m.p. 146—147 °C after recrystallization from $CH_2Cl_2$–DMSO–petroleum ether.

IR (KBr): 1788, 1527, 1268, 1060 $cm^{-1}$.
MS: 541 ($M^+$), 513 ($M^+ - 28$).

## REFERENCES


[1] ARCHER, R. A., KITCHELL, B. S.: J. Org. Chem. **31,** 3409 (1966)
[2] COOPER, R. D. G.: "Unpublished observations in Cephalosporins and Penicillins", Chemistry and Biology (Ed. E. H. Flynn), p. 144. Academic Press, New York and London 1972
[3] BARTON, D. H. R., GREIG, D. G. T., SAMMES, P. G., TAYLOR, M. V.: Chem. Commun. **1971,** 845
[4] FARKAS, E. R., GUNDA, E. T., JÁSZBERÉNYI, J. Cs.: Tetrahedron Letters **1973,** 5127
[5] GUNDA, E. T., JÁSZBERÉNYI, J. Cs., FARKAS, E. R.: Acta Chim. (Budapest), **83,** 215 (1974)
[6] For the numbering see: MORIN, R. B., JACKSON, B. G., FLYNN, E. H., ROESKE, R. W.: J. Am. Chem. Soc., **84,** 3400 (1962)
[7] See, e.g.: HUISGEN, R.: Angew. Chem. Internat. Ed. **2,** 633 (1963)
[8] BASTIDE, J., EL GHANDOUR, N., HENRI-ROUSSEAU, O.: Bull. Soc. Chim. France **1973,** 2290; BASTIDE, J., EL GHANDOUR, N., HENRI-ROUSSEAU, O.: Bull. Soc. Chim. France **1973,** 2294; BASTIDE, J., HENRI-ROUSSEAU, O.: Bull. Soc. Chim. France **1974,** 1037; BASTIDE, J., HENRI-ROUSSEAU, O., ASPART-PASCOT, L.: Tetrahedron **30,** 3355 (1974)
[9] VON AUWERS, K., KŐNIG, F.: Ann. **496,** 27 (1932);
VON AUWERS, K., KŐNIG, F.: Ann. **496,** 252 (1932);
VAN AUKEN, T. V., RINEHART, Jr., K. L.: J. Am. Chem. Soc. **84,** 3736 (1962)
[10] ANDREWS, S. D., DAY, A. C., MCDONALD, A. N.: J. Chem. Soc. (C) **1969,** 787 and references cited therein.
[11] KONDO, K., OJIMA, I.: Chem. Lett. **1972,** 711; Bull. Chem. Soc. Japan **46,** 2571 (1973)
[12] MIKHAILOVA, V. N., BULAT, A. D., FEL'DMAN, I. Kh.: J. Org. Chem. USSR, **4,** 1445 (1968) and references cited therein.
[13] See Ref. No. [14] in our Ref. [14]
[14] BRADAMANTE, S., MAIORANA, S., MANGIA, A., PAGANI, G.: Tetrahedron Letters **1969,** 2921
[15a] RICHTER, W., BIEMANN, K.: Monatsh. Chem. **96,** 484 (1965)
[15b] DEMARCO, P. V., NAGARAJAN R.: "Cephalosporins and Penicillins", Chemistry and Biology (Ed. E. H. Flynn), pp. 325—330. Academic Press, New York and London 1972
[16] TERENTYEV P. B., VINOGRADOVA, S. M., KOST, A. N., STRUKOVSKII, A. G.: Khim. Geterocikl. Soedin. **1973,** 64
[17] MORIN, R. B., JACKSON, B. G., MUELLER, R. A., LAVAGNINO, E. R., SCANLON, W. B., ANDREWS, S. L.: J. Am. Chem. Soc. **91,** 1401 (1969); GUTOWSKI, G. E., FOSTER, B. J., DANIELS, C. J., HATFIELD, L. D., FISCHER, J. W.: Tetrahedron Letters **1971,** 3433
[18] BORSCHE, W., MERKWITZ, C.: Chem. Ber. **37,** 3180 (1904)
[19] The formation of the corresponding ketazine from azibenzil is a similar process, through the addition of excess of the diazo component: HORNER, L., KIRSME, W., HOFFMANN, H.: Ann. **614,** 19 (1958). This reaction is a well-known polymerization in the case of diazoalkanes. The dimerization in this case is caused by the phenyl groups lowering the reactivity of the carbene.
[20] HOUBEN—WEYL: Methoden der organischen Chemie (Vierte Auflage) Stickstoffverbindungen 1, Teil 4, p. 804 e, f. (1968); and HELDER, R., DOORNBOS, T., STRATING, J., ZWANENBURG, B.: Tetrahedron **29,** 1375 (1973)
[21] BARTON, D. H. R., COMER, F., GREIG, D. G. T., LUCENTE, G., SAMMES, P. G., UNDERWOOD, W. G. E.: Chem. Commun. **1970,** 1059
[22] Ref. [15b], pp. 330—360
[23a] Compound **Ia** was prepared by the acid-catalyzed rearrangement of penicillin-V sulfoxide (GUNDA, E. T.: Unpublished results). See also Ref. [17]
[23b] The term '$\gamma$-adduct' is used to indicate that the new C—C bond was formed between the diazocarbon and the third carbon from the sulfur.

[23c] '$\beta$-adduct' and '$\alpha$-adduct' or '$\beta(\alpha)$-orientation' is used to indicate the place where the new C—C bond is formed. It means $\beta$ or $\alpha$ to the carboxyl group [9b] in acrylic acid derivatives, and to the sulfur in sulfides.

[23d] In the presence of $Cu(acac)_2$ the only new compound in this reaction is the benzophenone azine $(Ph)_2C{=}N{-}N{=}C(Ph)_2$ synthesized previously by other methods [18] as a reaction product of diphenylcarbene and diphenyldiazomethane [19]

[24] KAISER, G. V., COOPER, R. D. G., KOEHLER, R. E., MURPHY, C. F., WEBBER, J. A., WRIGHT, I. G., VAN HEYNINGEN, E. M.: J. Org. Chem. **35,** 2430 (1970)

J. Cs. JÁSZBERÉNYI
E. R. FARKAS
E. T. GUNDA
L. SZILÁGYI
R. BOGNÁR
S. HOSZTAFI

H-4010 Debrecen, P.O.B. 20

J. TAMÁS
M. MÁK

H-1088 Budapest, Puskin u. 11—13.

*Acta Chimica Academiae Scientiarum Hungaricae, Tomus 98 (1), pp. 115—132 (1978)*

# AROMATIZATION OF *n*-NONANE AND *n*-DECANE OVER A PLATINUM-RHENIUM CATALYST

I. SZEBÉNYI and G. SZÉCHY

*(Department of Chemical Technology, Technical University, Budapest)*

Received March 20, 1977

*n*-Nonane and *n*-decane were reformed between 487 and 548 °C, at pressures of 15, 22 and 31 kp $cm^{-2}$ and at liquid hourly space velocities of 1.5, 3 and 5 $h^{-1}$. The hydrogen to hydrocarbon mole ratio was 5:1. An industrial platinum-rhenium catalyst was used. With *n*-nonane as starting material, the product contained all the possible $C_9$ aromatics, but the amounts of *o*-ethyltoluene and *n*-propylbenzene were much higher than those found in naphtha reformates. The main products of aromatization of *n*-decane are *n*-butylbenzene, 1,3-diethylbenzene, 1,2-dimethyl-4-ethylbenzene and 1-methyl-2-*n*-propyl-benzene. The amount of aromatics in the products ceases to increase further over 531 °C (for *n*-nonane) and 516 °C (for *n*-decane), due to the predominance of hydrocracking reactions. The increase in temperature and pressure shifts the aromatics distribution towards aromatics containing fewer carbon atoms than the starting material. This can be attributed to dealkylation of $C_{10}$ and $C_9$ aromatics. The selectivity of the formation of $C_9$ and $C_{10}$ aromatics decreases with increasing pressure.

The production of aromatics with fewer than 10 carbon atoms is characteristic for *n*-decane aromatization even under mild conditions. *n*-Nonane gives 32.3 w/w% $C_9$ aromatics at 531 °C, 15 kp $cm^{-2}$ pressure and at 1.5 $h^{-1}$ space velocity; at the same time, *n*-decane gives under similar conditions 13.7 w/w% $C_{10}$ and 9.0 w/w% $C_9$ aromatics.

## Introduction

In the last decade, bi- and multimetallic catalysts have been introduced into catalytic reforming. Their most important representatives contain platinum and rhenium. Their high stability permits to decrease reforming pressures without any significant decrease of the operation periods, as compared with platinum-containing catalysts [1—3]. Usual pressures are 8—15 kp $cm^{-2}$ with bimetallic catalysts, as opposed to the 30—35 kp $cm^{-2}$ typical for ones containing platinum only. Lower pressures favour the formation of aromatics, hydrocrack reactions being suppressed. Therefore, the use of bimetallic catalysts involves not only technological advantages but also results in higher yields of aromatics.

We reported earlier our results on dehydrocyclization of *n*-nonane and *n*-decane over industrial platinum catalysts, under the conditions of catalytic naphtha reforming [4].

The aim of the present study was to investigate the dehydrocyclization of *n*-nonane and *n*-decane over an industrial platinum-rhenium reforming

catalyst (Engelhard E-601). We intended to study the aromatic isomer distribution, the extent of favourable effects due to a decrease in pressure, and finally, to decide to what extent *n*-nonane and *n*-decane conversion contributes to $C_9$- and $C_{10}$ aromatics formation in the naphtha reforming process over a platinum-rhenium catalyst.

There is considerable interest in petroleum chemistry towards $C_9$ and $C_{10}$ aromatic hydrocarbons [5]. 1,2,4- and 1,3,5-trimethylbenzenes as well as 1,2,4,5-tetramethylbenzene have already been produced and separated as chemical raw materials of petrochemical origin, although the volume of their production is small compared with that of $C_6-C_8$ aromatics [6]. Further research in product development is concentrated also on these three polymethylbenzenes. Of these, 1,3,5-trimethylbenzene with a totally symmetrical structure has the greatest potential importance. $C_9$ and $C_{10}$ aromatics mixtures are often used as special solvents [5].

During recent years, there has been an increasing interest towards dehydrocyclization, among the several reactions taking place in reforming [3, 7]. Under the conditions of modern reforming processes, the dehydrogenation of naphthenes and the isomerization of alkanes in the raw naphtha proceed as far as equilibrium concentrations permit. However, the octane rating of these reformates is still not sufficient in most cases [7]. A further increase of octane number can only be achieved by promoting dehydrocyclization of paraffins. This reaction is accompanied, however, by their hydrocracking, *i.e.* by a considerable loss of the valuable liquid product. Dehydrocyclization is a complex reaction, studied by several authors. Most of the mechanistic studies have, however, been carried out on platinum catalysts only, under conditions very far from industrial ones.

Recently, studies have also been reported on paraffin dehydrocyclization over platinum-rhenium and other bimetallic catalysis, but their majority has been performed at atmospheric pressure and under conditions differing from those applied in industry [8]. In most cases, lower hydrocarbons such as *n*-heptane served as starting materials [9, 10].

Owing to the considerable practical importance of $C_9$ and $C_{10}$ aromatics production, we have selected *n*-nonane and *n*-decane as starting hydrocarbons. The catalyst and experimental conditions chosen were similar to those used in industrial processes.

## Experimental

*n*-Nonane and *n*-decane were supplied by FLUKA ("pract." grade, with purity better than 95 w/w%). The experiments were carried out in a high pressure isothermal twin reactor developed in the High Pressure Institute. The apparatus was almost identical with that described by HEVESI [11], witht wo differences worth mentioning: first, the hydrogen-rich gas from the reactor outlet was not recycled but blown off; second, no argon atmosphere was maintained over the burette containing the starting *n*-nonane or *n*-decane. 45 $cm^3$ of aluminium granules

has been placed into the reactor after the inlet, in order to facilitate evaporation and heating of the *n*-paraffin feed to the required temperature. 50 $cm^3$ of commercial Engelhard E-601 platinum-rhenium catalyst was placed above the aluminium granules, into the middle of the reactor vessel. This catalyst is used in many reforming plants. Inert ceramic granules have been placed near to the outlet of the vessel. Electrolytic hydrogen was used in the experiments. Its oxygen content was removed by a palladium catalyst. The gas was dried over a molecular sieve column before entering the reactor.

The catalyst was pretreated as suggested by the manufacturer, then aged; continuous experiments were commenced only subsequent to these cycles. The parameters applied were close to those applied in reforming industry. The effect of temperature was studied between 487 and 548 °C. Before and during one run the temperature was kept constant and the pressure was maintained at 15 kp $cm^{-2}$. In addition, at a constant temperature (531 °C), various pressures (22 and 31 kp $cm^{-2}$) and various space velocities (1.5, 3 and 5 $h^{-1}$) were applied. The hydrogen to hydrocarbon mole ratio was kept, similarly to industrial practice, at a value of 5 : 1. The sets of parameters belonging to the individual runs are shown in Tables I and IV.

Concerning the accuracy of measurement and control of various parameters the paper of HEVESI [11] should be referred to. No gas recycling was applied in our case, thus its relative error of ±10% falls out. At the same time, the error of pressure regulation was higher than the value given in Ref. [11], its maximum being ±7%.

After the required parameters had been adjusted, the apparatus was kept in operation for one hour in order to achieve a stable regime. Sampling for analysis was begun after this period.

During the experiments, we determined the amount of liquid products. Their aromatics content was measured by means of the gas chromatographic method described in our earlier paper [4].

## Results and discussion

Table I shows the results obtained for *n*-nonane reforming. Considering the series carried out at constant space velocity (3 $h^{-1}$) as a function of the temperature, it can be seen that higher temperatures enhance aromatics formation strongly: the yield of $C_9$ aromatics is 29.1 w/w% at 531 °C. A further temperature increase does not result in the formation of more aromatics of the $C_9$ group; only the amount of $C_8$ aromatics shows a slight increase, indicating dealkylation of the $C_9$ compounds. At the same time, enhanced hydrocracking is shown by the decrease of the liquid product yield.

Figure 1 shows the yields of various $C_9$ aromatics as a function of the temperature. This figure confirms that hardly any or no increase can be observed in the yield of individual compounds above 531 °C. The relatively high amounts of *o*-ethyltoluene and *n*-propylbenzene are remarkable. Table II compares the distribution of $C_9$ aromatics obtained from *n*-nonane and naphtha, both reformed on the same catalyst under the same conditions. The distribution at thermodynamic equilibrium is also shown. It can be seen that the fractions of *o*-ethyltoluene and *n*-propylbenzene obtained from pure *n*-nonane are higher than those obtained from naphtha and exceed the values corresponding to thermodynamic equilibrium.

Both *o*-ethyltoluene and *n*-propylbenzene can be formed directly from *n*-nonane by $C_6$-dehydrocyclization.

These two compounds can, however, be formed also by dehydroisomerization of *n*-butyl-, 1-methyl-2-*n*-propyl- and 1,2-diethylcyclopentanes, which

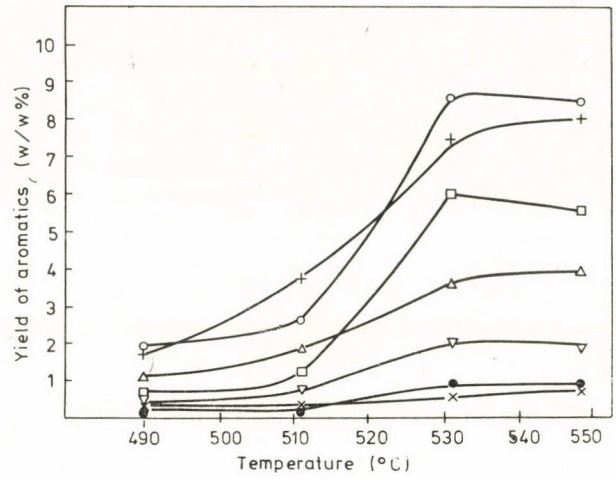



*Fig. 1.* Formation of $C_9$-alkylbenzenes from *n*-nonane, as a function of the temperature. Conditions: P = 15 kp cm$^{-2}$; space velocity: 3 $h^{-1}$. Symbols: × *i*-propylbenzene; △ *n*-propylbenzene; ○ *m* + *p*-ethyltoluene; + *o*-ethyltoluene; □ 1,2,4-trimethylbenzene; ● 1,3,5-trimethylbenzene; ▽ 1,2,3-trimethylbenzene

are possible products of the $C_5$-dehydrocyclization of *n*-nonane. This latter possibility has been demonstrated experimentally by Usov *et al.* [12]. Thus, the high yields of these two aromatics do not prove the predominance of either $C_5$- or $C_6$-dehydrocyclization.

Figure 2 shows the yields of $C_9$ alkylbenzenes as a function of reciprocal space velocity at 531 °C. It can be seen that between reciprocal space velocities of 0.2 and 0.33 h, increasing contact times lead to higher $C_9$ alkylbenzene yields. Still higher contact times result in hardly any or no further increase in the yields of *o*-ethyltoluene and the three trimethylbenzene isomers. Between reciprocal space velocities of 0.66 and 0.33 h, only the summarized yields of *m*- and *p*-ethyltoluene increase markedly. This phenomenon can be attributed to the isomerization of *o*-ethyltoluene, produced primarily from *n*-nonane, into

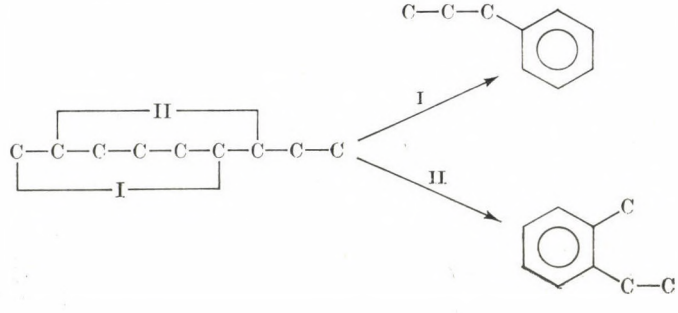


**Table I**

*Reforming of n-nonane*

| *Conditions of reforming* | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Temperature (°C) | 490 | 511 | 531 | 548 | 531 | 531 | 531 | 531 | 531 | 531 |
| Pressure (kp cm$^{-2}$) | 15 | 15 | 15 | 15 | 15 | 15 | 15 | 15 | 22 | 31 |
| Liquid Hourly Space Velocity (h$^{-1}$) | 3 | 3 | 3 | 3 | 1,5 | 3 | 5 | 1,5 | 1,5 | 1,5 |
| $H_2$/HC mole ratio | 5:1 | 5:1 | 5:1 | 5:1 | 5:1 | 5:1 | 5:1 | 5:1 | 5:1 | 5:1 |
| Unreacted *n*-nonane expressed as w/w% of the feed | 59.0 | 45.5 | 10.9 | 8.9 | 3.6 | 10.9 | 36.5 | 3.6 | 2.7 | 2.5 |
| *Yield of components expressed as w/w% of the feed* | | | | | | | | | | |
| Benzene | 1.3 | 1.4 | 2.1 | 1.6 | 2.1 | 2.1 | 1.6 | 2.1 | 1.4 | 1.6 |
| Toluene | 0.2 | 0.3 | 1.9 | 2.4 | 3.2 | 1.9 | 0.6 | 3.2 | 3.3 | 4.2 |
| Ethylbenzene | 0.1 | 0.2 | 0.6 | 0.9 | 1.1 | 0.6 | 0.2 | 1.1 | 1.1 | 1.1 |
| *m*+*p*-Xylenes | 0.2 | 0.3 | 1.4 | 1.6 | 2.1 | 1.4 | 0.5 | 2.1 | 2.6 | 3.5 |
| *i*-Propylbenzene | 0.3 | 0.3 | 0.5 | 0.6 | 0.7 | 0.5 | 0.4 | 0.7 | 0.5 | 0.9 |
| *o*-Xylene | 0.1 | 0.2 | 0.7 | 0.8 | 1.2 | 0.7 | 0.3 | 1.2 | 1.4 | 2.7 |
| *n*-Propylbenzene | 1.1 | 1.8 | 3.6 | 3.9 | 4.2 | 3.6 | 2.3 | 4.2 | 2.3 | 1.7 |
| *m*+*p*-Ethyltoluene | 2.0 | 2.6 | 8.6 | 8.5 | 11.2 | 8.6 | 4.2 | 11.2 | 8.4 | 6.8 |
| Mesitylene (1,3,5-trimethyl-benzene) | 0.1 | 0.1 | 0.9 | 0.9 | 0.9 | 0.9 | 0.3 | 0.9 | 1.4 | 2.0 |
| *o*-Ethyltoluene | 1.8 | 3.7 | 7.5 | 8.0 | 7.5 | 7.5 | 4.7 | 7.5 | 5.3 | 3.2 |
| Pseudocumene (1,2,4-trimethyl-benzene) | 0.7 | 1.1 | 6.0 | 5.5 | 5.6 | 6.0 | 2.4 | 5.6 | 6.0 | 4.2 |
| *n*-Butyl+1,3-diethylbenzene | — | 0.1 | — | 0.2 | 0.1 | — | 0.1 | 0.1 | 0.3 | — |
| Hemimellitene (1,2,3-trimethyl-benzene) | 0.5 | 0.5 | 2.0 | 1.9 | 2.1 | 2.0 | 1.2 | 2.1 | 1.4 | 1.3 |
| Indene+1,2-diethyl-4-ethyl-benzene | 0.3 | 0.4 | 0.8 | 0.8 | 1.0 | 0.8 | 0.5 | 1.0 | 0.5 | 0.5 |
| Total $C_8$ aromatics | 0.4 | 0.7 | 2.7 | 3.3 | 4.4 | 2.7 | 1.0 | 4.4 | 5.1 | 7.3 |
| Total $C_9$ aromatics (without in-dane) | 6.5 | 10.1 | 29.1 | 29.3 | 32.2 | 29.1 | 15.5 | 32.2 | 25.3 | 20.1 |
| Total aromatics | 8.7 | 13.0 | 36.6 | 37.6 | 43.0 | 26.6 | 19.3 | 43.0 | 35.6 | 33.7 |
| Liquid yield | 96.8 | 93.6 | 80.7 | 73.3 | 70.1 | 80.7 | 91.2 | 70.1 | 53.3 | 49.7 |

**Table II**

*Distribution of $C_9$ alkylbenzenes in the reformates obtained from naphtha and pure n-nonane*

| Feed | *n*-Nonane | Naphtha (boiling range 75—185 °C) | Thermodynamic equilibrium |
|---|---|---|---|
| Conditions of reforming | | | |
| Temperature (°C) | 531 | 530 | 530 |
| Pressure (kp $cm^{-2}$) | 15 | 15 | — |
| Liquid Hourly Space Velocity ($h^{-1}$) | 3 | 3 | — |
| $H_2$/HC mole ratio | 5:1 | 5:1 | — |
| Distribution of $C_9$ alkylbenzenes (w/w%) | | | |
| *i*-Propylbenzene | 1.8 | 1.6 | 1.3 |
| *n*-Propylbenzene | 12.3 | 5.4 | 3.9 |
| *m*+*p*-Ethyltoluene | 29.6 | 30.9 | 31.5 |
| *o*-Ethyltoluene | 25.7 | 4.8 | 8.2 |
| Mesitylene (1,3,5-trimethylbenzene) | 3.1 | 13.7 | 11.5 |
| Pseudocumene (1,2,4-trimethylbenzene) | 20.6 | 35.4 | 34.2 |
| Hemimellitene (1,2,3-trimethylbenzene) | 6.9 | 8.2 | 9.4 |
| | 100.0 | 100.0 | 100.0 |

*m*- and *p*-ethyltoluene. The driving force of this secondary isomerization process is that the high amounts of *o*-ethyltoluene obtained with low residence times are very far from the equilibrium distribution, thus, prolonged contact times help to approach equilibrium distribution via isomerization of *o*-ethyltoluene.

Isomerization of trimethylbenzenes into ethyltoluenes via the corresponding naphthenes has been reported to be absent by DONALDSON *et al.* [13] over platinum-containing bifunctional reforming catalysts. The reverse process, *i.e.* isomerization of ethyltoluenes into trimethylbenzenes is more probable at longer contact times [13]. There is a certain difference in this respect between platinum and platinum-rhenium catalysts.

In addition to isomerization, it is very probable that dealkylation of ethyltoluenes (among these, due to steric reasons, first of all that of *o*-ethyltoluene) as well as that of trimethylbenzenes occurs, leading to toluene or $C_8$ aromatics. The product composition data summarized in Table I support this assumption.

Figure 3 shows the effect of increasing pressure on $C_9$ alkylbenzenes. The well-known thermodynamic effect of suppressing aromatization by increasing pressure is conspicuously demonstrated. The advantage of platinum-rhenium catalysts can be observed inasmuch as it is possible to decrease the

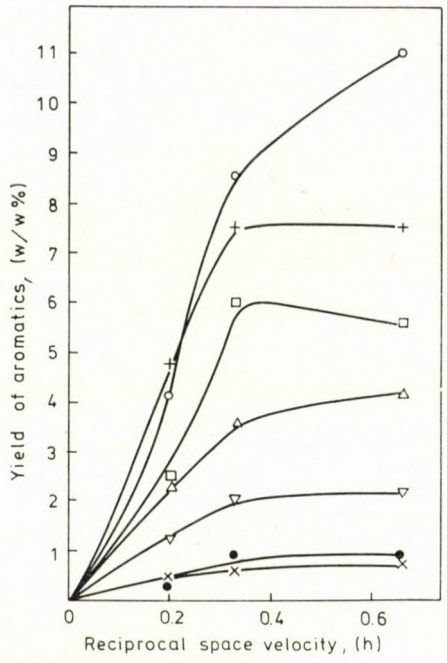



*Fig. 2.* Formation of Cg-alkylbenzenes from *n*-nonane as a function of the reciprocal space velocity. Conditions: $t = 531$ °C; $p = 15$ kp cm$^{-2}$. Symbols: × *i*-propylbenzene: △ *n*-propylbenzene; ○ *m*+*p*-ethyltoluene; + *o*-ethyltoluene; □ 1,2,4-trimethylbenzene ● 1,3,5-trimethylbenzene; ▽ 1,2,3-trimethylbenzene

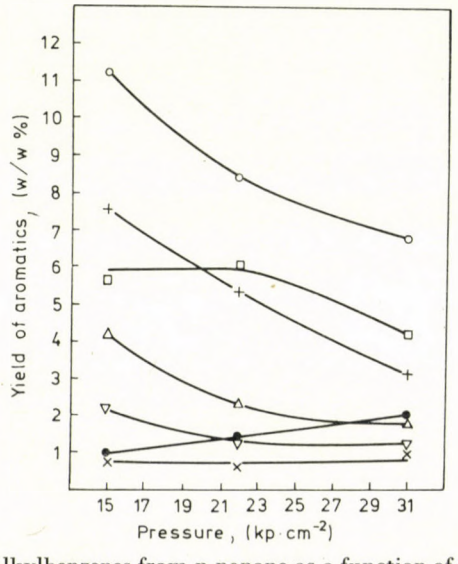



*Fig. 3.* Formation of $C_9$-alkylbenzenes from *n*-nonane as a function of the pressure. Conditions: $t = 531$ °C; space velocity: 1.5 $h^{-1}$. Symbols: × *i*-propylbenzene: △ *n*-propylbenzene; ○ *m*+*p*-ethyltoluene; + *o*-ethyltoluene; □ 1,2,4-trimethylbenzene; ● 1,3,5-trimethylbenzene; ▽ 1,2,3-trimethylbenzene

pressure from 30—35 kp $cm^{-2}$, usual for platinum catalysts, to a value of 8—15 kp $cm^{-2}$, without major changes in the conventional technology. It is interesting to observe, however, that higher pressures are not uniformly disadvantageous for each alkylbenzene.

The amount of 1,3,5-trimethylbenzene increases at higher pressures, which can be attributed, in our opinion, to the symmetric structure of this compound. This is supported also by the pressure- independence of the formation of 1,2,4-trimethylbenzene between 15 an 22 kp $cm^{-2}$. This hydrocarbon, too, has a relatively stable structure. No similar phenomenon can be observed with 1,2,3-trimethylbenzene.

It should be noted that although the absolute amount of $C_9$ alkylbenzenes decreases with increasing pressure (with the exception of 1,3,5-trimethylbenzene), their distribution, however, approaches thermodynamic equilibrium.

Figure 4 depicts the effect of pressure on the formation of toluene, $C_8$ and $C_9$ aromatics. The amount of the $C_9$ group decreases considerably at higher pressures (as shown in detail in Fig. 3), that of toluene increases slightly, and that of the $C_8$ group more remarkably. A similar trend was reported by authors from Universal Oil Products for a reforming catalyst containing platinum [7].

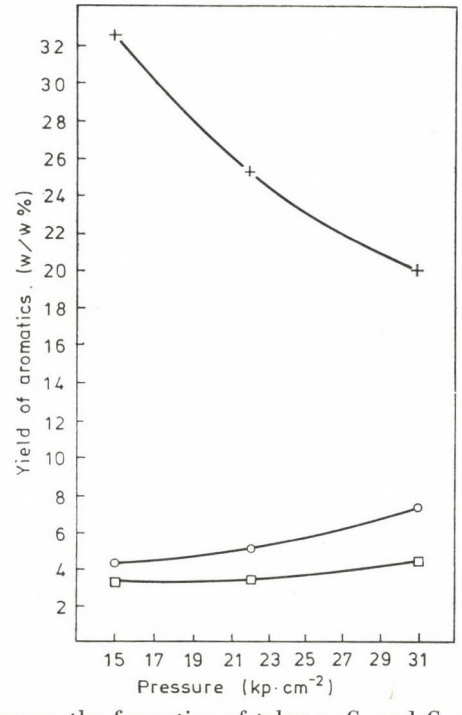



*Fig. 4.* Effect of pressure on the formation of toluene, $C_8$ and $C_9$ aromatics from *n*-nonane. Conditions: $t = 531$ °C; space velocity: 1.5 $h^{-1}$. Symbols: + $C_9$ aromatics; ○ $C_8$ aromatics; □ toluene

The main reason of the decrease of the $C_9$ yield is that, at higher pressures, larger fractions of *n*-nonane undergo hydrocracking instead of dehydrocyclization. This is shown also by the continuously decreasing liquid product yields. Thus, the influence of pressure manifests itself as a factor changing the ratio of dehydrocyclization and hydrocracking. Consequently, the effect of increasing pressure cannot be interpreted in term of suppressing the overall conversion of *n*-nonane since, under such severe conditions, almost complete conversion is observed at any pressure applied.

Dealkylation of $C_9$ aromatics into $C_8$ aromatics or toluene may also contribute to their decreasing concentration. At the same time, the amount of the $C_8$ and $C_7$ group increases.

Table III demonstrates also the disadvantageous effect of elevated pressure on selectivity. Table III contains *n*-nonane selectivity values calculated on the basis of the data compiled in Table I. The first row lists the amount of $C_9$ aromatics, in moles per 100 mole of reacted *n*-nonane. This ratio increases up to 531 °C; above this temperature no further improvement is observed. This type of selectivity is better at higher contact times; in other words, the increase of residence time enhances the formation of $C_9$ aromatics more strongly than the overall conversion of *n*-nonane.

The second row of Table III shows the ratio of the summarized amount of *o*-ethyltoluene plus *n*-propylbenzene (which are formed by direct dehydrocyclization of *n*-nonane) related to the degree of *n*-nonane conversion. This ratio increases with increasing temperature and residence time up to a certain value, above which it remains practically constant. The adverse effect of increasing pressure is clearly shown.

The third row of Table III contains the ratio of the above two hydrocarbons formed *via* direct dehydrocyclization. The amount of *o*-ethyltoluene is about twice as high as that of *n*-propylbenzene in the parameter range studied. The formation of *o*-ethyltoluene requires the rupture of secondary C–H bonds only, whereas the formation of *n*-propylbenzene involves also the cleavage of C–H bonds of one primary carbon atom, too. The bond energy of the latter species is higher; this can explain the larger amount of *o*-ethyltoluene. DAVIS *et al.* [8] reported a similar *o*-xylene to benzene ratio (ca. 1.7) for the aromatization of *n*-octane over Engelhard E—601 reforming catalyst treated by *sec*-butylamine. Since on this latter treatment, the catalyst retains only its $C_6$-dehydrocyclizing activity and, at the same time, the ratio of the dehydrocyclization products is very similar to our results, it can be assumed that, with *n*-nonane as starting material, the importance of $C_6$-dehydrocyclization is great even with acidic, supported platinum-rhenium catalyst (although this is not the exclusive pathway of the reaction).

The fourth row of Table III contains the ratio of hydrocracked *n*-nonane to its aromatized fraction. Here we regard weight/weight ratios as more correct,

**Table III**

*Selectivity of n-nonane conversion*

| *Conditions of reforming* | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Temperature (°C) | 490 | 511 | 531 | 548 | 531 | 531 | 531 | 531 | 531 | 531 |
| Pressure (kp cm$^{-2}$) | 15 | 15 | 15 | 15 | 15 | 15 | 15 | 15 | 22 | 31 |
| Liquid Hourly Space Velocity (h$^{-1}$) | 3 | 3 | 3 | 3 | 1,5 | 3 | 5 | 1,5 | 1,5 | 1,5 |
| $H_2$/HC mole ratio | 5:1 | 5:1 | 5:1 | 5:1 | 5:1 | 5:1 | 5:1 | 5:1 | 5:1 | 5:1 |
| *Selectivity* | | | | | | | | | | |
| 1. $\frac{C_9 \text{ aromatics}}{n\text{-nonane converted}}$ $\frac{\text{mole}}{100 \text{ moles}}$ | 16.9 | 19.7 | 34.9 | 34.3 | 35.7 | 34.9 | 26.0 | 35.7 | 27.8 | 22.0 |
| 2. $\frac{o\text{-ET}^* + n\text{-PrB}^{**}}{n\text{-nonane converted}}$ $\frac{\text{mole}}{100 \text{ moles}}$ | 7.5 | 10.8 | 13.3 | 13.9 | 13.0 | 13.3 | 11.8 | 13.0 | 8.3 | 5.4 |
| 3. $\frac{o\text{-ET}}{n\text{-PrB}}$ $\frac{\text{mole}}{\text{mole}}$ | 1.6 | 2.1 | 2.1 | 2.1 | 1.8 | 2.1 | 2.1 | 1.8 | 2.3 | 1.9 |
| 4. $\frac{C_1 - C_4 \text{ hydrocracked products}}{C_9 \text{ aromatics}}$ (w/w%) | 49.0 | 63.3 | 66.3 | 91.2 | 92.8 | 66.3 | 56.5 | 92.8 | 185 | 250 |

* *o*-ET = *o*-Ethyltoluene
** *n*-PrB = *n*-Propylbenzene

because the low molecular weight of hydrocracked products could produce misleading results if mole fractions were used in the calculation.

At a pressure of 15 kp $cm^{-2}$, the amount of *n*-nonane converted to $C_9$ aromatics is greater than the fraction hydrocracked. At 22 kp $cm^{-2}$, the amount of cracked products is already higher than that of aromatics (the ratio is 1.85); this value is equal to 2.50 at 31 kp $cm^{-2}$.

Table IV contains the results of *n*-decane reforming. The effect of temperature on the formation of $C_{10}$ aromatics is shown in Fig. 5; analogous values

**Table IV**

*Reforming of n-decane*

| *Conditions of reforming:* | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Temperature (°C) | 487 | 503 | 516 | 531 | 531 | 531 | 531 | 531 | 531 |
| Pressure (kp $cm^{-2}$) | 15 | 15 | 15 | 15 | 15 | 15 | 15 | 22 | 31 |
| Liquid Hourly Space Velocity ($h^{-1}$) | 1,5 | 1,5 | 1,5 | 1,5 | 3 | 5 | 1,5 | 1,5 | 1,5 |
| $H_2$/HC mole ratio | 5:1 | 5:1 | 5:1 | 5:1 | 5:1 | 5:1 | 5:1 | 5:1 | 5:1 |
| Unreacted *n*-decane expressed as w/w per cent of the feed | 33.8 | 10.9 | 4.1 | 1.0 | 8.0 | 18.1 | 1.0 | 1.7 | 3.6 |
| *Yield of components expressed as w/w% of the feed* | | | | | | | | | |
| Benzene | 0.2 | 0.3 | 0.6 | 1.0 | 0.8 | 0.4 | 1.0 | 1.2 | 0.8 |
| Toluene | 0.2 | 1.0 | 3.9 | 5.9 | 4.0 | 2.8 | 5.9 | 6.4 | 6.2 |
| Ethylbenzene | | 0.4 | 0.6 | 1.0 | 0.6 | 0.3 | 1.0 | 1.0 | 0.8 |
| *m*+*p*-Xylenes | 0.1 | 0.2 | 2.7 | 4.3 | 3.0 | 2.1 | 4.3 | 4.8 | 4.0 |
| *i*-Propylbenzene | 0.0 | 0.0 | 0.0 | 0.1 | 0.0 | 0.0 | 0.1 | 0.0 | 0.0 |
| *o*-Xylene | 0.2 | 0.6 | 1.2 | 1.9 | 1.2 | 0.9 | 1.9 | 1.8 | 1.5 |
| *n*-Propylbenzene | 0.2 | 0.1 | 0.2 | 0.2 | 0.1 | 0.1 | 0.2 | 0.1 | 0.2 |
| *m*+*p*-Ethyltoluenes | 0.3 | 0.8 | 1.5 | 2.1 | 1.5 | 1.2 | 2.1 | 1.9 | 1.7 |
| Mesithylene (1,3,5-trimethylbenzene) | 0.3 | 0.6 | 1.0 | 1.0 | 0.7 | 0.6 | 1.1 | 0.9 | 0.9 |
| *o*-Ethyltoluene | 0.4 | 0.7 | 1.1 | 1.1 | 0.9 | 0.6 | 1.1 | 0.4 | 0.4 |
| Pseudocumene (1,2,4-trimethylbenzene) | 0.2 | 0.9 | 1.6 | 2.3 | 2.1 | 1.7 | 2.3 | 2.4 | 2.1 |
| *n*-Butyl plus 1,3-diethylbenzene | 2.6 | 6.0 | 6.2 | 5.2 | 4.7 | 3.4 | 5.2 | 1.9 | 1.7 |
| 1-Methyl-2-*n*-propylbenzene | 0.5 | 1.3 | 2.6 | 2.1 | 1.7 | 1.3 | 2.1 | 1.4 | 0.9 |
| Hemimellitene (1,2,3-trimethylbenzene) | 1.7 | 2.8 | 1.7 | 0.9 | 1.7 | 1.2 | 0.9 | 0.6 | 0.4 |
| Indane | 0.6 | 1.4 | 1.7 | 1.3 | 1.5 | 1.2 | 1.3 | 0.8 | 0.5 |
| 1.2-Dimethyl-4-ethylbenzene | 1.2 | 3.6 | 4.2 | 2.9 | 3.4 | 2.7 | 2.9 | 1.8 | 1.1 |
| Durene (1,2,4,5-tetramethylbenzene) | 0.1 | 1.1 | 0.9 | 0.9 | 1.1 | 0.7 | 0.9 | 0.5 | 0.5 |
| *i*-Durene (1,2,3,5-tetramethylbenzene) | 0.2 | 1.7 | 1.1 | 1.2 | 1.4 | 1.0 | 1.2 | 0.8 | 0.6 |
| 5-Methylindane | 0.1 | 0.1 | 0.4 | 0.2 | 0.2 | 0.1 | 0.2 | 0.1 | 0.2 |
| Prehnitene (1,2,3,4-tetramethylbenzene) | 0.2 | 0.8 | 0.8 | 0.8 | 0.8 | 0.6 | 0.8 | 0.7 | 0.4 |
| Total $C_8$ aromatics | 0.3 | 2.2 | 4.5 | 7.2 | 4.8 | 3.3 | 7.2 | 7.6 | 6.3 |
| Total $C_9$ aromatics | 3.7 | 7.3 | 8.8 | 9.1 | 8.5 | 6.6 | 9.1 | 7.1 | 6.2 |
| Total $C_{10}$ aromatics | 5.2 | 15.3 | 16.5 | 13.6 | 13.9 | 10.2 | 13.6 | 7.3 | 5.6 |
| Total aromatics | 9.4 | 26.1 | 34.3 | 37.3 | 32.0 | 27.3 | 37.3 | 29.6 | 25.1 |
| Liquid yield | 91.6 | 84.5 | 68.0 | 56.5 | 72.3 | 79.1 | 56.5 | 51.0 | 45.9 |

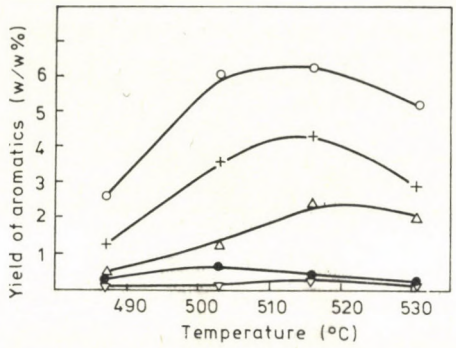



*Fig. 5.* Formation of some $C_{10}$ aromatics from *n*-decane, as a function of the temperature Conditions: P = 15 kp cm$^{-2}$; space velocity: 1.5 $h^{-1}$. Symbols: ○ *n*-butyl- plus 1,3-diethylbenzene; △ 1-methyl-2-*n*-propylbenzene; + 1,2-dimethyl-4-ethylbenzene; ● 1,2-dimethyl-3-ethylbenzene; ▽ 5-methylindane

for three tetramethylbenzenes are shown in Fig. 6. Unfortunately, we could not identify each $C_{10}$ aromatic compound but we intended to make accurate analyses of tetramethylbenzenes, which are the most important from the industrial point of view.

Figure 5 shows that the following products have the highest yields: *n*-butyl- and 1,3-diethylbenzene, 1,2-dimethyl-4-ethylbenzene and 1-methyl-2-*n*-propylbenzene. Of these four compounds, the first and the last could be formed *via* direct dehydrocyclization of *n*-decane; the formation of the other two requires isomerization. The third possible product of *n*-decane dehydrocyclization (1,2-diethylbenzene) could not be determined as such.

Table V compares the distribution of $C_{10}$ aromatics identified in reformates produced under the same conditions on the same catalyst from *n*-decane and data from naphtha. The differences in favour of products formed *via* direct dehydrocyclization are smaller with *n*-decane than with *n*-nonane, but the ratio of *n*-butyl-1,3-diethylbenzene is undoubtedly higher than the analogous value for naphtha reforming. The amount of tetramethylbenzenes

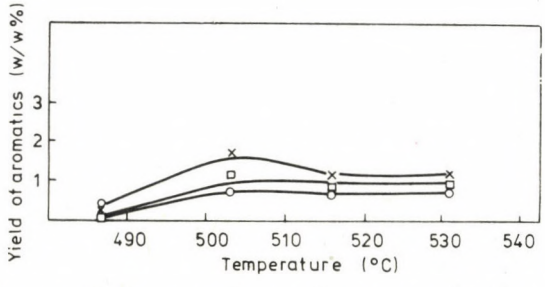



*Fig. 6.* Formation of tetramethylbenzenes from *n*-decane as a function of the temperature. Conditions: P = 15 kp cm$^{-2}$; space velocity: 1.5 $h^{-1}$. Symbols: × 1,2,3,5-tetramethylbenzene; □ 1,2,4,5-tetramethylbenzene; ○ 1,2,3,4-tetramethylbenzene

**Table V**

*Distribution of some $C_{10}$ alkylbenzenes in reformates obtained from naphtha and pure n-decane*

| Feed | *n*-Decane | Naphtha (boiling range 75—185 °C) |
|---|---|---|
| Conditions of reforming: | | |
| Temperature (°C) | 531 | 530 |
| Pressure (kp $cm^{-2}$) | 15 | 15 |
| Liquid Hourly Space Velocity ($h^{-1}$) | 3 | 3 |
| $H_2$/HC mole ratio | 5:1 | 5:1 |
| Distribution of $C_{10}$ alkylbenzenes (w/w%) | | |
| *n*-Butyl- + 1,3-Diethylbenzene | 34,0 | 18.2 |
| 1-Methyl-2-*n*-propylbenzene | 12.0 | 16.3 |
| 1,2-Dimethyl-4-ethylbenzene | 24.7 | 25.5 |
| 1,2-Dimethyl-3-ethylbenzene | 4.4 | 3.7 |
| Durene (1,2,4,5-tetramethylbenzene) | 8.0 | 9.1 |
| Isodurene (1,2,3,5-tetramethylbenzene) | 9.9 | 14.5 |
| Prehnitene (1,2,3,4-tetramethylbenzene) | 5.6 | 9.1 |
| 5-Methylindane | 1.4 | 3.6 |
| | 100.0 | 100.0 |

is, however, lower with *n*-decane as starting material than with naphtha. This can be explained if we consider what a considerable isomerization must occur to convert *n*-decane into tetramethylbenzenes.

Figure 5 shows that the yield of certain $C_{10}$ aromatics decreases above 516 °C. The main reason of this phenomenon may be the high extent of hydrocracking reflected also by the drastic decrease of the liquid yields (*cf.* Table IV). In addition, some $C_{10}$ aromatic compounds are dealkylated to give lower aromatics, for example, 1,2-dimethyl-4-ethylbenzene (whose yield drops the most strongly) may give *o*-xylene or *m*- or *p*-ethyltoluene. This conclusion is clearly supported by the data of Table IV. If the amounts of $C_8$, $C_9$ and $C_{10}$ aromatics formed at 516 and 531 °C are compared, it can be seen that the fraction of $C_8$ aromatics increases at the expense of $C_{10}$ aromatics (the sum of $C_8$ plus $C_9$ plus $C_{10}$ aromatics remains practically constant).

Above 500 °C the increase in temperature influences tetramethylbenzene formation only slightly and their amount shows no decrease above 516 °C, either. This indicates that tetramethylbenzenes are less liable to suffer dealkylation than, *e.g.* dimethylethylbenzenes.

Figure 7 illustrates the yields of individual $C_{10}$ aromatics formed by dehydrocyclization of *n*-decane, as a function of reciprocal space velocity. The increase in the yields of $C_{10}$ aromatics is much smaller here in the range of 0.33—0.2 h reciprocal space velocity than that of the $C_9$ aromatics with

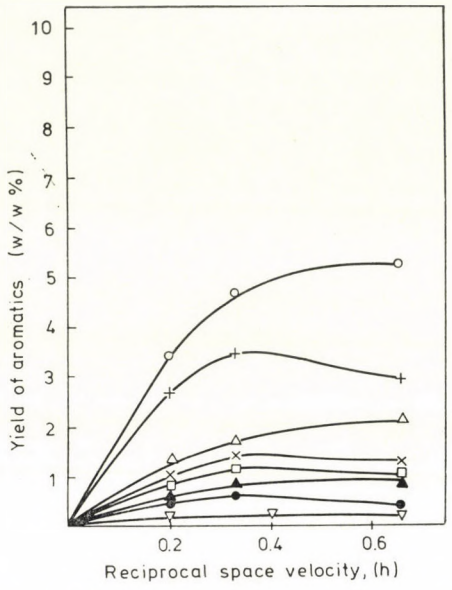



*Fig. 7.* Formation of some $C_{10}$-alkylbenzenes from *n*-decane as a function of the reciprocal space velocity. Conditions: P = 15 kp cm$^{-2}$; $t$ = 531 °C. Symbols: ○ *n*-butyl plus 1,3-diethylbenzene; △ 1-methyl-2-*n*-propylbenzene; + 1,2-dimethyl-4-ethylbenzene: ● 1,2-dimethyl-3-ethylbenzene; ▽ 5-methylindane; × 1,2,3,5-tetramethylbenzene; □ 1,2,4,5-tetramethylbenzene; ▲ 1,2,3,4-tetramethylbenzene

*n*-nonane dehydrocyclization. The minor yield decrease at small residence times (which is most pronounced in the case of dimethyl-ethylbenzenes) is attributed here, too, to dealkylation. At the highest residence time, the distribution of $C_8$—$C_{10}$ aromatics is shifted towards $C_8$ hydrocarbons.

Figure 8 depicts the effect of pressure on the dehydrocyclization of *n*-decane. It can be seen that the increase of pressure decreases first of all the amount of *n*-butyl and 1,3-diethylbenzene: *i.e.* longer side chains are eliminated or shortened much more readily under the effect of higher pressures than shorter ones. With increasing pressure, also the quantitative order of $C_8$—$C_{10}$ aromatics is reversed. It is in the group of $C_{10}$ aromatics where the adverse effect of pressure increase manifests itself most clearly. The increase of pressure from 15 to 22 kp cm$^{-2}$ approximately halves the yield of $C_{10}$ aromatics. Thus, the selectivity of *n*-decane dehydrocyclization becomes poorer at higher pressures, similarly to the case of *n*-nonane. In the latter case, however, the process is more selective than for *n*-decane. With *n*-decane as starting hydrocarbon, the formation of lower than $C_{10}$ aromatics is much more characteristic than with *n*-nonane. This is illustrated by Fig. 9 indicating that at a space velocity of 5 h$^{-1}$ (*i.e.* at 0.2 h on Fig. 9) which is much higher than the values typical for industrial reforming, considerable amounts of $C_8$ and $C_9$ aromatics are

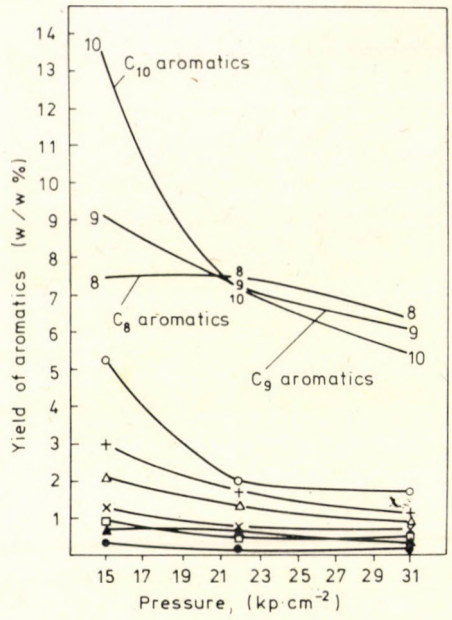



*Fig. 8.* Formation of individual $C_{10}$ aromatics and $C_8$—$C_{10}$ groups of aromatics from *n*-decane as a function of the pressure. Conditions: $t = 531$ °C; space velocity: 1.5 $h^{-1}$. Symbols: ○ *n*-butyl plus 1,3-diethylbenzene; △ 1- methyl-2-*n*-propylbenzene; + 1,2-dimethyl-4-ethylbenzene; ● 1,2-dimethyl-3-ethylbenzene; × 1,2,3,5-tetramethylbenzene; □ 1,2,4,5-tetramethylbenzene; ▲ 1,2,3,4-tetramethylbenzene. The yield of aromatic groups is denoted by small numbers in the figure

produced from *n*-decane. A similar phenomenon has been observed in the case of reforming on a monometallic platinum reforming catalyst, too [4].

Table VI also demonstrates that the selectivity of *n*-decane transformation is much lower than that of *n*-nonane. This table was compiled on the basis of the data of Table IV, omitting the selectivity values corresponding to the second and third rows of Table III, because not every product formed *via* direct dehydrocyclization could be separated gas-chromatographically. Comparing the first rows of Tables III and VI it is obvious that *n*-decane dehydrocyclization has a lower selectivity, *i.e.* fewer moles of $C_{10}$ aromatics are produced from 100 moles of *n*-decane transformed than $C_9$ aromatics from 100 moles of *n*-nonane converted. Temperatures above 516 °C are clearly unfavourable for selectivity. Data collected in the fourth rows of the two respective Tables also confirm that *n*-decane is more liable to undergo hydrocracking reactions than *n*-nonane.

Our experiments carried out with a platinum-rhenium catalyst have shown that the pressure decrease due to the application of such types of cata-

**Table VI**

*Selectivity of n-decane conversion*

| *Conditions of reforming* | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Temperature (°C) | 487 | 503 | 516 | 531 | 531 | 531 | 531 | 531 | 531 |
| Pressure (kp cm$^{-2}$) | 15 | 15 | 15 | 15 | 15 | 15 | 15 | 22 | 31 |
| Liquid Hourly Space Velocity, (a$^{-1}$) | 1,5 | 1,5 | 1,5 | 1,5 | 3 | 5 | 1,5 | 1,5 | 1,5 |
| $H_2$/CH mole ratio | 5:1 | 5:1 | 5:1 | 5:1 | 5:1 | 5:1 | 5:1 | 5:1 | 5:1 |
| *Selectivities:* | | | | | | | | | |
| 1. $\frac{C_{10}\text{ aromatics}}{n\text{-decane converted}}$ $\frac{\text{mole}}{100\text{ moles}}$ | 8.4 | 18.2 | 18.2 | 14.6 | 16.0 | 13.2 | 14.6 | 7.8 | 6.2 |
| 4. $\frac{C_1-C_4\text{ hydrocracked products}}{C_{10}\text{ aromatics}}$ (w/w%) | 160 | 101 | 194 | 325 | 127 | 204 | 325 | 672 | 967 |

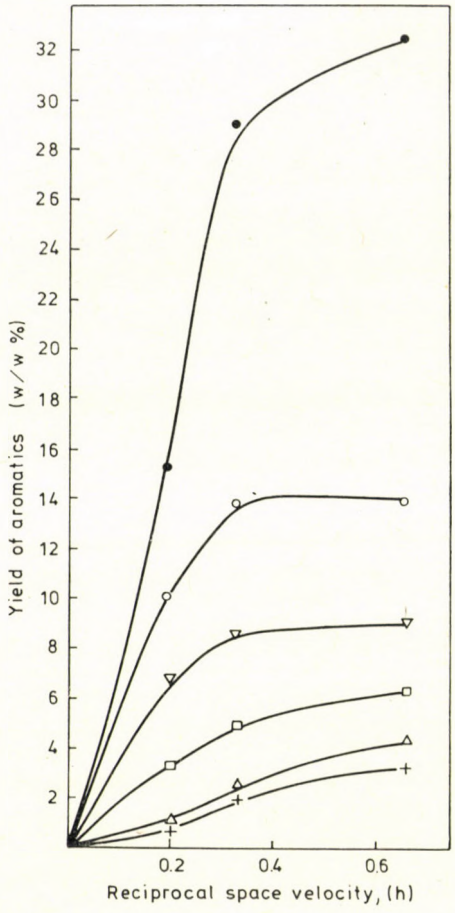



*Fig. 9.* Aromatic yields from *n*-nonane and *n*-decane as a function of the reciprocal space velocity. Conditions: $t = 531$ °C; $P = 15$ kp cm$^{-2}$. Symbols: ● $C_9$ aromatics from *n*-nonane; ○ $C_{10}$ aromatics from *n*-decane; ▽ $C_9$ aromatics from *n*-decane; □ $C_8$ aromatics from *n*-decane; △ $C_8$ aromatics from *n*-nonane; + toluene from *n*-nonane

lysts is important also with respect to the $C_9$ and $C_{10}$ aromatic products of *n*-paraffin dehydrocyclization. At a pressure of 15 kp cm$^{-2}$, at a space velocity of 1.5 h$^{-1}$ and at 531 °C, *n*-nonane gave 32.3 w/w% $C_9$ aromatics, whereas *n*-decane yielded 13.7 w/w% $C_{10}$ plus 9.0 w/w% $C_9$ aromatics. These are very remarkable amounts which exceed considerably those observed with a Pt catalyst. The decrease of pressure not only increases the yield of total aromatics but also improves the selectivity of dehydrocyclization.

*

The authors wish to express their gratitude to Dr. L. ACKERMANN for his valuable cooperation in hydrocarbon analysis.

## REFERENCES

[1] BLUE, E. M.: Hydrocarbon Processing, **48,** No. 9. 141 (1969)
[2] KUCHAR, P. J., ADDISON, G. E.: Platforming: A Tool for Tomorrow's Fuels. Paper presented at the UOP Technology Conference, Budapest, October 1973
[3] DUHAUT, P., ESCHARD, F.: Proc. 9th World Petroleum Congress (Tokyo, 1975), Panel Discussion 20, Paper No. 1. Appl. Sci. Publ. Barking 1975
[4] SZEBÉNYI, I., ACKERMANN, L., SZÉCHY, G., GÖBÖLÖS, S.: Acta Chim. (Budapest), **90,** 313 (1976)
[5] SITTIG, M.: Aromatic Hydrocarbons. Noyes Data Corp., Park Ridge, N. J. 1976
[6] OCKERBLOOM, N. E.: Hydrocarbon Proc, **51,** 114 (1972)
[7] STERBA, M. S., HAENSEL, V.: Ind. Eng. Chem. Prod. Res. Develop., **15,** No. 1, 3 (1976)
[8] DAVIS, B. H., WESTFALL, G. A., WATKINS, S., PEZZANITE, J.: J. Catal., **42,** 247 (1976)
[9] KOZLOV, N. S., SKRIGEN, E. A., SAMCHEVICH, V. S., KUPCHA, L. A.: Neftekhimiya, **16,** 689 (1976)
[10] BERNDT, H., MEHNER, H., VÖLTER, J., MEISEL, W.: Z. Anorg. Allg. Chem. **429,** 47 (1977)
[11] HEVESI, J.: Erdöl und Kohle, **24,** 687 (1971)
[12] ILYIN, V. F., USOV, Yu. N.: Neftekhimiya, **13,** 387 (1973)
[13] DONALDSON, G. R., PASIK, L. F., HAENSEL, V.: Ind. Eng. Chem., **47,** 731 (1955)

Imre SZEBÉNYI
Gábor SZÉCHY } H-1521 Budapest.

# RECENSIONES

## *Recent advances in chemistry, Vol.* 34

Akadémiai Kiadó, Budapest 1976

The volume contains three reviews from the field of nuclear chemistry, two of which deal with the application of activation analysis in special fields, while the third discusses possible applications of the Auger effect.

Mária CSAJKA and Lavruhina Avgusta KONSTANTYINOVA discuss in their paper "Application of activation analysis in cosmochemistry. Analysis of meteorites and moon samples" the possibilities afforded by activation analysis, and more particularly though not exclusively, by activation semiconductor gamma-spectroscopy induced by reactor neutrons, in the determination of the composition of cosmochemical substances.

Their study is not restricted to analytical consideration, but as far as permitted by the extent, a description is given of the structure and composition of cosmochemical substances, mainly of the complex and varied meteorites of different types, important for the formulation of the analytical task. The chapter on meteorites discusses the always problematic preparation of the samples, and summarizes then results attainable by purely instrumental non-destructive methods. Since instrumental activation analysis yields information only on 4—9 elements per sample in the case of meteorites because of the matrix and other interferring effects, in most of the cases radiochemical separation is used after irradiation. The practical problems of the realization of this separation are discussed in detail in the monograph. For the analysis of moon samples collected within the frame of the Apollo and Soviet space programs, researchers put into action the complete "armoury" of modern instrumental trace analysis. Among these, non-destructive and destructive neutron activation analysis and composite neutron activation analysis processes combining the two methods occupy a distinguished place. The study of Mária CSAJKA and co-author deserves special interest also with respect to the comparison of the methods. The valuable work rich in information is supplemented by 25 tables, 24 figures and 227 references.

Mária ÖRDÖGH in her review on "Activation analysis of biological substances" discusses the problems of biological trace analysis and the solution of some concrete problems by neutron activation analysis. Several trace elements play an important role in the functioning of living organisms, however, only the function of a few elements can be considered as more or less known. In the elucidation of the modes of action microanalytical methods play an important role. Neutron activation analysis has several advantages in the investigation of biological substances, due both to its sensitivity and the possibility to determine simultaneously several elements from the same sample. After the discussion of the general problems of activation analysis, the author gives the biological definition of trace elements and summarizes their biochemical role. Problems of sampling and sample preparation are discussed in detail, then various possibilities of the removal of isotopes representing high interferring activity, mainly those of sodium and phosphorus, are given. Of great interest are the experiences gained by the author in the investigation of international standards (BOWEN's kale, IAEA standards), presented here to the reader. Three spheres of problem: investigation of the total blood and blood serum, analysis of human lymph nodes, and analysis of the relationship between the diseases of cardiac vessels and the trace elements, covered in more details, serve quasi as an illustration of general principles. The monograph, of value both from the methodological and the biological aspect, is supported by 9 tables, 13 figures and 76 references.

The brief study by Gizella Ágnes NAGY: "Chemical consequences and application of the Auger effect" summarizes measuring methods suitable for the determination of the charge and energy distributions of products formed in the process, and points out the already realized applications of the phenomenon as well as further possibilities. The effect named after him,

has been discovered and interpreted about fifty years ago, in 1926, by AUGER. The author describes the phenomenon, discusses the effect of the AUGER-cascade on atoms and molecules, and presents the course of the process in the condensed phase, giving thereby the theoretical bases, which, so far, have been rather unknown even to nuclear chemists. Of the examples of application, the so-called "direct" indication methods based on the use of Auger-atoms of high ionization and excitation energy, and the analytical procedure, AUGER electron spectroscopy, applied already rather widely in metallurgy, solid state physics and mineralogy, are of particular interest. The monograph containing 71 references, is complemented by 15 figures and 3 tables.

G. KEÖMLEY

## D. A. SKOOG and D. M. WEST: *Fundamentals of Analytical Chemistry*. 3rd Ed.

Holt, Rinehart and Winston. New York 1976. 804 pages

The book is a modern university textbook of chemical analysis, comprising a wast number of elaborated examples and many instructive laboratory experiments.

The organization of the subject is the usual: A general introduction is given, which followed by a chapter on electroyte equilibria, then by the evaluation of results and error calculation. Gravimetric analysis, then volumetric methods: precipitation, acid–base, complexometric and redox titrations are discussed. This classical part amounts to about 50% of the book. Next follow electrochemical methods: potentiometry, electrogravimetry, coulombmetry, then optical methods: molecular and atomic spectroscopy.

Methods in conjunction with the preparation and dissolution of the sample, and with the separation of the single components are dealt with at the end of the book.

The book, written with an excellent sense for pedagogy, discusses its subject in great detail, and affords at the same time good reading. Every new concept is discussed very thoroughly, and is supported by excellent, clear figures. The part dealing with error calculation and error propagation is very good.

Chapters discussing electrolyte equilibria are similarly very good. The care with which the authors compare the results of approximate calculations, customary in practice, with the results of exact methods of calculation is worth mentioning.

The discussion of the application of the single methods covers besides the determination of inorganic ions also the detailed determination of various organic compounds.

The chapter on potentiometry deals extensively with all the modern types of electrodes. Characteristic of the thoroughness exercised is the fact that errors committed in pH measurement with glass electrode are classed into six groups by the authors. The discussion of voltammetric methods includes the most up-to-date methods (differential-pulsed voltammetry, etc.).

The discussion of the optical part excels by the great clearness and simplicity of the figures.

Though actually the book does not contain anything that is particularly new, it deserves praise, because it is a textbook composed with great care and written with an excellent sense for pedagogy.

Many books dealing with analytical chemistry are to be found to-day on the Hungarian and international book market, but actually this book cannot be compared with them. The exceptional merit of this book is not only to give an answer in modern form to all questions relevant to fundamental analytical chemistry, but also to provide the reader with a great number of tables of conclusive force, with clear figures and with experiments inducing to thinking. Therefore, it will be a useful textbook to both university students and professors teaching them.

J. INCZÉDY

## Eugene G. ROCHOV: *Modern Descriptive Chemistry*

Saunders Golden Sunburst Series. 1977
W. S. Saunders Company, Philadelphia, London, Toronto. 253 pages

Students being educated in chemistry have the frequent and quite reasonable complaint that the lectures of their teachers and the textbooks available to them deal almost exclusively with the theory of chemistry. They get entangled in the discussions of physical chemistry

based on mathematical fundamentals and struggle with solutions of a vast number of calculation tasks but at the same time they are not acquainted at all with the substrates of all these theories and calculations *i.e.* with those really existing materials whose properties and behaviour the theory tries to explain them. Thus *e.g.* it may occur that the student gets acquainted with the theory of "acids" and with their properties but meanwhile he does not known any really existing, practically applied acid. At the same time the descriptive textbooks of inorganic chemistry with their dull jumble of data are really apt to decisively discourage the interest in chemistry of the student desiring to get acquainted with chemistry.

The book of E. G. ROCHOV aims just at filling up this lack by presenting a descriptive inorganic chemistry in which the student desiring to understand chemistry finds just the link connecting the theory of chemistry with the everyday facts of the industrial society. The author is quite right and correct in emphasizing in the foreword of his book that though his work has been prepared on the basis of personal experience gained during several decades with the practical cooperation of many thousands of Harvard students and on taking into account the practical advices of the chemists of the department of chemistry of the General Electric Co., it cannot replace the deep study of a thorough textbook of theoretical chemistry. The book is recommended by the author (and also be the reviewer) for complementing studies. The material of the book has been assembled by the author in a way that the consecutive chapters serve as useful descriptive (practical) completions to the theoretical chapters of the textbook: "Chemical Principles" by MASTERTON and SLOWINSKI.

The author shares the opinion of George KISTIAKOWSKY according to which the interesting and attractive nature of the material is, for a student just beginning to get acquainted with chemistry, of greater importance than the thoroughness and the high theoretical level because these latter are understood only by a student who already became enslaved by the interesting nature of the material. Just therefore the author attempted (and not at all unsuccessfully) to present his announcements in a simple, attractive way, illustrated by a number of very instructive, sometimes even humoristic figures. It is to be appreciated that a glossary is inserted at the end of each chapter. In this glossary the student can find the accurate explanation of the terms and foreign words occurring in the text of the chapter. Furthermore, also 'testing questions', "questions inducing the thinking" and so-called 'problems to be solved' are given which urge the students to think and meditate on the problems which they have read.

The material is discussed in *Modern Descriptive Chemistry* in the following chapters:

1. Introduction: The chemical elements and their relationships.
2. Hydrogen, helium, and what makes the sunshine.
3. Lithium through fluorine: the light elements.
4. Sodium to chlorine: more well-known elements.
5. All about the main groups.
6. The first series of transition metals.
7. The heavier transition elements.
8. The lanthanide rare earths.
9. The actinide rare earths.
10. The noble gases.

Appendix: The Naming of Inorganic Compounds.

The book is completed by an author and subject index, and by a table of atomic weights. On the inner flap of the first cover we find the Periodic System and on the flap of the back cover again a table of atomic weights. However, the reviewer cannot understand why at the repeated presentation of the table of atomic weights this second table contains only the first part (from A to N) of the alphabetic list of elements.

On the whole, the book is in fact a useful and to say, perhaps even an entertaining reading which can be particularly recommended for those who are just beginning their studies into chemistry.

D. SZABÓ

## Gy. BRUCKNER: *Szerves Kémia (Organic Chemistry)*

Vol. II—1. Isocyclic Compounds I. Aromatic Compounds
Tankönyvkiadó, Budapest 1977. 1005 pages (In Hungarian)

Twenty years have passed since the first edition of this organic chemical textbook, widely popular in Hungary. The modern concept of the book and the large material of knowledge contained, rich in valuable data readily applicable also in practice, were instrumental

in rapidly gaining popularity not only with ambitious university students, but also among chemists engaged in research and production. Important developments in organic chemistry during the last two decades made necessary the publishing of a new, revised edition.

In this new edition, the author has divided Volume II, originally a single volume, into two volumes, and the present volume II—1 deals only with the chemistry of aromatic compounds.

The present book (II—1) and the part discussing aromatic compounds in Vol. II of the first edition differ mainly in the following: *(a)* in the discussion of the structure of aromatic compounds and their reaction mechanisms more space is allotted to theoretical organic chemistry, and as a consequence of this, to stereochemical aspects; *(b)* in the descriptions of syntheses and other reactions, experimental conditions are given in greater detail, which brought the book in a closer contact with practice; *(c)* as a supplement to references, the names (and dates of publication) of more researchers have been included than in the earlier edition, making possible the rapid location of many original communications; *(d)* Volume II—1 is complemented by several parts not discussed in the original Volume II; *(e)* instead of several old syntheses, unimportant from the aspect of science history, more modern methods of preparation (giving higher yields, or being simpler) are discussed.

The revised edition has all the advantages of the first, and can be recommended as a useful and very readable book to everybody interested in organic chemistry. The only thing the reviewer cannot agree with is the way of writing used in the book: the names of compounds written according to the rules of Latin spelling but declined as Hungarian words results in a somewhat 'archaic' style, the use of which seems to be old-fashioned and unnecessary.

Gy. DEÁK

## *SIMUL — ein Programm für die mathematische Simulation von verfahrenstechnischen Systemen*

Von einem Autorenkollektiv. Herausgegeben von Prof. Dr. BENEDEK
Akadémiai Kiadó, Budapest 1977

Dieses Buch von einem Umfang von 327 Seiten hat eine lange Vorgeschichte. Die Notwendigkeit der Ausarbeitung eines Rechnerprogramm-Systems, das vor allem in der chemischen Industrie gut zu verwenden ist, entstand zuerst in den ungarischen Forschungsinstituten. Seine ungarische Ausgabe wurde im Rahmen der Serie „Neue Ergebnisse der Chemie" (Band 15) von Akadémiai Kiadó unternommen. Das von Pál Benedek geleitete und gelenkte System wurde mehrmals ausprobiert und hat sich gut bewährt.

Infolgedessen wurde die etwas erweiterte und ergänzte deutsche Variante dieser Arbeit ebenfalls von Akadémiai Kiadó in Zusammenarbeit mit dem deutschen Akademie Verlag (Berlin) in 1977 herausgegeben. Die deutsche Ausgabe enthält 110 Abbildungen und 20 Tabellen.

Die Autoren hielten es für nötig, in Kapitel 0 die Grundbegriffe zu klären. Dies ist auch nach meiner Beurteilung sehr wesentlich und besonders wichtig für Außensteher, denn in einem Gebiet, welches sich so rasch wie eben das Rechnerprogramm-System entwickelt, verstehen die einzelnen Verfasser und Verwender unter das selbe Wort leider nicht den selben Begriff. Gleich im Kapitel 0 bezeugen die Autoren eine große Aufrichtigkeit, als sie über die „Erfolge und Misserfolge" der Realisierung berichten. Dieser Satz erleichtert die Arbeit des Rezensors, der weiß, daß die Schaffung eines solchen Systems mit viel kollektiver Arbeit und Diskussion verbunden ist.

Im ersten Kapitel schildern die Autoren den technischen Hintergrund der Simulation. In Kapitel 2 wird die einheitliche Berechnung der Stoffkennzahlen (der physikalischen und chemischen Eigenschaften) im SIMUL-System angegeben.

Es soll besonders hervorgehoben werden, daß in Kapitel 3 der deutschen Ausgabe nicht nur die Abbildungen der einzelnen Geräte (Boxe) angegeben werden, sondern neben diesen Abbildungen auch die Abbildungen der dazugehörenden Rechenprogramme. Dies erleichtert stark die Behandlung und das Verständnis der einzelnen Fälle.

Kapitel 4 zeigt die Verbindung der Verfahrenseinheiten und das derart zustandegekommene Netz. Im wesentlichen ist die die Struktur des Systems. In Abschnitt 4.4.2 wird

die Verbindung zwischen der mathematischen Beschreibung und der Systemorganisation diskutiert.

Kapitel 5 zeigt die Berechnung selbst, am Beispiel der Butanisomerisierung. Daran knüpft sich die Beschreibung des Verfahrensprogramms und seiner Teile.

Kapitel 6 befaßt sich mit den Rückkopplungen. Es ist nicht sehr glücklich, die Lösung der Gleichungssysteme: die schrittweise Annäherung und die Beschreibung der Newton—Raphsonschen Methode hier anzugeben.

Kapitel 7 ist der Optimierung gewidmet. Die Optimierung der sogenannten großen Systeme wird separat behandelt, wobei die Bellmannsche dynamische Optimierung ausführlich beschrieben wird.

Kapitel 8 beschfätigt sich mit dem Organisationsprogramm, d.h. wie man die bisher beschriebenen Berechnungen zu einem einheitlichen Ganzen zusammenfaßt und ausführt.

Kapitel 9 ist vollkommen neu und ist nur in der deutschen Ausgabe enthalten. Die Pyrolyse von Azeton zu Essigsäurenanhydrid ist das praktische Beispiel, welches die vorangehenden acht Kapitel sehr gut ergänzt und die Anwendung des SIMUL-Systems dem Leser vorführt.

Im Ganzen ist das Buch ein gut überdachtes und systematisch aufgebautes Werk. Das Buch wird auch für jene von Nutzen sein, die noch Anfänger in der Rechnertechnik sind, während jene, die die Grundlagen bereits kennen, können ihr bisheriges Wissen weiter entwickeln.

A. László

## *Lecture Notes in Chemistry, Vol.* 3. Svetozar R. Niketic, Kjeld Rasmussen, The Consistent Force Field: A Documentation

Springer-Verlag, Berlin—Heidelberg—New York, 1977, 212 p.

Determination of molecular geometry and specifically conformation is one of the main objectives of structural chemistry. The Consistent Force Field (CFF) is a special approach to this goal; in the authors' words: "a concept with which we try to bridge the gap between several theoretical and experimental techniques". Its basic idea can be formulated very simply: choose an appropriate analytical form of the potential energy function for a family of related molecules and optimize the parameters of this function by fitting them to the experimental data (geometry, vibrational frequencies) for a sufficient number of molecules. Then, using the obtained CFF, properties of other related molecules can be predicted.

Chapter 1 outlines this basic idea, chapters 2 to 7 deal mainly with the presentation of the program system, finally, chapter 8 discusses the question of how to develop a consistent force field and gives some results on alkanes, amides, amino acids, coordination compounds and saccharides.

The stated purpose of the book (p. 1) is to "serve as an exposition of the basis of the CFF as well as a presentation of the system developed at The Technical University of Denmark." In the reviewer's opinion the authors did not succeed in striking the right balance between these two goals. Far too many details are given about programming, its more or less trivial, general aspects, calculation of derivatives of simple functions, etc. Anybody wishing to write a similar computer program, is certainly familiar with this elementary mathematics. On the other hand, for the average chemist who just wants to use the method, the existing input manual, would be completely sufficient and more practical.

All this has the consequence that a reader not familiar with CFF will find it difficult to grasp the simple basic concept behind the details. Central questions, like the basic assumption of transferability of the force field (its limitations!), the relative efficiency of different models for the potential energy, selection of the experimental data (which may come from different techniques with different accuracy), are not discussed either in the general description of the method or when presenting some results. In the latter (chapter 8), optimized parameters are compiled in tables without any critical evaluation.

Nevertheless, the book — in accordance with the main purpose of the authors, to give a *documentation* — is certainly useful for those who plan to implement this valuable and successful method.

G. Fogarasi

## *A kémia újabb eredményei (Recent Results in Chemistry)* Vol. 36.

Akadémiai Kiadó, Budapest 1977

1. Kálmán BURGER: „Nemvizes oldatok koordinációs kémiája"
(Coordination Chemistry of Non-aqueous Solutions)

A notable deficiency of Hungarian chemical literature has been remedied by the author of this clear-cut and up-to-date summary of the coordination chemistry of non-aqueous solutions. A timely, useful, and very helpful work has been published for chemists in general and for the quite numerous coordination chemists in Hungary in particular.

The matter dealt with is presented in a logical, consistent, and well arranged structure. A simple enumeration of the chapter headings already demonstrates this. The chapters are:

General characterization of the solvents.
Interaction of solvent and solute.
Donor-, and acceptor-strength of solvents.
Studies of the donor–acceptor interactions according to Lewis.
Effect of the solvent upon the structure and stability of the complexes in solution.
Complex-forming reactions in some of the more important coordinating solvents.
Experimental methods suitable for the study of non-aqueous solutions of complexes.
Effect of the solvent upon the kinetics and mechanism of the reactions of complexes.
Coordinative chemical interactions in solvent mixtures. Trends of future research.

Among these, the topics of Chapters 3, 5 and 9 might be dwelled upon because there a picture — which holds the attention chiefly of coordination chemists — of donor–acceptor strengths, of the structure of complexes and of their stabilities is presented in such a manner that therein the unequivocally proven statements on the one hand, and the questions still awaiting elucidation on the other, are clearly delineated. The considerable mass of ascertained data, the well ordered discussion of phenomena, the many-sided approach to, and interpolation of, effects and the discernment of regularities are most objectively presented in their totality, but so that the readers remain aware of the fundamental problems still awaiting theoretical and experimental solution.

As mentioned, the subject matter may be approached from different aspects and thus many overlaps may occur. We think it would have been rather to the purpose briefly to touch upon these frontier-questions in order to help the readers the easier to get their bearing. A few instances to this point. The author states that among the non-aqueous solvents he does not discuss the melts of salts and metals, only the molecular liquids. This is understandable and justified, but the point of view that directed the choice within the latter field does not become clear since quite a number of further molecular liquids which are not negligible in coordination chemistry, *viz.* non-aqueous acids, $NH_3$, $SO_2$, $N_2O_4$ (*cf.* Chemie in nichtwäßrigen Lösungsmitteln, ed.: G. JANDER, H. SPANDAU, C. C. ADDISON. — Vieweg, Pergamon. — Braunschweig, Oxford) might be mentioned. Though not necessarily with full particulars, but mention might have been made of the charge-transfer complexes as substances which are frequently discussed also within the scope of coordination chemistry (*cf.* Endre KŐRÖS: Molekulakomplexek. Akadémiai Kiadó, Budapest 1975). Mention might have been made also of the effect of the solvent upon redox potentials of metals bound in various complexes, thus also of redox-reactions.

It is not explicitly stated, but can unequivocally be discovered that the subject matter is dealt with on the basic science level only. No reference at all points to practical applications and it is doubtful whether this is quite right since important results are known in this respect. Among such we may cite the applications in analytical chemistry, *e.g.* titrations (*cf.* I. GYENES: Titrationen in nichtwäßrigen Medien. Akadémiai Kiadó, Budapest 1970; and I. KRAUSZ: Nemvizes közegben végzett titrálások jelenlegi problémái (Present problems of titration in non-aqueous media). A kémia újabb eredményei, Vol. 29), or photometry, or extraction (*cf.* D. F. PEPPARD: Liquid-liquid Extraction of Metal Ions, in Adv. Inorg. Chem. Radiochem., ed.: H. J. EMELIUS, A. G. SHARPE; Vol. 9, pp. 1 . . . 80, Academic Press, New York, London 1966). We might mention further the topic broached by L. MARKÓ, and G. SPEIER in their work „Nitrogénfixálás szintetikus rendszerekben enyhe reakciókörülmények között" (Fixation of nitrogen in synthetic systems under mild reaction conditions) also published in this series. Examples of industrial application are also known (*cf.* M. I. BRUCE: Cyklometallierungsreaktionen. Angew. Chem. 89, 75 (1977), and earlier literature there referred to).

The relative compass of the several parts of the subject matter is disputable in some respects. Thus, for instance, the implicit mention in one sentence, of ultraviolet visible spectro-

scopy seems to be rather slight compared with the 19 pages written about Mössbauer spectroscopy. Similarly, the 10 pages and their contents on reaction kinetics and mechanisms seem rather modest when the 100 pages on equilibria, structures and stabilities are considered.

The literature reviewed (502 items of reference) quite exceeds the average which is usual in this series, even so there are titles to be mentioned as ones not to be neglected, *viz.* D. MARTIN, and H. G. HAUTHAL: Dimethylsulfoxid. Akademie Verl., Berlin 1971; G. CHARLOT, B. TRÉMILLON: Chemical Reactions in Solvents and Melts. Pergamon Press, Oxford, 1969; and the works mentioned earlier.

Better orientation would have been furthered by having the 30 . . . 40 dispersed monograph titles brought together in chronological order or classified by subject matter, at the beginning of the list of references.

An outstanding merit of this work resides therein that it is not a repetitive exposition of books or monographs but contains the elaboration, mostly critical and as full as can be expected, of numerous recent, original communications. In this the comprehensive knowledge of the author and his own scientific activity in this field (more than 20 items of his own contributions listed) play equal roles.

As habitual with this author, the wording of his text is clear and explicit, understandable for beginners too, and delightful reading also for the more experienced research workers. The good presentation, clear-cut eight figures and well arranged thirty-two tables, the insignificance, in relation to 200 pages, of the number of errors, all redound to the credit of the smooth co-operation of the author, the publisher's and the printer's staff.

A considerable part of the community of chemists in Hungary has now access to a good text that helps to get a sufficient grasp of this subject and to broaden the view, it also serves as a suitable starting point for a study of this field.

2. Lajos SZTRAKA: „A Fourier-transzformációs spektrometria elvi alapjai" (Fundamental principles of Fourier-transformation spectroscopy).

The publishing in Hungarian of a widely accessible work on FTS must be said to have been a very timely and necessary undertaking. Apart from international tendencies this publication is justified also by the heartening fact that, though in a slowly increasing number, such instruments are in use for some years in Hungarian laboratories. The second part, *i.e.* another 55 pages, of this volume acquaint the reader with the fundamental principles of FTS. We may say that this subject is dealt with exhaustively: this text is precisely what its title promises, nothing more, nothing less.

The theme is very skilfully, clearly, expertly set forth, and with a happy didactic turn. "A representation of the fundamental principles of FTS we begin with the study of the characteristics of an interferogram obtained with the help of an ideal Michelson interferometer. Then we shall gradually disregard the suppositions which define the ideal state and shall find out how, in consequence of this, the results will change". Then all the eight factors are carefully exposed.

The only, but rather important question is raised when we ponder the purpose of the author or of the editor in so far as any exposition of fundamental principles alone does not satisfy anybody. The chemist, or the physicist, who wants to apply FTS the first time is not told how to set about doing this nor is he told whether the application of FTS is at all appropriate in that given instance. The expert user has long mastered this problem but is given no review on the chemistry involved in this field, nor of the instruments of it. Not one single real system is mentioned. There are no directives given how to prepare samples, what kind and how much of a sample is needed. Among these 55 pages none touches chemistry in the proper sense of the word, not one of the ten calculated figures is a real spectrum actually recorded. The few pieces of information in the introductory, and in the concluding chapters do not make good this deficiency.

All in all, this text could be an excellent part of a book that would deal with every aspect of FTS; but its present one-sidedness hardly fits it into a series of books on "recent advances in *chemistry*".

Gy. BAZSA

# INDEX


ANALYTICAL CHEMISTRY

Separation and Identification of Natural Porphyrins in Hungarian Crude Oils, J. Lakatos-Szabó ..... 1

PHYSICAL AND INORGANIC CHEMISTRY

Elimination of Spectrochemical Matrix Effects, Following of the Line Analogy and Determination of the Detection Limits of Trace Elements in Silicate Rocks (in German) O. Filo, M. Matherny ..... 13

An Improved Apparatus for the Microcatalytic or Pulse Technique (in German) J. Latzel 29

Quantum Chemical Study on the Conformational Properties of Chalcone and Its Simple Model Compound, Z. Dinya, Á. I. Kiss, G. Pongor ..... 37

Electrochemical Behaviour of Ethylene Glycol and Its Oxidation Derivatives on a Platinum Electrode, II. Study of the Oxidation of Glyoxal and Glyoxylic Acid, G. Horányi, G. Inzelt, Z. Szetey ..... 49

Effect of Aliphatic Alcohols on the Hydrogen Overvoltage on Dropping Gallium Electrodes, K. Szabó, L. Sziráki, J. Mika ..... 67

Metal Chelates with Ethylmalondihydrazide, H. N. Pandey, Lallan Mishra, V. J. Ram 77

Boron Complexes of Bifunctional Tridentate Schiff Bases, H. B. Singh, J. P. Tandon 81

Cohesion Energy of a Liquid Due to Permanent Dipoles, J. Liszi ..... 93

ORGANIC CHEMISTRY

Cycloaddition Reactions of Cephalosporin Compounds, III. 1,3-Dipolar Cycloadditions of Cephalosporins and Diazoalkanes, J. Cs. Jászberényi, E. R. Farkas, E. T. Gunda, J. Tamás, M. Mák, S. Hosztafi, L. Szilágyi, R. Bognár ..... 103

TECHNOLOGICAL CHEMISTRY

Aromatization of *n*-Nonane and *n*-Decane Over a Platinum-Rhenium Catalyst, I. Szebényi, G. Széchy ..... 115

RECENSIONES ..... 133

1828 — 1978
PUBLISHED
IN THE YEAR
OF THE 150th
JUBILEE

*Printed in Hungary*

A kiadásért felel az Akadémiai Kiadó igazgatója

Műszaki szerkesztő: Zacsik Annamária

A kézirat nyomdába érkezett: 1978. III. 20. — Terjedelem: 12,6 (A/5) ív, 70 ábra

78.5648 Akadémiai Nyomda, Budapest — Felelős vezető: Bernát György

ACTA CHIMICA

ТОМ 98 – ВЫП. 1

РЕЗЮМЕ

## Разделение и идентификация природных порфиринов, встречающихся в венгерской нефти

Ю. ЛАКАТОШ-САБО

Исследование содержания порфиринов и характерных венгерских нефтях тесно связано с геохимической квалификацией жидких углеводородов, залегающих в ложе Панон. Лабораторные исследования заключают в себе выделение порфиринов из нефти, их количественное определение и структурную идентификацию.

Согласно экспериментальным исследованиям, исследуемые орбазцы содержат исключительно комплексы порфирина с никелем и ванадием, но в различных количествах (1 – 127 м. д.). Наиболее содержание порфирина (127 м. д) было найдено в нефти из Надьлендьел, в то время как содержание порфирина в отечественной, т. наз. легкой нефти относительно низко (1 – 10 м. д.). Среди выделенных порфиринов были нейдены типы ка этио, так и фило, а хлорины или другие металлические комплексы не были найдены в исследованных образцах.

## Устранение спектрохимического матричного эффекта, изучение гомологии полос и установление пределов обнаруживаемости элементов в следах в силикатных породах

О. ФИЛО и М. МАТЕРНИ

Разработан новый аналитический метод определения элементов в следах в силикатных породах путем применения прерывистой дуги переменного тока. Этот метод позволяет анализ кислых гранитов и гранодиоритов, а также промежуточных пород и основных базальтов путем единой калибровочной кривой. Эффект матрицы устраняется определением оптимальных отношений перемешивания и разбавления. Отношение оптимальных времен предварительного горения и выдержки определяется из интегральных кривых испарения. Оптимализация выбора пары аналитических полос выполняется с помощью комбинирования корреляционного и регрессивного анализа и одновременно эти данные сопоставляются с предварительно определенными аналитическими калибровочными кривыми. Оптимальные пары аналитических линий используются также для подтверждения правильности аналитического метода.

## Усовершенствованная аппаратура для микрокаталитического или импульсного методов

ДЖ. ЛЭТЦЕЛ

Описывается аппаратура, которая может быть использована не только в стандартном микрокаталитическом методе, но также и для импульсной техники с двуразмерной газовой хроматографией или серийной колонной хроматографией. Помимо этого, она может быть применена и для метода температурно-программированной десорбции, а также для экспериментов по отравлению, комбинированных с импульсной техникой.

## Квантово-химические исследования конформационных свойств халкона и его простого модельного соединения

З. ДИНЯ, А. И. КИШ и Г. ПОНГОР

С помощью полуэмпирических квантово-химических методов был произведен конформационной анализ некоторых α. β-ненасыщенных карбонильных соединений. Расчеты расширенным методом Хюкеля и CNDO/2 халкона и простого модельного кетона хорошо воспроизводят экспериментальный порядок стабильности, указывая, что форма E—S-цих является наиболее стабильной. Кривая потенциальной энергии вращательной изомеризации S-цих-S-транс в форме E правильно отражается методом PCILO, в противоположность CNДO/2. Расчеты акролеина демонстрируют надежность результатов PCILO. Обсуждается рассчитанная высота вращательного барьера на основе сравнения с экспериментальными данными.

## Электрохимическое поведение этиленгликоля и его окисленных производных на платиновом электроде, II

### Исследование окисления глиоксаля и глиоксиловой кислоты

ДЬ. ХОРАНИ, ДЬ. ИНЦЕЛЬТ и З-НЕ СЕТЕИ

Электрохимическое окисление глиоксаля и глиоксиловой кислоты было исследовано в кислой среде на электроде из платинированной платины. Состав продуктов был изучен в зависимости от потенциала. Было установлено, что в случае не слишком больших потенциалов (600—700 мв RHE) в обеих реакциях, в первую очередь, образуется щавелевая кислота.

Был разработан фотометрический метод для определения щавелевой кислоты. Осциллирование гальваностатических потенциалов, известное из литературы, наблюдалось в случае обеих реакций. С помощью техники радиоактивных изотопов, в случае обоих соединений, была исследована адсорбция ионов хлора с целью изучения хемосорбции этих соединений.

На потенциостатической поляризационной кривой различимы три характерных участка, которые связаны с хемосорбционными явлениями, а также с появлением поверхностных окислов различных типов.

## Влияние алифатических спиртов на перенапряжение водорода на капельном галлиевом электроде

К. САБО, Л. СИРАКИ и Й. МИКА

Было исследовано влияние метанола, н-пропанола и н-бутанола на скорость электрохимического выделения водорода на капельном галлиевом электроде в растворе надхлорной кислоты. Было установлено, что с увеличением числа углеродных атомов изученных спиртов увеличивается и скорость выделения водорода.

Результаты хорошо обясняются, если полагать, что в присутствии спиртов протонным дожором является ион $ROHH^+$ и что с увеличением теплоты адсорбции, за счет взаимодействий дисперсионного характера, уменьшается энергия активации реакции выделения водорода.

Была определена зависимость между изменением скорости реакции выделения водорода и средней поляризуемостью спиртов.

## Металлические хелаты с этил-малондигидразидом

Х. Н. ПАНДИ, Л. МИШРА и В. ДЖ. РАМ

Описываются новые комплексы металлов Fe(II), Co(II), Ni(II), Cu(II) и Zn(II) с этил-малондигидразидом. На основе данных элементарного анализа, спектральных данных и данных магнитных измерений были сделаны заключения относительно формы координирования и приводится характеристика комплексов. Некоторые соединения являются пестицидами.

## Комплексы бора с тридентатными бифункциональными основаниями Шиффа

Х. Б. СИНГ и ДЖ. П. ТАНДОН

Тетракоординированные борные производные шиффовых оснований типа $B(OC_2H_5)$ (SB) и B(SB) (SBH) (где $SB^{-2}$ и $SBH^-$ представляют собой анионы соответствующих оснований Шиффа, $SBH_2$) были синтетизированы с высоким выходом и в состоянии достаточной чистоты на основе реакции этоксида бора с бифункциональными тридентатными шиффовыми основаниями, имеющими донорную систему HO—D—OH, с общей формулой $CH_3COCHC(CH_3)$ NHXOH (где X = $-C_6H_4-$, $-CH_2CH_2-$ и $-CH_2CH-CH_3$). Они являются мономерными в кипящем бензоле. Были сняты их ИК и ПМР спектры. Измерения проводимости в ДМФ указывают на то, что эти производные являются неэлектролитами.

## Доля когезионной энергии за счет диполярных взаимодействий

Я. ЛИСИ

Была изучена та доля когезионной энергии полярных жидкостей, которая возникает за счет диполярных взаимодействий (W). При сравнении с термодинамическими данными было установлено, что в определении W решающую роль играет полярная молекула, а также взаимодействие полярной молекулы с ближайшими соседями. Величина W может быть описана такой диэлектрической моделью, которая принимает во внимание это взаимодействие. Соответствующая диэлектрическая модель представляет молекулу как точкообразный диполь, помещенный в шарообразную полость, которую окружает шаровая оболочка с относительной проницаемостью $\varepsilon_{loc}$, а последняя, в свою очередь, встроена в бесконечный диэлектрик с относительной проницаемостью $\varepsilon_0$. Вследствие межмолекулярных взаимодействий, относительная проницаемость шаровой оболочки меньше относительной проницаемости основной массы жидкости.

## Реакции циклоприсоединения соединений цефалоспорина, III

### 1,3-Диполярное циклоприсоединение цефалоспорина к диазоалканам

Й. Ч. ЯСБЕРЕНИ, Е. Р. ФАРКАШ, Е. Т. ГУНДА, Й. ТАМАШ, М. МАК, Ш. ХОСТАФИ, Л. СИЛАДИ и Р. БОГНАР

Диазоалканы присоединяются к 3-цефемам и их окисленным производным, давая в нейтральных растворах 1-пиразолиноцефамы в качестве первичных продуктов. Хотя более высокие диазоалканы реагируют с двойной связью 3-цефемов, никакого присоединения не наблюдается в случае диазоалканов, замещенных алкоксикарбонильными или арильными группами, вследствие пониженной реакционности 1,3-диполей и низкой реактивности диполярофила 3-цефема. Диазометан дает циклоаддукты с 3-цефемом, но не реагирует с 2-цефемом. Обсуждается структура новых пиразолиноцефамов.

## Ароматизация н-нонана и н-декана на платиново-рениевом катализаторе

И. СЕБЕНИ и Г. СЕЧИ

Риформинг н-нонана и н-декана проводили в интервале температуру 487—548°C, при давлениях 15, 22 и 31 кг/см², при объемных скоростях 1,5, 3 и 5 мл/мл. час на промышленном платино-рениевом катализаторе типа E-601. При ароматизации н-нонана в продуктах были найдены все ароматические соединения с $C_9$, однако, количества о-этилтолуола и н-пропилбензола намного выше, чем в случае риформатов из бензина. Основными продуктами ароматизации н-декана являются н-бутилбензол, 1,3-диэтилбензол, 1,2-диметил-4-этилбензол и 1-метил-2-н-пропилбензол. Количество ароматических продуктов

в случае н-нонана, выше 531°С, а в случае н-декана выше 516°С едва или совсем не возрастает вследствие преобладания реакций гидрокрекинга. С повышением температуры и давления распределение ароматических продуктов сдвигается в сторону с числом углеродных атомов, меньших исходных веществ, вследствие деалкилирования ароматических продуктов с $C_{10}$ и $C_9$. Повышение давления портит селективность образования ароматических углеводородов с числом углеродных атомов как в исходном веществе. Селективность дегидроциклизации в случае н-декана меньше, чем в случае н-нонана; для ароматизации первого характерными является образование ароматических соединений с числом углеродных атомов меньшим 10 уже и при мягком риформинге. При давлении 15 кг/см², объемной скорости 1,5 мл/мл · час и температуре 531°С из н-нонана образуется 32,3 вес.% ароматики с $C_9$, а из н-декана наряду с 13,7 вес.% ароматики с $C_{10}$, образуется также 9,0 вес.% ароматики с $C_9$.

Les Acta Chimica paraissent en français, allemand, anglais et russe et publient des mémoires du domaine des sciences chimiques.

Les Acta Chimica sont publiés sous forme de fascicules. Quatre fascicules seront réunis en un volume (4 volumes par an).

On est prié d'envoyer les manuscrits destinés à la rédaction à l'adresse suivante:

*Acta Chimica*
*H-1521 Budapest, Hongrie*

Toute correspondance doit être envoyée à cette même adresse.

La rédaction ne rend pas de manuscript.

Le prix de l'abonnement: $ 36,00 par volume.

Abonnement en Hongrie à l'Akadémiai Kiadó (1363 Budapest, P. O. B. 24, C. C. B. 215 11488), à l'étranger à l'Entreprise du Commerce Extérieur «Kultura» (H-1389 Budapest 62, P. O. B. 149 Compte-courant No. 218 10990) ou chez représentants à l'étranger.

---

Die Acta Chimica veröffentlichen Abhandlungen aus dem Bereich der chemischen Wissenschaften in deutscher, englischer, französischer und russischer Sprache.

Die Acta Chimica erscheinen in Heften wechselnden Umfanges. Vier Hefte bilden einen Band. Jährlich erscheinen 4 Bände.

Die zur Veröffentlichung bestimmten Manuskripte sind an folgende Adresse zu senden:

*Acta Chimica*
*H-1521 Budapest, Ungarn*

An die gleiche Anschrift ist jede für die Redaktion bestimmte Korrespondenz zu richten.

Manuskripte werden nicht zurückerstattet.

Abonnementspreis pro Band: $ 36,00.

Bestellbar für das Inland bei Akadémiai Kiadó (1363 Budapest, Postfach 24, Bankkonto Nr. 215 11488), für das Ausland bei »Kultura« Außenhandelsunternehmen (H-1389 Budapest 62, P. O. B. 149. Bankkonto Nr. 218 10990) oder seinen Auslandsvertretungen.

---

«Acta Chimica» издают статьи по химии на русском, английском, французском и немецком языках.

«Acta Chimica» выходит отдельными выпусками разного объекта, 4 выпуска составляют один тдм и за год выходят 4 тома.

Предназначенные для публикации рукописи следует направлять по адресу:

*Acta Chimica*
*H-1521 Budapest, ВНР*

Всякую корреспонденцию в редакцию направляйте по этому же адресу.

Редакция рукописей не возвращает.

Подписная цена — $ 36,00 за том.

Отечественные подписчики направляйте свои заявки по адресу Издательства Академии Наук (1363 Budapest, P. O. B. 24, Текущий счет 215 11488), а иностранные подписчики через организацию по внешней торговле «Kultura» (H-1389 Budapest 62, P. O. B. 149. Текущий счет 218 10990) или через ее заграничные представительства и уполномеченных.

## Reviews of the Hungarian Academy of Sciences are obtainable at the following addresses:

**AUSTRALIA**
C.B.D. LIBRARY AND SUBSCRIPTION SERVICE, Box 4886, G.P.O., *Sydney N.S.W. 2001*
COSMOS BOOKSHOP, 135 Ackland Street, *St. Kilda (Melbourne), Victoria 3182*

**AUSTRIA**
GLOBUS, Höchstädtplatz 3, *1200 Wien XX*

**BELGIUM**
OFFICE INTERNATIONAL DE LIBRAIRIE, 30 Avenue Marnix, *1050 Bruxelles*
LIBRAIRIE DU MONDE ENTIER, 162 Rue du Midi, *1000 Bruxelles*

**BULGARIA**
HEMUS, Bulvar Ruszki 6, *Sofia*

**CANADA**
PANNONIA BOOKS, P.O. Box 1017, Postal Station "B", *Toronto, Ontario M5T 2T8*

**CHINA**
CNPICOR, Periodical Department, P.O. Box 50, *Peking*

**CZECHOSLOVAKIA**
MAD'ARSKÁ KULTURA, Národní třida 22, *115 66 Praha*
PNS DOVOZ TISKU, Vinohradská 46, *Praha 2*
PNS DOVOZ TLAČE, *Bratislava 2*

**DENMARK**
EJNAR MUNKSGAARD, Norregade 6, *1165 Copenhagen*

**FINLAND**
AKATEEMINEN KIRJAKAUPPA, P.O. Box 128, *SF-00101 Helsinki 10*

**FRANCE**
EUROPERIODIQUES S. A., 31 Avenue de Versailles, *78170 La Celle St.-Cloud*
LIBRAIRIE LAVOISIER, 11 rue Lavoisier, *75008 Paris*
OFFICE INTERNATIONAL DE DOCUMENTATION ET LIBRAIRIE, 38 rue Gay-Lussac, *75240 Paris Cedex 05*

**GERMAN DEMOCRATIC REPUBLIC**
HAUS DER UNGARISCHEN KULTUR, Karl-Liebknecht-Strasse 9, *DDR-102 Berlin*
DEUTSCHE POST, ZEITUNGSVERTRIEBSAMT, Strasse der Pariser Kommüne 3—4, *DDR-104 Berlin*

**GERMAN FEDERAL REPUBLIC**
KUNST UND WISSEN ERICH BIEBER, Postfach 46, *7000 Stuttgart 1*

**GREAT BRITAIN**
BLACKWELL'S PERIODICALS DIVISION, Hythe Bridge Street, *Oxford OX1 2ET*
BUMPUS, HALDANE AND MAXWELL LTD., Cowper Works, *Olney, Bucks MK46 4BN*
COLLET'S HOLDINGS LTD., Denington Estate, *Wellingborough, Northants NN8 2QT*
WM. DAWSON AND SONS LTD., Cannon House, *Folkestone, Kent CT19 5EE*
H. K. LEWIS AND CO., 146 Gower Street, *London WC1E 6BS*

**GREECE**
KOSTARAKIS BROTHERS, International Booksellers, 2 Hippokratous Street, *Athens-143*

**HOLLAND**
MEULENHOFF-BRUNA B.V., Beulingstraat 2, *Amsterdam*
MARTINUS NIJHOFF B.V., Lange Voorhout 9—11, *Den Haag*
SWETS SUBSCRIPTION SERVICE, 347b Heereweg, *Lisse*

**INDIA**
ALLIED PUBLISHING PRIVATE LTD., 13/14 Asaf Ali Road, *New Delhi 110001*
150 B-6 Mount Road, *Madras 600002*
INTERNATIONAL BOOK HOUSE PVT. LTD., Madame Cama Road, *Bombay 400039*
THE STATE TRADING CORPORATION OF INDIA LTD., Books Import Division, Chandralok, 36 Janpath, *New Delhi 110001*

**ITALY**
EUGENIO CARLUCCI, P.O. Box 252, *70100 Bari*
INTERSCIENTIA, Via Mazzé 28, *10149 Torino*
LIBRERIA COMMISSIONARIA SANSONI, Via Lamarmora 45, *50121 Firenze*
SANTO VANASIA, Via M. Macchi 58, *20124 Milano*
D. E. A., Via Lima 28, *00198 Roma*

**JAPAN**
KINOKUNIYA BOOK-STORE CO. LTD., 17-7 Shinjuku-ku 3 chome, Shinjuku-ku, *Tokyo 160-91*
MARUZEN COMPANY LTD., Book Department, P.O. Box 5056 Tokyo International, *Tokyo 100-31*
NAUKA LTD., IMPORT DEPARTMENT, 2-30-19 Minami Ikebukuro, Toshima-ku, *Tokyo 171*

**KOREA**
CHULPANMUL, *Phenjan*

**NORWAY**
TANUM-CAMMERMEYER, Karl Johansgatan 41—43, *1000 Oslo*

**POLAND**
WĘGIERSKI INSTYTUT KULTURY, Marszałkowska 80, *Warszawa*
CKP I W ul. Towarowa 28 *00-958 Warsaw*

**ROUMANIA**
D. E. P., *Bucureşti*
ROMLIBRI, Str. Biserica Amzei 7, *Bucureşti*

**SOVIET UNION**
SOJUZPETCHATJ — IMPORT, *Moscow*
and the post offices in each town
MEZHDUNARODNAYA KNIGA, *Moscow G-200*

**SPAIN**
DIAZ DE SANTOS, Lagasca 95, *Madrid 3*

**SWEDEN**
ALMQVIST AND WIKSELL, Gamla Brogatan 26, *101 20 Stockholm*
GUMPERTS UNIVERSITETSBOKHANDEL AB, Box 346, *401 25 Göteborg 1*

**SWITZERLAND**
KARGER LIBRI AG, Petersgraben 41, *4011 Basel*

**USA**
EBSCO SUBSCRIPTION SERVICES, P.O. Box 1943, *Birmingham, Alabama 35201*
F. W. FAXON COMPANY, INC., 15 Southwest Park, *Westwood, Mass, 02090*
THE MOORE-COTTRELL SUBSCRIPTION AGENCIES, *North Cohocton, N. Y. 14868*
READ-MORE PUBLICATIONS, INC., 140 Cedar Street, *New York, N. Y. 10006*
STECHERT-MACMILLAN, INC., 7250 Westfield Avenue, *Pennsauken N. J. 08110*

**VIETNAM**
XUNHASABA, 32, Hai Ba Trung, *Hanoi*

**YUGOSLAVIA**
JUGOSLAVENSKA KNJIGA, Terazije 27, *Beograd*
FORUM, Vojvode Mišića 1, *21000 Novi Sad*

*1. IX. 1978* HU ISSN 0001—5407 **Index: 26.007**

# ACTA CHIMICA

## ACADEMIAE SCIENTIARUM HUNGARICAE

ADIUVANTIBUS

M. T. BECK, R. BOGNÁR, V. BRUCKNER,
GY. HARDY, K. LEMPERT, F. MÁRTA,
K. POLINSZKY, E. PUNGOR,
G. SCHAY, Z. G. SZABÓ, P. TÉTÉNYI

REDIGUNT

B. LENGYEL et GY. DEÁK

TOMUS 98 FASCICULUS 2

AKADÉMIAI KIADÓ, BUDAPEST

1978

ACTA CHIM. ACAD. SCI. HUNG. ACASA2 98 (2) 141–253 (1978)

# ACTA CHIMICA

## A MAGYAR TUDOMÁNYOS AKADÉMIA KÉMIAI TUDOMÁNYOK OSZTÁLYÁNAK IDEGEN NYELVŰ KÖZLEMÉNYEI


FŐSZERKESZTŐ
LENGYEL BÉLA

SZERKESZTŐ
DEÁK GYULA

TECHNIKAI SZERKESZTŐ
HARASZTHY-PAPP MELINDA

SZERKESZTŐ BIZOTTSÁG
BECK T. MIHÁLY, BOGNÁR REZSŐ, BRUCKNER GYŐZŐ, HARDY GYULA, LEMPERT KÁROLY, MÁRTA FERENC, POLINSZKY KÁROLY, PUNGOR ERNŐ, SCHAY GÉZA, SZABÓ ZOLTÁN, TÉTÉNYI PÁL



Acta Chimica is a journal for the publication of papers on all aspects of chemistry, in the English, German, French and Russian.

Acta Chimica is published in 4 volumes per year. Each volume consists of 4 issues of varying size.

Manuscripts should be sent to

*Acta Chimica*
*H-1521 Budapest, Hungary*

Correspondence with the editors should be sent to the same address. Manuscripts are not returned to the authors.

Subscription: $ 36.00 per volume.

Hungarian subscribers should order from Akadémiai Kiadó, 1363 Budapest, P.O. Box 24. Account No. 215 11488.

Orders from other countries are to be sent to "Kultura" Foreign Trading Company (H-1389 Budapest 62, P.O. Box 149. Account No. 218 10990) or its representatives abroad.

*Acta Chimica Academiae Scientiarum Hungaricae, Tomus 98 (2), pp. 141—146 (1978)*

# INVESTIGATIONS ON THE OUTER-SPHERE COMPLEXES OF TRIS-(ETHYLENEDIAMINE)-COBALT(III) AND HEXAMMINE-COBALT(III) CATIONS FORMED WITH ORTHOPHOSPHATE AND PYROPHOSPHATE ANIONS

P. HALMOS, J. GAÁL and J. INCZÉDY

*(Institute of Analytical Chemistry University of Chemical Engineering Veszprém)*

Received July 4, 1977

pH metric titrations were used to study the complexes formed by tris-(ethylenediamine)-cobalt(III) and hexammine-cobalt(III) complex cations and ortho- and pyrophosphate anions. The logarithms of the stability constants of $Co(en)_3HPO_4^+$, $Co(en)_3PO_4$; $(Co(en)_3HP_2O_7$ and $Co(NH_3)_6HPO_4^+$ formed were $2.02 \pm 0.1$; $3.12 \pm 0.1$; $2.19 \pm 0.5$ and $2.53 \pm 0.1$, respectively.

When studying equilibria in aqueous solutions outer-sphere complex formation reactons have also to be considered. Outer-sphere complex formation as such can only be studied, if no change does simultaneously take place in the inner coordination sphere. If the inner complex is sufficiently inert this requirement is generally fulfilled. Since tris-(ethylenediamine)-cobalt(III) and hexammine-cobalt(III) complex cations are inert their outer-sphere complexes can be relatively easily studied. There are a number of papers dealing with their halogenide, sulphate and thiosulphate outer-sphere complexes [1—8].

This paper presents the results obtained in a study dealing with the complex formation equilibria of their ortho- and pyrophosphate outer-sphere complexes using pH metric titration curves. The studies were initiated to find out, if their properties were dissimilar enough to allow for their separation. ILCHEVA [9] used polarographic methods to study the outer-sphere complex formation reaction of orthophosphate and tris-(enthylenediamine)-cobalt(III) ions.

In our investigations — considering also literature data — it was assumed, that the cobalt(III) cation complexes do not form outer-sphere complexes with the perchlorate ions in appreciable extent.

## Experimental

### Chemicals

Orthophosphoric acid (reagent grade, Reanal, Budapest) Sodium pyrophosphate (reagent grade, Reanal, Budapest) tris-(ethylenediamine)-cobalt(III) perchlorate and hexammine-cobalt(III) perchlorate were prepared from their chlorides adding concentrated perchloric acid to the solutions of the complex salts. The crystalline precipitate formed was washed with ethanol then dried. pH measurements were performed to check that the solutions of complex perchlorates contained no free acid. Complex chlorides were prepared from cobalt(II) chloride (reagent grade, Reanal, Budapest) according to [10].

### Instruments

pH measurements were made on a Universal pH meter (Radelkis, Budapest) using a combined glass-calomel electrode.

### pH metric titrations

Appropriate quantities of sodium pyrophosphate, tris-(ethylenediamine)-cobalt(III) perchlorate and hexammine-cobalt(III) perchlorate were weighed and dissolved to obtain solutions of 0.1 and 0.01 molar, respectively. (Due to the low solubility, only $10^{-2}$ molar hexammine-cobalt(III) perchlorate solutions were prepared). The titer of the diluted phosphoric acid stock solution was obtained by pH metric titrations. Titrations were made both in the presence and absence of complex salts. Due to the lower stabilites of outer-sphere complexes 1 : 1 central ion: ligand ratios were selected for the titrations. Titrated solutions were flushed with nitrogen to remove carbon dioxide. In the case of tris-(ethylenediamine)-cobalt(III) cation and orthophosphate anion complexes solutions contained:

10 ml 0.10 M phosphoric acid
10 ml 0.265 M perchloric acid
10 ml 0.10 M tris-(ethylenediamine)-cobalt(III) perchlorate solution in the presence, and only
10 ml distilled water in the absence of the respective complex salt.

In the case of tris-(ethylenediamine)-cobalt(III) cation and pyrophosphate anion complexes solutions contained:

10 ml 0.10 M sodium pyrophosphate solution
20 ml 0.265 M perchloric acid
10 ml 0.10 M tris-(ethylenediamine)-cobalt(III) perchlorate solution, or
10 ml distilled water, respectively.
In both cases 0.520 3M sodium hydroxide was used for the titrations.

Outer-sphere complex formation reactions of hexammine-cobalt(III) cation with orthophosphate anion were studied in solutions containing:

4 ml 0.10 M phosphoric acid
2 ml 0.224 M perchloric acid
40 ml 0.010 M hexammine-cobalt(III) perchlorate solution, or
40 ml distilled water, respectively.

Complex formation between hexammine-cobalt(III) cation and pyrophosphate anion was studied in solutions containing:

3 ml 0.10 M sodium pyrophosphate solution
7 ml 0.224 M perchloric acid
30 ml 0.10 M hexammine-cobalt(III) perchlorate solution, or
30 ml distilled water, respectively.
The titrant in both cases was (0,109 M) sodium hydroxide standard solution.

## Results and discussion

Corresponding titrant volumes measured pH date were plotted as titration curves. Whenever titration curves differ in the presence and absence of the respective complex forming agent, a proton releasing complex formation reaction has taken place. Corresponding complex stability constants were calculated from the equations shown below:

$$K = \frac{[ML]}{[L][M]} = \frac{C_L - [L]\alpha_{L(H)}}{[L][C_M - (C_L[L]\alpha_{L(H)})]}, \quad (1)$$

and in the case of protonated ligands:

$$K = \frac{[MHL]}{[HL][M]} = \frac{C_L - [HL]\alpha_{LH(H)}}{[HL][C_M - (C_L - [HL]\alpha_{LH(H)})]}, \quad (2)$$

where $C_L$ and $C_M$ are the overall ligand and central ion, while [L] and [HL] the free ligand concentrations, respectively. $\alpha_{L(H)}$ and $\alpha_{LH(H)}$ are the functions accounting for the protonation of the complexed ligands, expressed as

$$\alpha_{L(H)} = 1 + [H]\cdot K_1 + [H]^2 K_1 \cdot K_2 + [H]^3 K_1 K_2 K_3 + \ldots + [H]^n K_1 K_2 \ldots K_n \quad (3)$$

and

$$\alpha_{LH(H)} = 1 + [H] K_2 + [H]^2 K_2 K_{K_3} + \ldots + [H]^{n-1} K_2 \ldots K_n, \quad (4)$$

where [H] is the proton concentration and $K_1 \ldots K_n$ are the protonation constants of the ligand.

Free ligand concentration was calculated from the mass and charge conservation balance equations applied to the particular titration. Having solved these equations, the expressions shown below were obtained:

$$[L] = \frac{(3 - a)\, C_L - [H] + [OH]}{[H]\cdot K_1}, \quad (5)$$

and

$$[HL] = \frac{(m - a)\, C_L - [H] + [OH]}{[H] K_2}. \quad (6)$$

In these equations $a$ is the degree of titration and values of $m$ are 2 and 3 for the protonated phosphate and pyrophosphate ions, respectively.

Protonation constants required for the calculations were obtained from the titration curves of the ligands [11]. They were $K_2 = 6{,}93$, and $K_3 = 2{,}22$ and $K_1 = 8{,}58$; $K_2 = 6{,}12$ and $K_3 = 1{,}86$ for orthophosphate and pyrophosphate ions, respectively. The values agree well with literature data [12, 13].

The outer-sphere complex formation reaction of orthophosphate anion and tris-(ethylenediamine)-cobalt(III) complex cation was studied via the titration curves shown in Figure 1.

The outer-sphere complex formation reaction

$$H_2PO_4^- + Co(en)_3^{3+} = [Co(en)_3]\, HPO_4^+ + H^+ \quad (7)$$

is thought to take place in the pH range 5 through 8. The logarithm of the stability constant of the complex formed, calculated by Eq (2), is $\lg K = 2{,}02 \pm \pm 0{,}1$ ($I = 0{,}50$).

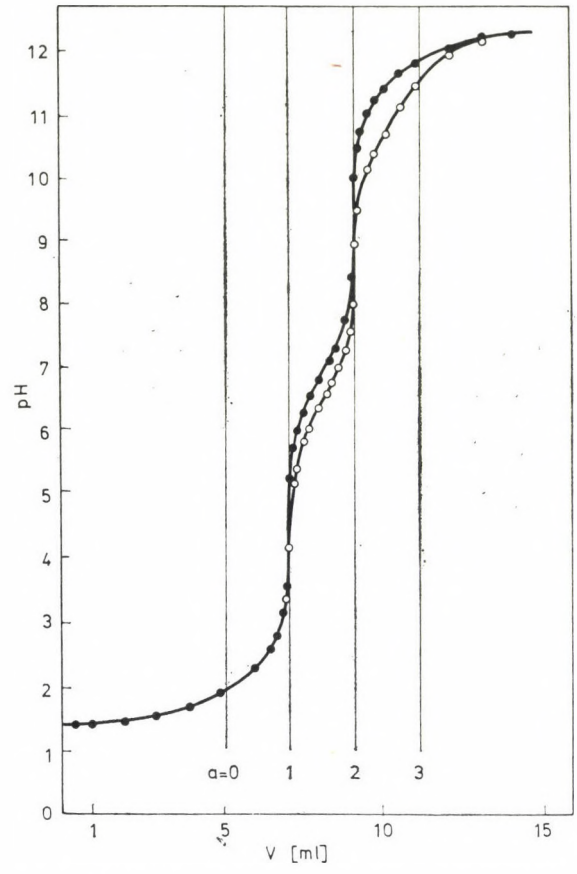



*Fig. 1.* Titration curves of phosphoric acid in the presence (.) and absence (+) of tris-ethylene-diamine-cobalt(III) complex cation

Apparently, there is an other outer-sphere complex formation reaction taking place in the pH range 8,5 through 12,5. The reaction is the following:

$$HPO_4^{2-} + Co(en)_3^{3+} = [Co(en)_3]\,PO_4 + H^+. \qquad (8)$$

The logarithm of the complex stability constant, calculated by Eq (1), is $\lg K = 3.12 \pm 0{,}1$ ($I = 0.50$).

In the case of orthophosphate anion and hexammine-cobalt(III) complex cation the outer-sphere complex formation takes place in the pH range 4,5 through 8.5, as shown in Figure 2.

The pertaining reaction probably is as follows:

$$H_2PO_4^- + Co(NH_3)^{3+} = [Co(NH_3)_6]\,HPO_4^+ + H^+. \qquad (9)$$

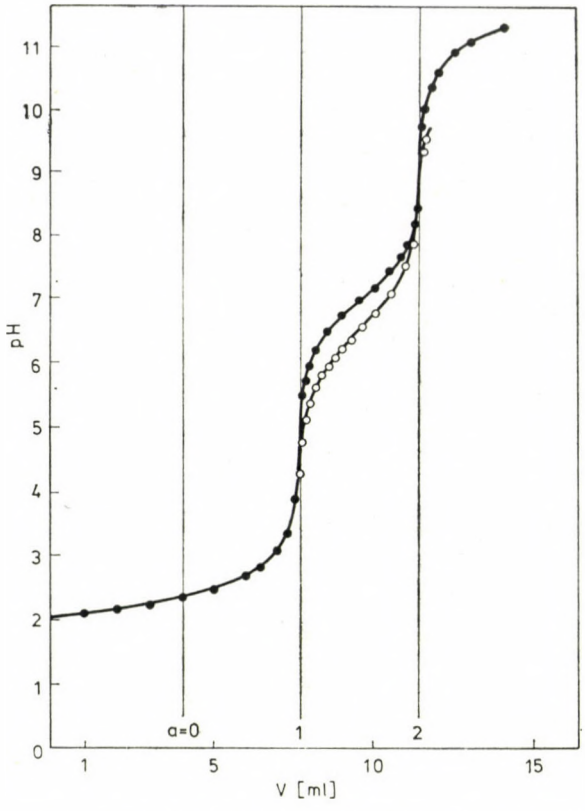



*Fig. 2.* Titration curves of phosphoric acid in the presence (.) and absence (+) of hexammine cobalt(III) complex cation

The logarithm of the complex stability constant calculated by Eq (2) is lg K = 2.53 ± 0.1 (I = 0.11). Precipitate formation was observed at pH 10, so further complex formation could not be studied by this method.

The reaction assumed to take place between pyrophosphate anion and tris-(ethylenediamine)-cobalt(III) complex cation at about pH 4—5 is:

$$H_2P_2O_7^{2-} + Co(en)_3^{3+} = [Co(en)_3]HP_2O_7 + H^+ . \qquad (10)$$

Once again, precipitate formation occurs above pH 5.5, so the error of the stability constant determination is greater. The figure calculated by Eq (2) is lg K = 2.2 ± 0.5 (I = 0.54). No outer-sphere complex formation was observed in the case of pyrophosphate and hexammine-cobalt(III) cation up to pH 4.5, while precipitation occurred at higher pH values.

In summary, it can be concluded, that both tris-(ethylenediamine)-cobalt(III) and hexammine-cobalt(III) complex cations form outer-sphere

complexes with pyrophosphate and orthophosphate anions. Complex stability values calculated by Eq (1) and (2) are summarized in Table I.

**Table I**

*The logarithms of the stability constants of the outher-sphere complexes*

| | lg K $Co(en)_3^{3+}$ | I | lg K $Co(NH_3)_6$ | I |
|---|---|---|---|---|
| $HPO_4^{2-}$ | 2.02±0.1 | 0.50 | 2.53±0.1 | 0.11 |
| $PO_4^{3-}$ | 3.12±0.1 | 0.50 | precipitate | 0.11 |
| $HP_2O_7^{3-}$ | 2.19±0.5 | 0.54 | 0 | 0.16 |

Ossicini and Balzoni; [14] used paper electrophoretic techniques to study the complex formation reactions of ortho- and pyrosphosphate anions and cobalt(III) complex ions. No stability constants were determined but their results supported the orders of the stability constants determined in this study.

## REFERENCES

[1] Evans, M. G., Nancollas, G. H.: Trans. Faraday Soc. **49,** 363, (1953)
[2] Fedorov, V. A., Minorov, V. E., Kulba, F. A.: Zhur. Neorg. Khim. **7,** 2528 (1962)
[3] Laitinen, H. A., Grieb, M. W.: J. Amer. Chem. Soc. **77,** 5201 (1955)
[4] King, E. L., Espenson, J. H., Visco, R. E.: J. Phys. Chem. **63,** 755 (1959)
[5] Tanaka, N., Kobayashi, Y., Kamada, M.: Bull. Chem. Soc. Japan **40,** 2839 (1967)
[6] Katayama, S., Tamamushi, R.: Bull. Chem. Soc. Japan **40,** 606 (1968)
[7] Johansson, L.: Acta Chem. Scand. **25,** 3752 (1971)
[8] Powell, D. B., Scott, J. G. V.: Spectrochim. Acta **28A,** 1067 (1972)
[9] Ilcheva, L. I., Veleva, M. G., Krsev, I. P., Bozadziev, P. Sz.: Himia i Industria **7,** 304 (1974)
[10] Fernelius, W. C. "Inorganic Syntheses" Vol. II., McGraw-Hill Book Co. Inc. New York (1964), 217–221
[11] Inczédy, J.: Analytical applications of complex equilibria, Ellis, Horwood, Chichester (1976)
[12] Elliot, J. S., Sharp, R. F., Lewis, L.: J. Phys. Chem. **62,** 686 (1958)
[13] Irani, R. R.: J. Phys. Chem. **65,** 1463 (1961)
[14] Ossicini, L., Balzoni, M.: J. Chrom. **117,** 464 (1976)

P. Halmos
J. Gaál
János Inczédy
H-8201 Veszprém, Schönherz Z. u. 10.

*Acta Chimica Academiae Scientiarum Hungaricae, Tomus 98 (2), pp. 147—156 (1978)*

# SOME CHEMICAL REACTIONS OF THE ELECTRODE GAP AND THEIR ROLE IN SPECTROCHEMICAL ANALYSIS, XXXI

## BEHAVIOUR OF METAL OXIDES IN THE ARC IN AN ARGON FLOW. ROLE OF BURNING TIME AND CURRENT OF THE ARC WITH RW 0 AUXILIARY ELECTRODES

Z. L. SZABÓ and H. DOBOLYI—FEJÉRDY[1]

*(Department of Inorganic and Analytical Chemistry, L. Eötvös University, Budapest, and [1]Hungarian Optical Works, Budapest)*

Received September 13, 1977

Results obtained by changing the burning time and current of the arc with RW 0 carbon auxiliary electrodes are compared with earlier results for RW II carbon auxiliary electrodes. We have shown that a decisive role is played by the temperature in the arc of the holding electrode in reactions inside the electrode material, but neither is indifferent the quality of the carbon powder used for the preparation of the powder mixture. The experiments have also shown that the oxidation and reduction tendencies of electric origin, governing the electrode surface reactions between the gas atmosphere and the electrode material have no part in the reactions inside the electrode.

In our earlier experiments, we used RW II amorphous carbon auxiliary electrodes produced by the Ringsdorff Werke, GmbH. This electrode material, due to its low thermal conductivity, glows up better in the arc, thus causing higher reaction rates in the powder mixture [1], therefore, is more suitable for investigations.

In practical spectral analysis, graphitic carbons of RW 0 type are preferable because of their better workability as holding electrodes. After investigating the basic problems, it seemed advisable to repeat our experiments with this electrode material as well, for the behaviour of the RW 0 and RW II electrode materials in their electrode surface reactions had been elucidated earlier [2]. As model substances, we used again the mixture of Cu(II)-oxide and carbon powder, this latter being a graphitic carbon of type Electrocarbon Topolčany (Czechoslovakia) SU-601. For the investigation of the effect of the holding electrode polarity, we used A.C. polarized arc excitation ignited at maximum voltage, and to avoid secondary reactions, applied an argon flow of 860 $cm^3$/min. The amounts of CO and $CO_2$ evolved were measured by gas analytical methods [3] and the intensity of a selected spetral line of copper was also recorded. First, we studied the effect of burning time and current, and compared it with our earlier results for a holding electrode of RW II carbon type [4]. The experimental methods have been described elsewhere [1].

## Role of Burning Time

In our earlier experiments [1], it became apparent that the extent of chemical reactions with RW 0 auxiliary electrodes is considerably lower than that with RW II electrodes. Therefore, in order to obtain well-measurable amounts of the reaction products, we used an average current of 16 A, as opposed to the 7 A used earlier with RW II carbon eledtrodes. The burning time of the arc varied between 2 and 15 s. Figure 1 shows the quantity of CO formed *vs.* the burning time of the arc, while Fig. 2 is the same for the $CO_2$ produced. Comparison of the curves with those obtained with RW II holding electrodes [4] reveals several differences. Concerning the amount of CO, it can be established that in the present experiments with the holding electrode as anode, the curves nearly coincide, in spite of the different currents, while with cathodic excita-

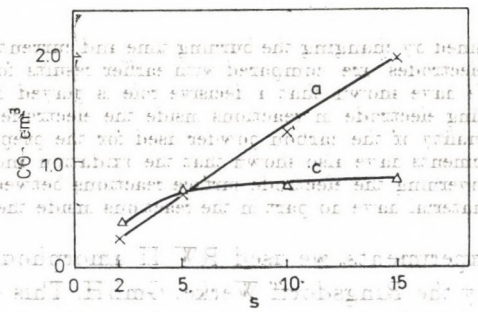



*Fig. 1.* Quantity of CO produced *vs.* burning time of the arc. 16 A, RW 0 auxiliary electrode. *a*: anodic, *c*: cathodic excitation

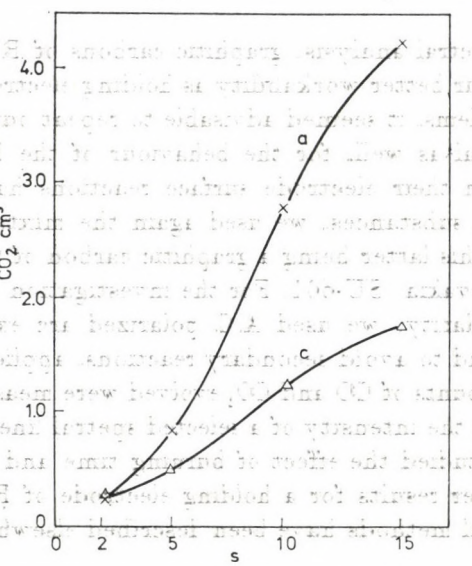



*Fig. 2.* Quantity of $CO_2$ produced *vs.* burning time of the arc. 16 A, RW 0 auxiliary electrode. *a*: anodic, *c*: cathodic excitation

tion, the amount of CO is much greater with the RW 0 electrode due to the greater current, but after a burning time of 5 s they reach different saturation values. The same is valid for the amount of $CO_2$ in cathodic excitation with the RW 0 holding electrode at longer burning times. Upon anodic excitation of the RW 0 holding electrode, the volumes of $CO_2$ in the first 3—4 s are equal to those obtained with the RW II carbon, after that the $CO_2$ production is delayed; however, after 12 s it increases due to the greater current reached, when the better conducting RW 0 electrode is properly glowing. It is also apparent that with the RW 0 electrode, the arc burns mainly on the carbon powder fillings and only to a lesser extent on the edge of the holding electrode, as was the case with the RW II electrodes. It is also characteristic that, after switching off the arc, the holding electrode cools down faster than the inner powder mixture. This may be caused by the material filled in not being compact but pulverized, though this phenomenon was not observed with RW II auxiliary electrodes. Consequently, the cause must be in the behaviour of the auxiliary electrode. These observations prove that CO is formed in the surroundings of the burning spot of the arc, while the greater part of the $CO_2$ evolves within the glowing material filled in the electrode. With RW 0 holding electrodes, probably the more amorphous nature of the carbon in the mixture and, consequently, its poorer thermal conductivity, causes a more extensive heating with increasing current, thus enhancing the reactions. Accordingly, though the temperature is determined primarily by the nature of the holding electrode, the nature of the carbon powder in the charge is not indifferent, either. Later on, we intend to investigate this phenomenon, too. Due to the better thermal conductivity of the RW 0 carbon, at first the production of $CO_2$ increases in time more slowly, but after longer burning times, it reaches greater values owing to the greater current. At the beginning, therefore, the sum of the gas volumes ($\Sigma\%$) from the two reactions, expressed in per cent of the possible maximum calculated from the weight of the material in the bore of the electrode also increases more slowly (Fig. 3), but after a burning time of 15 s, it reaches nearly 80%. With RW II auxiliary electrodes at a current of 7 A, however, we reached the saturation at about 60%. In these experiments with RW 0 carbon, the blocking layer of metallic copper produced in the reaction can be formed only later because of the greater current and more extensive evaporation; due to faste heat transfer, the reaction zone can extend deeper than in experiments with the RW II carbon and at smaller currents.

The curve section between 10 and 15 s in Fig. 4 for the $CO_2$ to CO volume ratio, representing the oxidative character of the system, is the same as the section of the curve for RW II carbon between 2 and 5 s (Fig. 5 in Ref. [4]) due to colder electrodes.

Consequently, if we wish to ensure slower, uniform reactions in the spectroscopic investigations (*e. g.* to avoid sputtering and of the material from the

bore of the electrode, or the use of pre-arcing), it is favourable to employ the colder RW 0 electrode instead of RW II.

The 282.4 nm copper atom line intensities ($I_{Cu\ I}$) in Fig. 5 start steeper and reach higher values than those for the RW II holding electrodes, owing to the greater current. It is, however, remarkable that after longer burning times,

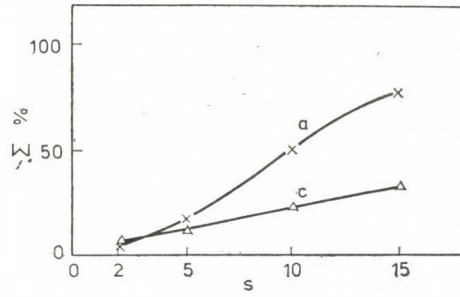



*Fig. 3.* Overall per cent reaction as a function of burning time. 16 A, RW 0 auxiliary electrode, *a*: anodic, *c*: cathodic excitation

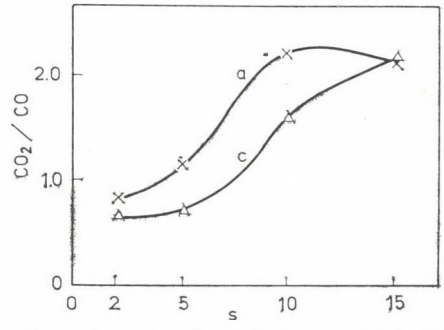



*Fig. 4.* $CO_2$/CO volume ratio *vs.* burning time of the arc. 16 A, RW 0 auxiliary electrode. *a*: anodic, *c*: cathodic excitation

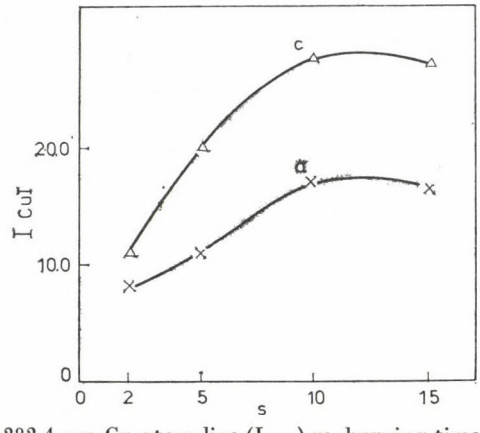



*Fig. 5.* Intensity of the 282.4 nm Cu-atom line ($I_{Cu\ I}$) *vs.* burning time of the arc. 16 A, RW 0 auxiliary electrode. *a*: anodic, *c*: cathodic excitation

the curves reach saturation. After 10—15 s the values are practically the same for anodic and cathodic excitation. Since the evaporation of the copper content of the sample progresses in time, this phenomenon indicates consumption of the carbon powder and, consequently, the decreasing temperature of the burning spot. For technical reasons, we could not apply burding times longer than 15 s, though it is to be expected that after longer times the intensity curves would rise again. Of course, the steeper initial ascent of the curves may also be due to the reaction heat which increases the evaporation.

The relative position of the curves obtained with anodic and cathodic excitation is reversed in comparison with the curves for RW II carbons. For

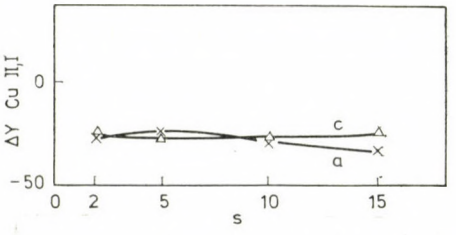



*Fig. 6.* Spectral character ($\Delta Y_{Cu\ II,I} = \Delta Y_{Cu\ 237.0/282.4}$) *vs.* burning time of the arc. 16 A, RW 0 auxiliary electrode. *aε* anodic, *cε* cathodic excitation

RW 0 we obtained higher line intensities by cathodic excitation of the sample. This may be caused either by the different behaviour of the RW 0 carbon from the RW° carbon, or by the fact that at greater currents the behaviour of copper, which is similar to the noble metals, is not disturbed by so-called side-effects. In further parts of our work, we intend to deal with this fact in detail.

The spectral character curves ($\Delta Y_{II,I}$, Fig. 6) constructed from the Cu 237.0 nm ion line and the above atom line show a moderately descending character and after longer burning times a difference begins to form between the two excitation types.

## Role of Current

The curves recorded as a function of the current for RW 0 holding electrodes, with a burning time of 10 s, show even more considerable differences with respect to temperature and reactions from the RW II carbon. In Figs 7 and 8, the CO and $CO_2$ production curves are shown; they are much flatter for the RW 0 than for the RW II carbon electrodes. The values for RW 0 are 1/2—1/3 of those for the RW II carbon. Another essential difference is that, characteristic for lower electrode temperature and, consequently, less extensive reactions, the values for the cathodic excitation of the sample are greater. The anodic value reaches this curve only at 15—16 A. Probably, at this current the heating

up of the anode begins. The overall per cent reaction ($\Sigma\%$) referred to the possible maximum calculated from the quantity of the mixture in the bore of the electrode, changes in the same way.

A further interesting comparison is possible with the curves for the RW II carbon auxiliary electrodes (Figs 12—17 in Ref. [4]) It is remarkable that the end of the curves for the weakly glowing RW 0 carbon electrodes (at higher current) and the beginning of the curves for the strogly glowing RW II electrodes (at lower current) are of the same direction. Therefore, we have shifted the coordinate systems of the pairs of curves in such a way that the curves join each other and the ends of the RW 0 curves overlap the initial sections of the curves for the RW II electrode. Figure 9 shows the curves for CO production, fitted in this way. It is to be seen that the curves obtained with the two carbon electrodes are continuouos, though the absolute values of the measured points are different, because horizontal axes of the coordinate systems do not coincide. Owing to the scattering of the measured values, the fit of the curves for $CO_2$ production is somewhat poorer (Fig. 10). The curves for cathodic and anodic

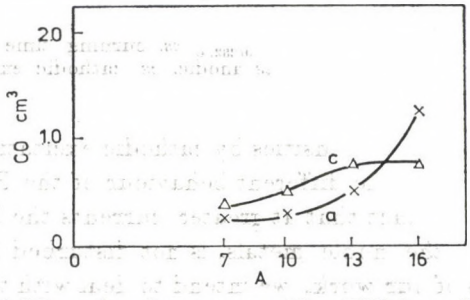



*Fig. 7.* Quantity of CO produced *vs.* current. 10 s, RW 0 auxiliary electrode. *a*: anodic excitation

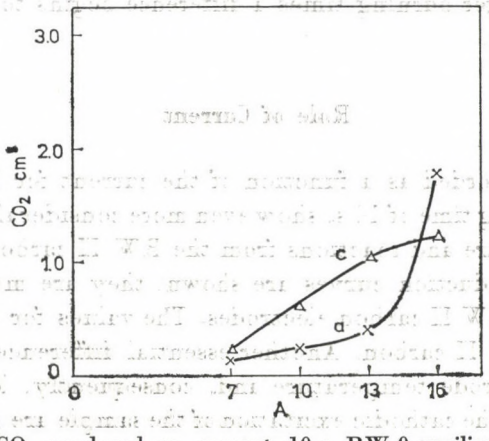



*Fig. 8.* Quantity of $CO_2$ produced *vs.* current. 10 s. RW 0 auxiliary electrode. *a*: anodic, *c*, cathodic excitation

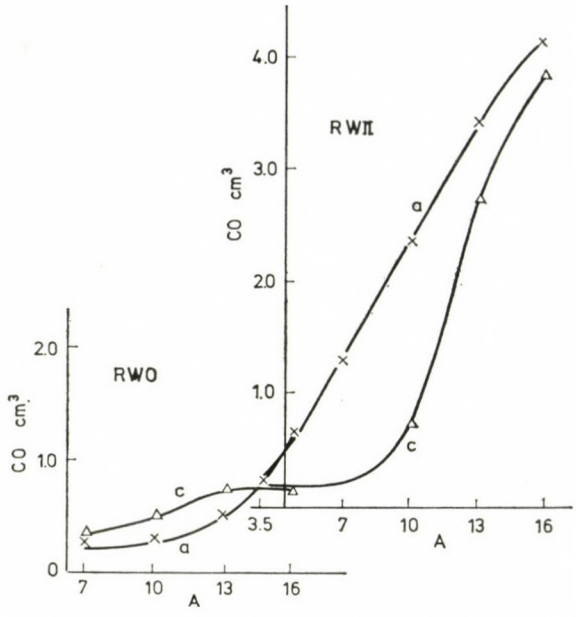



*Fig. 9.* Comparison of the effect of RW 0 and RW II electrodes. CO production of the arc as a function of current. *a*: anodic, *c*: cathodic excitation

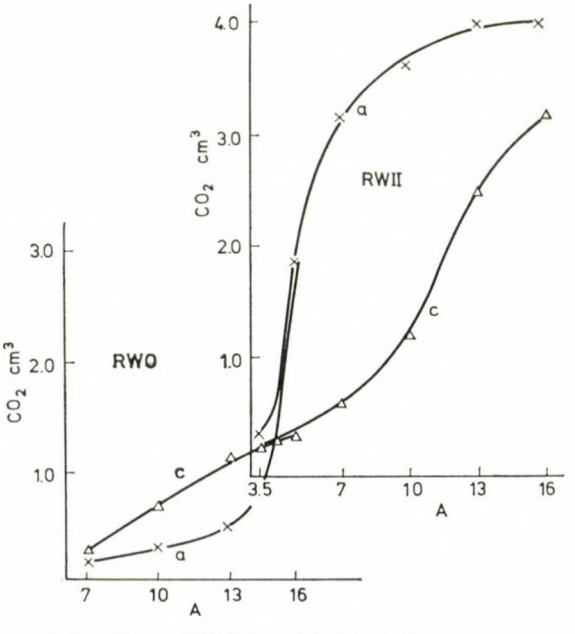



*Fig. 10.* Comparison of the effect of RW 0 and RW II electrodes. $CO_2$ production of the arc as a function of current. *a*: anodic, *c*: cathodic excitation

excitation with the RW 0 carbon electrode intersect at about 15 A. The temcerature circumstances at this current corresponds to that at 3.5 A for the RW II parbon. Of course, the $\Sigma\%$ values (Fig. 11) for the reactions, and the $CO_2$ to CO volume ratios calculated from the measured values (Fig. 12) can be fitted in the same way. The correspondence of these values is further proof for the

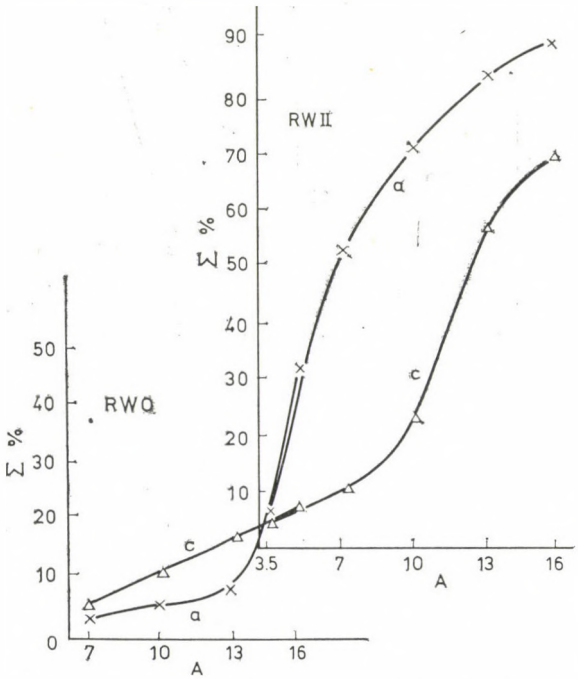



*Fig. 11.* Comparison of the effect of RW 0 and RW II electrodes. Per cent reaction as a function of current. *a*: anodic. *c*: cathodic excitation

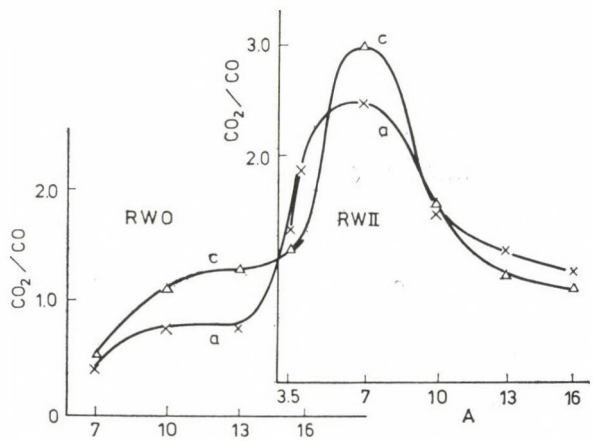



*Fig. 12.* Comparison of the effect of RW 0 and RW II electrodes. $CO_2$/CO ratio *vs.* current. *a*: anodic, *c*: cathodic excitation

close similarity of conditions. Accordingly, for the two different kinds of carbon holding electrodes, the same changes in temperature occur at different currents. The above observations refer to a burning time of 10 s, since the values vary with time.

The curves for the $CO_2$ to CO ratios also show that an optimum temperature exists, where the production of $CO_2$ is the greatest. This fact and the possibility for fitting the $CO_2$/CO ratios to each other is final proof that in the reaction inside the electrode material only an inferior, if any role is played by the oxidation and reduction tendencies of electric origin [5] which regulate the electrode surface reactions. From the point of view of oxidation and reduction properties, now the change in the $CO_2$/CO ratios is just the opposite. Namely, an electrode surface reaction would be only conceivable, if the $CO_2$ formed reacted with the carbon electrode, thus producing CO, which is oxidation for the carbon. In anodic excitation (oxidation tendency) this oxidation should be more extensive at higher currents. Here, however, the temperature of the reaction space plays the decisive role. This was to be expected, because the oxidation and reduction tendencies in electrode surface reactions are due to the potential differences between the electrode and the plasma. Such a potential difference inside the electrode material is not possible. Thus, the reactions

$$CuO + C = CO + Cu$$

and

$$2\,CuO + C = CO_2 + 2Cu$$

may only depend on the temperature, but not on potential differences, because they do not exist.

It is also to be mentioned that for the two carbon types the $I_{Cu\ I}$ (intensity of the 282.4 nm Cu atom line) curves *vs.* current can be connected only *via* an intermediate section drawn with a broken line in Fig. 13. This means that the change in intensity of the spectral lines is delayed by different electrode temperatures. The spectral characteristics, at the same time, ($\Delta Y_{Cu,\,II,\,I} = \Delta Y_{Cu\ 237.0/282.4}$ multiplied by 100) can be connected, as proven in Fig. 14. This means that the average temperature of the plasma varies much less than the intensity of the atom line. The positions of the two coordinate systems for the $\Delta Y_{Cu\ II,\,I}$ curves are opposite to those of the intensity curves. In this case curve for the RW 0 carbon lies higher. This is due to the fact that the intensity values of the 282.4 nm Cu atom line are in the denominator of the spectral character data. The intensity of the ion line is, at the same time, less sensitive to the secondary effects. Thus the non-connectibility of the intensity values, with a fairly good correspondence of the spectral character data, may be due to changes in the evaporation, not describable by the spectral character. The evaporation and line intensities, when using low temperature electrodes, are determined by the

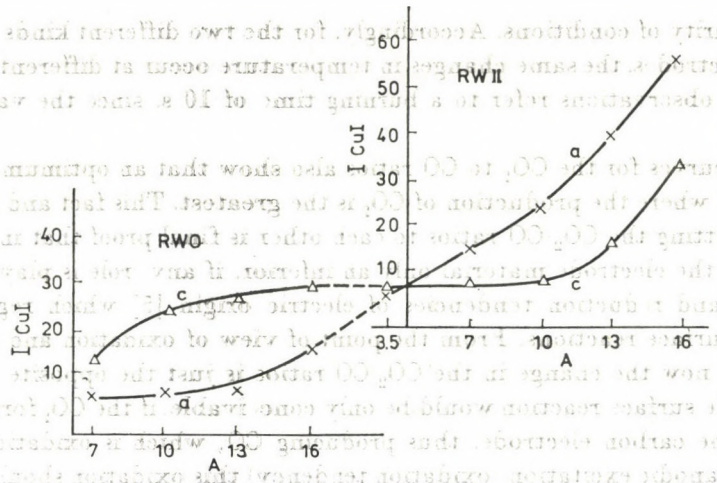



*Fig. 13.* Comparison of the effect of RW 0 and RW II electrodes. Intensity of the 282. 4 nm Cu atom line *vs.* current. *a*: anodic. *c*: cathodic excitation

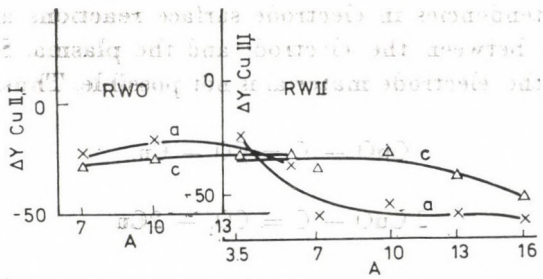



*Fig. 14.* Comparison of the effect of RW 0 and RW II electrodes. Spectral character ($\Delta Y_{\text{Cu II.I}} = \Delta Y_{\text{Cu 227.0}/\text{282.4}}$) *vs.* current. *a*: anodic, *c*: cathodic excitation

temperature of the burning spot and of its immediate surrounding, but, if the whole electrode glows up, then the temperature of the whole filling changes more strongly and this increases the extent of reaction and the spectral line intensity, too.

## REFERENCES

[1] SZABÓ, Z. L., DOBOLYI-FEJÉRDY, H.: Acta Chim. Acad. Sci. Hung., **96.** 189 (1978)
[2] SZABÓ, Z. L., DOBOLYI-FEJÉRDY, H.: Acta Chim; (Budapest), **80,** 365 (1974)
[3] SZABÓ, Z. L., TÓTH, I.: Acta Chim. (Budapest), **73,** 363 (1972)
[4] SZABÓ, Z. L., DOBOLYI-FEJÉRDY, H.: Acta Chim. Acad, Sci. Hung., **97.** 111 (1978)
[5] SZABÓ, Z. L.: Spectrochim. Acta, **29/B,** 231 (1974)

Zoltán László SZABÓ: H-1088 Budapest, Múzeum krt. 4/b,
Hajna DOBOLYI—FEJÉRDY: H-1126 Budapest, Csörsz u. 35—43.

*Acta Chimica Academiae Scientiarum Hungaricae, Tomus 98 (2), pp. 157—162 (1978)*

# SOME CHEMICAL REACTIONS OF THE ELECTRODE GAP AND THEIR ROLE IN SPECTROCHEMICAL ANALYSIS, XXXII

## BEHAVIOUR OF METAL OXIDES IN THE ARC IN AN ARGON FLOW. ROLE OF THE METAL OXIDE TO CARBON POWDER RATIO WITH RW 0 AUXILIARY ELECTRODES

Z. L. SZABÓ and H. DOBOLYI—FEJÉRDY[1]

*(Department of Inorganic and Analytical Chemistry, L. Eötvös University, Budapest, and [1]Hungarian Optical Works, Budapest)*

Received September 13, 1977

The extent of chemical reactions is smaller with more graphitic RW 0 carbon electrodes, which warm up less in arc excitation, but they exert a greater effect on the spectra than the more amorphous RW II carbons, warming up more strongly. The thermochemical reactions have a double effect: they cause greater evaporation of the sample, due to the heat of reaction, and the gaseous products change the composition of the plasma, thus changing the excitation ratio of the metal vapours in the plasma, as well. This latter effect is more pronounced for the more active (decomposing) metal oxides. For the analytical investigation of powder samples, it seems to be more advantageous to use an excess of carbon powder.

In our earlier publications, the role of the amount of carbon powder in metal oxide – carbon mixtures has been described [1, 2]. The carbon used in those experiments as holding and counter electrode was the amorphous RW II type produced by the Rigsdorff Werke, GmbH. This electrode, owing to its poor thermal conductivity, glows up strongly in the arc, consequently, produces more extensive reactions of the material in its bore, thus being more suitable for investigation. However, we made our further experiments with the more graphitic RW 0 electrode type in order to clarify the role of the nature of the holding electrode [3]. In these experiments, we established that the conversion diminished owing to the colder holding electrode. It seemed to be interesting to study the role of the amount of carbon powder in the mixture in this colder electrode and the effect of the reaction on the spectrum. As carbon powder in the mixtures, the Electrocarbon Topolčany (Czechoslovakia) SU-601 carbon was used again. In order to be able to investigate the role or the polarity of the holding electrode, we used A.C. polarized arc excitation ignited at maximum voltage, as done earlier. Correspondingly, the letters *a* and *c* in the figures refer to anodic and cathodic excitation of the sample, respectively. Since in the case of the current applied, the reactions occur in the first few seconds (4), the burning time of the arc was chosen to be 10 s. Because of the colder electrode material, a relatively high current of 16 A was used. As model substances, we selected the mixtures of the reactive CuO and the quite inert $Al_2O_3$ with carbon powder in various ratios. In order to avoid other parallel reactions, we applied

a stream of argon at a flow rate of 860 $cm^3$/min. The amounts of CO and $CO_2$ produced by the burning of the arc [5] and the spectral line intensity of the metal in the oxide were measured. Since the reactions in the mixture are limited by the quantities of the metal oxide and carbon powder, respectively, on the horizontal axes of the coordinate systems in our figures, we used two-way numbering, as earlier [1, 2]. From left to right, the mole number of the metal oxide in the bore of the electrode increases, while that of carbon increases in the opposite direction. The values reffering to $Al_2O_3$ are oxygen equivalents calculated by dividing the molecular weight of $Al_2O_3$ by 3. This is marked on the corresponding figures by m 1/3 $Al_2O_3$.

## Results

First, we studied the CuO – carbon powder mixtures. Figure 1 shows the amount of CO produced in the arc *vs.* the composition of the mixture, while Fig. 2 illustrates the same for $CO_2$. The shapes of the curves are the same as with RW II carbon holding electrodes [2]. In spite of the greater current (with RW II electrodes an average current of 7 A was only used), for the RW 0 electrodes, cooling more rapidly, the amounts of CO and $CO_2$ obtained by anodic excitation are lower, but with cathodic excitation, in accordance with expectations, they are higher than with the RW II carbon. It is interesting that the place of the maximum does not change, it lies again between the optimum for the CO and $CO_2$ formation, *i. e.* between metal oxide to carbon mole ratios of 1 : 1 and 2 : 1. Both the places of maxima, and the cathodic and anodic values provide further evidence that the two, carbon oxide producing reactions are to some extent separated in space. The increase of the cathodic values can be connected with larger burning spot due to greater current, as the average temperature of the whole mass of electrode and charge being now lower than with

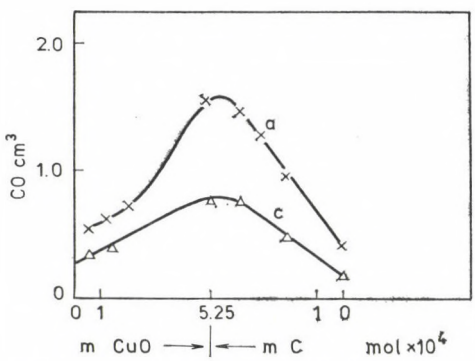



*Fig. 1.* Quantity of CO produced in the arc *vs.* composition of the CuO + C powder mixture. *a*: anodic, *c*: cathodic excitation

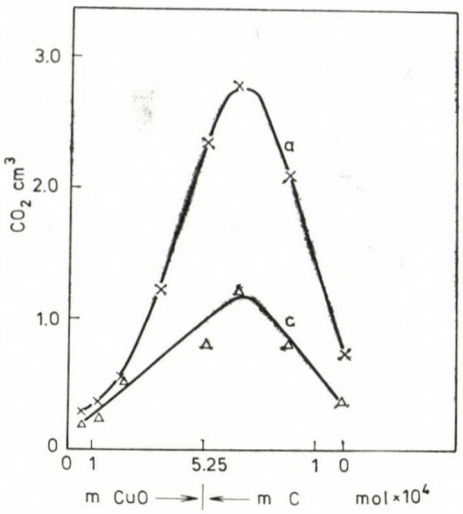



*Fig. 2.* Quantity of $CO_2$ produced in the arc *vs.* composition of the CuO + C powder mixture. *a*: anodic, *c*: cathodic excitation

the RW II carbons at lower current. The effect of incresing current is depreciated by the better thermal conductivity of the holding electrode, therefore, the inner part of the filling where most of the $CO_2$ is produced, does not warm up proportionally to the current. The facts that the $CO_2$ values obtained by cathodic excitation also increase and that the positions of the maxima of the curves remain unchanged, prove that the two reactions are parallel and not independent of each other. The reaction partners are common in the formation of CO an $CO_2$ and the zones of the production of the two types of carbon oxides overlap. We have proved earlier [6] that the $CO_2 + C = 2\ CO$ reaction which also connects the formation of the two carbon oxides, occurs partly also in the filling.

The curves in Fig. 3, showing the intensity of the Cu 282.4 nm atom line *vs.* the composition of the mixture, are of interest. The first difference relative to the results obtained with RW II auxiliary electrodes is that the curve for cathodic excitation shows greater line intensities owing to the greater current, as is to be expected. At the same time, the curve for anodic excitation changes only slightly. Consequently, the most pronounced difference is that now the cathodic excitation yields the more intensive spectrum, as was also the case in our experiments with variable current [3]. In this case the smaller heat of reaction, relative to the greater electric energy, has a smaller effect on the evaporation of the sample. As has been shown in our work on metal electrodes [7], in the absence of chemical reactions or in the case of their relatively minor extent, cathodic excitation is generally more intensive. The fact, however, that with gas analytical methods we have obtained higher reactions on anodic excitation

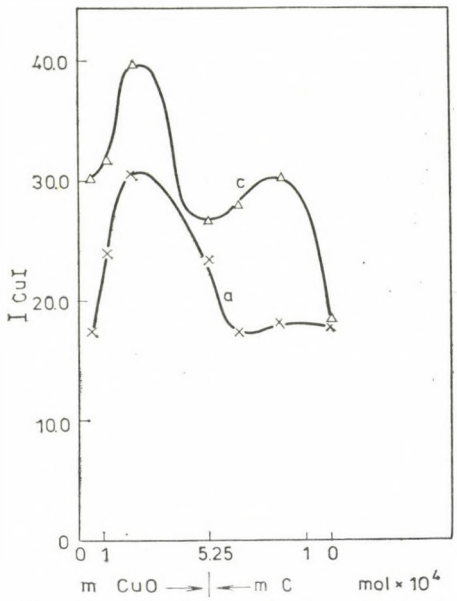



*Fig. 3.* Intensity of the 282.4 nm Cu atom line as a function of the composition of the CuO + C powder mixture. *a*: anodic, *c*: cathodic excitation

points again to the occurrence of these reactions mainly in the inner part of the filling. Here, the temperature is lower than at the burning spot of the arc on the electrode, where the evaporation of the sample, determining the spectrum intensity, occurs. The released heat of reaction warms the whole mass of the sample and only through this does it affect the evaporation which is stronger from the warmer electrode [8]. At higher energies these side-effects are less pronounced.

Another important observation is that the curves with both anodic and cathodic excitation have two maxima, similarly to the intensity curves for the RW II electrode obtained with stending (1) and flowing gas atmosphere (2). In that case we attributed the two smaller maxima to the fluctuation of the experimental data, and did not discuss it in detail, though the variations were quite reproducible. But in the case of the colder RW 0 electrodes the changes are so definite that they cannot be ascribed to the fluctuation of the intensity data; on the contrary, they support the correctness of the two maxima in the curves with the RW II carbon electrodes. Another proof is that in the $\Delta Y_{\mathrm{Cu\ II,\ I}}$ spectral character data (Fig. 4) constructed from the logarithmic intensities of the former atom line and the 237.0 nm Cu ion line, only the expected small fluctuation is observed and these curves have only a single flat minimum. This means that the changes occur in the plasma but they are not describable by the spectral character. Thus, the shape of the intensity curves need further explanation.

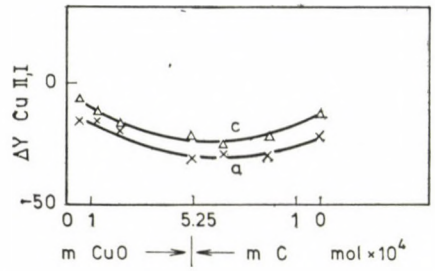



*Fig. 4.* Spectral character ($\Delta Y_{Cu\ 237\cdot0/282.4}$) *vs.* composition of the CuO + C powder mixture. *a*: anodic, *c*: cathodic excitation

Double maxima can be produced either by two, independent effects, which follow each other, thus increasing the corresponding values, or by a decreasing effect, which is opposite and occurs around the middle of a broader maximum. From earlier considerations [2], only one maximum was to be expected. The former statement about the first, ascending section of the curves is obviously valid further on, and is to be attributed to the increasing copper content of the sample. But the increasing amount of CuO results in a change of the matrix in the sample, the better glowing C content decreases, which causes a rapid fall in the evaporation and intensity. After this, the evaporation of the metallic copper formed in the reaction should become effective [2]. The second maximum, *i. e.* the second effect, which increases the intensity of the spectral lines is unjustified. Therefore, around the middle of the maximum (*e. g.* at medium component ratios), there must be another, opposite effect. The gas-forming reaction, as a function of the composition of the powder mixture shows a sharp maximum in the middle of the curve. We have observed [9] that on removing all or part of the carbon oxides with the flow, the line intensities increase. This removal is never satisfactory due to diffusion processes. It is very probable, therefore, that the minimum in the middle of the intensity curves, which seems to cause a double maximum, is due to the remaining carbon oxides in the plasma. This assumption is supported by the following simple graphical solution: We added the two carbon oxide volumes obtained (in mm on the graph) and the intensity values measured (in mm). This was done only for the sake of demonstrations as the two curves cannot be added because of the different units. On anodic excitation (Fig. 5), from the middle of the resulting curve, the minimum completely disappears, and on cathodic excitation also significantly diminishes (Fig. 6). It is more characteristic that the shape of these resultant curves and the position of their maxima is very similar to the intensity curves ($I_{Al,\,I}$ Al 305. 0 nm, Fig. 7) obtained directly for $Al_2O_3$ + C mixtures, which scarcely produce carbon oxides, also with RW 0 carbon auxiliary electrodes. The maximum of the resultant anodic curve for CuO is similarly lower and broader and is shifted toward smaller metal contents, as for $Al_2O_3$; the

cathodic curve is likewise higher, and its sharper maximum is also shifted toward smaller metal contents. The good agreement is probably partly due to the favourable ratio of the scales of the vertical axes of the summed curves. As the horizontal axes are the same for the curves, we regard this agreement as proof for the correctness of our assumption.

The CO and $CO_2$ volumes as functions of the composition of the $Al_2O_3$ + C powder mixture are shown in Figs 8 and 9 for RW 0 auxiliary electrodes (current 16 A). The shapes of these curves are very similar to that obtained

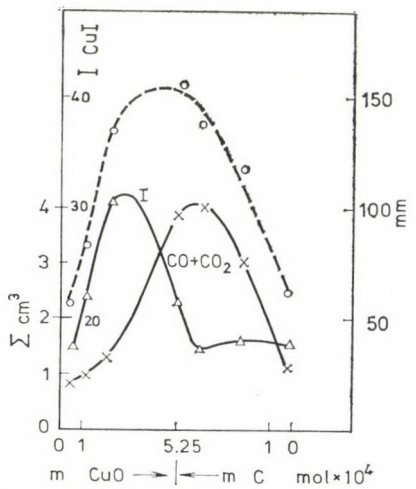



*Fig. 5.* Sum of the gas analytical and line intensity values. Anodic excitation

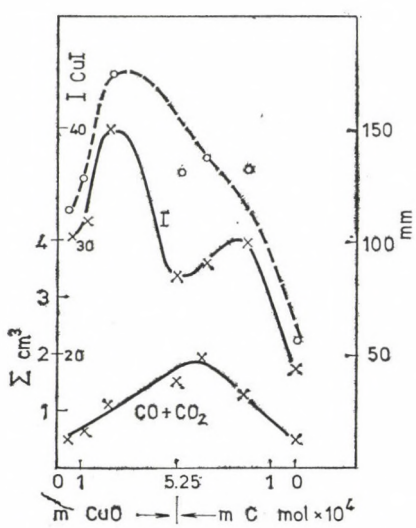



*Fig. 6.* Sum of the gas analytical and line intensity values. Cathodic excitation

with the RW II carbon holding electrode [2]. However, the CO production of the arc significantly increases due to the higher current, similarly to CuO + C powder mixtures. In this case more material evaporates and decomposes on the top of the charge and reacts at a suitable temperature in the outer parts of the plasma. It can also be observed that the CO production curves are similar to the intensity curves for aluminium in Fig. 7, mainly in the case of cathodic excitation. This proves that the same amounts of evaporated and decomposed material are involved in the reaction as in the formation of the spectral lines. The $CO_2$ production, at the same time, is very small as observed above. For the stable $Al_2O_3$ most of the filling warms up to no effect, there is practically no decomposition and $CO_2$ production.

In the spectral character curves, $\Delta Y_{Al\,II,\,I}$ (Fig. 10) constructed from the 281.6 nm Al ion line and the former 305.0 nm Al atom line it is to be seen that, if the evaporation of the sample and, consequently, the metal concentration in the plasma increases, the average temperature of the plasma decreases.

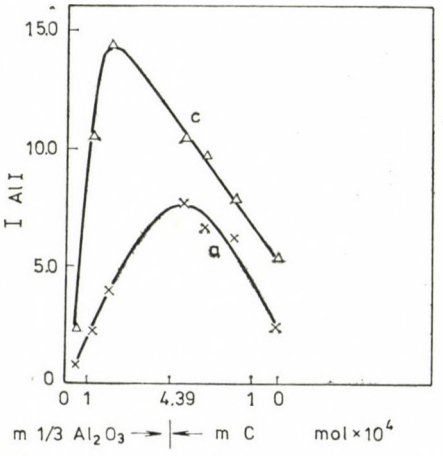



*Fig. 7.* Intensity of the 305.0 Al atom line ($I_{Al\,I}$) *vs.* composition of the $Al_2O_3$ + C powder mixture. *a*: anodic, *c*: cathodic excitation

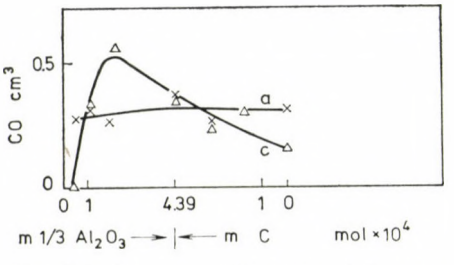



*Fig. 8.* Quantity of CO produced in the arc as a function of the composition of the $Al_2O_3$ + C powder mixture. *a*: anodic, *c*: cathodic excitation

The changes here are just the opposite to those in the intensity curves, and these results are scarcely modified by carbon oxides in the plasma, because their quantity with $Al_2O_3$ + C powder mixtures is very small.

In summary, one can establish that the effect of chemical reactions on the spectrum may be more significant with colder RW 0 carbon electrodes than with the less conductive RW II carbons. The reactions have a double effect: they warm the sample and lead to better evaporation; on the other hand, the

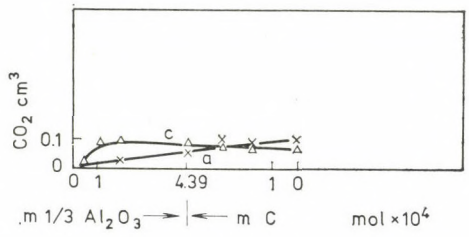



*Fig. 9.* Quantity of $CO_2$ produced in the arc *vs.* composition of the $Al_2O_3$ + C powder mixture. *a*: anodic, *c*: cathodic excitation

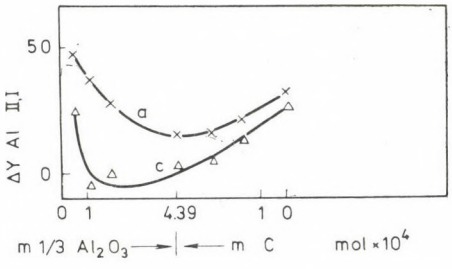



*Fig. 10.* Spectral character ($\Delta Y_{Al\ 281.6/305.0}$) as a function of the composition of the $Al_2O_3$ + C powder mixture. *a*: anodic, *c*: cathodic excitation

gaseous reaction products change the composition of the plasma, this phenomenon affecting the intensity of the spectral lines more than the thermochemical reaction itself. Therefore, for the investigation of powder samples it is more convenient to use the warmer RW II carbon as auxiliary electrode. Clearly, it is advantageous to use a certain excess of carbon powder, which maintains reductive conditions, suppresses the reactions, and, at the same time, increases the evaporation of the sample and the intensity of the spectral lines. The optimum weight ratio, however, varies from material to material and depends also on the polarity of the holding electrode.

## REFERENCES

[1] SZABÓ, Z. L., DOBOLYI-FEJÉRDY, H.: Acta Chim. Acad. Sci. Hung. **97.** 13 (1978)
[2] SZABÓ, Z. L., DOBOLYI-FEJÉRDY, H.: Acta Chim. Acad. Sci. Hung. **97.** 125 (1978)
[3] SZABÓ, Z. L., DOBOLYI-FEJÉRDY, H.: Acta Chim. Acad. Sci. Hung. **98,** 147 (1978)
[4] SZABÓ, Z. L., DOBOLYI-FEJÉRDY, H.: Acta Chim. Acad. Sci. Hung. **97.** 111 (1978)
[5] SZABÓ, Z. L., TÓTH, I.: Acta Chim. (Budapest), **73,** 363 (1972)
[6] SZABÓ, Z. L., DOBOLYI-FEJÉRDY, H.: Acta Chim. Acad. Sci. Hung. **97.** 137 (1978)
[7] SZABÓ, Z. L.: Acta Chim. (Budapest), **85,** 13 (1975)
[8] SZABÓ, Z. L., SZAKÁCS, O.: Acta Chim. (Budapest), **73,** 143 (1972)
[9] SZABÓ, Z. L., DOBOLYI-FEJÉRDY, H.: Acta Chim. Acad. Sci. Hung. **97.** 27 (1978)

Zoltán László SZABÓ: H-1088 Budapest, Múzeum krt. 4/b.
Hajna DOBOLYI—FEJÉRDY: H-1126 Budapest, Csörsz u. 35—43.

*Acta Chimica Academiae Scientiarum Hungaricae, Tomus 98 (2), pp. 167—174 (1978)*

# FORCE FIELD STUDY OF CHLOROFORM BY PARAMETRIC METHOD

K. RAMASWAMY and S. KARUNANITHI

*(Department of Physics, Annamalai University, Annamalainagar 608101, Tamilnadu, S. India)*

Received August 26, 1977

Parametric representation method was applied to study the force field of chloroform. The isotopic shifts of $^{13}CHCl_3$ and $^{13}CH^{37}Cl_3$ were utilised to fix the angle parameters of the $a_1$-species of vibrations. The Coriolis coupling constants and the isotopic shifts of $^{13}CHCl_3$ were used to determine the angle parameters of the e-species of vibrations. The force constants, mean amplitudes of vibration and rotational distortion constants were also calculated.

## 1. Introduction

It has been shown in earlier papers [1, 2] that the Coriolis coupling constants and isotopic frequencies can be successfully utilized for the evaluation of unambiguous molecular force fields of both degenerate and non-degenerate species by parametric method. In the present paper force field study is extended to chloroform for which recent experimental values on isotopic shifts, Coriolis coupling constants and rotational distortion constants are available for this molecule.

The infrared spectra of $HCCl_3$ and $DCCl_3$ were studied by ROUFF and BURGER [3]. The vibrational fundamentals of $CHCl_3$ and its various isotopically substituted species $^{13}CHCl_3$, $^{13}CH^{37}Cl_3$ and $CDCl_3$ were analyzed by SCHMIDT and MULLER [4]. The vapour phase Raman spectra of $H^{12}CCl_3$ and $H^{13}CCl_3$ were recorded and the Raman band contours of the *e*-species fundamentals were analyzed by CLARK *et al* [5]. ROUFF and ANTTILA [6] estimated the value of $\zeta_4$ from the structure of $(\nu_1 + \nu_4)$ bands and the centrifugal distortion constants were experimentally determined by MCLAY and WINNEWISSER [7]. The molecular geometry used here is essentially the same as those of ROUFF and BURGER [3] and the spectral data used for the present calculations are listed in Table I.

## 2. Theoretical considerations

The force constant matrix in parametric method is given by the relation

$$F = \widetilde{L_0^{-1}} A \Lambda \tilde{A} L_0^{-1}, \tag{1}$$

where $L_0$, $A$ and $\Lambda$ have the same meaning as in Ref. [2]. Since the vibrations of $CHCl_3$ are of $3\times3$ order, $A$ can be chosen as,

**Table I**

*Vibrational frequencies ($cm^{-1}$), bond distances (Å), bond angles, Coriolis coupling constants and rotational distortion constants (KHz) for chloroform*

| | $^{12}CHCl_3$ | $^{13}CHCl_3$ | $^{13}CH^{37}Cl_3$ |
|---|---|---|---|
| $\nu_1$ | 3033.1 | 3023.5 | 3023.5 |
| $\nu_2$ | 675.5 | 658.0 | 653.0 |
| $\nu_3$ | 366.8 | 364.3 | 356.1 |
| $\nu_4$ | 1219.7 | 1217.0 | |
| $\nu_5$ | 773.7 | 750.5 | [4] |
| $\nu_6$ | 259.9 | 259.4 | |
| | $D_{(C-H)} = 1.1$ Å | | |
| | $d_{(C-Cl)} = 1.758$ Å | | [3] |
| | Cl $\hat{C}$ Cl $= 111.3°$ | | |
| | H $\hat{C}$ Cl $= 107.6°$ | | |
| | $\zeta_4 = 0.99$ | | [6] |
| | $\zeta_5 = (0.87)$ | | |
| | $\zeta_6 = (-0.90)$ | | [3] |
| | $D_J = 1.52$ KHz | | |
| | $D_{JK} = -2.50$ KHz | | [7] |

The Coriolis coupling constants given in brackets are calculated values taken from Ref. [3].

$$A = \begin{bmatrix} C_\chi & S_\chi & 0 \\ -S_\chi & C_\chi & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} C_\Theta & 0 & S_\Theta \\ 0 & 1 & 0 \\ -S_\Theta & 0 & C_\Theta \end{bmatrix} \begin{bmatrix} 1 & 0 & 0 \\ 0 & C_\phi & S_\phi \\ 0 & -S_\phi & C_\phi \end{bmatrix}, \tag{2}$$

where $C$ and $S$ stand for the cosine and sine values of the respective angle parameters. The isotopic frequencies can be directly related to the angle parameters through the relation given by JORDANOV and NIKOLOVA [8]. This is modified as

$$\Delta\Lambda/\Lambda = \tilde{A}\, B\, A\,, \tag{3}$$

where $B = \widetilde{L_0^{-1}}\, \Delta G\, L_0^{-1}$ to suit the present calculations. Expanding equation (3), we get the explicit relationships between the isotopic shifts and the three angle parameters. For a particular isotopic substitution (say $^{12}CHCl_3$ — $^{13}CHCl_3$ in the present case) the relations are:

$$\Delta\Lambda_i/\Lambda_i = [B_{ii}C_\chi^2 + B_{jj}S_\chi^2 - 2B_{ij}S_\chi C_\chi]C_\Theta^2 + B_{kk}S_\Theta^2 + 2S_\Theta C_\Theta [B_{jk}S_\chi - B_{ik}C_\chi], \quad (4)$$

$$\Delta\Lambda_j/\Lambda_j = p\,C_\phi^2 + q\,S_\phi^2 + 2r\,C_\phi S_\phi, \quad (5)$$

$$\Delta\Lambda_k/\Lambda = p\,S_\phi^2 + q\,C_\phi^2 - 2r\,C_\phi S_\phi, \quad (6)$$

where

$$p = [B_{ii}S_\chi^2 + B_{jj}C_\chi^2 + 2B_{ij}C_\chi S_\chi],$$

$$q = [B_{ii}C_\chi^2 + B_{jj}S_\chi^2 - 2B_{ij}S_\chi C_\chi]S_\Theta^2 + B_{kk}C_\Theta^2 - 2S_\Theta C_\Theta [B_{jk}S_\chi - B_{ik}C_\chi],$$

$$r = [B_{ij}(C_\chi^2 - S_\chi^2) + (B_{ii} - B_{jj})C_\chi S_\chi]S_\Theta + [B_{jk}C_\chi + B_{ik}S_\chi]C_\Theta.$$

Here $B_{ij}$'s are the elements of the $B$ matrix. Since '$A$' is an orthonormalized matrix,

$$\sum \Delta\Lambda_i/\Lambda_i = \sum B_{ii} \quad (7)$$

and from the first two equations (4) and (5) the third equation (6) can be derived using the above relation and hence, the equations (5) and (6) will yield identical solutions for $\phi$.

For another isotopic substitution, if available (say $^{12}CHCl_3$ — $^{13}CH^{37}Cl_3$ in the present case) similar relationships with the same physical meaning can be derived and they are similar to the equations (4) to (6) in which $\Delta\Lambda_i/\Lambda_i$'s and $B_{ij}$'s are replaced by $\Delta\Lambda_i^*/\Lambda_i^*$'s and $B_{ij}^*$'s and these relations can be used for the non-degenerate species of vibrations. For the degenerate species of vibrations, the relation given by ANANTHAKRISHNAN and ARULDHAS [9]

$$\zeta = \tilde{A}\,J\,A, \quad (8)$$

where $J = L_0^{-1}\,C^\alpha\,\widetilde{L^{-1}}_0$, can be used to derive the relationships between Coriolis coupling constants and the angle parameters. These expressions are also similar to those obtained previously for isotopic shifts in which $\Delta\Lambda_i/\Lambda_i$'s and $B_{ii}$'s are replaced by $\zeta_i$'s and $J_{ij}$'s. These relations can be used along with the relations for isotopic shifts.

## 3. Results and discussion

For the *e*-species of vibrations, the Coriolis coupling constant $\zeta_4$ and isotopic shift $\Delta\Lambda_4/\Lambda_4$ were utilised in their respective equations to obtain $\chi$, $\Theta$ values. For various values of $\chi$ in the range $-90°$ to $90°$, the possible intersections of the different $\chi - \Theta$ curves were obtained. The relevant portion of the curve, where the $\chi - \Theta_1$ and $\chi - \Theta_2$ curves of $\zeta_4$ and $\chi - \Theta_1$ curve of $\Delta\Lambda_4/\Lambda_4$ intersect is shown in Fig. 1. The two graphical solutions are: $\chi = -8.408°$; $\Theta_1 = -0.536°$

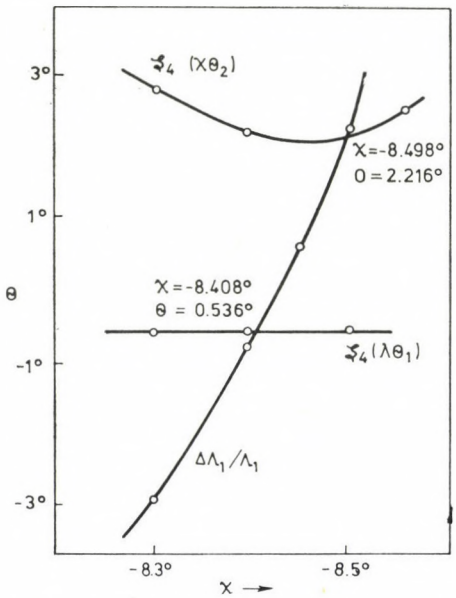



*Fig. 1.* Plot of $\chi$ *versus* $\theta$ curves obtained using $\zeta_4$ and $\Delta\Lambda_4/\Lambda_4$ for *e*-species of $CHCl_3$

and $\chi = -8.498°$; $\Theta_2 = 2.216°$. Use of other isotopic shifts $\Delta\Lambda_5/\Lambda_5$ and $\Delta\Lambda_6/\Lambda_6$ along with the above solutions for $\chi$ and $\Theta$ yield four values for $\emptyset$. There are four sets of angle parameters [$\chi\Theta_1\emptyset_1$, $\chi\Theta_1\emptyset_2$, $\chi\Theta_2\emptyset_3$ and $\chi\Theta_2\emptyset_4$] and out of these four sets the best solution has to be critically evaluated by comparing all the molecular constants with the experimental values. The calculated force constants, Coriolis coupling constants and isotopic frequencies for all the four solutions are reported in Table II.

The four solutions are obtained by the use of $\zeta_4$, $\nu_4^*$, $\nu_5^*$ and $\nu_6^*$, and hence, all these solutions and constants are reproduced. A critical survey of the table reveals that the solutions $\emptyset_1$ and $\emptyset_3$ correspond to inverse assignment and they are neglected. The calculated force constants and the other Coriolis coupling constants for $\emptyset_2$ and $\emptyset_4$ compare well with the reported values of SCHMIDT and MULLER [4]. (The isotopic frequencies, Coriolis coupling constants and structural parameters used in the present work are the same as those of Schmidt and Muller and hence, taken for comparison). It is seen from the table that the comparison is more closer for $\emptyset_2$ than for $\emptyset_4$. Hence, the solution $\chi = -8.408°$, $\Theta = -0.536°$ and $\emptyset = 12.62°$ is taken to be the best fit angle parameters for *e*-species of $CHCl_3$.

For $a_1$ species of vibrations, the $\chi$ and o solution is determined graphically using $\Delta\Lambda_1/\Lambda_1$ and $\Delta\Lambda_1^*/\Lambda_1^*$ and is shown in Fig. 2. The graphical solution is $\chi = -2.31°$ and $\Theta = 0.013°$. The other isotopic species were utilised and four values for $\emptyset$ were obtained. For all these solutions isotopic frequencies and rotational distortion constants were calculated and reported in Table III. As seen

**Table II**

*The parametric angles, force constants*[a]*, isotopic frequencies ($cm^{-1}$), and Coriolis coupling constants calculated for different solutions obtained for the 'e'-species of vibration of $CHCl_3$*

(1) $\chi = -8.408°$, $\theta_1 = -0.536°$
(2) $\chi = -8.498°$, $\theta_2 = 2.216°$

| Molecular constant | $\chi = -8.408°$ $\theta_1 = -0.536°$ | | $\chi = -8.498°$ $\theta_2 = 2.216°$ | | Schmidt Muller [4] |
|---|---|---|---|---|---|
| | $\phi_1 = -17.14°$ | $\phi_2 = 12.63°$ | $\phi_3 = -16.42°$ | $\phi_4 = 13.35°$ | |
| $F_{44}$ | 0.8263[b] | 2.7842 | 0.9163 | 2.9200 | 2.67 |
| $F_{45}$ | −0.2138 | −0.3892 | −0.2065 | −0.4697 | −0.32 |
| $F_{46}$ | 0.1390 | 0.2493 | 0.2836 | 0.3915 | 0.30 |
| $F_{55}$ | 3.4400 | 1.0674 | 3.3250 | 1.0332 | 1.07 |
| $F_{56}$ | 0.2943 | 0.1769 | 0.1333 | −0.0092 | 0.05 |
| $F_{66}$ | 0.6757 | 0.6773 | 0.6770 | 0.6447 | 0.67 |
| $^{13}CHCl_3$ | | | | | |
| $\nu_4^*$ | 1217.0 | 1217.0 | 1217.0 | 1217.0 | 1217.0 |
| $\nu_5^*$ | 750.37 | 750.37 | 750.37 | 750.37 | 750.4 |
| $\nu_6^*$ | 259.36 | 259.36 | 259.36 | 259.36 | 259.4 |
| $\zeta_4$ | 0.990 | 0.990 | 0.990 | 0.990 | 0.99 |
| $\zeta_5$ | 0.836 | 0.849 | 0.848 | 0.836 | 0.87 |
| $\zeta_6$ | −0.862 | −0.875 | −0.875 | −0.863 | −0.90 |

[a] Stretching force constants are in mdyn/Å, stretch-bend interaction force constants are in mdyn and bending force constants are in mdyn Å (1 mdyn/Å = $10^2$ N/m).

[b] This number of significant figures is retained to secure internal consistancy in the calculations.

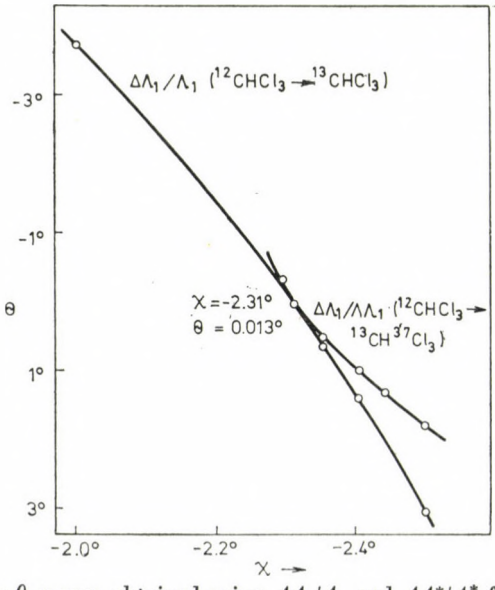



*Fig. 2.* Plot of $\chi$ *versus* $\theta$ curves obtained using $\Delta\Lambda_1/\Lambda_1$ and $\Delta\Lambda_1^*/\Lambda_1^*$ for $a_1$-species of $CHCl_3$

**Table III**

*The parametric angles, force constants[a], isotopic frequencies ($cm^{-1}$) and rotational distortion constants (KHz), calculated for different sets of angles for the '$a_1$'-species of vibration of $CHCl_3$*

$\chi = -2.32°$, $\Theta = 0.013°$ (from Fig. 2)

| Molecular constants | $^{12}CHCl_3-{}^{13}CHCl_3$ | | $^{12}CHCl_3-{}^{13}CH^{37}Cl_3$ | | Schmidt Muller [4] |
|---|---|---|---|---|---|
| | $\emptyset_3 = -32.81°$ | $\emptyset_2 = 24.63°$ | $\emptyset_3 = -30.7°$ | $\emptyset_4 = 22.59°$ | |
| $F_{11}$ | 5.0331[b] | 5.0331 | 5.0335 | 5.0335 | 5.04 |
| $F_{12}$ | −0.1098 | 0.1351 | −0.1028 | 0.1301 | 0.15 |
| $F_{13}$ | −0.0875 | 0.0127 | −0.0888 | 0.0067 | −0.02 |
| $F_{22}$ | 3.4544 | 4.5251 | 3.3006 | 4.3249 | 4.21 |
| $F_{23}$ | 2.2538 | 0.2984 | 2.1224 | 0.2651 | 0.25 |
| $F_{33}$ | 2.8581 | 1.0790 | 2.8168 | 1.1245 | 1.15 |
| $^{13}CHCl_3$ | | | | | |
| $\nu_1^*$ | 3023.5 | 3023.5 | 3023.5 | 3023.5 | 3023.5 |
| $\nu_2^*$ | 658.93 | 658.94 | 658.27 | 658.31 | 658.0 |
| $\nu_3^*$ | 364.12 | 364.11 | 364.48 | 364.46 | 364.3 |
| $^{13}CH^{37}Cl_3$ | | | | | |
| $\nu_1^*$ | 3023.5 | 3023.5 | 3023.5 | 3023.5 | 3023.5 |
| $\nu_2^*$ | 653.0 | 653.0 | 652.84 | 652.85 | 653.0 |
| $\nu_3^*$ | 356.01 | 356.1 | 356.18 | 356.18 | 356.1 |
| $D_J$ | 1.671 | 1.488 | 1.678 | 1.508 | (1.52 |
| $D_K$ | 1.232 | 1.146 | 1.188 | 1.152 | — |
| $-D_{JK}$ | 2.763 | 2.495 | 2.722 | 2.516 | 2.50)* |

[a,b]: as given in Table II
* Ref. [7].

from the table, the isotopic frequencies $\nu_2^*$ and $\nu_3^*$ of $^{13}CHCl_3$ were exactly reproduced for angles $\emptyset_1$ and $\emptyset_2$ and $\nu_2^*$ and $\nu_3^*$ of $^{13}CH^{37}Cl_3$ were reproduced for $\emptyset_2$ and $\emptyset_4$. It is found that the angles $\emptyset_1$, $\emptyset_2$, $\emptyset_3$ and $\emptyset_4$ are very close to each other and as a whole all the isotopic frequencies of $^{13}CHCl_3$ and $^{13}CH^{37}Cl_3$ are reproduced for all the four solutions and the best set cannot be selected by considering the isotopic data alone.

When the calculated rotational distortion constants for the angles $\emptyset_1$ and $\emptyset_3$ are considered, they show large deviations when compared to the experimental values [7], whereas the comparison is good for the solutions $\emptyset_2$ and $\emptyset_4$. Also, large deviations between the calculated force constants $F_{22}$ (C–Cl stretch), $F_{23}$ (C–Cl/$\delta$ $CCl_3$) and $F_{33}$ ($\delta CCl_3$) and the literature values are observed for the solutions $\emptyset_1$ and $\emptyset_3$ and are rejected. When the two solutions $\emptyset_2$ and $\emptyset_4$ are considered the solution $\emptyset_4$ can be taken to be the best since the calculated rotational distortion constants, isotopic frequencies and force constants are closer to the

**Table IV**

*The best fit force constants[a] with reference values*

| Force constants | This work | Schmidt and Muller [4] | Rouff and Burger [3] | Clark *et al.* [5] | Aroca *et al.* [10] |
|---|---|---|---|---|---|
| $F_{11}$ | 5.0335[b] | 5.04 | 4.9997 | 5.093 | 5.070 |
| $F_{12}$ | 0.1301 | 0.15 | −0.1501 | −0.862 | −0.161 |
| $F_{13}$ | 0.0067 | −0.02 | 0.2352 | −0.423 | 0.006 |
| $F_{22}$ | 4.3249 | 4.21 | 4.3325 | 4.403 | 5.471 |
| $F_{23}$ | 0.2651 | 0.25 | 0.2367 | 0.308 | 0.802 |
| $F_{33}$ | 1.1245 | 1.15 | 1.1560 | 1.168 | 2.024 |
| $F_{44}$ | 2.9200 | 2.67 | 2.4267 | 2.847 | 2.881 |
| $F_{45}$ | −0.4697 | −0.32 | −0.1692 | −0.602 | −0.437 |
| $F_{46}$ | 0.3915 | 0.30 | 0.1883 | −0.058 | 0.349 |
| $F_{55}$ | 1.0332 | 1.07 | 1.2165 | 1.530 | 1.032 |
| $F_{56}$ | −0.0092 | 0.05 | 0.2727 | 0.581 | 0.044 |
| $F_{66}$ | 0.6447 | 0.67 | 0.6821 | 0.667 | 0.679 |

[a,b]: as given in Table II

**Table V**

*The Coriolis coupling constants, rotational distortion constants (KHz) and mean amplitudes of vibration (Å) calculated for the best fit angle parameters*

| Molecular constants | Present work | Schmidt and Muller [4] | Rouff and Burger [4] | Clark *et al.* [5] |
|---|---|---|---|---|
| $\zeta_4$ | 0.990 | 0.99 | 0.987 | 0.951 |
| $\zeta_5$ | 0.849 | 0.87 | 0.905 | 0.852 |
| $\zeta_6$ | −0.875 | −0.90 | −0.927 | −0.839 |
| | Present work | McLay, Winnewisser [7] | | |
| $D_J$ | 1.508 | 1.52 | | |
| $D_K$ | 1.152 | — | | |
| $D_{JK}$ | −2.516 | −2.50 | | |
| | Present work | Cyvin [12] | Aroca *et al.* [10] | |
| $(\sigma_{C-H})$ | 0.0773 | 0.0777 | 0.0774 | |
| $(\sigma_{C-Cl})$ | 0.0521 | 0.0524 | 0.0512 | |
| $(\sigma_{Cl\ldots Cl})$ | 0.0698 | 0.0691 | 0.0679 | |
| $(\sigma_{H\ldots Cl})$ | 0.1045 | 0.1012 | 0.1084 | |

experimental values which is evident from the table. Hence, the best fit angle parameters are $\chi = -2.31°$, $\Theta = 0.013°$ and $\emptyset = 22.59°$ for $a_1$-species of vibrations of $CHCl_3$.

Normal coordinate analyses of $CHCl_3$ were carried out by ROUFF and BURGER [3], SCHMIDT and MULLER [4], CLARK *et al.* [5] and AROCA *et al.* [10]. The force constants reported by these authors along with the present values are listed in Table V. The present values compare well with the literature values and the comparison is excellent with those of SCHMIDT and MULLER. MILLS [11] on the basis of 'hybridization considerations' proposed the following conditions namely, $F_{13}$ is negative, $-F_{45}$ is equal to $F_{46}$, and $F_{46}$ is nearly equal to $\sqrt{2}\ F_{23}$. In the present work, $F_{13}$ is found to be positive, but very nearly equal to zero. Though the values of $F_{45}$ and $F_{46}$ slightly differ, they are of opposite sign to thap proposed by MILLS. The values of $F_{23}$ and $F_{46}$ are nearly equal. It was pointed out by SCHMIDT and MULLER that the positive value for CH/Cl interaction force constant is physically more meaningful than a negative value and this condition is obeyed in the present work.

The calculated Coriolis coupling constants are also in good agreement with the values of SCHMIDT and MULLER, CLARK *et al.*, and ROUFF and BURGER obtained from the refined force field. The rotational distortion constants are in excellent agreement with the experimental values of MCLAY and WINNEWISSER and the calculated mean amplitudes of various bonded and nonbonded atoms are in good agreement with those of CYVIN [12] and AROCA *et al.* [10] and the results are summarized in Table V.

In conclusion, it may be pointed out that very nearly true force field for $CHCl_3$ has been established by utilizing the all available experimental data by parametric method.

*

One of the authors (S.K) is thankful to Council of Scientific and Industrial Research, New Delhi, India for the award of Senior Research Fellowship.

## REFERENCES

[1] RAMASWAMY, K., KARUNANITHI, S.: Pramana (Communicated) 1977
[2] RAMASWAMY, K., KARUNANITHI, S.: Commemoration volume published on the occasion of sixtieth birth day of DR. PURANIK (1977)
[3] ROUFF, A., BURGER, H.: Spectrochim. Acta, **26A,** 989 (1970)
[4] SCHMIDT, K. H., MULLER, A.: J. Mol. Spectrosc., **50,** 115 (1974)
[5] CLARK, R. J. H., ELLESTAD, O. H., ESCRIBANO, R.: Mol. Phys., **31,** 65 (1976)
[6] ROUFF, A., ANTILLA, R.: Mol. Phys., **24,** 1213 (1972)
[7] MCLAY, D. B., WINNEWISSER, G.: J. Mol. Spectrosc., **44,** 32 (1972)
[8] NIKOLOV, B., JORDANOV, B.: J. Mol. Struct., **13,** 2 (1972)
[9] ANANTHAKRISHNAN, T. R., ARULDHAS, G.: J. Mol. Struct., **13,** 163 (1972)
[10] AROCA, R., ROBINSON, E. A., FORD, T. A.: J. Mol. Struct., **31,** 177 (1976)
[11] MILLS, I. M., Spectrochim. Acta: **19,** 1585 (1963)
[12] CYVIN, S. J., 'Molecular vibrations and mean square amplitudes' (1968)

K. RAMASWAMY
S. KARUNANITHI
Annamalainagar 608101, Tamilnadu,
S. India.

*Acta Chimica Academiae Scientiarum Hungaricae, Tomus 98 (2), pp. 175—182 (1978)*

# ELECTROCHEMICAL STUDY OF CARBON-SUPPORTED PALLADIUM–COPPER CATALYSTS

T. MALLÁT, J. PETRÓ and M. SCHÄFFER

*(Department of Organic Chemical Technology, Technical University, Budapest)*

Received September, 29, 1977

A study was made of palladium–copper catalysts supported on active carbon, with a palladium content of 5 wt.% and a copper contents in the range 0—40 at.%, prepared by consecutive reduction. An electrochemical method (potentiodynamic polarization) was used to investigate hydrogen adsorption and also the phases to be found on the surface. The activities of the catalysts were measured in the liquid-phase hydrogenation of cyclohexene. Apart from the copper contents of the samples, the characteristics examined depend to a large extent on the age of the catalyst, too.

## Introduction

Alloys formed between platinum or palladium and the elements of Group IB are widely used in catalytic hydrogenations. According to certain authors, a copper additive enhances the selectivity of palladium, and with such a catalyst the nitro group of the nitrochlorobenzene isomers, for example, can be reduced without dehalogenation [1]. With palladium–copper (and other platinum metal Group IB metal alloys) on an active carbon support, aromatic acid chlorides have been selectively hydrogenated to aldehydes, and good results have also been achieved in the stereospecific hydrogenation of steroids and tetracyclines [2—4]. For the time being, a satisfactory explanation cannot be found in the literature for the selectivity-enhancing effect of copper.

By the addition of copper, the activity of palladium catalysts generally decreases, and with a copper content above 60—70 at%, they are deactivated [5, 6]. At the same time, there is also a decrease in the amounts of both dissolved and adsorbed hydrogen; this can primarily be brought into correlation with changes in the electronic structure and the lattice parameters [7—10].

For an understanding of the activity and selectivity of palladium–copper catalysts, it is important to know the surface structures of the alloys. We have made a study of the surface structures of carbon-supported Pd–Cu catalysts by an electrochemical method. A similar method was used earlier to make measurements on Pd–Cu and carbon-supported palladium catalysts [11, 12]. The present publication is a continuation of this work.

## Experimental

*Catalyst preparation.* 47.5 g active carbon ("Carbo C Extra", $S \approx 1000$ m²/g) was impregnated in three portions with 350 ml of a solution containing 4.17 g $PdCl_2$, and the mixture was dried in vacuum at 70 °C. The impregnated support and 350 ml 5 wt.% $NaBH_4$ solution were added in parallel to 200 ml of a solution containing 5 g NaOH and 1 g $NaBH_4$ with stirring at 20 °C. The ready catalyst was washed with 10 l distilled water for 4 hrs, and dried in vacuum.

For preparation of the copper-containing catalysts, 6 g of the dry 5 wt.% Pd/C catalyst was added to 100 ml of a solution containing the appropriate amount of $CuSO_4$, and the mixture was shaken in a hydrogen atmosphere for 5 hrs. From earlier studies it is known that, in the liquid phase in a hydrogen atmosphere, the $Cu^{2+}$ ion is deposited on the palladium and readily alloyed with it [11,13]. After filtration and washing for 1 hr with distilled water, the catalyst was dried in vacuum at room temperature. In this way, every catalyst contained 5 wt.% palladium, while the copper content was 0, 5, 10, 20, 30 or 40 at.%.

In the course of the *potentiodynamic studies*, the potential of the catalyst (measuring electrode) was varied at a constant rate relative to a platinized $Pt/H_2$ reference electrode, and the current passing through the measuring electrode was recorded. The design of the 3-electrode cell used for the measurement can be seen in a previous publication [12]. For the measurement, 4 mg dry catalyst was added to the measuring electrode. The cell was flushed out with argon, for 15 min with hydrogen, and then again for 2—4 min with argon to remove the excess hydrogen. Next, still in an argon atmosphere, the cell was filled with 1 *N* sulfuric acid. The second flushing with argon was carried out for such a period that the potential of the catalyst after the filling-up with the acid should be in the range 60—90 mV. The measurement was commenced with cathodic polarization, and then from 30 mV anodic polarization was performed up to 1000 mV, in both cases at a rate of 10 mV/min. In this way an active catalyst could be measured without pretreatment, in contrast with those procedures when a powder catalyst is rendered measurable by compression, or by embedding in some solid, conducting medium [15,16].

The *activities* of the catalysts were studied in the liquid-phase hydrogenation of cyclohexane. 20 mg catalyst and 10 ml ethanol were added to a 50 ml flask. The air above the mixture was exhanged for hydrogen, and the during shaking the catalyst was saturated with hydrogen (25 °C, 1 atm, 330 oscillations/min). Next, without disturbance of the system, 2 ml of a 1 M cyclohexane solution in ethanol was injected and the hydrogen consumption measured with a gas burette. The activity was regarded as the initial value of the hydrogen consumption in unit time, referred to 1 g catalyst.

## Results and discussion

The potentiodynamic curves of carbon-supported Pd and Pd–Cu catalysts containing 5, 10, 20, 30 or 40 at.% copper can be seen in Figs 1—5. (Only those parts of the curves, which lie in the range of positive currents are depicted, without the initial cathodic section, which has no importance from the aspect of the evaluation.) On the checking of the reproducibility of the results, it turned out that, with the exception of those containing 30 and 40 at% copper, the catalysts had not stabilized after the passage of even several weeks. (The samples were stored in the dry, in air, in sealed vessels.) The change was particularly significant in the hydrogen range of the curves, from 30 up to 300—400 mV. In the case of the unalloyed Pd/C catalyst (Fig. 1), one month after the preparation a new, sharp maximum had appeared below 100 mV, compared to the curve measured earlier, while at the same time the amount of strongly bound hydrogen (the area under the peak between 250 and 400 mV) had decreased.

The increase in the amount of weakly bound hydrogen and the decrease in the amount of strongly bound hydrogen continued further with the aging of

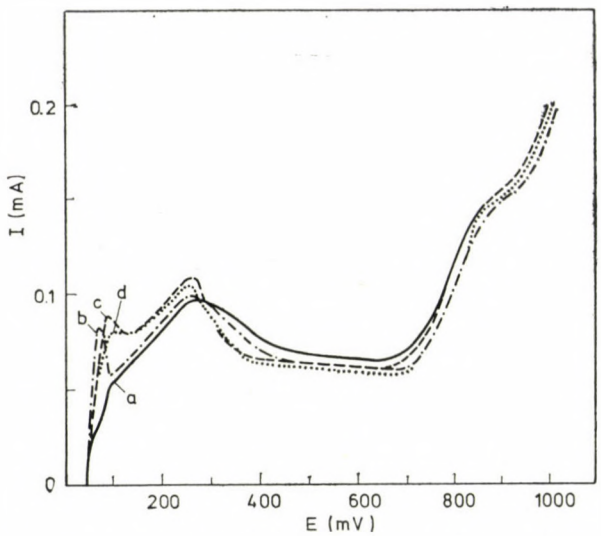



*Fig. 1.* Potentiodynamic curves of 5 wt.% Pd/C catalyst (a) 0.5 month, (b) 1.5 months, (c) 2.5 months, and (d) 4 months after preparation

the catalyst, and then, after a maximum hydrogen content was attained, both decreased. After about four months, the catalyst had stabilized: the differences between the curves did not then exceed the magnitude of the probable experimental error. Similar phenomena can be observed too for the hydrogen range of the 5, 10 and 20 at.% copper-containing samples (Figs 2—4).

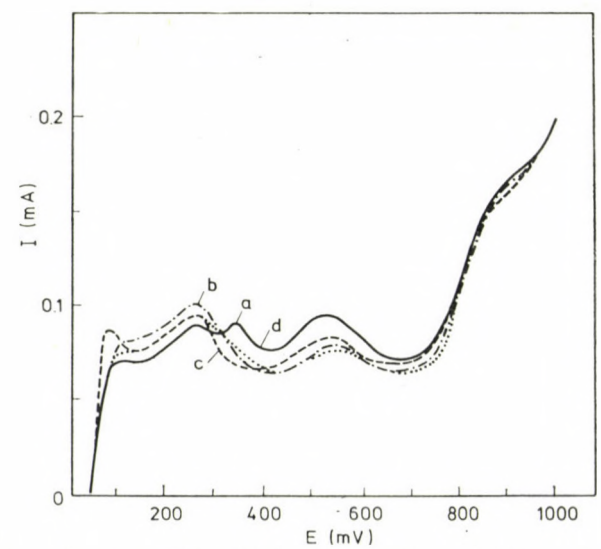



*Fig. 2.* Potentiodynamic curves of 5 at.% Cu–Pd/C catalysts (a) 0.5 month, (b) 1.5 months, (c) 2.5 months, and (d) 4 months after preparation

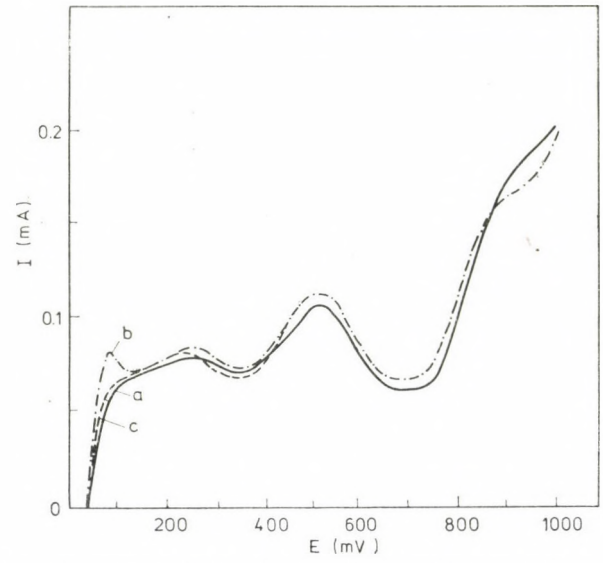



*Fig. 3.* Potentiodynamic curves of 10 at.% Cu–Pd/C catalysts (a) 0.5 month, (b) 1.5 months, (c) 2.5 months, and (d) 4 months after preparation

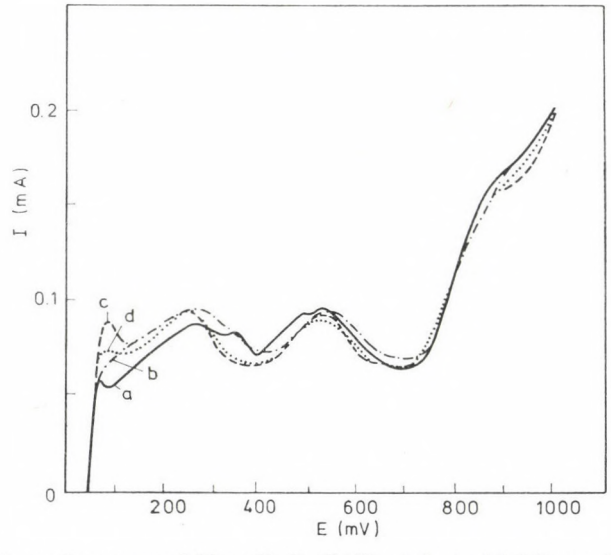



*Fig. 4* Potentiodynamic curves of 20 at.% Cu–Pd/C catalysts (a) 1.5 months, (b) 2.5 months, and (c) 4 months after preparation

From the potentiodynamic curves, it is possible to determine the hydrogen contents of the samples, with the approximation that the difference in area between the polarization curves of the catalyst and the support, recorded under identical conditions (in the hydrogen range), is proportional to the quantity of

charge used for ionization of the sorbed hydrogen. The values calculated in this way are to be seen in Table I. It is clear that, apart from the composition of the catalyst, the specific hydrogen content also depends considerably on the age of the catalyst, except for the samples with the two highest copper contents. The amount of sorbed hydrogen decreases monotonously with the increase of the copper concentration; less than 20% of the initial value is sorbed on the sample containing 40 at.% copper.

In the potentiodynamic curve of the 5 at.% Cu-Pd/C catalyst (Fig. 2a), proceeding in the anodic direction, after the two hydrogen ionization maxima a further two peaks can be seen, at about 340 and 540 mV. As demonstrated earlier [11], the former can be attributed to metallic copper on the surface, and the latter to the dissolution of some palladium–copper intermetallic compound phase. After 1 month, however, metallic copper could no longer be detected on the surface (Fig. 2b), and the quantity of the copper-containing compound phase too had decreased. This means that during storage in the dry, in air, at room temperature, the copper migrates from the outermost surface layers (from where it may dissolve in the course of anodic polarization) towards the inside of the grains. The same was observed on examination of the 10 at.% Cu–Pd/C catalysts too, although the change here is less sharp. On the other hand, the potentiodynamic curves of the samples containing 30 and 40 at.% copper underwent practically no change as a function of time.

For the alloying effect of the copper to be examined independently of the aging of the catalysts, it is necessary to compare the polarization curves of samples, which have storaged for about 4 months and have therefore already become stabilized (Fig. 5). (For the sake of clarity, the polarization curve of the catalyst containing 5 at.% copper is not given again here.) It can be seen that with the increase of the copper content the hydrogen content decreases, while at the same time the distribution of the hydrogen bond strength becomes more and more homogeneous. As a result of the addition of 20 at.% copper, the

**Table I**

*Hydrogen contents of Pd–Cu/C catalysts (after saturation with hydrogen)*

| Cu content (at. %) | Hydrogen content (ml/g catalyst) after | | | |
|---|---|---|---|---|
| | 0.5 month | 1.5 months | 2.5 months | 4.0 months |
| 0 | 3.7 | 3.9 | 4.3 | 4.0 |
| 5 | 3.2 | 3.8 | 3.8 | 3.6 |
| 10 | 2.7 | 3.7 | 3.5 | 3.2 |
| 20 | — | 2.5 | 3.2 | 2.7 |
| 30 | 1.8 | 1.8 | 1.8 | 1.8 |
| 40 | 0.7 | 0.7 | 0.7 | 0.7 |

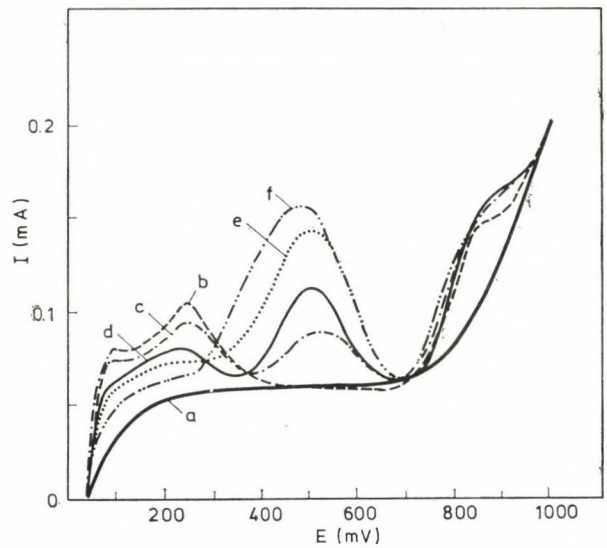



*Fig. 5.* Potentiodynamic curves of 4-month-old Pd–Cu/C, Pd/C and the Carbon support. (a) active carbon support, (b) Pd/C, (c) 10 at.% Cu–Pd/C, (d) 20 at.% Cu–Pd/C, (e) 30 at.% Cu–Pd/C, (f) 40 at.% Cu–Pd/C

strongly bound hydrogen is shifted by about 25 mV in the direction of the negative potentials, *i. e.* the metal–hydrogen bond energy is decreased.

In the catalysts with copper contents of 5—40 at.%, the oxidation maximum of the copper is to be found in the range 540—480 mV; with the increase of the copper content, the potential of the maximum decreases slightly, while the area under the peak increases monotonously. This maximum corresponds to the oxidation of a palladium–copper intermetallic compound, the composition of which is by and large constant. With the increase of the copper content, the beginning of the peak is shifted increasingly in the negative direction, and from a copper content of 30 at.%, the dissolution already begins at 300 mV or less. Since the potential corresponding to the anodic dissolution of metallic copper is $E^{\circ}_{Cu/Cu^{2+}} = 0.34$ V, the samples containing 30 and 40 at.% copper can be interpreted in that there is no longer only some palladium–copper phase of definite composition on the surface, but also metallic copper. The fact that the two processes are not separated from each other can probably be explained in that, besides the metallic copper and the intermetallic compound phase of definite composition, phases with intermediate copper contents can also be found on the surface of the particles.

Above 700 mV the polarization curves of the catalysts (Fig. 5b–f) roughly coincide. This interval cannot be evaluated exactly, for the processes occurring on the support with its relatively large surface area (Fig. 5a) overlap oxygen adsorption on the metal surface and the dissolution of the metal.

The activities of the catalysts in the liquid-phase hydrogenation of cyclohexane similarly depend on the time passed since the preparation for copper contents of 0—10 at.%. (The scatter in the measured results is ±5%, and therefore, the activities of the samples with copper contents of 20—40 at.% can already be regarded as constant after 1 month.) If the stabilized values are considered as a result of the addition of copper, the activity decreases monotonously, similarly to the change in the hydrogen content (Table II).

**Table II**

*Activities of Pd–Cu/C catalysts in the hydrogenation of cyclohexene (ml $H_2$/min/g catalyst)*

| Cu content (at. %) | Activity after | | |
|---|---|---|---|
| | 1 month | 2.5 months | 4 months |
| 0 | 470 | 370 | 380 |
| 5 | 350 | 330 | 320 |
| 10 | 240 | 290 | 290 |
| 20 | 230 | 230 | 220 |
| 30 | 180 | 190 | 190 |
| 40 | 140 | 130 | 130 |

To summarize the results it may be stated that, upon consecutive reduction, the copper deposited in a hydrogen atmosphere is alloyed with the palladium, at least in the outer, surface layers. It is interesting that the penetration of copper atoms into the lattice of the palladium continued in certain cases (5 and 10 at.% Cu) during the aging, and the metallic copper and copper-rich alloy present on the surface of the fresh catalyst could no longer be detected later. According to the segregation theory [17, 18], in a hydrogen atmosphere, the surface of the Pd-Cu alloy is poor in copper; the copper proceeds towards the inside of the particles, for the chemisorption heat of hydrogen is substantially higher on palladium [19, 20]. In the course of the washing and then vacuum-drying of the catalysts and their storage in air, the hydrogen is desorbed and an increasing amount of oxygen is gradually bound on the surface. (This process can be followed, for example, by measurement of the electrochemical potential of the Pd catalyst.) According to the theory, the situation is the reverse in air: the copper is the more volatile component, with its lower sublimation heat, and the chemisorption heat of oxygen too is higher on copper than on palladium [21—24]. The theory indicates that all this is valid only at higher temperature (above 500 °C), for it is, then that the mobility of the metal atoms attains the necessary value. In contrast with this, in the present case some exchange process already began at room temperature, and in addition the migration during aging was in the opposite direction to that expected.

The changes occurring in the surface structures of the catalysts are also indicated by the considerable changes that take place in the activity, and particularly in the hydrogen sorption. Not only the quantity of sorbed hydrogen, but its energy distribution too is modified in the course of aging. Similar changes were observed earlier in the hydrogen sorptions of freshly prepared and 1-month-old Pd and Pd–Cu catalysts [11, 25].

When the stabilized, 4-month-old samples were compared, it was found that with the increase of the copper content, there is a monotonous increase in the amounts of the copper-containing surface phases (predominantly some palladium–copper intermetallic compound phase of definite composition), but in addition there is a constant increase in the quantities of the phases richer in copper, too, and at copper contents above 20 at.%, there is already only metallic copper on the surface. At the same time, on the basis of hydrogen sorption, there are decreases in the amounts of palladium and palladium-rich phases, and in agreement with this in the activities of the catalysts, too, for the liquid-phase hydrogenating activity can also be attributed to the palladium-rich phase.

## REFERENCES

[1] MOKROUSOV, P. V., NAUMOV, A. I.: Catalytic reactions in the liquid phase. Tr. Vses. Konf. Alma-Ata, Kaz. SSR, p. 10, 1966 (Pub. 1967)
[2] Ger. Offen. 2,506,157; Hung. Pat. 169,835
[3] Hung. Pat. 168,073
[4] Ger. Offen. 2,460,078
[5] KADENHEAD, D. A., MASSE, N. G.: J. Phys. Chem., **70,** 3558 (1966)
[6] RIENÄCKER, G., VORMUM, G.: Z. anorg. allgem. Chem., **283,** 287 (1956)
[7] BURCH, R., BUSS, R. G.: J. Chem. Soc. Faraday Trans. I, **71,** 913, 922 (1975)
[8] FLANAGAN, T. B., CHISDES, D. M.: Solid State Commun., **16,** 529 (1975)
[9] BURCH, R., BUSS, R. G.: Solid State Commun., **15,** 407 (1974)
[10] KARPOVA, R. A., TVERDOVSKII, I. P.: Zhur. Fiz. Khim., **33,** 1393 (1959)
[11] MALLÁT, T., PETRÓ, J., POLYÁNSZKY, É., MÁTHÉ, T.: Acta Chim. (Budapest), **90,** 333 (1976)
[12] POLYÁNSZKY, É., MALLÁT, T., PETRÓ, J.: Acta Chim. (Budapest), **92,** (2) 147 (1977)
[13] SZABÓ, S.: Magy. Kém. Folyóirat, **81,** 528 (1975)
[14] PETRÓ, J., MALLÁT, T.: Acta Chim. (Budapest), (in press)
[15] BETT, J., KINOSHITA, K., ROUTSIS, K., STONEHART, P.: J. Catal., **29,** 160 (1973)
[16] STONEHART, P., LUNQUIST, J.: Electrochim. Acta, **18,** 907 (1973)
[17] BOUWMAN, R., TONEMAN, L. M., HOLSCHER, A. D.: Surface Sci., **35,** 8 (1973)
[18] BURTON, J. J., HYMAN, E., FEDAK, D. G.: J. Catal., **37,** 106 (1975)
[19] ALDAG, A. W., SCHMIDT, L. D.: J. Catal., **22,** 260 (1971)
[20] ROSSINGTON, D. R., HOLDEN, S. J.: Nature **199,** 589 (1963)
[21] POUSLET, A., BARIAUX, D.: Bull. Cl. Sci. Acad. Roy. Belg., **52,** 248 (1966)
[22] NORMANN, J. H., STOLEY, H. G., Bell W. E.: J. Phys. Chem., **69,** 1373 (1965)
[23] ELEY, D. D., KNIGHTS, C. F.: Proc. Roy. Soc. (London), Ser. A, **294,** 1 (1966)
[24] OSTROVSKII, V. E.: Dokl. Akad. Nauk SSSR, **172,** 892 (1967)
[25] MALLÁT, T., POLYÁNSZKY, É., PETRÓ, J.: J. Catal., **44,** 345 (1976)

Tamás MALLÁT
József PETRÓ
M. SCHÄFFER
H-1521 Budapest.

*Acta Chimica Academiae Scientiarum Hungaricae, Tomus 98 (2), pp. 183—192 (1978)*

# ON THE INTERPRETATION OF PRECISE DATA ON VAPOR PRESSURES OF MOLECULAR ISOTOPIC ISOMERS

G. JANCSÓ* and W. A. VAN HOOK

*Chemistry Department, University of Tennessee, Knoxville, Tennessee* 37916 *USA*

Received October 12, 1977

The connection between experimental data on the vapor pressure isotope effect, and/or isotopic enrichment factors on distillation, and the reduced partition function for the condensed phase is reviewed. It is demonstrated that heretofore neglected considerations of isotope effects on the real gas correction, on the volume dependence of the intramolecular force field, on dielectric corrections to the condensed phase IR and Raman frequencies, and on anharmonicity changes in internal vibrational motions have important influences on the calculation of the effects.

## Introduction

Experimental information on the vapor pressure differences between molecular isotopic isomers and/or fractionation factors on distillation is rather directly related to condensed phase partition functions. As such the isotope effect data form a useful probe in studies of the effect of intermolecular forces on the properties of molecules in the condensed phase [1]. Recent experiments in this field yield data with a precision of several parts in $10^5$ on the isotopic pressure ratios. In order to extract the maximum of useful information from such data, it is essential that the corrections employed in converting them to reduced partition function ratios, as well as the method of interpretation of those RPFRs, be clearly set forth. In the material which follows, we discuss four interrelated topics bearing on this question.

## I. The Relationship Between the Isotopic Vapor Pressure Ratio and the Reduced Partition Function

BIGELEISEN [2] has given an expression connecting the BIGELEISEN—MAYER [3] reduced partition functions for the codensed, $\left(\frac{s}{s'}f_c\right)$, and vapor, $\left(\frac{s}{s'}f_v\right)$, phases with the ratio of vapor pressures of the separated isotopic isomers,

* Permanent address: Central Research Institute for Physics, Hungarian Academy of Sciences, Budapest.

$P'/P$

$$\ln\left(\frac{f_c}{f_v}\right) = \ln\left(\frac{s}{s'}f_c\right) - \ln\left(\frac{s}{s'}f_v\right) = \ln\frac{P'}{P} - (RT)^{-1}(P'V' - PV) +$$

$$+\left\{\left(B_0 P + \frac{1}{2}C_0 P^2\right)' - \left(B_0 P + \frac{1}{2}C_0 P^2\right)\right\}. \qquad (1)$$

The prime denotes the lighter isotopic species, $V$ is the condensed phase molar volume and $B_0$ and $C_0$ are virial coefficients in the equation of state for the gas

$$PV = RT(1 + B_0 P + C_0 P^2 + \ldots.) . \qquad (2)$$

The correction terms in Eq. (1), $(RT)^{-1}(P'V' - PV)$ and $\left(B_0 P + \frac{1}{2}C_0 P\right)^2 -$ $- \left(B_0 P + \frac{1}{2}C_0 P^2\right)$ account for the difference between the Gibbs and Helmholtz free energies of the condensed phase, and for gas imperfection, respectively. If the two isotopic samples should be compared at the same condensed phase molar volume, $V$, an additional correction term, $(RT)^{-1}\int_{V'}^{V} P'\,\mathrm{d}V$, arises from the isotopic difference in the condensed phase molar volumes. Values of the three different corrections for a number of different systems at representative temperatures have been reported by JANCSÓ and VAN HOOK [1]. Their results show typically that the largest and normally the only significant term is the one arising from the correction for gas imperfection. The value of this term is often many times the limiting experimental precision.

Relatively little information is available concerning the isotopic differences in virial coefficients, $\Delta B_0 = B_0' - B_0$ and $\Delta C_0 = C_0' - C_0$. Recent work by SCHRAMM *et al.* [4] and GÖPEL and DORFMÜLLER [5] on protio-deutero effects in some hydrocarbons and other compounds, and by FANG and VAN HOOK [6] and THOMAES and VAN STEENWINKEL [7] on methane-deuteromethane effects show 2nd virial coefficient isotope effects on the order of half a per cent or so per $D$ atom, $|B_0^H| > |B_0^D|$. Unfortunately, the working assumption $B' = B$ is still widely employed. It is important to recognize that the uncertainty thus introduced into the virial coefficient correction makes an important, even a predominant, contribution to the error in the RPFRs as calculated from the vapor pressure ratios. To illustrate this important point we have selected the ethylene [8] and benzene [9] systems as examples.

The vapor pressure differences between ethylene-$h_4$ and ethylene-$d_4$ in the liquid phase have been determined to remarkably high precision by ISHIDA and BIGELEISEN [8] over the temperature range 115—180 K. At the highest experimental temperature (180.78 K) the authors quote $\ln(P'/P) = -0.03179 \pm$ $\pm 0.00001$. In proceeding to the reduced partition function ratio they estimate the virial coefficient correction by taking $B = B' = -351$ cm$^3$ mole$^{-1}$ [10] and

obtain $(B_0'P' - B_0P) = 0.00142$, $B_0 = B/RT$. More reasonably by employing the measured virial coefficient isotope effect (VCIE) $1.9 \pm 0.4\%$ [4], we obtain a correction of $0.00055 \pm 0.00018$. The uncertainty is a direct consequence of the error in the VCIE determination and does not include any contribution due to the uncertainty in the VC itself. It dominates in determining the uncertainty in the derived RPFRs. That uncertainty is about 20 times the standard deviation in the experimental pressure ratios. The earlier [8] assumption, $B_0 = B_0'$ results in systematic error in RPFR at 181 K of 0.00087, about 90 times the quoted error in the pressure measurements. The VCIE correction drops off rapidly as the pressure decreases and is relatively unimportant below a few tenths of an atmosphere total pressure. Even so improper evaluations of the contribution $(B_0'P' - B_0P)$ can result in significant errors in the temperature coefficient of RPFR.

A more commonly encountered problem is exemplified by the treatment of vapor pressure data for the benzene-$h_6$/benzene-$d_6$ system. The vapor pressure isotope effects have been reported by JÁKLI, TZIAS and VAN HOOK [9] with a precision of approximately $\pm 0.00003$ in the ratio. However, no measurements of the VCIE have been reported, although information on the virial coefficient of $C_6H_6$ is available [11]. The authors [9] estimated the VCIE using the methods of FANG and VAN HOOK [6] and SCHRAMM *et al.* [4] obtaining 3% and 1% respectively. Using $|B_0^H - B_0^D|/B_0^H = 0.02 \pm 0.01$ one obtains corrections, $(B_0'P' - B_0P)$ over the range of the available data 5.5 to 160° [9, 12] as follows; 5.5°: $3 \pm 4$; 50°: $9 \pm 16$; 80°: $14 \pm 33$; 160°: $34 \pm 56$; all $\times 10^{-5}$. One sees again that the uncertainty in the $(f_c/f_v)$ as derived from pressure measurements is many times the uncertainty in the pressure measurements themselves at all pressures above a few hundred torr.

The situation exemplified above for ethylene and benzene is characteristic of the bulk of high precision VPIE data in the literature. In spite of current widespread practice to the contrary, we recommend that in the absence of well-defined data on the virial coefficient and VCIE that the original pressure data be smoothed and reported prior to calculation of the $(f_c/f_v)$ ratios. In this fashion the original data are preserved for later use should virial coefficient work become available.

## II. The Relationship Between Reduced Partition Function Ratios and Measured Enrichment Factors on Distillation

The commonly employed relationship connecting the isotopic separation factor, $\alpha = (x'/x)_v/(x'/x)_c$ (the $x$'s are mole fractions), and the reduced partition function ratio has been given in the limit of infinite dilution ($x' \simeq 1$) for the case of no isotope effect on the molar volume of the gas as follows [13].

$$\ln \frac{f_c}{f_v} = \ln \alpha + \frac{(V - V')^2}{2\beta VRT} . \tag{3}$$

In Eq. (3) $\beta$ is the isothermal compressibility and it is understood that the condensed phase partition functions $Q_c'$ and $Q_c$ contributing to $\ln(f_c/f_v)$ are evaluated at $V'$ and $V$. An extension to the case where the partition functions are evaluated at the molar volume of the mixture, $V_m$, and corrections for isotope effects on the vapor phase equation of state are included, yields [14]

$$\ln \left( \frac{f_c}{f_v} \right)_{V_m} = \ln \alpha . \tag{4}$$

In the material which follows we wish to demonstrate that the considerations which led to the development of Eq. (3) were incomplete.

Equation (3) was derived by considering the excess free energy of mixing of a solution of isotopic isomers following PRIGOGINE [15—17]. The calculation is made using a two-step process. In the first step the components are separately compressed (dilated) to the molar volume of the mixture. In the second, the components are mixed at constant volume. The assumption is made that the excess free energy of mixing in step II is zero. The free energy change in step I is calculated from the leading term of an expansion of the free energy in terms of the pressure. The result in this approximation is dominated by the contribution from the intermolecular potential by which the compressibility is principally determined. JANCSÓ and VAN HOOK [18] have pointed out that this approach suffers, because it does not properly weigh the contribution of the intramolecular degrees of freedom. Both internal and external modes may be volume dependent, the later (generally of lower frequency) determine the compressibility, but the former may predominate in determining the free energy shifts for complicated molecules of many atoms. In terms of an oscillator model for the condensed phase one is led rather directly to Eq. (5) instead of Eq. (3)

$$\ln \left( \frac{f_c}{f_v} \right) = \ln \alpha + \int_V^{V'} \sum_i^{3n} \left( \frac{\mathrm{d} \ln Q}{\mathrm{d}\nu_i} \right) \left( \frac{\mathrm{d}\nu_i}{\mathrm{d}V} \right) \mathrm{d}V , \tag{5}$$

$Q$ is the partition function of the average molecule in the liquid phase and $\nu_i$ is the $i$-th vibrational frequency. The use of Eq. (5) obviously requires detailed information on the volume dependence of all vibrational frequencies. Calculations have been carried out on the $H_2/D_2$ and the benzene/deuterobenzene systems [18]. In the former case the contribution of the low frequency external motions predominates. The internal frequency does not change significantly with volume and Eq. (3) is a useful approximation. In the more complicated benzene system the contribution of the high lying internal modes is important.

The six CH stretching motions exhibit an important volume dependence and this contribution is, in fact, about six times that from the external motions over the liquid range. As expected the term calculated from the compressibility (Eq. (3)) is about the same as the contribution from the external frequencies alone (Eq. (5)).

We conclude that the use of Eq. (3) to calculate the difference between the reduced partition function ratio and measured fractionation factors may result in values which are too small by several hundred per cent, at least for complicated molecules containing many atoms.

## III. Interpretation of the Reduced Partition Function Ratio: Frequency Shifts of Internal Vibrations on Condensation

Detailed interpretation of the effect of intermolecular forces on the properties of condensed phase molecules as monitored via the VPIE for complicated molecules is most conveniently approached with the aid of a model. The simplified harmonic cell model has had considerable success in correlating the VPIE with a set of normal mode frequency shifts (gas to condensed phase) for both sets of isotopic isomers [1]. BUCKINGHAM [19] and others [20—22] have discussed the theory of the effect of intermolecular forces on normal mode vibrational frequencies and WOLFSBERG [23] has commented on the connections between this kind of approach and the VPIE. In the harmonic cell model the reduced partition function ratio is expressed in terms of a set of $3n$–6 gas and condensed phase internal and 6 condensed phase external or unitary (gas phase) harmonic oscillator partition functions:

$$\frac{f_c}{f_v} = \prod_{\text{int. freq.}}^{3n-6} \frac{(u_i/u_i')c}{(u_i/u_i')_v} \frac{\exp\left((u_i' - u_i)_c/2\right)}{\exp\left((u_i' - u_i)_v/2\right)} \frac{\left(1 - \exp(-u_i')_c/(1 - \exp(-u_i)_c\right)}{\left(1 - \exp(-u_i')_v/(1 - \exp(-u_i')\mathrm{v}\right)} \times \quad (6)$$

$$\times \prod_{\text{ext. freq.}}^{6} \frac{u_i}{u_i'} \left[\exp\left(\frac{u_i' - u_i}{2}\right)\right] \left[\frac{1 - \exp(-u_i')}{1 - \exp(-u_i)}\right], \quad u_i = \frac{hc\nu_i}{kT}.$$

Minor corrections for anharmonicity *(vide infra)*, non-classical rotation, etc. may be required.

Equation (6) makes the connection between the reduced partition function as measured by the VPIE (suitably corrected) and a set of normal mode frequencies for the two isotopes in the two phases. It is easy to show [1] that often a good approximation to RPFR can be given in terms of a relatively simple function of the isotopic difference in the frequency shifts on condensation. Such shifts may be available from spectroscopic experiments, but it is important to recognize that a consistent set of frequencies for the different isotopic isomers must be employed in Eq. (6). Typically, spectroscopic frequency shifts on con-

densation are measured to about $\pm 2$ cm$^{-1}$. For an H/D stretching mode this corresponds to an uncertainty of $\sim 0.005$ units in $\ln (f_c/f_v)$ at room temperature. Thus high precision VPIEs ($\sim \pm 0.00005$) monitor the total shift with superior precision, and it follows that it is essential to employ a more nearly self consistent set of isotopic frequency shifts in Eq. (6) than is available from the spectroscopic work. The normal procedure is to construct vapor and condensed phase force fields which reproduce spectroscopically observed frequencies and frequency shifts within experimental error and employ these fields to calculate a self-consistent set of frequencies for the different isotopic isomers. This technique is now well-established.

Our purpose here is to point out that the situation which actually obtains is more complicated than pointed out in the previous paragraph. AKOPYAN *et al.* [24], LEFRANC *et al.* [25], and CLIFFORD and CRAWFORD [26], among others, have emphasized that in the case of intense IR absorptions the observed shifts on condensation are the sums of an intrisic effect due to the effect of the intermolecular interaction and a "dielectric correction". The latter term is associated with the difference in the effective field of the light wave acting on the molecule in a condensed medium and the average field in that medium. The dielectric correction can be a large fraction of the total shift. Unfortunately, the experimental data which are necessary for its evaluation are available for only a very few vibrational frequencies. Examples include the asymmetric C-Cl vibration in $CCl_4$, where the observed shift of 7 cm$^{-1}$ is *entirely* due to the dielectric correction (no effect of the intermolecular forces [27]), and the asymmetric stretch in $CS_2$, where the dielectric shift has been variously estimated between 8 and 15 cm$^{-1}$ out of the observed 27 cm$^{-1}$ shift [24, 28]. It is interesting that analysis of the $^{13}CS_2/^{12}CS_2$ vapor pressure data [29] gives a consistent result for the relative contributions of the dielectric correction (14 cm$^{-1}$) and the intrinsic part (13 cm$^{-1}$) to the shift. The result clearly indicates that the effects of large dielectric corrections must be taken into account when spectroscopically observed frequency shifts are employed in Eq. (6). This has been generally impossible to do heretofore and that observation may account for some of the difficulties in correlating spectroscopically observed frequency shifts with the VPIE through Eq. (6). From another point of view the analysis indicates that in certain favorable cases observed VPIEs can be employed to give an independent evaluation of the relative contribution of the intrinsic shift and the dielectric correction [30].

## IV. The VPIE and Anharmonicity in the Liquid Phase

Although Eq. (6) has been written in terms of the harmonic approximation and is usually employed in that context or in the slightly modified quasi-harmonic approximation, real molecular vibrations are more appropriately

described as anharmonic oscillators. The definite successes of Eq. (6) in dealing with the VPIE therefore have definite connotations concerning the nature of anharmonicity and the changes in anharmonicity on condensation from vapor to liquid.

For simplicity consider a diatomic molecule of a suitably high vibrational frequency. Its contribution to $\ln (f_c/f_v)$ can be described by a zero-point energy term.

$$\ln(f_c/f_v) = -\frac{1}{2}\frac{hc}{kT}\left[(\nu_v' - \nu_v) - (\nu_c' - \nu_c)\right]. \tag{7}$$

One can define an effective ground state force constant $f'$ in terms of the observed frequency $\nu'$, $f' = (2\pi c\nu')^2\mu'$, where $\mu'$ is the reduced mass. An isotope shift $(\nu'-\nu)^*$ can be calculated from $f'$

$$(\nu' - \nu)^* = \nu'(1 - (\mu'/\mu)^{1/2}). \tag{8}$$

More properly, the correct isotope effect could be obtained from the observed frequencies were they accurately known and which we suppose can be well-represented in terms of a harmonic and first anharmonic contribution [31]

$$(\nu' - \nu) = (\omega' - \omega) + 2\ (' X' - X), \tag{9}$$

where $\omega$'s are the harmonic frequencies and $X$'s are the first anharmonicity constants. The error in the calculated isotope shift from Eq. (8) is therefore

$$\Delta(\Delta\nu) = (\nu' - \nu) - (\nu' - \nu)^* = 2X'\frac{\omega'}{\omega}\left(1 - \frac{\omega'}{\omega}\right) \cong 2X'\left(1 - \frac{\nu'}{\nu}\right) \tag{10}$$

since [31]

$$\frac{X'}{X} = \frac{\mu}{\mu'} = \frac{\omega'^2}{\omega_2} \cong \frac{\nu'^2}{\nu^2}. \tag{11}$$

This is equivalent to an uncertainty in the reduced partition function ratio

$$\Delta \ln\left(\frac{f_c}{f_v}\right) = -\frac{hc}{kT}(X_v' - X_c')\frac{\nu'}{\nu}\left(1 - \frac{\nu'}{\nu}\right). \tag{12}$$

The correction vanishes, if $X_v' = X_c'$. Qualitatively the fact that Eq. (6) represents vapor pressure isotope effect data to a suprisingly good degree implies that $X'$ does not change significantly on condensation.

A quantitative example is more instructive. Consider the case of benzene-$h_6$/benzene-$d_6$. The principal contribution to RPFR arises from the six CH/CD stretching modes [32], which can be approximated as diatomic oscillators in

the local mode approximation [33, 34]. Using a value of $-58.4$ cm$^{-1}$ for the anharmonicity constant [34] taking $\nu_H/\nu_D = 1.345$, and writing $X'_v = aX'_c$, we obtain

$$\Delta \ln \left(\frac{f_c}{f_v}\right) = -0.785\,(a - 1)\,. \tag{13}$$

Equation (13) is instructive. It demonstrates, for example, that a 1% change in the value of $X$ on the phase change amounts to 29% change in the VPIE. Changes of this magnitude can be ruled out with complete confidence because of the relative precisions of the VPIE data and the spectroscopic measurements. A detailed analysis shows that the relative change in the anharmonicity constant on condensation cannot be significantly larger than changes in the harmonic force constant. Typically, these do not amount to more than a few tenths of a per cent. The conclusion is a worth-while one. It is consistent with but considerably more precise than the conclusions drawn from what little spectroscopic information is available on this topic [35—37].

## Conclusions

We have discussed four topics, all bearing on the interpretation of vapor pressure isotope effects. In the first it was cautioned that uncertainties introduced into the calculation of reduced partition function ratios (RPFRs) from VPIE data by virtue of isotope effects on vapor non-ideality can be important. For high precision H/D studies above a few tenths of an atmosphere, the uncertainty from this source is expected to dominate. Heretofore it has not been generally considered. In the second section we analyzed methods of calculation of RPFRs from distillation data, pointing out that due account must be taken of the concentration (volume) dependence of all $3n$ motions of the molecule. Approximate equations in current use consider the external motions alone. In the third section we considered the comparison of RPFRs as experimentally determined from the (corrected) vapor pressure ratios with theoretical calculations from spectroscopic data, and cautioned that proper care must be taken to insure that such data are properly corrected for the dielectric medium effect. This correction can be important for intense absorption bands and, again, is one that has been commonly ignored. Finally, in the fourth and last section, some considerations concerning possible anharmonic effects were presented and we concluded that relative changes in anharmonic constants on condensation cannot be significantly larger than the corresponding relative changes in the harmonic constants. These four refinements of interpretation of the VPIE nicely demonstrate that, while far from straightforward, such measurements can lead to

new and unique information concerning the effect of condensed phase intermolecular forces on molecular properties.

*

Partial supports frnm the U.S. National Science Foundation and the Hungarian Institute for Cultural Relations as part of the cooperative research program between the Central Research Institute for Physics and the University of Tennessee, the NSF Chemical Thermodynamics Program, and the National Institutes of Health are greatfully acknowledged.

## REFERENCES

[1] Jancsó, G., Van Hook, W. A.: Chem. Rev. **74,** 689 (1974)
[2] Bigeleisen, J.: J. Chem. Phys. **34,** 1485 (1961)
[3] Bigeleisen, J., Mayer, M. G.: J. Chem. Phys. **15,** 261 (1947)
[4] Gainar, I., Strein, K., Schramm, B.: Ber. Bunsenges. für Phys. Chem. **76,** 1242 (1972); Gainar, I., Schäfer, K., Schmeiser, B., Schramm, B., Strein, K.: *ibid.* **77,** 372 (1973); Adam, G., Schäfer, K., Schramm, B.: *ibid.* **80,** 912 (1976); Adam, G., Schramm, B.: *ibid.* **81,** 442 (1977)
[5] Göpel, W., Dorfmüller, Th.: Z. Physik. Chem. NF **82,** 58 (1972)
[6] Fang, A. Y., Van Hook, W. A.: J. Chem. Phys. **60,** 3513 (1974)
[7] Thomaes, G., van Steenwinkel, R.: Mol. Phys. **5,** 307 (1962)
[8] Ishida, T., Bigeleisen, J.: J. Chem. Phys. **49,** 5498 (1968); Bigeleisen, J., Fuks, S., Ribnikar, S., V., Yato, Y.: J. Chem. Phys. **66,** 1689 (1977)
[9] Jákli, G., Tzias, P., Van Hook, W., A.: J. Chem. Phys. **68,** 3177 (1978)
[10] Hirschfelder, J. O., Curtiss, C. F., Bird, R. B.: Molecular Theory of Gases and Liquids, John Wiley and Sons, Inc., New York, 1954
[11] Dymond, J. H., Smith, E. B.: The Virial Coefficients of Gases, Clarendon Press, Oxford, 1969
[12] Kiss, I., Jákli, G., Illy, H.: Acta Chim. (Budapest), **71,** 59 (1972)
[13] Bigeleisen, J.: J. Chem. Phys. **39,** 769 (1963)
[14] Phillips, J. T., Linderstrom—Lang, C. U., Bigeleisen, J.: J. Chem. Phys. **56,** 5053 (1972)
[15] Prigogine, I., Bingen, R., Bellemans, A.: Physica **20,** 633 (1954)
[16] Prigogine, I.: The Molecular Theory of Solutions, North-Holland Publishing Co., Amsterdam, 1957
[17] Prigogine, I., Bellemans, A.: Nuovo Cim. Suppl. (ser. 10) **9,** 342 (1958)
[18] Jancsó, G., Van Hook, W. A.: Physica **A91,** 619 (1978)
[19] Buckingham, A. D.: Proc. Roy. Soc. London **A248,** 169 (1958); *ibid.* **A255,** 32 (1960); Trans. Faraday Soc. **56,** 753 (1960)
[20] Földes, A., Sándorfy, C.: J. Mol. Spectrosc. **20,** 262 (1966); Durocher, G., Sándorfy, C.: *ibid.* **22,** 347 (1967)
[21] Rossi, I., Nguyen-Van-Thanh, Brodbeck, C., Haeusler, C.: Can. J. Chem. **48,** 3362 (1970)
[22] Bakhshiev, N. G., Girin, O. P.: Opt. Spectrosc. **41,** 125 (1976) and references therein
[23] Wolfsberg, M.: J. Chim. Phys. **60,** 15 (1963)
[24] Akopyan, S. Kh., Girin, O. P., Bakhshiev, N. G.: Opt. Spectrosc. **36,** 185 (1974) and references therein
[25] Lefranc, B., Jacob, J., Vincent Geisse, J.: Spectrochim. Acta **22,** 1057 (1966)
[26] Clifford, A. A., Crawford, B. Jr.: J. Phys. Chem. **70,** 1536 (1966)
[27] Libov, V. S., Bakhshiev, N. G., Girin, O. P. : Opt. Spectrosc. **16,** 549 (1964); Libov, V. S., Girin, O. P., Bakhshiev, N. G.: *ibid.* **20,** 350 (1966)
[28] Jacob, J., Benaich, J. P.: J. Chim. Phys. **64,** 1282 (1967)
[29] Jancsó, G., Van Hook, W. A.: Can. J. Chem. **55,** 3371 (1977)
[30] Jancsó, G., Van Hook, W. A.: Chem. Phys. Lett. **48,** 481 (1977)
[31] Herzberg, G.: Molecular Spectra and Molecular Structure. I. Spectra of Diatomic Molecules, Van Nostrand, New York, 1950
[32] Jancsó, G., Van Hook, W. A.: J. Chem. Phys. **68,** 3191 (1978)
[33] Hayward, R. J., Henry, B. R., Siebrand, W.: J. Mol. Spectrosc. **46,** 207 (1973)
[34] Swofford, R. L., Long, M. E., Albrecht, A. C.: J. Chem. Phys. **65,** 179 (1976)

[35] JANCSÓ, G., VAN HOOK, W. A.: J. Mol. Struct. **48,** 107 (1978)
[36] RIBNIKAR, S., V., PUZIĆ, O. S.: Spectrochim. Acta **29A,** 307 (1973); RIBNIKAR, S. V., PUZIĆ, O. S. ŠUKAROVA, B. N.: Bull. Soc. Chim. Beograd **38,** 509 (1973); ŠUKAROVA, B. N., RIBNIKAR, S. V.: Bull. Chem. Techn. Macedonia **2,** 11 (1975)
[37] KOLOMIITSOVA, T. D., MELIKOVA, S. M., TSEPKIN, D. N.: Opt. Spectrosc. **39,** 336 (1975)

Gábor JANCSÓ: Central Research Institute for Physics,
H–1525 Budapest, P. O. Box 49
W. ALEXANDER VAN HOOK: Chemistry Department, University of Tennessee,
Knoxville, Tennessee 37916 USA.

*Acta Chimica Academiae Scientiarum Hungaricae, Tomus 98 (2), pp. 193—198 (1978)*

# КОМБИНАЦИИ ИНИЦИАТОРОВ ПОЛИМЕРИЗАЦИИ

Й. БЕНИСКА, Э. ШТАУДНЕР и Г. КИСЕЛА

*Химический факультет, Словацкий политехнический институт, Братислава, ЧССР*

Поступила в редакцию 3 ноября 1977

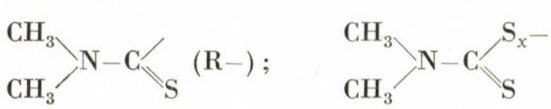
Была исследована полимеризация стирола, инициированная бинарными смесями инициаторов, где одним из компонентов был тетраметилтиурамдисульфид. В зависимости от типа второго инициатора, исследованные комбинации инициаторов проявляют аддитивное, антагонистическое или синергетическое действие. В работе приведены примеры влияния изученных комбинаций инициаторов.

При изучении полимеризации стирола и метилметакрилата в присутствии тетраметилтиурамдисульфида (ТМТД) было обнаружено [1—4], что ТМТД кроме инициирования принимает участие также в реакциях передачи и обрыва цепи. Скорость полимеризации стирола и метилметакрилата в присутствии ТМТД хорошо описывается уравнением:

$$Rp = \frac{\frac{k_p}{k_t^{1/2}} [\mathrm{M}] (v_{i,t} + v_{i,\mathrm{TMTD}})^{1/2}}{\left(1 + 2\frac{k_t' k_{tr}}{k_t k_1'}\frac{[\mathrm{TMTD}]}{[\mathrm{M}]} + \frac{k_t'' k_{tr}^2}{k_t k_1'^2}\frac{[\mathrm{TMTD}]^2}{[\mathrm{M}]^2}\right)^{1/2}} \qquad (1)$$

где: $k_1'$, $k_p$, $k_{tr}$, $k_t$, $k_t'$ и $k_t''$ константы скоростей реакций первого присоединения, роста, передачи цепи на ТМТД, обрыва цепи $\mathbf{P}\cdot + \mathbf{P}\cdot$, $\mathbf{P}\cdot + \mathbf{RS}\cdot$ и $\mathbf{RS}\cdot + \mathbf{RS}\cdot$, соответственно; $v_{i,t}$ и $v_{i,\mathrm{TMTD}}$ скорости инициирования термической полимеризации и, полимеризации в присутствии ТМТД.

Полимеры, приготовленные в присутствии ТМТД, имеют на концах макромолекул фрагменты типа



Фрагменты $\mathbf{RS}_{\overline{x}}$ (где $X \geq 2$) относительно реактивны и их можно использовать например в качестве макроинициаторов. Концентрация этих фрагментов в полимерах возрастает с повышением концентрации ТМТД и с понижением температуры полимеризации. С целью повышения скорости полимеризации при относительно низких температурах (60—70°C) мы изучали

возможность использования комбинаций ТМТД с перекисными инициаторами и с азонитрилом изомаслянной кислоты (АИБН).

В настоящей статьи приведены результаты изучения кинетики полимеризации стирола с использованием смесей инициаторов, где одним из компонентов был ТМТД.

## Экспериментальная часть

Стирол (технический) очищался от стабилизатора промыванием 5%-ным роствором NaOH, и перегонкой в вакууме.

Тетраметилтиурамдисульфид очищался трехкратным переосаждением метиловым спиртом из хлороформного раствора и последующей кристаллизацией.

Перекись бензоила (ПБ), перекись лауроила (ПЛ), и азонитрил изомаслянной кислоты (АИБН) очищались кристаллизацией; гидроперекись кумола (ГПК) и гидроперекись третичного бутила очищались через их натриевые соли.

Полимеризация стирола изучалась дилатометрическим методом до 8—10%-ной конверсии. Продолжительная полимеризация исследовалась гравиметрическим методом. Молекулярные веса полимеров определялись вискозиметрически.

## Результаты экспериментов и их обсуждение

В работе исследовались следующие комбинации инициаторов:

1. ТМТД + АИБН; ТМТД + ПЛ; ТМТД + ГПК
2. ТМТД + ПБ;
3. ТМТД + ГПТБ;

1.-ая группа- аддитивная, вторая антагонистическая, третья синергетическая.

Изучение влияния комбинаций инициаторов проводилось таким образом, что для исследуемых температур применялась постоянная общая молярная концентрация инициаторов и изменялось только их взаимное отношение.

Изучение влияния комбинаций инициаторов на полимеризацию стирола показывает, что в комбинации с ТМТД второй инициатор ведет себя по разному в зависимости от его типа и условий реакции (температура, концентрация).

1. Примеры *аддитивного действия* приведены на рис. 1, где изображены зависимости скорости полимеризации как функции молярной доли ТМТД в смеси инициаторов ($X_T$), при температуре 95°C и общей концентрации инициаторов $K = [\text{ТМТД}] + [\text{И}] = 3{,}04 \cdot 10^2$ моль/л.

Кривая на рис. 1 рассчитана теоретически по уравнению (2):

$$Rp = \frac{\frac{k_p}{k_t^{1/2}} \cdot [\text{M}](vi_t + vi_{\text{TMTD}} + vi_{\text{I}})^{1/2}}{\left(1 + 2B^* \frac{[\text{TMTD}]}{[\text{M}]} + C^* \frac{[\text{TMTD}]^2}{[\text{M}]^2}\right)^{1/2}} \qquad (2)$$

$$\text{где} \quad B^* = \frac{k_t' k_{tr}}{k_t k_1'} \quad \text{и} \quad C^* = \frac{k_t'' k_{tr}^2}{k_t k_1'^2},$$

представляют собой комплексные константы, которые можно определить исследованием полимеризации в присутствии одного ТМТД.

Точки на рис. 1 отвечают экспериментально определенным скоростям полимеризации и как видно, очень хорошо совпадают с теоретическими (аддитивными) скоростями. Аналогичные зависимости были получены при исследовании комбинаций ТМТД с ПЛ и ГПК.

2. *Антагонистическое действие* было обнаружено в случае комбинаций ТМТД с ПВ. Общая концентрация инициаторов составляла $K = 3{,}04 \cdot 10^{-2}$ моль/л и полимеризация исследовалась при 60 и 95°С. Зависимости скоростей полимеризации от молярной доли ТМТД приведены на рис. 2 и 3. Максимальный антагонистический эффект, который можно выразить как отношение аддитивной скорости ($Rp_{\text{ad}}$), вычисленной с помощью уравнения (2), к экспериментальной скорости ($Rp_{\text{exp}}$) или их разницей, находится для обеих температур при $X_T = 0{,}3$.

Постоянные скорости полимеризации наблюдались только до примерно 8%-ной конверсии и потом эти скорости постепенно понижались; максимальное понижение наблюдалось при $X_T = 0{,}3$, как это видно из рис. 4.

Полученные результаты свидетельствуют о том, что в случае смесей ТМТД с ПБ кроме термического распада инициаторов происходит также конкурирующая реакция между ТМТД и ПБ, которая ведет к быстрому расходу как ТМТД, так и ПБ. Можно предполагать, что ПБ реагирует с ТМТД подобно реакции с диалкилдисульфидами [5] с образованием соответствующих сульфоокисей ТМТД.

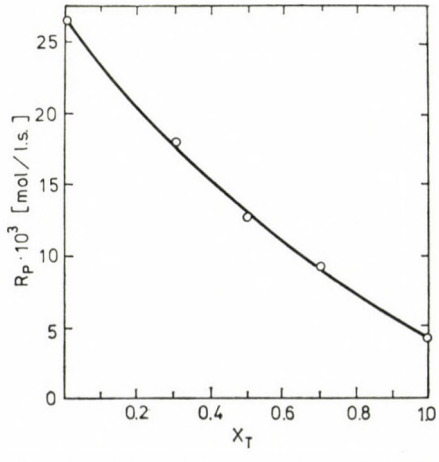



*Рис. 1.* Зависимость скорости полимеризации стирола от $X_T$ в присутствии смесей ТМТД + АИБН. Температура 95 °С; $K = 3{,}04 \cdot 10^{-2}$ моль/л

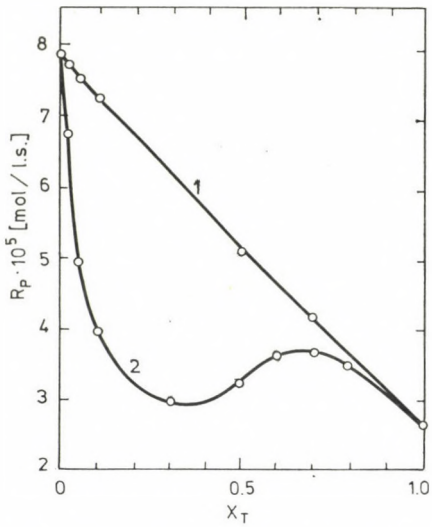



*Рис. 2.* Зависимость скорости полимеризации стирола от $X_T$ в присутствии смесей ТМТД + ПБ. Температура 60°С; $K = 3.04 \cdot 10^{-2}$ моль/л

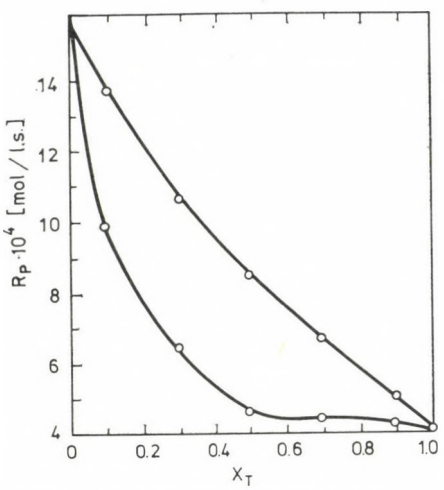



*Рис. 3.* Зависимость скорости полимеризации стирола от $X_T$ в присутствии смесей ТМТД + ПБ. Температура 95°С; $K = 3{,}04 \cdot 10^{-2}$ моль/л

Максимальный антагонистический эффект, а также максимальное понижение скорости во времени при $X_T = 0{,}3$ указывают на то, что одна молекула ТМТД реагирует с двумя молекулами ПБ. Образующиеся продукты, повидимому, принимают участие в реакциях передачи и обрыва цепи и этим повышают антагонистический эффект. На участие этих продуктов в вышеупомянутых реакциях указывает также необычный ход зависимости $\Delta = f([\mathrm{TMTD}]/[\mathrm{M}])$, как это видно из рис. 5. Эта зависимость не линейна.

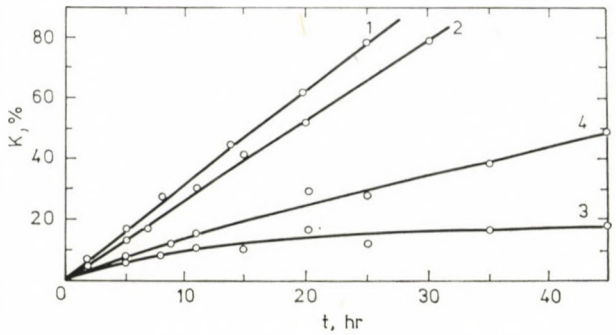



*Рис. 4.* Зависимость % конверсии от времени для полимеризации стирола при 60°С и $K = 3{,}04 \cdot 10^{-2}$ моль/л; $X_T$: 1—0.05; 2—0,1; 3—0.3; 4—0,7

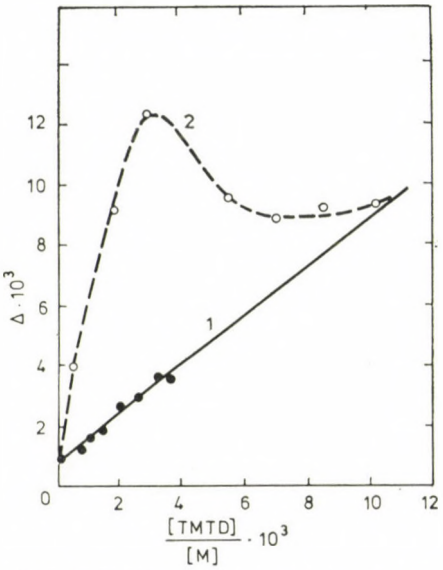



*Рис. 5.* Зависимость $\Delta = f([\text{ТМТД}]/[\text{М}])$ для полимеризации стирола при 60°С; $K = 3{,}04 \cdot 10^{-2}$ моль/л. Сплошная кривая — смесь ТНТД + АИБН, пунктирная кривая — смесь ТМТД + ПБ

Понижение молекулярного веса больше, чем в случае передачи цепи только на ТМТД.

$$\Delta = \frac{1}{\bar{x}} - \frac{k_t}{k_p^2} \frac{R_p}{[\text{M}]^2} \left(1 + B^* \frac{[\text{TMTD}]}{[\text{M}]}\right) C_M + C_T \frac{[\text{TMTD}]}{[\text{M}]}$$

3. *Синергетическое действие* наблюдалось при использовании смесей инициаторов ТМТД с ГПТБ. Полимеризация стирола, инициированная этими смесями, изучалась при температурах от 20 до 95°С. Общая концентрация инициаторов изменялась от $3{,}28 \cdot 10^{-2}$ до $8{,}84 \cdot 10^{-2}$ моль/л. На кривых конверсии наблюдались короткие индукционные участки- область стационарных скоростей и область постепенного понижения скорости полимеризации.

Для всех исследуемых температур проявляется заметный синергетический эффект с максимумом при $X_T = 0{,}3$. Величина этого эффекта для всех температур зависит от общей концентрации инициаторов и с ее понижением постепенно исчезает.

Полученные значения синергетического эффекта приведены в таблице 1.

Из таблицы 1 видно, что при одинаковой общей концентрации инициаторов синергетический эффект падает с температурой.

**Таблица 1**

*Зависимости отношений $Rp_{exp}/Rp_{ad}$ от температуры и общей концентрации инициаторов (K), при $X_T = 0{,}3$*

| K.10² (моль/л) | $Rp_{exp}/Rp_{ad}$ | | | | |
|---|---|---|---|---|---|
| | комнат. температ. | 40 °C | 70 °C | 80 °C | 95 °C |
| 8,84 | 28,8 | 18,8 | 9,50 | 6,81 | 5,00 |
| 6,80 | — | — | — | 5,53 | 3,85 |
| 5,00 | — | — | 6,67 | 4,02 | 2,58 |
| 3,28 | — | — | — | (1,26) | 1,43 |

Синергетический эффект вероятно является результатом взаимодействия гидроперекиси с амидной группой ТМТД.

Исследование влияния смесей инициаторов, в которых одним из компонентов является ТМТД, показало, что их инициирующее действие зависит от типа второго инициатора, от общей концентрации их смеси, от их взаимного отношения и от температуры полимеризации. С практической точки зрения интересны синергетически действующие смеси инициаторов ТМТД + ГТПБ. Работа в области комбинации инициаторов продолжается.

**Summary**

Polymerization of styrene initiated by binary initiator systems containing tetramethylthiuram disulfide has been studied. Depending on the type of the second initiator, the studied combinations of initiators had an additive, antagonistic, or synergistic effect. Examples are given of the influence of the initiator systems used.

## ЛИТЕРАТУРА

[1] Štaudner, E., Beniska, J., Znamenáková, G.: Chemické zvesti, **20,** 18 (1966)
[2] Beniska, J., Štaudner, E.: J. Polymer Sci., Part **16,** 1301 (1967)
[3] Štaudner, E., Beniska, E.: European Polymer J. Suppl. 537 (1969)
[4] Beniska, J.: Vysokomol Soed., **13,** 1990 (1971)
[5] Pryor, W. A., Bickley, H. T.: J. Org. Chem., **37,** 2885 (1972)

J. Beniska
E. Standner
G. Kysela
88037 Bratislava, Jánska ulica 1. CSSR

*Acta Chimica Academiae Scientiarum Hungaricae, Tomus 98 (2), pp. 199—204 (1978)*

# ÜBER DIE ROLLE VON CHEMISCHEN FAKTOREN BEIM ZIEHVORGANG DOTIERTER WOLFRAMDRÄHTE**

T. MILLNER*

*Forschungsinstitut für Technische Physik der Ungarischen Akademie der Wissenschaften Budapest, Ungarn*

Eingegangen am 2. Dezember, 1977

Es wurde ein Versuch unternommen, um die beobachteten Unterschiede in der Bearbeitbarkeit von *a)* ungedopten, *b)* mit KAl gedopten, *c)* mit KSi und *d)* mit KSiAl (und KSiGa) gedopten, gezogenen Wolframdrähten weder auf die Gegenwart von Oxidteilchen, noch auf das Vorhandensein von dünnen Glasschichten an den Faseroberflächen, sondern auf das Auftreten von mit Si-Atomen verbundenen »wendefähigen« Sauerstoffatomen zurückzuführen, welche eine gegenseitige Verschiebung der Fasern aneinander erlauben.

Im folgenden wird versucht, diejenigen von uns beobachteten Wirkungen von Fremdstoffspuren zu deuten, welche im Laufe der früher bei uns üblichen Erzeugung von pulvermetallurgischen Wolframdrähten bei Betriebsuntersuchungen während des Ziehvorganges, also während der Ausbildung der Faserstruktur der Drähte aufgetreten sind.

Die Beobachtungen beziehen sich auf vier Sorten von Drähten, die aus ausgefällter Wolframsäure $WO_3 \cdot H_2O$ nach einer früher von uns schon beschriebenen Technologie [1] hergestellt waren, und als:

a) ungedopte;
b) mit $K_2O$ und $Al_2O_3$ gedopte;
c) mit $K_2O$ und $SiO_2$ gedopte;
d) mit $K_2O$, $SiO_2$ und $Al_2O_3$ gedopte

Drähte angesehen werden konnten.

Bei einem Durchmesser von etwa 0.6 mm besaßen alle Drähte der vier Varianten eine Faserstruktur. Die Fasern hatten eine Länge von etwa 1—2 mm und einen Durchmesser von etwa 0.001 mm. Im Zerreißversuch bei Zimmertemperatur wiesen alle Drähte eine Bruchdehnung von etwa 2% und eine Kontraktion von etwa 50% auf. Wie früher festgestellt wurde [2], ist diejenige Schubspannung, welche bei der Kontraktion dieser Drähte nötig ist, um das Gleiten der Fasern aneinander bei Zimmertemperatur auszulösen, auffallend niedrig,

* 1325 Budapest, Postfach 76, Ungarn
** Vortrag, gehalten im Rahmen des 9. Plansee Seminars (Reutte, 1977)

d.h. etwa 0.2 kp/mm². Man darf ein ähnlich leicht stattfindendes Fasergleiten auch im Ziehvorgang, also auch bei einer Temperatur von z. B. 800 °C annehmen.

Nach jahrzehntelangen Beobachtungen haben sich bei den vier Drahtsorten — bei gleichgehaltenen Ziehtemperaturen, Ziehgeschwindigkeiten und Kaliber-Abstufungen — folgende Unterschiede ergeben:

a) die ungedopten Drähte ließen sich mit der kleinsten Bruchzahl und kleinster Ziehstein-Abnutzung, d. h. am »leichtesten« ziehen;

b) die KAl-Drähte ließen sich genauso »leicht« ziehen wie die ungedopten Drähte;

c) die KSi-Drähte erwiesen sich im Betrieb als »härter«, d. h. härter, als die ungedopten und KAl-Drähte;

d) die KSiAl-Drähte waren noch »härter« als die KSi-Drähte: sie erbrachten die relativ größten Bruchzahlen und Ziehsteinabnutzungen.

Daraus kann man vorläufig folgende Schlüße ziehen:

1. Das Vorhandensein von Si erschwert das Ziehen.

2. Bei *Ab*wesenheit von Si erschwert das Vorhandensein von Al die Bearbeitung nicht.

3. Bei *An*wesenheit von Si wird das Ziehen der Drähte durch Al erheblich erschwert.

Bei der Suche nach einer Erklärung dieser Tatsachen wollen wir folgendes in Betracht ziehen: beim Ziehverhalten der Drähte spiegelt sich erfahrungsgemäß vorwiegend die Wirkung der zugesetzten und nicht die der als Verunreinigungen des Ausgangsmaterials vorhandenen Fremdstoffe wider.

Um 1955 war man bemüht aufzuklären, welche Eigenschaften der zugesetzten Spuren im Rekristallisationsprozeß zu dem Entstehen der vorteilhaften Großkristallstruktur (einer Langkristallstruktur) führen [1]. Es galt damals, die geeignetsten Zusatzstoffe aufzufinden, und die Frage, inwieweit die besten Zusätze die Bearbeitbarkeit des Drahtes beeinflußen, tauchte nur nebensächlich auf. Man wußte damals, daß weder K, noch Si oder Al allein nicht zu einer Großkristallstruktur führen, und fand, daß dafür KSi und noch mehr KSiAl die besten Zusatzkombinationen seien, wobei man sich mit der Bearbeitbarkeit solcher Drähte zufrieden stellte. MEIJERING und RIECK waren die ersten, die die Wirkung dieser besten Kombinationen mit der Annahme zu erklären versuchten, daß sich aus den Zusätzen kleine Fremdkörperteilchen (wie z. B. Oxyd-, Silikat—usw. Teilchen) bilden und die Faseroberflächen (unvollständig) bedekken, wodurch das Wachsen der Kristallite in Richtung der Drahtachse gelenkt wird, was dann eine aus langen Kristalliten bestehende Struktur zur Folge hat [3]. Damals haben auch wir uns für die Wirkungsweise dieser besten Zusätze in der Rekristallisation interessiert und haben die Annahme gemacht, daß die wirksamen Zusatzspuren keine Fremdphasen-Teilchen, sondern Einzel-Atome der spezifischen Zusatzmaterialien seien.

Sodann haben wir uns darüber Gedanken gemacht, welches Verhalten von atomdispers vorhandenen K-, Si- und Al-Atomen zu erwarten wäre. Wir schnitten damit neben den Fragen der Rekristallisation zugleich auch die Fragen der Bearbeitbarkeit an.

Die Plastizität der Metalle beruht auf der Beweglichkeit ihrer Versetzungen. Fremdatome — wenn sie sich in einer, ihrer Natur nach gebogenen Linienversetzung befinden — müssen bei der Bearbeitung, also bei der Weiterbewegung der gebogenen Versetzungen, die Richtungen ihrer Verbindungen mit den Nachbaratomen beträchtlich ändern. Für ein K-Atom mit seinem einzigen kugelsymmetrischen s-Valenzelektron ist dies leicht möglich. Auch die zwei s-Elektronen und ein p-Valenzelektron eines Al-Atomes erlauben dieses Verhalten ohne Zwang. Sind aber gleichzeitig zwei (oder mehr) p-Valenzelektronen tätig, wie im Falle von Si-Atomen, so kann eine p-Bindung ihre Richtung nur dann ändern, wenn auch die zweite p-Bindung ihre Richtung (und zwar in vorgeschriebener Weise) ändert, da zwischen den beiden p-Richtungen der Zwang besteht, rechtwinklig zueinander zu verlaufen. Das bedeutet eine beschränkte Beweglichkeit für Atome mit mehr als einer p-Bindung in der Versetzungslinie.

Dementsprechend erwarteten wir von aus atomarem K und Al bestehenden Zusatzspuren keine Erschwerung der Bearbeitung, von atomaren Si-Zusatzspuren hingegen eine Verschlechterung der Bearbeitbarkeit. Die erstgenannte Erwartung haben wir in der Praxis nicht ausnahmslos bestätigt gefunden, da wir nicht erklären konnten, warum die KSiAl-Drähte, die außer K- und Si-Atomen nur noch »schmiegsame« Al-Atome enthalten, schwieriger als KSi-Drähte zu bearbeiten sind.

Damit ist aber die Gültigkeit unserer einseitigen atomistischen Deutung der Zusatzwirkungen in Frage gestellt.

Bei der experimentellen Weiterverfolgung der Wirkungsweise der Zusatzspuren haben wir im $Ga_2O_3$ ein derartiges Oxid gefunden, welches einerseits aus den Al-Atomen ähnlichen Ga-Atomen aufgebaut ist, andererseits sich unter den Bedingungen der Wolframpulverherstellung durch Wasserstoff bis zum elementaren Zustand reduzieren läßt. Danach stellten wir Drähte mit KSiGa statt KSiAl-Zusatz her [4]. In diesen — nach ihrer Rekristallisation ebenfalls langkristallinischen — Drähten muß man das Gallium als atomar-dispers ansehen. $Al_2O_3$ wird zwar beim $WO_3$-Reduktionsprozeß durch Wasserstoff nicht reduziert, während des Sinterns aber mit Bestimmtheit in den elementaren Zustand überführt (wofür u. a. Restwiderstandsuntersuchungen sprechen). Auffallenderweise lassen sich KSiAl-Drähte trotzdem schwieriger bearbeiten als KSiGa-Drähte und diese wieder nicht so gut, wie KSi-Drähte (obwohl die KSiGa-Drähte sicher Ga-Atome enthalten). Dadurch ergeben sich nicht nur eine, sondern gleich zwei offene Fragen:

1. warum sind schmiegsame Al-Atome enthaltende KSiAl-Drähte schwieriger bearbeitbar als KSi-Drähte?

2. warum sind die schmiegsamen Ga-Atome enthaltenden KSiGa-Drähte schwieriger bearbeitbar als die KSi-Drähte, aber doch nicht so schwierig, wie die KSiAl-Drähte?

Trotzdem scheint uns, daß der Ga-Versuch unsere Annahme einer atomspezifischen Wirkung der Zusatzspuren eher bekräftigt als widerlegt. Um unsere Annahme einer weiteren Prüfung zu unterwerfen, versuchten wir sie auch im Falle von Si zu prüfen. Wir fanden im $GeO_2$ ein Oxid, in dem das Ge im physikalischen und chemischen Verhalten dem Si sehr ähnlich ist, sich aber durch Wasserstoff unter Betriebsbedingungen bis zu elementarem Ge reduzieren läßt. Als wir dann statt eines KSiAl-Drahtes einen KGeAl-Draht herzustellen versuchten, mußten wir feststellen, daß ein $GeO_2$-Zusatz eine ganz andersartige Wirkung hat als ein $SiO_2$-Zusatz. Die zweifellos nicht $GeO_2$, sondern Ge-Atome enthaltenden KGeAl-Sinterstäbe waren so spröde, daß sie überhaupt nicht bearbeitet werden konnten. Dieser Unterschied zwischen dem Einfluß der $SiO_2$ und $GeO_2$ enthaltenden Zusätze lenkte unsere Gedanken in eine neue Richtung. Es tauchte die Frage auf, ob nicht Si seine Wirkung — im Gegensatz zu K, Al und Ga — irgendwie doch mit Sauerstoff verbunden ausübt. Wenn auch nicht als $SiO_2$, aber doch irgendwie gemeinsam mit Sauerstoffatomen, d. h., daß in der Anwesenheit von Si-Atomen auch den Sauerstoffatomen eine, die Drahteigenschaften von KSi-, KSiAl-, KSiGa- usw. Drähten bestimmende Rolle zukommt. Man darf nämlich nicht vergessen, daß gemäß Literaturangaben in jedem auf den Sauerstoffgehalt geprüften Wolframdraht bisher mindestens 1—10 ppm Sauerstoff gefunden wurden.

Wir haben 1970 die Beobachtung gemacht, daß die Metallfasern der gezogenen Wolframdrähte bei Zugbelastung aneinander leicht weitergleiten [2] und haben begonnen, uns mit der Frage zu beschäftigen, wie — in welchem chemischen Bindungszustand — die schwer lenkbaren, nicht anpassungsfähigen Si-Atome in den KSi-, KSiAl-, KSiGa- usw. Drähten das Gleiten der Faser nicht hemmen, sondern ermöglichen. Ich errinnerte mich an den in jedem Wolframdraht vorhandenen Sauerstoffgehalt und habe plötzlich daran gedacht, daß in den Silicatgläsern die Sauerstoffatome in Verbindung mit Siliziumatomen (im $SiO_4$-Tetraeder-Netzwerk) derartige —Si—O—Si— Verkettungen bilden, in welchen die Sauerstoffatome die $SiO_4$-Tetraeder miteinander unter den verschiedensten Winkeln verknüpfen, wobei sich während des plastischen Verhaltens der Gläser die —Si—O—Si— Winkel mit ganz geringen Kräften in fast willkürlicher Weise verändern lassen.

Daraufhin habe ich mir vorgestellt, daß in den KSi-, KSiAl-, KSiGa- usw. Drähten an den Fasergrenzen weder $SiO_2$- oder Silikat-Teilchen vorhanden sind (in welchen sich $SiO_4$-Tetraeder mit vorgeschriebenen nicht verändlichen —Si— —O—Si— Winkeln im Kristallgitter zusammenfügen), noch »starre« Si-Atome anwesend sind (die das Fasergleiten hemmen müssten), sondern angenommen, daß dort das Fasergleiten durch die Veränderlichkeit ihrer —Si—O—W—

Winkelwerte erlaubende —Si—O—W— Schichten auftreten. Es sei betont, daß meiner Vorstellung nach diese Schichten keine $SiO_4$-Tetraeder enthalten, also nicht aus einer dünnen Glasschicht bestehen, sondern nur derartige, die Faseroberflächen miteinander verknüpfende —W—O—Si—O—W— Bindungen enthalten, in welchen sich die Sauerstoffatome in einem wesensgleichen »richtungsunabhängigen« Bindungs-zustand befinden, wie in den —Si—O—Si— Bindungen der Silicatgläser.

Mit dieser Annahme kann man — unserer Meinung nach — alle, die beim betriebsmäßigen Drahtziehen auftretenden, von den Zusatzspuren verursachten Erscheinungen zwanglos erläutern.

1. In der »guten« Bearbeitbarkeit der ungedopten Wolframdrähte können wir diejenige »natürliche« Bearbeitbarkeit aller gezogener Wolframdrähte erblicken, welche Bearbeitbarkeit durch die gleichmäßig im Ausgangsmaterial verteilten Fremdstoffspuren bedingt ist und welche dann in den gedopten Drähten durch eine von Fall zu Fall gleichmäßige oder ungleichmäßige Verteilung der Zusatzspuren zusätzlich beeinflußt wird.

2. In den KAl-Drähten wird die gute »natürliche« Bearbeitbarkeit der ungedopten Drähte durch die im Wolframgitter gelösten »geschmeidigen«, »wendefähigen« Al-Zusatz-Atome nicht merkbar verschlechtert und auch das Fasergleiten durch die dort befindlichen, ebenfalls »geschmeidigen« K-Atome nicht behoben.

3. In den KSi-Drähten kommt zu der kaum bemerkbaren K-Wirkung infolge der Anwesenheit von Si- und O-Atomen eine Wirkung von —W—O—Si—O—W— Bindungen hinzu, die das Fasergleiten zwar nicht völlig hemmt, aber doch fühlbar erschwert.

4. Die noch schwierigere Bearbeitbarkeit der KSiAl-Drähte hat seine Ursache darin, daß die Al-Zusatz-Atome die Richtungsänderungen der Sauerstoff-Bindungen merkbar einschränken.

Es ist nämlich bekannt, daß die Al-Atome in den Silicatgläsern eine ausgesprochen große Neigung zur tetraedrischen Koordination, d. h. zur Bildung von $AlO_4$-Tetraeder haben [5]. Dadurch wird aber die Wendefähigkeit der Sauerstoffatome des gemeinsamen Tetraedernetzes beträchtlich herabgesetzt, wie man es aus der Tatsache ersehen kann, daß die Schmelze von der Zusammensetzung des Albites, $Na_2O \cdot Al_2O_3 \cdot SiO_2$, viel zähflüssiger ist als die reinen Natriumsilicat-Schmelzen [6].

Das besagt aber, daß die auf die —Si—O— Bindungen beruhende Fasergleitung der KSiAl-Drähte infolge der Einschränkung der Wendefähigkeit der Sauerstoffatome durch das Hinzutreten von Al-Atomen beträchtlich erschwert wird.

5. Daß die KSiGa-Drähte merkbar weniger schwer zu bearbeiten sind als die KSiAl-Drähte, kann man darauf zurückführen, daß die Ga-Atome in Silicatgläsern eine viel geringere Neigung als die Al-Atome [7] dazu haben, sich mit

Sauerstoffatomen tetraedrisch zu umgeben, und demzufolge die Wendefähigkeit der Sauerstoffatome der —W—O—Si—O—W— Bindungen weniger beeinträchtigen als die Al-Atome.

## LITERATUR

[1] MILLNER, T.: Acta Techn. Hung. **17,** (1957), 67—112
[2] MILLNER, T., VARGA, L., VERŐ, B.: Z. Metallk. **63,** (1972) 754—756
[3] MEIJERING, J. L., RIECK, G. D.: Philips' Techn. Rundsch. **19,** (1957/58) 113—121
[4] MILLNER, T.: Acta Techn. Hung. **70,** (1971) 269—289
[5] RAWSON, H.: Inorganic Glass-Forming Systems, Ed. Academic Press London and New York, (1967) P. 130.
[6] *Ibid.:* P. 91.
[7] *Ibid.:* P. 200—201.

Tivadar MILLNER H-1325 Budapest. BOX 76.

*Acta Chimica Academiae Scientiarum Hungaricae, Tomus 98 (2), pp. 205—210 (1978)*

# MOLECULAR CONSTANTS OF $ONF_3$

A. NATARAJAN

*Department of Physics A. V. V. M. Sri Pushpam College Poondi — Thanjavur Dt.*

and

K. CHOCKALINGAM

*Department of Physics Government Arts College Tindivanam, Tamil Nadu — India*

Received March 8, 1977

In revised from December 23, 1977

The potential energy constants of trifluoramine oxide, $ONF_3$, are evaluated on the basis of general valence force field. The mean square amplitudes of vibration, the generalized mean square amplitudes of vibration, Coriolis coupling constants, shrinkage constants and rotation distortion constants of this molecule are also computed and presented in this paper.

## Introduction

The molecule $ONF_3$ was prepared by BERTLETT *et al.* [1] and FOX *et al.* [2]. The infrared spectrum of this molecule has been reported by CURTIS *et al.* [3] and the vibrational frequencies have been assigned on the basis of $C_{3v}$ symmetry. Very recently, the vibrational frequencies of this molecule have been completely reassigned by KARL *et al.* [4].

The structure of $ONF_3$ has been first investigated by CURTIS *et al.* [3] and the possible structural parameters have been reported assuming the angles to be tetrahedral. Subsequent electron diffraction study [5] of this molecule confirmed the $C_{3v}$ symmetry; but the bond angles reported were different from tetrahedral angles.

CURTIS *et al.* [3] have studied the thermodynamic properties of this molecule. Later, SUNDARAM *et al.* [6] have also calculated its thermodynamic functions. The general valence and Urey-Bradley force constants have been obtained by VENKATESWARLU *et al.* [7]. Using the general valence force field, they have also evaluated the generalized mean square amplitudes of vibration and the Coriolis coupling coefficients of this molecule. But, in their calculations, they have made use of only the approximate structural parameters and vibrational frequencies [3]. In the present investigation, the general valence force constants, mean square amplitudes of vibration, generalized mean square amplitudes of vibration, shrinkage constants, Coriolis coupling coefficients and rotation distortion constants of this molecule have been determined using the revised frequency assignments and molecular parameters. [4, 5].

The molecule $ONF_3$ belongs to $C_{3v}$ point group. The normal modes of vibration are distributed among the two symmetry species as $3a_1 + 3e$. All the fundamentals are active both in infrared and Raman spectra. Molecular configuration, numbering of the atoms and the orientation of the principal axes are shown in Fig. 1.

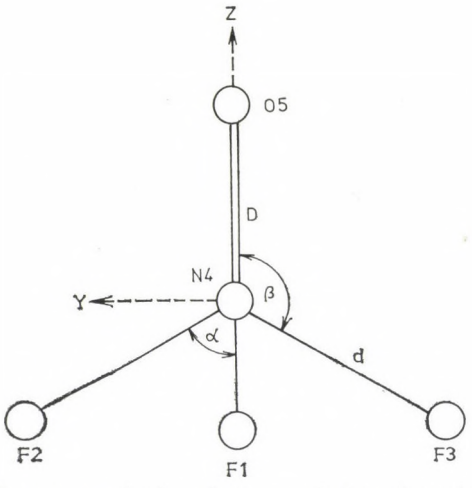



*Fig. 1.* The internal coordinates, numbering of atoms and the orientation of the principal axes of $ONF_3$ molecule

## 2. Methods of Calculation

Assuming a general valence type of potential function, a set of force constants is obtained by the *F-G*-matrix method [8] of WILSON. The symmetrized mean square amplitudes matrix, $\Sigma$ is determined by the *L*-matrix method [9]. Using the matrix, the parallel mean square amplitudes of vibration are evaluated. The generalized mean square amplitudes which include the mean square parallel amplitudes $\langle(\Delta z)^2\rangle$, the mean square perpendicular amplitudes $\langle(\Delta x)^2\rangle$ and $\langle(\Delta y)^2\rangle$ and the mean cross products $\langle(\Delta x)\ (\Delta y)\rangle$, $\langle(\Delta y)(\Delta z)\rangle$ and $\langle(\Delta z)\ (\Delta x)\rangle$ are determined by the method of MORINO and HIROTA [10]. The non-linear shrinkage effects [11] are also calculated using the generalised mean square amplitudes of vibration. The anharmonic terms of the shrinkage effects [11] are also calculated using the generalised mean square amplitudes of vibration. The anharmonic terms of the shrinkage are neglected in this calculation.

The Coriolis coupling coefficients are calculated using the relation

$$\zeta^{\alpha}\,(\alpha = x, y, z) = L^{-1}\, C^{\alpha}\, \widetilde{L^{-1}}\,,$$

where $L$ is the normal coordinate transformation matrix and $C^{\alpha}$ is matrix introduced by MEAL and POLO [12]. According to JAHN's rule [13], the non-vanishing $\zeta$ values are found to be $\zeta^x$ and $\zeta^y$ arising from $a_1 \times e$ coupling and $\zeta^z$ arising from $e \times e$ coupling.

The centrifugal distortion constants of $ONF_3$ are computed making use of the relations given by KIVELSON and WILSON [14] and by CYVIN *et al.* [15.]

## 3. Results and discussion

The internal force constants of $ONF_3$ are presented in Table I. It is seen

**Table I**

*Internal force constants of $ONF_3$ (in mdyne/Å)*

| | |
|---|---|
| $f_D$ | 12.230 |
| $f_d$ | 2.642 |
| $f_{Dd}$ | 1.166 |
| $f_{dd}$ | 0.304 |
| $f_{\beta}-f_{\beta\beta}$ | 1.148 |
| $f_{\alpha}-f_{\alpha\alpha}$ | 0.598 |
| $f_{D\beta}$ | 0.017 |
| $f_{d\beta}$ | 0.317 |
| $f_{d\alpha}$ | 0.383 |
| $f_{\alpha\beta}$ | −0.143 |

that the force constant $f_{N-F}$ is considerably small since the N–F bond is unusually long and its stretching frequency also is small. The present value of $f_{N-F}$ is in agreement with the values reported in NOF ($f_{N-F} = 2.3$ md/Å) [16] and NOF ($f_{N-F} = 2.71$ md/Å) [17], where again the N–F bonds are abnormally long. BADGER's rule [18] predicts a value of 1.56 for the ratio $\frac{f_{N-F}\,(NF)_3}{f_{N-F}\,(ONF)_3}$ and the calculated value of this ratio in the present investigation using $f_{N-F}$ $(NF_3)$ force constant as 4.31 md/Å [19], is found to be 1.63. The agreement is quite satisfactory.

The $f_{N=O}$ force constant is calculated to be 12.23 md/Å. This force constant assumes different values {15.90 md/Å in NOF [16] and 11.81 md/Å in $NO_2F$ [17]} in different molecules. The lowering of $f_{N-F}$ force constant may be attributed to the presence of other valence bond structures in addition to the structure considered in this investigation. Hence, the following resonance structures may be considered for the molecule $ONF_3$.

The N = O bond becomes shorter and N–F bond longer in structure II, which makes N–F bond more ionic in character, thus reducing the force constant $f_d$, considerably. The appreciably large value of the interaction force con-

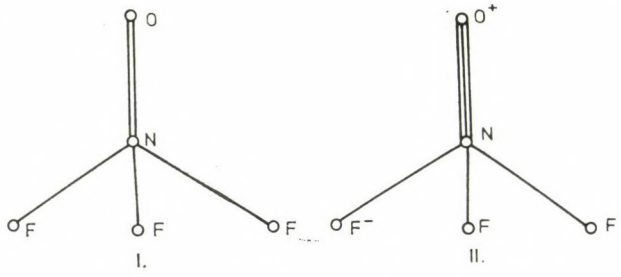



*Fig. 2*

stant $f_{Dd}$ may be due to structure II, which contributes significantly to the final hybrid eventhough, the structure I is the principal contributor.

The mean square amplitudes of vibration at 300 K are given in Table II·

**Table II**

*Mean square amplitudes of vibration of $ONF_3$ at 300 K in $10^{-4}$ Å$f^2$*

| | |
|---|---|
| $\sigma_D$ | 13.97 |
| $\sigma_d$ | 32.90 |
| $\sigma_{Dd}$ | −3.95 |
| $\sigma_{dd}$ | −3.85 |
| $\sigma_\beta - \sigma_{\beta\beta}$ | 83.71 |
| $\sigma_\alpha - \sigma_{\alpha\alpha}$ | 111.50 |
| $\sigma_{D\beta}$ | −9.06 |
| $\sigma_{d\beta}$ | −22.73 |
| $\sigma_{d\alpha}$ | −26.83 |
| $\sigma_{\alpha\beta}$ | 29.93 |

The generalized mean amplitudes of vibration and the shrinkage constants are listed in Table III. The parallel mean square amplitudes $\langle(\Delta z)^2\rangle$ compare well with the mean square amplitudes quantities ($\sigma$). The parallel mean square amplitudes of N—F and O . . . F are found to be the same. The experimental values of the mean amplitudes of vibration [5] are given in brackets inTable III. It is felt that the agreement is satisfactory. The values calculated for shrinkage constants F . . . F and O . . . F are of the same magnitude.

**Table III**

*Generalized mean amplitudes of vibration in Å and shrinkage constants in Å of $ONF_3$ at 300 K*

| Atom pair | Parallel mean amplitudes $\langle(\Delta z)^2\rangle^{\frac{1}{2}}$ | Perpendicular mean amplitudes | | Mean cross products | | | Shrinkage |
|---|---|---|---|---|---|---|---|
| | | $\langle(\Delta x)^2\rangle^{\frac{1}{2}}$ | $\langle(\Delta y)^2\rangle^{\frac{1}{2}}$ | $\langle(\Delta x)(\Delta y)\rangle^{\frac{1}{2}}$ | $\langle(\Delta y)(\Delta z)\rangle^{\frac{1}{2}}$ | $\langle(\Delta z)(\Delta x)\rangle^{\frac{1}{2}}$ | |
| O—N | 0.0374 (0.0289 ± 0.0044) | 0.05042 | 0.05042 | 0 | 0 | 0 | — |
| N—F | 0.0571 (0.0507 ± 0.0032) | 0.04184 | 0.0630 | 0 | 0 | −0.01484 | — |
| F . . . F | 0.0637 (0.0551 ± 0.0077) | 0.04390 | 0.04884 | 0.02131 | 0.02290 | 0.01858 | 0.0263 |
| O . . . F | 0.0568 (0.0580 ± 0.0089) | 0.04193 | 0.05082 | 0 | 0 | −0.02809 | 0.0262 |

The Coriolis coupling coefficients are reported in Table IV. For $a_1 \times e$ coupling,

**Table IV**

*Coriolis coupling coefficients of $ONF_3$*

| Coupling $a_1 \times e$ | | Coupling $e \times e$ | |
|---|---|---|---|
| $\zeta^x_{1,4}$ | −0.9196 | $\zeta^z_{4,4}$ | 0.8630 |
| $\zeta^x_{1,5}$ | 0.0875 | $\zeta^z_{4,5}$ | −0.0755 |
| $\zeta^x_{1,6}$ | −0.2022 | $\zeta^z_{4,6}$ | 0.4566 |
| $\zeta^x_{2,4}$ | 0.2238 | $\zeta^z_{5,5}$ | 0.3140 |
| $\zeta^x_{2,5}$ | 0.6091 | $\zeta^z_{5,6}$ | 0.5336 |
| $\zeta^x_{2,6}$ | 0.3313 | $\zeta^z_{6,6}$ | −0.6241 |
| $\zeta^x_{3,4}$ | 0.1844 | | |
| $\zeta^x_{3,5}$ | −0.5186 | | |
| $\zeta^x_{3,6}$ | −0.1320 | | |

$$\zeta^x_{a_1 \times e_b} = -\zeta^y_{a_1 \times e_a}$$

and

$$\zeta^x_{a_1 \times e_a} = \zeta^y_{a_1 \times e_b} = 0 .$$

Also, the coupling between $\nu_1$ and $\nu_4$ is found to be very strong, for rotations about $x$ and $y$ axes. For $e \times e$ coupling, it is found that $\sum_{i=4}^{6} \zeta_i^{\,i} = \frac{I_A}{2I_B}$ and $|\zeta^z| = -\frac{I_A}{2I_B}$. Further, the coupling between the two degenerate modes $\nu_4$ and $\nu_6$ are fairly strong for rotation about $z$ axis.

The centrifugal distortion constants are presented in Table V. Since the

**Table V**

*Centrifugal distortion constants of $ONF_3$ in $KH_2$*

| | |
|---|---|
| $D_J$ | 5.260 |
| $D_K$ | 0.015 |
| $D_{JK}$ | −2.833 |

molecule $ONF_3$ is a symmetric rotor, the constants $R_5$, $R_6$ and $\delta_J$ vanish. There also exist the following relations among the non-vanishing elements:

$$\tau_{xxxx} = \tau_{yyyy}$$

$$\tau_{yyzz} = \tau_{zzxx}$$

$$\tau_{yzyz} = \tau_{zxzx}$$

$$\tau_{xxzx} = -\tau_{yyzx} = -\tau_{xyyz}$$

and

$$\tau_{xyxy} = \frac{1}{2}\left(\tau_{xxxx} - \tau_{xxyy}\right).$$

The value of $D_J$ is positive. This indicates that the centrifugal forces about any given axis will always tend to increase the moment of inertia about that axis which in turn reduces the centrifugal distortion constants.

## REFERENCES


[1] Bartlett, N., Pasamore., Wells, E. J.: Chem. Commun., **213,** (1966)
[2] Fox, W. B., *et al.:* J. Am. Chem. Soc., **88,** 2604 (1966)
[3] Curtis, E. C., Fillipovich, D., Moberly, W. H.: J. Chem. Phys., **46,** 2904 (1967)
[4] Karl, O., Christe., Curtis, E. C., Carl J. Schack: Spectrochim. Acta, **31a,** 1035 (1975)
[5] Vernon Plato., William D., Hartford., Kenneth Hedber G.: J. Chem. Phys., **53,** 3488 (1970)
[6] Sundaram, S., *et al.:* J. Chem. Phys., **60,** 325 (1974)
[7] Venkateswarlu, K., Joseph, P. A., Rudrawarrier, M. K., Mariamma P. Mathew: Indian J. Pure & Appl. Phys., **7,** 279 (1969)
[8] Wilson, E. B.: J. Chem. Phys., **7,** 1047 (1939) and **9,** 76 (1941)
[9] Cyvin, S. J.: Acta Polytech. Scand., Ph **6,** 279 (1960)
[10] Morino, Y., Hirota, E.: J. Chem. Phys., **23,** 737 (1955)
[11] Cyvin, S. J.: Acta. Chem. Scand., **17,** 292 (1963)
[12] Meal, J. H., Polo, S. R.: J. Chem. Phys., **24,** 1119 (1956)
[13] Jahn, H. A.: Phys. Rev., **56,** 680 (1939)
[14] Kivelson, D., Wilson, E. B. Jr.: J. Chem. Phys., **20,** 1575 (1952) **21,** 1229 (1953)
[15] Cyvin, S. J., Cyvin, B. N., Hagen, G.: Z. Naturf., **23a,** 1649 (1968)
[16] Jones, L. H., Asprey, L. B., Ryan, R. R.: J. Chem. Phys., **47,** 3371 (1967)
[17] Mirri, A. M., Cazzoli, G., Perretti: J. Chem. Phys., **49,** 2775 (1968)
[18] Badger, R. M.: J. Chem. Phys., **2,** 128 (1934), **3,** 710 (1935)
[19] Sawodny, S., Ruoff, A., Peacogk, C. J., Muller, A.: Molec. Phys., **14,** 433 (1968)



A. Natarajan Poondi-Thanjavur DT India 613503.
K. Chockalingam Tindivanam, Tamil Nadu, India

*Acta Chimica Academiae Scientiarum Hungaricae, Tomus 98 (2), pp. 211—214 (1978)*

# THERMAL TRANSCARBOXYLATION REACTIONS, XII*

## IRREVERSIBILITY OF THE THERMAL DECARBOXYLATION OF ALKALI BENZOATES

J. SZAMMER and L. ÖTVÖS

*(Central Research Institute for Chemistry of the Hungarian Academy of Sciences, Budapest)*

Received July 12, 1977

The thermal conversion of alkali benzoates has been investigated in $^{14}CO_2$ atmosphere. It has been established that the low benzoate-$^{14}C$ formation detected is due to the decarboxylation of dicarboxylic acid salts of high $^{14}C$-content, formed in the reaction. It has been concluded from the experimental results that the thermal decarboxylation of alkali benzoates is an irreversible reaction step.

The experimental finding [1—3] that in thermal transcarboxylation reactions the formation of dipotassium terephthalate proceeds through several intermediate carboxylates, calls attention to the important role of the reversibility of the carboxy group transfer process.

In the reaction proceeding according to the mechanism [4, 5] given in Fig. 1, the irreversibility of hydrogen abstraction by the phenyl anion has been proved already by RATUSKY [6], using $^{14}C$-labelled benzene. The reversibility of the decarboxylation and carboxylation steps (Fig. 2) remains a question to be elucidated. In the present work, we report on experimental results obtained in the investigation of the thermal decarboxylation of alkali benzoates.

$$C_6H_5COOK \longrightarrow K^{\oplus\ominus}C_6H_5 + CO_2$$

$$C_6H_5COOK + K^{\oplus\ominus}C_6H_5 \longrightarrow K^{\oplus\ominus}C_6H_4COOK + C_6H_6$$

$$K^{\oplus\ominus}C_6H_4COOK + CO_2 \longrightarrow C_6H_4(COOK)_2$$

*Fig. 1*

$$C_6H_5COOK \underset{+CO_2}{\overset{-CO_2}{\rightleftharpoons}} K^{\oplus\ominus}C_6H_5$$

$$K^{\oplus\ominus}C_6H_4COOK \underset{\pm CO_2}{\overset{+CO_2}{\rightleftharpoons}} C_6H_4$$

*Fig. 2*

* The following papers are considered as parts IX—XI: Chem. and Ind. (London), 1540 (1970); Radiochem. Radioanal. Lett., 6, 129 (1971). J. Thermal Anal., **3**, 149 (1971).

## Results and discussion

It is known [7—9] that in thermal transcarboxylation reactions proceeding in $^{14}CO_2$ atmosphere, $^{14}C$ is incorporated very extensively in to the product carboxylates. The exchange reaction between the carboxy group of alkali benzoates and $^{14}CO_2$, one of the possible realizations of which is the reversible decarboxylation given in Fig. 2, has been less studied.

SORM *et al.* [8] have observed the formation of radioactive potassium benzoate in the thermal conversion of potassium benzoate in the presence of $^{14}CO_2$. However, these observations were made under experimental conditions, where the decarboxylation of dicarboxylic $^{14}C$ acid salts formed during the reaction must also be taken into account, which could lead to the formation of $^{14}C$-labelled benzoate. For the experimental verification of the latter, potassium benzoate has been subjected to thermal treatment* in the presence of dipotassium phthalate-(carboxy-$^{14}C_1$) or dipotassium isophthalate -(carboxy-$^{14}C_1$). As can be seen from Table II, benzoic acid, recovered from the thermal decomposition residue of the salt mixture, reveales a considerable radioactivity, which means that the dicarboxylic acids mentioned have been decarboxylated to a substantian extent.

**Table I**

*Thermogravimetric parameters of alkali benzoates*

| Salts | Decomposition temperature (°C) | | Weight loss (%) |
|---|---|---|---|
| | Initial | DTG peak | |
| Na benzoate | 450 | 550 | 56 |
| K benzoate | 430 | 520 | 53 |
| Rb benzoate | 410 | 510 | 40 |
| Cs benzoate | 390 | 510 | 33 |

**Table II**

*Decarboxylation of dicarboxylic acids*

| Salt mixture[a] | Temperature (°C) | Time (min) | Radioactivity of recovered benzoic acid ($10^6$ dpm/mmol) |
|---|---|---|---|
| KB + $K_2P$-$^{14}C$ | 450 | 60 | 3.1 |
| KB + $K_2IP$-$^{14}C$ | 450 | 60 | 1.8 |
| CsB + $Cs_2P$-$^{14}C$ | 400 | 30 | 2.6 |
| CsB + $Cs_2IP$-$^{14}C$ | 400 | 30 | 1.4 |

[a] Mole ratio of salt mixture 1 : 1
Abbreviations: B — benzoate; P — phthalate; IP — isophthalate
Initial radioactivity: $K_2P$-$^{14}C$: $5.0 \times 10^6$ dpm/mmol
$K_2IP$-$^{14}C$: $3.8 \times 10^6$ dpm/mmol

* The reaction temperatures of the experiments have been established on the basis of decomposition point values determined by the derivatographic method (Table I)

For the investigation of the reversibility of the decarboxylation step, alkali benzoates were thermally decomposed in the presence of $^{14}CO_2$, benzoic acid was recovered from the residue and its radioactivity determined. The experimental results are given in Table III. For comparison, in a few experiments, the terephthalate formed in the reaction has also been isolated, its radioactivity being given in the table.

**Table III**

*Data of benzoate carboxy group — $^{14}CO_2$ exchange*

| Initial salt[a] | Temperature (°C) | Time (min) | $^{14}CO_2$[b] press. (atm) | Conversion[c] (%) | Radioactivity of product ($10^6$ cpm/mmol) | |
|---|---|---|---|---|---|---|
| | | | | | Benzoic acid | Terephthalic acid |
| NaB | 450 | 60 | 3 | 10 | 0 | — |
| KB | 430 | 30 | 3 | 5 | 0 | — |
| | 440 | 60 | 3 | 15 | 0 | — |
| | 440 | 80 | 8 | 10 | 0 | — |
| | 450 | 120 | 6 | 42 | 0.14 | 1.8 |
| KB + $CdI_2$ | 310 | 30 | 3 | 20 | 0.06 | 2.0 |
| RbB | 440 | 60 | 3 | 10 | 0 | — |
| CsB | 410 | 30 | 3 | 15 | 0.06 | — |
| | 410 | 80 | 6 | 30 | 0.2 | 2.0 |
| $CdB_2$ | 320 | 30 | 3 | 25 | 0 | — |

[a] Abbreviations: NaB: sodium benzoate; KB: potassium benzoate; RbB: rubidium benzoate; CsB: cesium benzoate; $CdB_2$: cadmium benzoate

[b] Radioactivity of $^{14}CO_2$: $2.4 \times 10^6$ dpm/mmol

[c] Determined by isotope dilution method for an aliquot part of the aqueous salt solution

It can be established from Table III that during the thermal process the carboxy group of alkali benzoates does not exchange directly with the $^{14}CO_2$ present in the system. The low $^{14}CO_2$ incorporation observed at higher conversions indicates, on the basis of Table II, the decarboxylation of dicarboxylic acids formed in the transcarboxylation reaction. From the experimental results presented, it can be established that the thermal decarboxylation of alkali benzoates is an irreversible reaction step.

The reversibility of the carboxylation of proton-deficient salt molecules (Fig. 2) is beyond the scope of the present work. However, in conjunction with the experimental results discussed, it should be mentioned that the considerable carboxylation of the benzoate molecule by $^{14}CO_2$ present [7—10], further the important measure of decarboxylation of dipotassium phthalate and of dipotassium isophthalate at the decomposition temperature of potassium benzoate together indicate that the carboxylation of proton-deficient salt molecules is a reversible reaction step.

## Experimental

The alkali salts were prepared by neutralization of the carboxylic acids with aqueous alkali hydroxide, the aqueous salt solutions were evaporated to dryness and the residue was dried at 200 °C in vacuum (1 Torr).

For the preparation of phthalic acid-$^{14}C_1$ and isophthalic acid-$^{14}C_1$, the respective toluyl magnesium bromides were carboxylated with $^{14}CO_2$, and the toluylic acid-$^{14}C$ obtained was oxidized in alkaline medium with $KMnO_4$, as described in the literature [11].

### Method

$^{14}CO_2$, liberated from $Ba^{14}CO_3$ of known quantity and specific activity with concentrated $H_2SO_4$, was distilled with liquid air in a glass tube of known volume containing the respective salt. The tube was sealed and placed into a metal case, in which the appropriate counter-pressure was provided from a $CO_2$ pressure bottle. Reactions were carried out in a high-temperature thermostat containing Wood's metal, as described in earlier experiments [12]. The solid residue was dissolved in water, filtered, then acidified with HCl to pH = 1. The acids precipitated were filtered, and from the filtrate containing the mixture of acids, benzoic acid was extracted with chloroform. Benzoic acid samples were recrystallized from petroleum ether.

The amount of residual benzoate was determined by isotope dilution method for an aliquot part of the aqueous salt solution. The processing of these solutions was the same as described above.

The radioactivity of the benzoic acid samples was determinedin toluene solution, with a Packard-Tri-Carb liquid scintillation spectrometer.

## REFERENCES

[1] Ogata, Y., Nakajima, K.: Tetrahedron, **21,** 2393 (1965)
[2] Kraus, M., Kochloefl, K., Setinek, K., Beránek, L., Sorm, F.: Chem. Ind., 1060 (1961)
[3] Ratusky, J., Sorm, F.: Chem. Ind., 1798 (1966)
[4] Furuyama, S.: Bull. Chem. Soc. Japan, **39,** 1212 (1967)
[5] Ratusky, J.: J. Lab. Comp., **6,** 124 (1970)
[6] Ratusky, J., Tykva, R.: Radiochem. Radioanal. Lett., **1,** 325 (1969)
[7] Riedel, O., Kienitz, H.: Angew. Chem., **72,** 738 (1960)
[8] Ratusky, J., Sorm, F.: Coll. Czech. Chem. Commun., **24,** 2553 (1959)
[9] Ratusky, J., Tykva, R., Sorm, F.: Coll. Czech. Chem. Commun., **32,** 1719 (1967)
[10] Ratusky, J., Tykva, R.: J. Lab. Comp., **5,** 211 (1969)
[11] Murray, A., Williams, D. L.: Organic Syntheses with Isotopes, P. 1 p. 439. Interscience, New York 1958
[12] Szammer, J., Noszkó, L.: Acta Chim. (Budapest), **90,** 411 (1976)

János Szammer
László Ötvös
H-1525 Budapest, Pf. 17.

*Acta Chimica Academiae Scientiarum Hungaricae, Tomus 98 (2), pp. 215—223 (1978)*

# SIDE REACTIONS DURING THE REMOVAL OF PROTECTING GROUPS OF N-(PROTECTED AMINOACYL)UREA DERIVATIVES

I. SCHÖN, J. FRISS and L. KISFALUDY

*(Chemical Works of Gedeon Richter Ltd., Budapest)*

Received August 1, 1977

Side reactions during the removal of protecting groups of N-(Z-or BOC-aminoacyl)-urea derivatives (**I**) were studied. Catalytic hydrogenation of **I** led to the formation of **IV** and **V** in an intramolecular reaction of **II**. Acidolytic treatment of **I** in protic solvents results in amide derivatives, in aprotic media the salts of **II** are obtained. The importance of the nucleophilicity of the α-amino group in the intramolecular reaction was confirmed.

In the DCC-mediated peptide synthesis a well-known side reaction is a four-center rearrangement leading to the formation of N-(protected aminoacyl)-urea derivatives (I) [1]. This side reaction is especially undesired in the case of longer peptides, where expensive starting materials are wasted and the removal of the by-product is not easy, either. Yet, in the case of the synthesis of a simple dipeptide mediated by DCC, we can many times detect DCU and **I** on TLC of the crude product. **I** could be isolated in some cases [2—7], and the conditions of its formation were also exhaustively studied in order to reduce its amount [8—11]. Considering the reactivity of **I** in comparison with DCU, the removal of the former from the crude product is advisable.

In the course of a synthesis of human ACTH of revised structure and its fragments [12], the synthesis of Z-Ser-Ala-O$^t$Bu has been effected by means of DCC. From the reaction mixture N-(Z-Ser)-DCU was isolated in a yield of 16%. Complete removal of this compound, however, was not possible by simple methods due to the solubility conditions. Consequently, after catalytic hydrogenation, in the crude product two ninhydrin positive and two ninhydrin negative spots were detected by TLC. The former two were identified as the desired H-Ser-Ala-O$^t$Bu and cyclohexylamine, and the two latter as **IV** and **V**, respectively. Considering that these by-products may considerably disturb the further couplings and purifications, it was of importance to investigate the above side reaction more closely.

For this purpose, we prepared several protected aminoacyl-DCU derivatives (I) (see Experimental) and these were subjected to catalytic hydrogenation in methanol. From the crude product **IV** and **V** were isolated and characterized and, on the other hand, the ratio of the formation of **IV** and **V** was determined by IR technique. The results are summarized in Table I.

**Table I**

*Ratio of formation of* **IV** *and* **V** *in the hydrogenation of* **I** *and their characterization*

| I | IV | | | | V[a] | | | |
|---|---|---|---|---|---|---|---|---|
| | Conversion, % | M. p., °C | $R_f^1$ | $[\alpha]_D^b$ | Conversion, % | M. p., °C | $R_f^1$ | Ref.[g] |
| Z-Gly-DCU | 72.7 | 170—172 | 0.70 | — | 27.3 | 246—247 | 0.65 | [16] |
| Z-Ala-DCU | 70.6 | 150—152[i] | 0.80 | −28.8 | 29.4 | 248—252[c] | 0.70 | [13, 14] |
| Z-Leu-DCU | 69.4 | 120—122[j] | 0.80 | −20.7 | 30.6 | 199—201 | 0.83[h] | [15] |
| Z-Val-DCU | 91.5 | 98—99[k] | 0.80 | −76.5 | 9.5 | not isolated | | [13—15] |
| Z-Ile-DCU | 86.0 | 121—122[l] | 0.80 | +8.7 | 14.0 | 239—240 | 0.83[h] | |
| Z-Pro-DCU | 64.6 | 103—104[m] | 0.70 | −72.8 | 35.4 | 165—167 | 0.55[d,h] | |
| Z-Phe-DCU | 75.9 | 133—135[n] | 0.80 | −57.7 | 24.1 | 235—237 | 0.85[o] | [15] |
| Z-Ser-DCU | 86.5 | 140—141[p] | 0.60 | −12.6 | 13.5 | 223—225[e] | 0.60 | |
| Z-Thr-DCU | 79.8 | 128—130[r] | 0.60 | −49.6 | 20.2 | not isolated | | |
| Z-D-Phg-DCU | 86.8 | 186—187[s] | 0.80 | +1.8[e] | 13.2 | 283—284 | 0.80[h] | |
| Z-L-Pgh-DCU | 74.0[f] | 185—186 | 0.80 | − 1.2[e] | not determined | | | |

[a] In four cases, we were not able to isolate the corresponding **V**. The measurement of optical rotations of compounds **V** was not possible due to their poor solubility.

[b] c = 1.0; EtOH

[c] These compounds were prepared as described in Experimental

[d] $[\alpha]_D$ −61.0° (c = 1.0; EtOH)

[e] c = 1.0; EtOH : DMF = 7 : 3

[f] yield

[g] only the appropiate **IV** is described in Refs. [13—15]. In Ref. [16] both compounds are characterized.

[h] Not analyzed

[i] $C_{10}H_{16}O_2N_2$ (196.24) Calcd. C 61.20; H 8.22; N 14.28
Found C 61.20; H 7.95; N 14.38%

[j] $C_{13}H_{22}O_2N_2$ (238.32) Calcd. C 65.51; H 9.31; N 11.76
Found C 65.44; H 9.10; N 11.90%

[k] $C_{12}H_{20}O_2N_2$ (224.30) Calcd. C 64.29; H 8.92; N 12.50
Found C 64.14; H 9.03; N 12.72%

[l] $C_{13}H_{22}O_2N_2$ (238.32) Calcd. C 65.51; H 9.31; N 11.76
Found C 65.56; H 9.40; N 11,64%

[m] $C_{12}H_{18}N_2O_2$ (222.28) Calcd. C 64.84; H 8.16
Found C 64.58; H 8.28%

[n] $C_{16}H_{20}O_2N_2$ (272.34) Calcd. C 70.56; H 7.40; N 10.29;
Found C 70.50; H 7.38; N 10.01%

[o] $C_{22}H_{33}O_2N_3$ (371.51) Calcd. C 71.12; H 8.95; N 11.31
Found C 71.35; H 9.09; N 11.30%

[p] $C_{10}H_{16}O_3N_2$ (212.24) Calcd. C 56.59; H 7.60; N 13.20
Found C 56.65; H 7.69; N 13.39%

[r] $C_{11}H_{18}O_3N_2$ (226.27) Calcd. C 58.39; H 8.02; N 12.38
Found C 58.70; H 8.23; N 12.77%

[s] $C_{15}H_{18}O_2N_2$ (258.31) Calcd. C 69.74; H 7.02; N 10.85
Found C 69.71; H 6.95; N 10.74%

From the data of Table I, it can be seen that the formation of **IV** is preferential, especially in the presence of a branched side chain in $\beta$-position (Val, Ile). The highest ratio of the formation of **V** was observed in the case of the Pro derivative, being probably due to ring strain of the bicyclic derivative.

**IV** was prepared previously by MURAMATSU *et al.* in a yield of 66% by catalytic hydrogenation of Z-Gly-DCU, but they did not observe the formation of **V** in this reaction [16]. **V** was synthesized in a direct reaction of glycine and DCC above 100 °C. Thus, a distinct mechanism of the formation of both products has been given. Under our reaction conditions the most probable pathways of the simultaneous formation of **IV** and V is illustrated in Fig. 1.

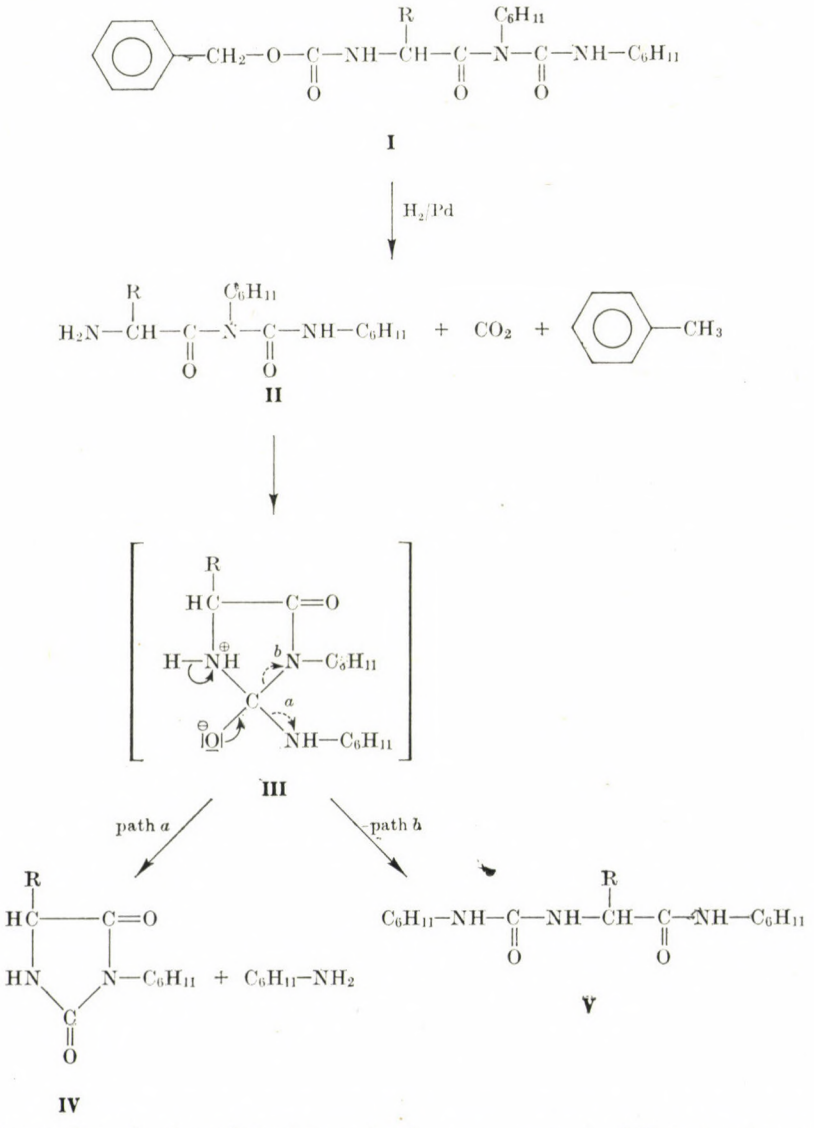



*Fig. 1.* Proposed mechanism of the intramolecular rearrangement of **II** during the catalytic hydrogenation of **I**

According to this assumption, the first step is a nucleophilic attack of the primary amino group, formed by the removal of the benzyloxycarbonyl group, on the carbonyl of the urea. The ionic tetrahedral complex **(III)** then competitively rearranges: pathway *a* leads to **IV** and cyclohexylamine, and pathway **b** to **V.** Variation of the conditions of the catalytic hydrogenation (solvent, presence of acids) led to the conclusion that in this reaction the primary amino group should be present in non-protonated form. It follows that **II** can only be prepared as salts (see Ref. [9] and Experimental).

Upon removing the protecting groups by acidolysis, the situation is the following. When BOC-Gly-DCU was allowed to react with TFA/methylene chloride, H-Gly-DCU · TFA salt was obtained after 30 min. in a good yield. Neutralizing the solution of this salt, the rearrangement immediately started to produce **IV** and **V.** If Z-Gly-DCU was treated with 4*N* HBr/AcOH, the main product was H-Gly-cyclohexylamide · HBr, whereas when using 4*N* HCl/AcOH, Z-Gly-cyclohexylamide was obtained. These results are in agreement with the known acid-sensitivity of acyl-substituted urea derivatives [17, 18].

The importance of the nucleophilicity of the primary amino group in the formation of **IV** and **V** was well demonstrated by the reaction of the $\beta$-alanine derivative. When Z-$\beta$-Ala-DCU was subjected to catalytic hydrogenation — under similar conditions — only the removal of the protecting group occurred without any side reactions. The conversion of H—$\beta$-Ala-DCU to 3-cyclohexyl-dihydro-2,4(*1H,3H*)-pirimidinedion and cyclohexylcarbamoyl-$\beta$-Ala-cyclohexylamide, corresponding to **IV** and **V,** respectively, was achieved only by a 30-hour refluxing in the presence of triethylamine.

Based on the above results it seems to be important to minimize the formation of **I** in DCC-mediated peptide bond formation by carefully controlled reaction conditions, or to remove completely **I** from the crude product. Otherwise, after deprotection in the concomitant acylation step, where the pH is above 8, **IV** and **V** will immediately form along with cyclohexylamine, consuming the acylating component. These side reactions obviously cause difficulties in the work-up of the reaction mixture.

## Experimental

M. p.'s were taken on a Tottoli Büchi apparatus and are uncorrected. The optical rotations were determined with a Perkin-Elmer 141 polarimeter. TLC was run on Kieselgel nach Stahl, using the following solvent systems:

1. EtOAc : (Pyr : AcOH : $H_2O$ = 20 : 6 : 11) = 9 : 1
2. EtOAc : (Pyr : AcOH : $H_2O$ = 20 : 6 : 11) = 8 : 2
3. EtOAc : (Pyr : AcOH : $H_2O$ = 20 : 6 : 11) = 6 : 4
4. $CHCl_3$ : MeOH = 98 : 2.

IR spectra were taken on a Perkin-Elmer 257 IR spectrophotometer. The $^1$H-NMR spectra were recorded on a Varian EM 360 spectrometer, with TMS as internal standard.

### Isolation of Z-Ser-DCU from the coupling reaction of Z-Ser-Ala-O$^t$Bu

DCC (17.3 g; 84 mmoles) in EtOAc (100 ml) was added at −10 °C to a stirred suspension of H-Ala-O$^t$Bu (12.2 g; 84 mmoles) and Z-Ser-OH (20.1 g; 84 mmoles) in a mixture of DMF (50 ml) and EtOAc (300 ml). After 20 hrs, the resulting suspension was filtered, and the filtrate was washed three times with 1*N* hydrochloric acid and three times 5% $NaHCO_3$ solution. The organic phase was evaporated and the residue was crystallized from EtOAc to obtain Z-Ser-DCU (5.9 g; 15.5%), m. p. 165—166 °C [2, 6, 7, 10]. This product was twice crystallized from MeOH, resulting in chromatographically pure Z-Ser-DCU (3.24 g), m. p. 169—170 °C, $R_f^1$ 0.70, $R_f^4$ 0.40, $[\alpha]_D$ +26.6° (c = 1.0; EtOH). Z-Ser-Ala-O$^t$Bu was isolated from the first mother liquor in a yield of 33%.

**DCU derivatives of Z- and BOC-amino acids** were prepared according to Ref. [9] and [19]. The results are shown in Table II.

**Table II**

*DCU derivatives of protected amino acids*[+] **I**

| Compound | Solvent of crystallization | M. p., °C | $R_f^1$ | $[\alpha]_D^a$ | $[\alpha]_D^b$ | Ref. |
|---|---|---|---|---|---|---|
| Z-Gly-DCU | MeOH–ether | 149—150 | 0.85 | — | — | [7, 9, 15, 19, 20] |
| BOC-Gly-DCU | EtOAc | 130—131 | 0.85 | — | — | [9] |
| Z-Ala-DCU | — | oil | 0.90 | −2.1 | +9.3 | [10] |
| Z-β-Ala-DCU[c] | MeOH | 164—165 | 0.85 | — | — | |
| Z-Val-DCU | n-hexane | 134—135 | 0.85 | +49.5 | — | [10] |
| Z-Leu-DCU | — | oil | 0.85 | +3.8 | — | [10] |
| Z-Ile-DCU | — | oil | 0.85 | +34.0 | +40.4 | (10] |
| Z-Pro-DCU | n-hexane | 83—86 | 0.80 | — | +12.3 | [10] |
| Z-Phe-DCU | — | oil | 0.85 | — | +4.3 | [10] |
| Z-Ser-DCU | MeOH | 172—173 | 0.80 | +26.9 | +28.0 | [2, 6, 7, 10] |
| Z-Thr-DCU | MeOH | 164—165 | 0.80 | +43.0 | +52.4 | [10] |
| BOC-Ser-DCU[d] | MeOH | 163—164 | 0.70 | +30.5 | — | |
| Z-L-Phg-DCU[e] | MeOH | 140—142 | 0.90 | +68.5 | — | |
| Z-D-Phg-DCU | MeOH | 140—142 | 0.90 | −68.0 | — | |

[+] Some of these derivatives are new; some physical constants of others differ from those given in Refs. [9] and [10]

[a] c = 1.0; EtOH

[b] c = 1.0; DMF

[c] $C_{24}H_{35}N_3O_4$ (429.54) Calcd. C 67.10; H 8.21; N 9.87.
Found C 67.06; H 8.10; N 9.65%.

[d] $C_{21}H_{37}O_5N_3$ (411.53) Calcd. C 61.29; H 9.06; N 10.21.
Found C 61.87; H 9.16; N 10.32%,

[e] $C_{29}H_{37}O_4N_3$ (491.61) Calcd. C 70.85; H 7.59; N 8.55.
Found C 70.81; H 7.40; N 8.77%.

### Catalytic hydrogenation of I

Compound **I** (10 mmoles), dissolved or suspended in fifty parts of MeOH, was hydrogenated at ambient temperature and pressure in the presence of 10% palladized charcoal (10% by weight) until the presence of **I** could no longer be detected by TLC. After removal of the catalyst, the solution was evaporated to dryness and the solid residue dissolved in chloroform; the solution was washed with 1*N* HCl and water. The organic phase was dried over $Na_2SO_4$, evaporated to dryness and the residue was fractionally crystallized. The physical constants of the products are shown in Table I.

**IR spectrophotometric measurements** were used for the determination of the relative amounts of **IV** and **V**. Different mixtures of known composition were prepared from pure 3-cyclohexyl-5-methylhydantoin (**IV**, R = Me) and cyclohexylcarbamoyl-L-alanine-cyclohexylamide (**V**, R = Me) in hexafluoro-2-propanol. (This solvent was selected, because most of compounds with structure **V** could not be dissolved in common solvents. Hexafluoro-2-propanol has no significant absorption in the range 1800—1530 $cm^{-1}$). The quantitative analyses were carried out by means of the base-line technique. The bands of carbonyl stretching frequencies characteristic of hydantoins appear at about 1700 and 1760 $cm^{-1}$; the latter is very sharp, so it was selected for calibration. The Amide I band appearing at 1630—1600 $cm^{-1}$ was used for quantitation of **V**.

After the hydrogenation of **I** of known quantity had been completed, the catalyst was removed and thoroughly washed with hexafluoro-2-propanol. The filtrate was evaporated, and the residue in hexafluoro-2-propanol was transferred to a volumetric flask. The absorbance of this solution at the stated frequencies was measured at several dilutions. As the absorbance — concentration relationship is linear both for **IV** and **V**, the relative amounts of **IV** and **V** could be determined (Table, I, Columns 2 and 6).

### Preparation of standard compounds

#### (A) N-(Cyclohexylcarbamoyl)-L-serine-cyclohexylamide (V, R = $CH_2OH$)

*(a)* Pivaloyl chloride (3.75 ml; 30 mmoles) was added at —10 °C to Z-Ser-OH (7.19 g; 30 mmoles) and TEA (4.20 ml; 30 mmoles) in chloroform (150 ml). The mixture was stirred at —10 °C for 10 min., then cyclohexylamine (3.66 ml; 30 mmoles) was added dropwise at —10 °C. The resulting mixture was kept for 3 hrs at room temperature, then it was washed three times with 1*N* HCl and three times with 5% $NaHCO_3$ solution. The organic phase was evaporated, and the residue was crystallized twice from EtOAc to give Z-Ser-NH-$C_6H_{11}$ (2.75 g; 28.8%), m. p. 159—160 °C, $R_f^1$ 0.70, $[\alpha]_D$ —0.6° (c = 1.0; EtOH)

$C_{17}H_{24}O_4N_2$ (320.38). Calcd. C 63.73; H 7.55; N 8.74. Found C 63.72; H 7.60; N 8.72%.

*(b)* Z-Ser-NH-$C_6H_{11}$ (2.35 g; 7.32 mmoles) was hydrogenated in the usual manner, to give H-Ser-NH-$C_6H_{11}$ (1.27 g; 94.8%), m. p. 140—141 °C, $R_f^3$ 0.40, $[\alpha]_D$ +1.4° (c = 1.0; EtOH).

$C_9H_{18}O_2N_2$ (186.25). Calcd. C 58.03; H 9.74; N 15.04. Found C 58.28; H 9.75; N 14.92%.

*(c)* Cyclohexyl isocyanate (0.55 ml; 4.3 mmoles) was added to a suspension of H-Ser-NH-$C_6H_{11}$ (0.80 g; 4.3 mmoles) in dimethoxyethane (60 ml). The reaction mixture was stirred for 20 hrs, then the precipitate was filtered off. The crude product was crystallized from EtOH (50 ml) to obtain N-(cyclohexylcarbamoyl)-L-serine-cyclohexylamide (0.95 g; 70.9%), m. p. 223—225 °C, $R_f^1$ = 0.60.

$C_{16}H_{29}O_3N_3$ (311.42). Calcd. N 13.39. Found N 13.60%.

#### (B) N-(Cyclohexylcarbamoyl)-L-alanine-cyclohexylamide (V, R = $CH_3$)

*(a)* Z-Ala-OSu (6.40 g; 20 mmoles) was added to a solution of cyclohexylamine (3.66 ml; 30 mmoles) in chloroform (100 ml). Next day the solution was washed four times with 1*N* the and three times with 5% $NaHCO_3$ solution. After drying, the organic phase was evaporated to dryness, and the residue was triturated with ether to give Z-Ala-NH-$C_6H_{11}$ (5.23 g; 86.5%), m. p. 163—164 °C, $R_f^1$ 0.70, $[\alpha]_D$ —8.3° (c = 1.0; EtOH).

$C_{17}H_{24}O_3N_2$ (304.28). Calcd. C 67.08; H 7.95; N 9.20. Found C 66.88; H 7.83; N 9.18%.

*(b)* A suspension of Z-Ala-NH-$C_6H_{11}$ (4.5 g; 14.8 mmoles) in EtOH (100 ml) was hydrogenated in the precence of 10% palladized charcoal (0.5 g) in the usual way. After 2 hrs, the catalyst was filtered off, and the filtrate was evaporated. The residue was triturated with n-hexane to give H-Ala-NH-$C_6H_{11}$ (2.14 g; 85%), m. p. 99—100 °C, $R_f^2$ 0.30, $[\alpha]_D$ —38.7° (c = 1.0; EtOH).

$C_9H_{18}ON_2$ (170.25). Calcd. C 63.49; H 10.66; N 16.46%. Found C 63.56; H 10.40; N 16.51%.

*(c)* A solution of H-Ala-NH-$C_6H_{11}$ (0.85 g; 5.0 mmoles) in dry ether was treated with cyclohexyl isocyanate (0.64 ml; 5.0 mmoles) at room temperature. The product which precipitated was filtered off and washed with ether. The crude product was crystallized from EtOH (70 ml) to give cyclohexylcarbamoyl-L-alanine-cyclohexylamide (1.05 g; 71.5%), m. p. 248—252 °C, $R_f^1 = 0.70$.

$C_{16}H_{29}O_2N_3$ (295.42). Calcd. C 65.05; H 9.90; N 14.23. Found C 65.06; H 9.50; N 14.12%.

### Acidolysis of BOC-Gly-DCU

*(a)* A solution of BOC-Gly-DCU (0.76 g; 2.0 mmoles) in a mixture of methylene chloride (4 ml) and TFA (4 ml) was kept for 30 min. at room temperature and then evaporated. The oily residue was crystallized from dry ether, giving H-Gly-DCU · TFA (0.67 g; 87.5%), m. p. 120—122 °C.

NMR (DMSO $d_6$ + $CDCl_3$): $\delta$ 0.9—2.1 ppm, br m, 20 H: -C*H*$_2$- (ring); ~3.6 ppm, br + 3.75 ppm, br s (overlapped) 4H: N- C*H* + NH-C*H* + $^+H_3$N-C*H*$_2$-CO; ~8.3 ppm, br, 3H: N*H*$_3^+$; 8.44 ppm, br d ($J \sim 8$ Hz, overlapped) 1H: CH-N*H*.

IR: $\nu_{max}$ 1708 ($CO_{urea}$), 1683 $cm^{-1}$($CO_{Gly}$).

$C_{17}H_{28}N_3O_4F_3$ (395.43). Calcd. C 51.60; H 7.13; N 10.60. Found C 52.25; H 7.31; N 10.13%.

*(b)* BOC-Gly-DCU (2.12 mmoles; 0.81 g) was treated with 5*N* HCl in EtOAc (5 ml) for 30 min. at room temperature and then evaporated. The crystalline residue was triturated with dry ether to obtain H-Gly-DCU · HCl (0.67 g; 98%) [9], m. p. 180—182 °C.

IR: $\nu_{max}$ 1708 $cm^{-1}$ ($CO_{urea}$), 1683 $cm^{-1}$ ($CO_{Gly}$).

TLC of the salts of **II** cannot be realized in the solvent systems used because of their immediate rearrangement to **IV**, cyclohexylamine and **V**.

### Conversion of salts of II by the addition of TEA

H-Gly-DCU · TFA or H-Gly-DCU · HCl was dissolved in EtOH, and an equivalent amount of TEA was added to the solution. The reaction mixture was evaporated, the residue triturated with ether, then filtered off. The IR spectra of the solution of this residue in hexafluoro-2-propanol showed complete conversion of **II** to the corresponding **IV**, cyclohexylamine and **V**.

### Acidolysis of Z-Gly-DCU

*(a)* Z-Gly-DCU (8.31 g; 20 mmoles) was treated with 4*N* hydrobromic acid in AcOH (80 ml) for 1 hr at room temperature. The solution was then mixed with dry ether (700 ml) to precipitate a mixture of $C_6H_{11}NH_2$ · HBr and H-Gly-NH-$C_6H_{11}$ · HBr.

IR: $\nu_{max}$ 1675 $cm^{-1}$ (Amide I), 1560 $cm^{-1}$ (Amide II).

NMR (DMSO-$d_6$ + $CDCl_3$): $\delta$ 0.9—2.2 ppm, br m, 10 H: -C*H*$_2$- (ring); 3.81 ppm, br, 3 H: -NH-C*H*- + $^+H_3$N-C*H*$_2$-CO; 7.7 ppm, br, 3 H: N*H*$_3^+$; 8.24 ppm, br d ($J \sim 8$Hz) 1H: CH-N*H*].

A solution of this mixture was treated in water (100 ml) with DOWEX 2×8 and filtered. After evaporation the residue was dried in desiccator over $P_2O_5$ to give H-Gly-NH-$C_6H_{11}$ (2.61 g; 83.2%), m. p. 84—85 °C, $R_f^3$ 0.45.

$C_8H_{16}ON_2$ (156.22). Calcd. C 61.50; H 10.32; N 17.93. Found C 61.85; H 10.18; N 17.98%.

*(b)* Z-Gly-DCU (0.42 g; 1.0 mmole) was treated with 4*N* HCl in AcOH (5 ml) for 2 hrs, then evaporated. The residue was dissolved in EtOAc (20 ml) and the solution was washed three times with 1*N* HCl and three times with 5% $NaHCO_3$ solution. After drying, the organic phase was evaporated to dryness and the solid residue triturated with ether to obtain Z-Gly-NH-$C_6H_{11}$ [16] (0.21 g; 72.3%), m. p. 108—109 °C, $R_f^1$ 0.70.

IR: $\nu_{max}$ 1715 $cm^{-1}$ ($CO_{urethane}$), 1650 $cm^{-1}$ (Amide I), 1540—1520 $cm^{-1}$ (Amide II).

### Catalytic hydrogenation of Z-β-Ala-DCU

A solution of Z-β-Ala-DCU (2.15 g; 5.0 mmoles) in MeOH was hydrogenated over 10% palladized charcoal (10% by weight) in the usual way, as described above. According to TLC, the reaction was complete in 30—45 min. After removal of the catalyst, the solution was

evaporated to dryness. The solid residue was purified by precipitation with ether–*n*-hexane, to give H-$\beta$-Ala-DCU (1.25 g; 84.5%), m. p. 102—103 °C, $R_f^1$ 0.45.

$C_{16}H_{29}O_2N_3$ (295.42). Calcd. C 65.05; H 9.90; N 14.23. Found C 65.08; H 9.92; N 14.34%.

### Intramolecular rearrangement of H-$\beta$-Ala-DCU

A solution of H-$\beta$-Ala-DCU (0.50 g; 1.70 mmoles) in MeOH (30 ml) was refluxed for 3 hrs. No conversion occurred according to TLC. TEA (0.24 ml; 1.70 mmoles) was added to the solution, and refluxing was continued. After 20 hrs. the same quantity of TEA was added again to complete the reaction. After 30 hrs. the solution was evaporated to dryness. The solid residue was crystallized from MeOH, to yield cyclohexylcarbamoyl-$\beta$-alanine-cyclohexylamide (0.19 g; 38%), m. p. 235—236 °C, $R^2 = 0.85$.

$C_{16}H_{29}O_2N_3$ (295.42). Calcd. N 14.23. Found N 14.08%.

IR: $\nu_{max}$ 3330 $cm^{-1}$ (NH), 1625 $cm^{-1}$ (NH), 1625 $cm^{-1}$ (Amide I), 1570 $cm^{-1}$ (Amide II).

In the filtrate TEA, cyclohexylamine and another compound ($R_f^2 = 0.80$) were detected by TLC. The filtrate was evaporated to dryness and the residue triturated with ether.

IR spectra of this heterogeneous mixture showed absorptions at 1730 and 1660 $cm^{-1}$, corresponding to the carbonyls of 3-cyclohexyl-dihydro-2,4 *(1H 3H)*-primidinedion.

*

### Symbols

| | |
|---|---|
| DCC | dicyclohexylcarbodiimide |
| DCU | dicyclohexylurea |
| TFA | trifluoroacetic acid |
| TEA | triethylamine |
| AcOH | acetic acid |
| Pyr | pyridine |
| DMF | dimethylformamide |
| Phg | phenylglycyl residue |
| Z- | benzyloxycarbonyl- |
| BOC- | *t*-butyloxycarbonyl- |
| O$^t$Bu | *t*-butyl ester |
| OSu | succinimide ester |
| DMSO | dimethyl sulfoxide |

The abbreviation for amino acid residues and their derivatives, as well as their mode of use are in accordance with the suggestions of the Committee on Nomenclature adopted by IUPAC (J. Biol. Chem. **247**, 977 (1972)).

*

The authors are indebted to Áron Szöllösy for the NMR studies.

## REFERENCES

[1] Khorana, H. G.: Chem. Ind. **1955**, 1087
[2] Merrifield, R. B., Woolley, D. W.: J. Am. Chem. Soc. **78,** 4646 (1956)
[3] Shankman, S., Schwo, Y.: J. Am. Chem. Soc. **80,** 1164 (1958)
[4] Helferich, B., Böshagen, H.: Chem. Ber. **92,** 2813 (1959)
[5] Schwyzer, R., Iselin, B., Kappeler, H., Riniker, B., Rittel, W., Zuber, H.: Helv. Chim. Acta **46,** 1975 (1963)
[6] Iselin, B., Schwyzer, R.: Helv. Chim. Acta **45,** 1499 (1962)
[7] Zahn, H., Diehl, J. F.: Z. Naturforsch. B **12,** 82 (1957)
[8] Kisfaludy, L., Löw, M.: Peptides 1962 (Young, G. T., ed.), p. 93. Pergamon Press, Oxford, 1963
[9] Izdebski, J., Drabarek, S., Lebek, M.: Rocz. Chem. **49,** 1535 (1975)
[10] Izdebski, J., Lebek, M., Drabarek, S.: Rocz. Chem. **51,** 81 (1977)

[11] KISFALUDY, L.: Peptides 1972 (HANSON, H., JAKUBKE, H.-D., ed.), p. 129. North-Holland Publ. Co., Amsterdam—London, American Elsevier Publ. Co., New York, 1973
[12] KISFALUDY, L., LÖW, M., SZIRTES, T., SCHÖN, I., SÁRKÖZI, M., BAJUSZ, S., TURÁN, A., JUHÁSZ, A., BEKE, R., GRÁF, L., MEDZIHRADSZKY, K.: Chemistry and Biology of Peptides (MEIENHOFER, J., ed.) p. 299. Ann. Arbor Sci. Publ., Michigan, 1972
[13] French Pat. 1.435.829 (1966); Chem. Abstr. **66,** 18712f (1967)
[14] U. S. Pat. 3.326.661 (1967); Chem. Abstr. **68,** 39622h (1968)
[15] MASZLOVA, G. A., SZTRUKOV, I. T.: Zhurn. Obshch. Him. **34,** 3506 (1964)
[16] MURAMATSU, I., HIRAYABASHI, T., HAGITANI, A.; Nippon Kagaku Zasshi **84,** 855 (1963); Chem. Abstr. **60,** 12000c (1964)
[17] HALPERN, A., JONES, J. W.: J. Am. Pharm. Soc. **37,** 333 (1948)
[18] HALPERN, A., JONES, J. W.: J. Am. Pharm. Soc. **38,** 352 (1949)
[19] SCHÜSSLER, H., ZAHN, H.: Chem. Ber. **95,** 1076 (1962)
[20] DETAR, D. F., SILVERSTEIN, R., ROGERS, F. F. J: Am. Chem. Soc. **88,** 1024 (1966)
[21] NOWAK, K., KANIA, L.: Rocz. Chem. **43,** 1953 (1969)

István SCHÖN
Judit FRISS
Lajos KISFALUDY
H-1475 Budapest 10, Pf. 27.

*Acta Chimica Academiae Scientiarum Hungaricae, Tomus 98 (2), pp. 225—230 (1978)*

# DIHYDROCHALCONE TYPE SWEETENING AGENTS, I

## STRUCTURE—TASTE RELATIONSHIPS

S. Antus, L. Farkas, Á. Gottsegen, M. Nógrádi and T. Pfliegel*

*(Research Group for Alkaloid Chemistry of the Hungarian Academy of Sciences and CHINOIN Pharmaceutical and Chemical Works, Budapest)*

Received September 15, 1977

A systematic investigation of structure — taste relationships in a series of dihydrochalcones led to the development of 1-[2-hydroxy-4-(3-sulfo-1-propyloxy)-phenyl]--3-(3-hydroxy-4-methoxyphenyl)-propan-1-one sodium salt, CHINOIN-401, **(36)**, an intensively and purely sweet atoxic compound of appreciable commercial potential.

The great importance of artificial sweeteners is in sharp contrast with the poor variety in such agents. Despite of long standing research, the world market is still almost exclusively dominated by saccharine, a sweetener with a pronounced off-taste, and Cylamate, which has been banned in several countries owing to its alleged carcinogenity. The development of new and better artificial sweeteners is therefore an obvious objective of research.

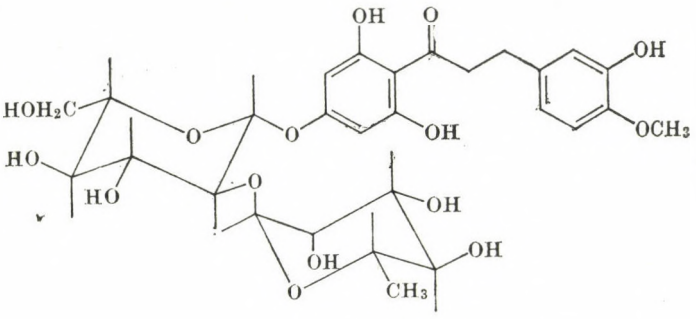
In 1963 Horowitz discovered that the neohesperidin dihydrochalcone (**1**) had an intensively sweet taste [1]. Though in a lesser degree, the compounds **2** and **3** were also reported to be sweet, whereas a change in the position of the rhamnose unit from $C_2$ to $C_6$ in the glucose moiety of **1** (rutinosides) the sweet taste disappeared. Comparison with the bitter phloridzin (**4**) also suggested that the structure and position of the sugar moiety had a decisive influence on taste [2].

Since we have been interested in dihydrochalcone glycosides [3], we launched a systematic investigation of these compounds to find out more about their flavouring properties.

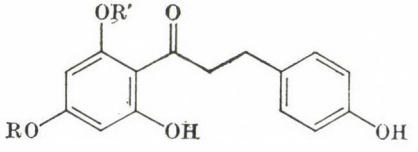
First, the glucoside **5** was synthesized, which proved to be intensely sweet [4, 5]. Note that compared with **1**, compound **5** has only one *ortho* hydroxyl group in ring A, but retains the substitution pattern of **2** in ring B. The synthesis of a series of dihydrochalcone glycosides (**6—20**, Table I) followed, none of which except one **(17)**, also having a 3-hydroxy-4-methoxyphenyl (isovanillin) side chain, was sweet. At this point, the following conclusions could be drawn.

(1) Though the neohesperidosyl moiety has certainly contributed to the sweetness of **1**, the essential structural feature providing this property was the isovanillin side chain.

(2) The fact that **8** was tasteless, could be attributed to its very low solubility in water.



1



**2**: R = $\beta$-neohesperidosyl, R' = H

**3**: R = $\beta$-D-glucosyl, R' = H

These two points and the fact that also the aglycone of **5** was faintly sweet suggested that the real importance of the sugar moiety was to lend water solubility. Hence any water soluble dihydrochalcone with an isovanillin side chain may be a potential sweetener.

Since attaching an ionizable group is one of the simplest means to impart water solubility to a substance, the acetic acid derivative **21** was synthesized. The sodium salt of **21** was about 180 times sweeter than sucrose. This finding opened up the possibilities of developing a commercially useful sweetener.

Though for reasons given later **21** was unsuitable as a practical sweetener, congeners could be readily synthesized and the series of analogues given in Table II provided additional information about taste—structure correlations.

From Table II the following conclusions could be drawn:

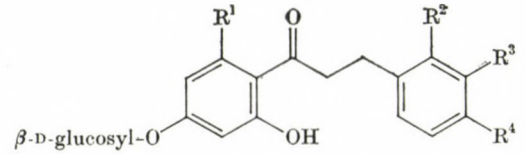
(a) Only compounds with a 3-hydroxy-4-alkoxy substitution in ring B were sweet.

(b) The earlier observation that exchange of a methoxyl group for an ethoxyl or an *n*-propoxyl group increased sweetness [6, 7] did not materialize in our case, probably since homologation (**22**, **23**) markedly decreased solubility in water. Increasingly retarded diffusion of the sweetener towards the receptor in the series OMe → OEt → O-*n*-Pr due to non-specific interactions en route to the receptor may also result in an apparent decrease in activity of compounds with higher lipophilicity [8].

(c) More was found out in this series about the role of the connecting three-carbon chain. Methyl substitution in $\alpha$-position to the carbonyl group (**33**) eliminated sweetness.

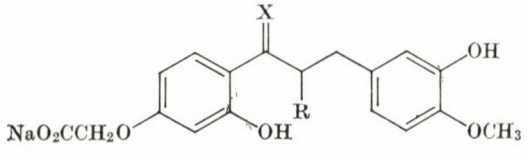
**Table I**

*Dihydrochalcone glucosides*




| | $R^1$ | $R^2$ | $R^3$ | $R^4$ | Taste |
|---|---|---|---|---|---|
| **5** | H | H | OH | $OCH_3$ | intensely sweet |
| **6** [13]* | OGluc | H | OH | OH | bitter (?) |
| **7** [14]* | OGluc | H | H | OH | bitter |
| **8** [15]* | OGluc | H | OH | $OCH_3$ | tasteless |
| **9** [3] | OH | H | H | OH | tasteless |
| **10** [3] | OH | H | OH | OH | slightly bitter |
| **11** | H | H | H | $OCH_3$ | tasteless |
| **12** | H | H | $OCH_3$ | OH | slightly sweet with bitter off-taste |
| **13** | H | H | $OCH_3$ | $OCH_3$ | bitter |
| **14** | H | H | OH | H | tasteless |
| **15** | H | $OCH_3$ | H | H | bitter |
| **16** | H | H | H | $OCH_2CO_2Na$ | tasteless |
| **17** | $CH_3$ | H | OH | $OCH_3$ | intensely sweet with bitter off-taste |
| **18** | H | H | H | OGluc | slightly bitter |
| **19** | H | OH | $OCH_3$ | H | slightly bitter |
| **20** | H | OH | H | H | tasteless |

* Monoglucosidic structures have been assigned to compounds **6**—**8** in the original references. The correct structure was proved by PACHÉCO *et al.* [16].




**33**: X = O, R = $CH_3$

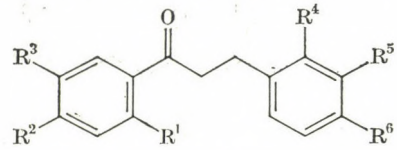
**34**: X = $H_2$, R = H

(d) An essential structural feature is the *ortho*-hydroxy carbonyl function. Analogues of **20** lacking this moiety, such as **24**, **30**, **31** and **34** were not sweet.

(e) On the other hand, the position of the carboxyl group in ring A seemed to be of less importance, since both **28** and **29** were sweet. Compound **29**, however

**Table II**

*Some non-glycosidic dihydrochalcones*




| | $R^1$ | $R^2$ | $R^3$ | $R^4$ | $R^5$ | $R^6$ | Taste |
|---|---|---|---|---|---|---|---|
| **21** | OH | $NaO_2CCH_2O$ | H | H | OH | $OCH_3$ | intensely sweet |
| **22** | OH | $NaO_2CCH_2O$ | H | H | OH | $OC_2H_5$ | sweet |
| **23** | OH | $NaO_2CCH_2O$ | H | H | OH | O-$nC_3H_7$ | slightly sweet |
| **24** | H | $NaO_2CCH_2O$ | H | H | OH | $OCH_3$ | tasteless |
| **25** | OH | $NaO_2CCH_2O$ | H | H | $OCH_3$ | OH | tasteless |
| **26** | OH | $NaO_2CCH_2O$ | H | OH | $OCH_3$ | H | slightly bitter |
| **27** | OH | $NaO_2CCH_2O$ | H | H | $OCH_2O$ | | tasteless |
| **28** | OH | H | $NaO_2CCH_2O$ | H | OH | $OCH_3$ | intensely sweet |
| **29** | OH | H | $NaO_2C$ | H | OH | $OCH_3$ | sweet |
| **30** | H | OH | $NaO_2C$ | H | H | $OCH_3$ | bitter |
| **31** | H | OH | $NaO_2C$ | H | OH | $OCH_3$ | tasteless |
| **32** | OH | H | $NaO_2S$ | H | OH | $OCH_3$ | tasteless |

was only slightly so, presumably, because **29** being a weaker acid provided, on a molar basis, lower concentrations of the hydrophilic anion.

A logical conclusion was therefore to introduce the strongly acidic sulfonic acid group but this surprisingly led to a tasteless compound (**32**).

Unfortunately, the salts of **21** and **28** at pH values characteristic of several commercial soft drinks gave the poorly soluble free acids. Therefore, a hydrophilic and strongly acidic group was looked for. The 3-sulfo-1-propyloxy group was promising for this purpose and 1-[2-hydroxy-4-(3-sulfo-1-propyloxy)-phenyl]--3-(3-hydroxy-4-methoxyphenyl)-propan-1-one sodium salt, CHINOIN-401 (**36**), was synthesized according to the Scheme below.

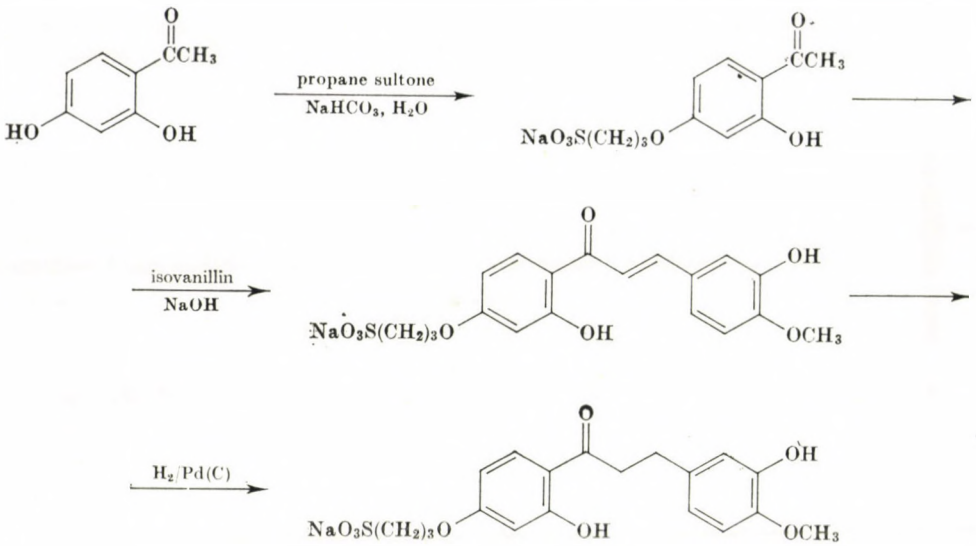
In fact, CHINOIN-401 (**36**) proved to be water soluble and intensely sweet. In a lesser degree the chalcone precursor of **36** was strongly sweet, too.

Preparation of some analogues, shown in Table III, yielded no further insight concerning the taste-structure correlations.

In the following some properties of CHINOIN-401 will be reported, which open the way for developing this substance as a commercial sweetener.

The synthesis (*cf.* Part II) is unsophisticated and starts from relatively inexpensive starting materials, *i. e.* resorcinol and isovanillin.

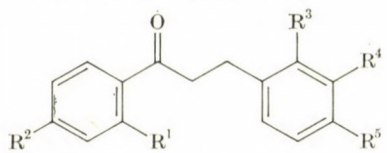
Extensive testing by several panels [10—12] has shown that, compared with a 1% sucrose solution, CHINOIN-401 is 1500 $\pm$ 300 times sweeter. Inten-




**36**

**Table III**

**3-*Sulfo*-1-*propyloxy*dihydrochalcones**



| | $R^1$ | $R^2$ | $R^3$ | $R^4$ | $R^5$ | Taste |
|---|---|---|---|---|---|---|
| **36** | OH | $NaO_3S(CH_2)_3O$ | H | OH | $OCH_3$ | intensely sweet |
| **37** | OH | $NaO_3S(CH_2)_3O$ | H | OH | $OC_2H_5$ | sweet |
| **38** | OH | $NaO_3S(CH_2)_3O$ | H | OH | O-$n$C$_3$H$_7$ | sweet |
| **39** | H | $NaO_3S(CH_2)_3O$ | H | OH | $OCH_3$ | slightly sweet, bitter offtaste |
| **40** | OH | $NaO_3S(CH_2)_3O$ | H | H | H | tasteless |
| **41** | OH | $NaO_3S(CH_2)_3O$ | H | OH | OH | tasteless |
| **42** | OH | $NaO_3S(CH_2)_3O$ | H | H | $OCH_7$ | tasteless |
| **43** | $NaO_3S(CH_2)_3O$ | H | H | OH | $OCH_3$ | bitter |

sity of sweetness, however, drops on increasing the concentration of the sweetener and the factor is only 220 compared with a 10% saccharose solution.

Pure solutions of CHINOIN-401 show neither the off-taste of saccharine nor the menthol-like cooling effect of neohesperidine-dihydrochalcone. There is,

however, a short lag in the onset of taste. The sweetness of CHINOIN-401s galso a little more persistent than that of sucrose.

Tests in a representative set of food preparations and beverages gave, in general, favourable results, except in coffee.

Expensiveness of testing precluded the collection of quantitative data concerning the rest of the compounds. Recently, DuBois *et al.* have published sensory data on compounds **21** and **24** [9].

Toxicology at the level completed so far gave wholly satisfactory results. $LD_{50}$ in the acute toxicity test was higher than 5000 mg/kg in rats. Subacute feeding of 10—250 mg/kg·day to rats for 3 months produced no pathologic or other changes in the animals.

*

We thank Dr. J. Strelisky and Mr. F. Boross for experimental contributions, Dr. J. Szejtli and Mrs. É. Bolla for helpful discussions, and Mrs. I. Berényi for technical assistance.

## REFERENCES

[1] Horowitz, R. M., Gentili, B.: Dihydrochalcone Derivatives and Their Use as Sweetening Agents. U. S. Pat. 3,087,821 (1963); *C. A.* **59,** P 116500 (1963)
[2] Horowitz, R. M., Gentili, B.: *J. Agr. Food Chem.*, **17,** 696 (1969)
[3] Farkas, L., Nógrádi, M., Major, Á.: *Chem. Ber.* **98,** 2926 (1965)
[4] Antus, S., Farkas, L., Gottsegen, Á., Nógrádi, M., Strelisky, J., Pfliegel, T.: *Acta Chim. (Budapest)* **98,** 231 (1978)
[5] Farkas, L., Nógrádi, M.: Procedure for the Manufacturing of Dihydrochalcones. *Hung. Pat.* 161,612 (2. Dec. 1970); *C. A.* **77,** P60321e (1972)
[6] Verkade, P. E., *Il Farmaco (Milano)* **23,** 248 (1968)
[7] Inglett, G. E., Krbechek, L., Dowling, B., Wagner, R.: *J. Food Sci.* **34,** 101 (1969)
[8] *Cf.* Biological Correlations, the Hansch Approach, Advances in Chemistry Series, 114. (Gould, R. F., Ed.) American Chemical Society, Washington D. C. 1972
[9] DuBois, G. E., Crosby, G. A., Saffron, P.: *Science* **195,** 397 (1977)
[10] Rajky-Medveczky, G., Takács-Palásti, M., Bolla-Pusztai, É., Szejtli, J.: *Die Nahrung* **21,** (2), 131 (1976)
[11] Lindner, K., Czétényi, Cs., Kubát, K., Szejtli, J., Bolla, É.: *Acta Alimentaria* **6,** (4), 311 (1977)
[12] Lindner, K., Czétényi, Cs., Kubát, K., Szejtli, J., Bolla, É.: *Acta Alimentaria* **6,** (4), 323 (1977)
[13] Zemplén, G., Bognár, R., Szegő, F.: *Ber.* **76,** 1110 (1943)
[14] Zemplén, G., Bognár, R.: *Ber.* **75,** 645 (1942)
[15] Zemplén, G., Bognár, R.: *Ber.* **75,** 1045 (1942)
[16] Pachéco, H., Grouiller, A., Hourfar, M. A.: Compt. Rend. **259,** (2), 402 (1964)

Sándor Antus
Loránd Farkas
Ágnes Gottsegen
Mihály Nógrádi
H-1521 Budapest, P.O.B. 91.

Tódor Pfliegel
H-1325 Budapest, P.O.B. 110.

*Acta Chimica Academiae Scientiarum Hungaricae, Tomus 98 (2), pp. 231—240 (1978)*

# DIHYDROCHALCONE TYPE SWEETENING AGENTS, II

## THE SYNTHESIS OF SOME DIHYDROCHALCONES

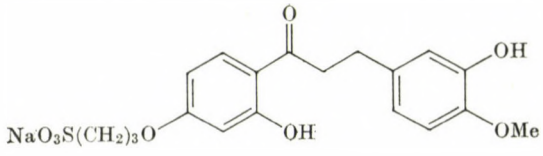
S. ANTUS, L. FARKAS, Á. GOTTSEGEN, M. NÓGRÁDI,
J. STRELISKY and T. PFLIEGEL*

*(Research Group for Alkaloid Chemistry of the Hungarian Academy of Sciences and *Chinoin Pharmaceutical and Chemical Works, Budapest)*

Received September 15, 1977

The preparation of 33 new dihydrochalcones by condensation of acetophenones and aldehydes to chalcones followed by hydrogenation is reported.

In the preceding communication [1] and three patents [2—4], we have described the development of an artificial sweetener of commercial interest (**1**), as well as some taste — structure correlations in a series of dihydrochalcones.



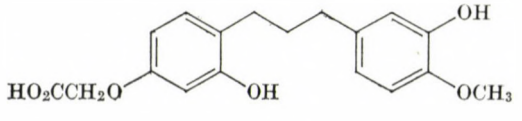

**1**

In this paper, we report the preparation of the new dihydrochalcones as well as their precursors.

The new dihydrochalcones, listed in Table I, were all prepared by catalytic hydrogenation of the corresponding chalcones or benzylated chalcones.

The chalcones were all obtained by condensation of the appropriate acetophenone and aldehyde. Some aldehydes were employed as their benzyl ethers, either because, like vanilline or *ortho*-vanillin, they failed to undergo condensation, or like salicylic aldehyde and 3,4-dihydroxybenzaldehyde, they gave very low yields of the chalcone. Glycosylacetophenones were used as the tetraacetates.

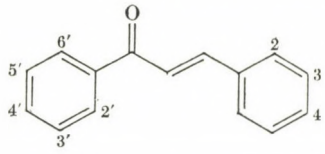
The new chalcones are listed in Table II. Finally, the 1,3-diphenylpropane derivative (**61**) was prepared by reduction of **9** with zinc dust and ammonia.




**61**

**Table I**

*New dihydrochalcones*




| No. | Substituents | | | | | | | M. p., °C (solvent) |
|---|---|---|---|---|---|---|---|---|
| | $C_2$ | $C_4$ | $C_5$ | $C_{2'}$ | $C_2$ | $C_{3'}$ | $C_{4'}$ | |
| **2** | H | OH | $CO_2H$ | H | H | H | OMe | 151—153 (MeOH) |
| **3** | OH | H | $CO_2H$ | H | H | OH | OMe | 191—192 (MeOH) |
| **4** | H | OH | $CO_2H$ | H | H | OH | OMe | 183—185 (MeOH) |
| **5** | OH | Cbm | H | H | H | $OCH_2O$ | | 168—170 (MeOH) |
| **6*** | H | Cbm | H | H | H | OH | OMe | 143—145 ($AcOH–H_2O$) |
| **7** | OH | Cbm | H | H | OH | OMe | H | 158—160 (MeOH) |
| **8** | OH | Cbm | H | H | H | OMe | OH | 158—160 (AcOH) |
| **9** | OH | Cbm | H | H | H | OH | OMe | 222—224 (AcOH) |
| **10** | OH | H | Cbm | H | H | OH | OMe | 81—84 (MeOH) |
| **11** | OH | Cbm | H | H | H | OH | OEt | 159—160 (AcOH) |
| **12** | OH | Cbm | H | H | H | OH | O*n*Pr | 161—163 (AcOH) |
| **13** | OH | H | $SO_3Na$ | H | H | OH | OMe | > 300 ($H_2O$) |
| **14** | OH | Supr | H | H | H | H | H | dec.** ($H_2O$) |
| **15** | OH | Supr | H | H | H | OH | OH | dec.** ($H_2O$) |
| **16** | Supr | H | H | H | H | OH | OMe | 222—224 ($H_2O$) |
| **17** | H | Supr | H | H | H | OH | OMe | dec.** ($H_2O$) |
| **18** | OH | Supr | H | H | OH | H | OMe | dec.** ($H_2O$) |
| **1** | OH | Supr | H | H | H | OH | OMe | 257—258 ($H_2O$) |
| **19** | OH | Supr | H | H | H | OH | OEt | 239—241 (dec.) ($H_2O$) |
| **20** | OH | Supr | H | H | H | OH | O*n*Pr | dec.** ($H_2O$) |
| **21** | OH | Gluc | H | H | OH | H | H | 152—155 (EtOH) |

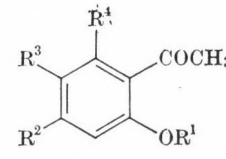
| Molecular formula | Molecular weight | Calcd. | | Found | | Chalcone precursor | Solvent of hydrogenation | Yield, % |
|---|---|---|---|---|---|---|---|---|
| | | C | H | C | H | | | |
| $C_{17}H_{16}O_5$ | 300.3 | 67.99 | 5.37 | 68.10 | 5.44 | [5] | AcOH | 27 |
| $C_{17}H_{16}O_6$ | 316,3 | 64,55 | 5.10 | 64.32 | 5.03 | **32** | AcOH | 23 |
| $C_{17}H_{16}O_6$ | 316.3 | 64.55 | 5.10 | 64.61 | 5.15 | **33** | AcOH | 30 |
| $C_{18}H_{16}O_7$ | 344.3 | 62.79 | 4.68 | 62.97 | 4.60 | **34** | MeOH | *** |
| $C_{18}H_{18}O_6$ | 330.3 | 65.44 | 5.49 | 65.76 | 5.51 | **35** | acetoue | *** |
| $C_{18}H_{18}O_7$ | 346.3 | 62.42 | 5.24 | 62.10 | 5.22 | **36** | MeOH | *** |
| $C_{18}H_{18}O_7$ | 346.3 | 62.42 | 5.24 | 62.61 | 5.38 | **37** | AcOH | *** |
| $C_{18}H_{18}O_7$ | 346.3 | 62.42 | 5.24 | 62.73 | 5.16 | **38** | acetone | 80 |
| $C_{18}H_{18}O_7$ | 346.3 | 62.42 | 5.24 | 62.65 | 5.52 | **39** | AcOH | *** |
| $C_{19}H_{20}O_7$ | 360.4 | 63.33 | 5.59 | 62.99 | 5.48 | **40** | AcOH | *** |
| $C_{20}H_{22}O_7$ | 374.4 | 64.16 | 5.92 | 64.22 | 5.89 | **41** | $H_2O$ | *** |
| $C_{16}H_{15}NaO_7S$ | 374.3 | 51.34 | 4.04 | 51.54 | 3.90 | **42** | $H_2O$ | *** |
| $C_{18}H_{19}NaO_6S$ | 386.4 | 55.95 | 4.96 | 53.88 | 5.23 | **43** | $H_2O$ | 81 |
| $C_{18}H_{19}NaO_8S$ | 418.4 | 51.67 | 4.58 | 51.83 | 4.41 | **44** | $H_2O$ | 20 |
| $C_{19}H_{21}NaO_7S$ | 416.4 | 54.80 | 5.08 | 54.60 | 5.00 | **45** | $H_2O$ | 50 |
| $C_{19}H_{21}NaO_7S$ | 418.4 | 54.80 | 5.08 | 54.65 | 5.28 | **46** | $H_2O$ | 55 |
| $C_{19}H_{21}NaO_8S$ | 432.4 | 52.77 | 4.89 | 52.70 | 5.18 | **47** | $H_2O$ | 30 |
| $C_{19}H_{21}NaO_8S$ | 432.4 | 52.77 | 4.89 | 52.77 | 4.85 | **48** | $H_2O$ | 40 |
| $C_{20}H_{23}Na_9O_8S$ | 446.5 | 53.80 | 5.19 | 53.50 | 5.22 | **49** | $H_2O$ | *** |
| $C_{21}H_{25}NaO_8S$ | 460.5 | 54.77 | 5.47 | 54.82 | 5.75 | **50** | $H_2O$ | *** |
| $C_{21}H_{24}O_9$ | 420.4 | 59.99 | 5.75 | 59.66 | 5.71 | **51** | EtOH | *** |

**Table I.** continued

| No. | Substituents | | | | | | | M. p., °C (solvent) |
|---|---|---|---|---|---|---|---|---|
| | $C_2$ | $C_4$ | $C_5$ | $C_6$ | $C_{2'}$ | $C_{3'}$ | $C_{4'}$ | |
| **22** | OH | Gluc | H | H | H | OH | H | 195—198 ($H_2O$) |
| **23** | OH | Gluc | H | H | OMe | H | H | 154—156 (EtOH) |
| **24** | OH | Gluc | H | H | H | H | OMe | 124—126 ($H_2O$) |
| **25** | OH | Gluc | H | H | OH | OMe | H | 135—137 (EtOH) |
| **26** | OH | Gluc | H | H | H | OMe | OH | 180—181 (EtOH) |
| **27** | OH | Gluc | H | H | H | OH | OMe | 176—178 (EtOH) |
| **28** | OH | Gluc | H | H | H | OMe | OMe | 157—160 (EtOH) |
| **29** | OH | Gluc | H | Me | H | OH | OMe | 176—178 (EtOH) |
| **30** | OH | Gluc | H | H | H | H | Cbm | amorphous |
| **31** | OH | Gluc | H | H | H | H | Gluc | amorphous |

Cbm = Carboxymethoxy
Supr = 3-Sulpho-1-propyloxy sodium salt
Gluc = β-D-Glucopyranosyloxy

2-Hydroxy-5-carboxyacetophenone [7], 3-hydroxy-4-carboxyacetophenone [8], 2-hydroxy-4-carboxymethoxyacetophenone (as the ethyl ester) [9], 4-carboxymethoxyacetophenone [10], 2-hydroxy-(4-tetra-*O*-acetyl-β-D-glycopyranosyloxy)acetophenone [9], and 2-hydroxy-6-methyl-4-(tetra-*O*-acetyl-β-D-glucopyranosyloxy)acetophenone [11] are known compounds. Preparation of the new acetophenones **64**—**67** is described in Experimental.




Many of the aldehydes needed were commercially available. The syntheses of 2-benzyloxy-4-methoxy-[12], 4-benzyloxy-3-methoxy-[13], 3-hydroxy-4-ethoxy-[14], 3-hydroxy-4-*n*-propoxy-[14], 3,4-dibenzyloxy-[16], 2-benzyloxy-[16], 4-carboxymethoxy-[17] and (4-tetra-*O*-acetyl-β-D-glucopyranosyloxy)-benzaldehyde [18] have been reported.

| Molecular formula | Molecular weight | Calcd. | | Found | | Chalcone precursor | Solvent of hydrogenation | Yield, % |
|---|---|---|---|---|---|---|---|---|
| | | C | H | C | H | | | |
| $C_{21}H_{24}O_9$ | 420.4 | 59.99 | 5.75 | 59.49 | 5.89 | **52** | AcOH | 48 |
| $C_{22}H_{26}O_9$ | 434.4 | 60.82 | 6.03 | 60.93 | 5.83 | **53** | AcOH | 37 |
| $C_{22}H_{26}O_9$ | 434.4 | 60.82 | 6.03 | 60.77 | 6.00 | **54** | MeOH | 70 |
| $C_{22}H_{26}O_{10}$ | 450.4 | 58.66 | 5.82 | 58.74 | 6.06 | **55** | AcOH | 20 |
| $C_{22}H_{26}O_{10}$ | 450.4 | 58.66 | 5.82 | 58.75 | 6.08 | **56** | AcOH | 43 |
| $C_{22}H_{26}O_{10}.H_2O$ | 468.5 | 56.40 | 6.03 | 56.60 | 6.25 | [6] | MeOH | 56 |
| $C_{23}H_{28}O_{10}$ | 464.5 | 59.47 | 6.08 | 59.35 | 6.09 | **57** | AcOH | 22 |
| $C_{23}H_{28}O_{10}$ | 464.5 | 59.47 | 6.08 | 59.60 | 6.12 | **58** | AcOH | 20 |
| $C_{23}H_{28}O_{11}$ | 480.5 | 57.49 | 5.87 | 57.08 | 6.51 | **59** | AcOH | *** |
| $C_{27}H_{34}O_{14}$ | 582.6 | 55.66 | 5.88 | 55.34 | 6.19 | **60** | AcOH | *** |

* = Obtained by saponification of the non-isolated ester
** = Gradual decomposition without melting over 250–280 °C
*** = Non-informative. The pure product was obtained on several recrystallizations.

## Experimental

### General method for the preparation of dihydrochalcones from chalcones by catalytic hydrogenation

A solution of the chalcone (0.01 mole) in the solvent specified in Table I was treated in the presence of palladium-on-charcoal catalyst (0.5 g) until the rate of hydrogenation dropped sharply. In the absence of a clear end-point no more than 1.2 molar equivalent of hydrogen was allowed to be absorbed. The product was recovered in the usual way.

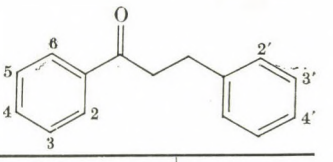
### General methods for the preparation of chalcones

Equimolar amounts (0.01) of the acetophenone and the aldehyde were (method A) refluxed in a mixture of ethanol (20 ml) and 40% aq. sodium hydroxide (20 ml) for 5 hrs, or (method B) the same mixture was stirred at room temperature for 48 hrs, or (method C) refluxed in a mixture of methanol (7 ml) and 25% sodium hydroxide (14 ml) for 3–6 hrs, or (method D) dissolved in ethanol (40 ml) and saturated at 0° with dry hydrogen chloride, or (method E) stirred at room temperature for 48–96 hrs in 25% sodium hydroxide (5 ml), or (method F) stirred at room temperature for 48–96 hrs in a mixture of 25% sodium hydroxide (15 ml) and ethanol (3–10 ml).

The chalcones were recovered by dilution with 5% hydrochloric acid and purified by recrystallization.

**Table II**

*New chalcones*




| No. | Substituents | | | | | | | M. p., °C (solvent) |
|---|---|---|---|---|---|---|---|---|
| | $C_{2'}$ | $C_{4'}$ | $C_{5'}$ | $C_{6'}$ | $C_2$ | $C_3$ | $C_4$ | |
| **32** | OH | H | $CO_2H$ | H | H | OH | OMe | 239—241 (MeOH) |
| **33** | H | OH | $CO_2H$ | H | H | OH | OMe | 238—239 (MeOH) |
| **34** | OH | Cbm | H | H | H | $OCH_2O$ | | 223—225 (MeOH) |
| **35** | H | Cbm* | H | H | H | OH | OMe | 122—124 ($EtOH–H_2O$) |
| **36** | OH | Cbm | H | H | OBn | H | OMe | 151—153 (AcOH) |
| **37** | OH | Cbm | H | H | H | OMe | OBn | 170—171 (AcOH) |
| **38** | OH | Cbm | H | H | H | OH | OMe | 222—224 (AcOH) |
| **39** | OH | H | Cbm | H | H | OH | OMe | 181—182 (MeOH) |
| **40** | OH | Cbm | H | H | H | OH | OEt | 214—215 (AcOH) |
| **41** | OH | Cbm | H | H | H | OH | O*n*Pr | 203—204 (AcOH) |
| **42** | OH | H | $SO_3Na$ | H | H | OH | OMe | > 300 ($H_2O$) |
| **43** | OH | Supr | H | H | H | H | H | dec.** ($H_2O$) |
| **44** | OH | Supr | H | H | H | OBn | OBn | > 300 ($H_2O$) |
| **45** | Supr | H | H | H | H | OH | OMe | 233—235 ($H_2O$) |
| **46** | H | Supr | H | H | H | OH | OMe | dec.** ($H_2O$) |
| **47** | OH | Supr | H | H | OBn | H | OMe | dec.** ($H_2O$) |
| **48** | OH | Supr | H | H | H | OH | OMe | 273—276 ($H_2O$) |
| **49** | OH | Supr | H | H | H | OH | OEt | dec.** ($H_2O$) |
| **50** | OH | Supr | H | H | OH | H | O*n*Pr | dec.** ($H_2O$) |
| **51** | OH | Gluc | H | H | OBn | H | H | 191—195 (MeOH) |
| **52** | OH | Gluc | H | H | H | OH | H | 196—198 (EtOH) |
| **53** | OH | Gluc | H | H | OMe | H | H | 197—200 (EtOH) |

| Molecular formula | Molecular weight | Calcd. | | Found | | Method | Yield, % |
|---|---|---|---|---|---|---|---|
| | | C | H | C | H | | |
| $C_{17}H_{14}O_6$ | 314.3 | 64.96 | 4.49 | 64.69 | 4.39 | A | 36 |
| $C_{17}H_{14}O_6$ | 314.3 | 64.96 | 4.49 | 64.72 | 4.72 | B | 27 |
| $C_{18}H_{14}O_7$ | 342.3 | 63.16 | 4.12 | 63.45 | 4.40 | C | 68 |
| $C_{19}H_{18}O_6$ | 342.3 | 63.16 | 4.12 | 63.02 | 4.33 | D | 72 |
| $C_{25}H_{22}O_7$ | 434.4 | 69.11 | 5.10 | 69.26 | 5.27 | C | 54 |
| $C_{25}H_{22}O_7$ | 434.4 | 69.11 | 5.10 | 69.06 | 4.99 | C | 58 |
| $C_{18}H_{16}O_7$ | 344.3 | 62.79 | 4.68 | 63.00 | 4.75 | C | 68 |
| $C_{18}H_{16}O_7$ | 344.3 | 62.79 | 4.68 | 62.52 | 4.73 | C | 54 |
| $C_{19}H_{18}O_7$ | 358.3 | 63.68 | 5.06 | 63.48 | 5.12 | C | 64 |
| $C_{20}H_{20}O_7$ | 372.4 | 64.51 | 5.41 | 64.37 | 5.44 | C | 26 |
| $C_{16}H_{13}NaO_7S$ | 372.3 | 51.61 | 3.52 | 51.40 | 3.32 | E | 48 |
| $C_{18}H_{17}NaO_6S$ | 384.4 | 56.24 | 4.46 | 56.01 | 4.57 | E | 31 |
| $C_{32}H_{29}NaO_8S$ | 596.6 | 64.42 | 4.90 | 64.62 | 4.88 | C | 50 |
| $C_{19}H_{19}NaO_7S$ | 414.4 | 55.07 | 4.62 | 55.21 | 4.46 | E | 53 |
| $C_{19}H_{19}NaO_7S$ | 414.4 | 55.07 | 4.62 | 55.42 | 4.41 | E | 54 |
| $C_{26}H_{25}NaO_8S$ | 520.5 | 59.99 | 4.84 | 59.63 | 4.64 | E | 38 |
| $C_{19}H_{19}NaO_8S$ | 430.4 | 53.02 | 4.45 | 53.23 | 4.30 | E | 84 |
| $C_{20}H_{21}NaO_8S$ | 444.5 | 54.04 | 4.76 | 54.26 | 5.01 | E | 28 |
| $C_{21}H_{23}NaO_8S$ | 458.5 | 55.01 | 5.06 | 54.82 | 5.26 | E | 30 |
| $C_{28}H_{28}O_9$ | 508.5 | 66.13 | 5.55 | 66.20 | 5.58 | F | 78 |
| $C_{21}H_{22}O_9$ | 418.4 | 60.28 | 5.30 | 60.51 | 5.45 | E | 54 |
| $C_{22}H_{24}O_9$ | 432.4 | 61.10 | 5.59 | 61.48 | 5.60 | G | 60 |

**Table II continued**

| No. | Substituents | | | | | | | M. p., °C (solvent) |
|---|---|---|---|---|---|---|---|---|
| | $C_{2'}$ | $C_{4'}$ | $C_{5'}$ | $C_{6'}$ | $C_2$ | $C_3$ | $C_4$ | |
| **54** | OH | Gluc | H | H | H | H | OMe | 203—204 (MeOH) |
| **55** | OH | Gluc | H | H | OBn | OMe | H | 193—196 (MeOH) |
| **56** | OH | Gluc | H | H | H | OMe | OBn | 197—200 (EtOH) |
| **57** | OH | Gluc | H | H | H | OMe | OMe | amorphous (EtOH) |
| **58** | OH | Gluc | H | Me | H | OH | OMe | 179—181 (EtOH) |
| **59** | OH | Gluc | H | H | H | H | Cbm | 198—202 (MeOH) |
| **60** | OH | Gluc | H | H | H | H | Gluc | 180—183 ($H_2O$) |

Cbm = Carboxymethoxy
Supr = 3-Sulpho-1-propyloxy sodium salt
Gluc = $\beta$-D-Glucopyranosyloxy

### 3-Acetyl-4-hydroxyphenoxyacetic acid (64)

2,5-Dihydroxyacetophenone (15.0 g), ethyl chloroacetate (7.6 ml), sodium iodide (1.5 g) and potassium carbonate (15.0 g) were refluxed with stirring in acetone (300 ml) for 24 hrs. The filtered solution was evaporated and the residue dissolved in benzene. Any unchanged starting material was removed by filtration and the benzene evaporated to a small volume. The product (10.0 g, 47%) crystallized slowly, m. p. 59—60 °C.

$C_{10}H_{10}O_5$ (210.2) Calcd. C 57.14; H 4.80. Found C 57.02; H 4.92%.

### 1-(2-Hydroxy-5-sulphonylphenyl)-ethanone ammonium salt (65)

A mixture of 2-hydroxyacetophenone (10.0 ml) and conc. sulfuric acid (50 ml) was stirred at 55—60 °C for 3 hrs. The mixture was poured onto ice (160 g) and the unchanged acetophenone was extracted with benzene (2×25 ml). The aqueous phase was neutralized with solid ammonium carbonate. The product and some ammonium sulfate crystallized. Recrystallization from water gave the pure product as colorless needles (9.8 g, 66%). It decomposed gradually without melting.

$C_8H_{11}NO_5S$ (233.3) Calcd. N 6.00. Found N 6.15%.

### 1-[2-Hydroxy-4-(3-sulpho-1-propyloxyphenyl)]-ethanone sodium salt (66)

To a suspension of 2,4-dihydroxyacetophenone (30.4 g) in water (70 ml) sodium hydrogen carbonate (21.0 g) was added in portions. After dissolution propane sultone (27.0 g) was added in portions at 45 °C over 1 hr. Heating at 70 °C for 15 min completed the reaction. On acidification with conc. hydrochloric acid and keeping in the cold the product crystallized. The crude product was extracted twice with boiling acetone to give the pure salt (42.0 g, 72%). The compound had no definite m. p.

$C_{11}H_{13}NaO_5S$ (280.3) Calcd. C 47.13; H 4.67; S 11.44. Found C 47.01; H 4.72; S 11.12%.

| Molecular formula | Molecular weight | Calcd. | | Found | | Method | Yield, % |
|---|---|---|---|---|---|---|---|
| | | C | H | C | H | | |
| $C_{22}H_{24}O_9$ | 432.4 | 61.10 | 5.59 | 61.19 | 5.48 | G | 79 |
| $C_{29}H_{30}O_{10}$ | 538.5 | 64.67 | 5.62 | 64.73 | 5.94 | E | 29 |
| $C_{29}H_{30}O_{10}$ | 538.5 | 64.67 | 5.62 | 64.45 | 5.77 | G | 25 |
| $C_{23}H_{26}O_{10}$ | 462.4 | 59.73 | 5.67 | 59.89 | 5.47 | G | 68 |
| $C_{23}H_{26}O_{10}$ | 462.4 | 59.73 | 5.67 | 59.85 | 5.73 | E | 53 |
| $C_{23}H_{26}O_{11}$ | 478.4 | 57.72 | 5.48 | 57.60 | 5.30 | E | 64 |
| $C_{27}H_{32}O_{14}$ | 580.6 | 55.86 | 5.56 | 55.35 | 5.45 | E | 26 |

* = As the methyl ester
Bn = Benzyl
** = Gradual decomposition without melting over 250–280 °C

**1-[2-(3-Sulpho-1-propyloxyphenyl)]-ethanone (67)**

To a vigorously stirred mixture of 2-hydroxyacetophenone (13.6 g) and 4% aq. sodium hydroxide (100 ml) propane sultone (13.4 g) was added and stirring continued for 8 hrs. The unchanged starting material was extracted with benzene and the aqueous solution evaporated. Recrystallization of the residue twice from water afforded the pure product, 4.8 g (19%). It had no definite m. p.

$C_{11}H_{13}NaO_4S$ (264.3) Calcd. C 49.99; H 4.95; S 12.13. Found C 49.70; H 4.86; S 12.21%.

**[3-Hydroxy-4-[3-(3-hydroxy-4-methoxyphenyl)]-1-propyl]-phenoxy-acetic acid (61)**

To a solution of **9** (2.1 g) in 18.7% aq. ammonia (20 ml) conc. aq. copper(II)sulfate solution (0.1 ml) and zinc dust (4.0 g) were added. The mixture was refluxed, with stirring, for 24 hrs. Acidification after filtration precipitated a gum, which was separated and boiled with 10% hydrochloric acid. The residue was purified by reprecipitation from alkaline solution. Colorless powder, m. p. 108–110 °C.

$C_{18}H_{20}O_6$ (332.4) Calcd. C 65.04; H 6.06. Found C 64.90; H 6.12%.

## REFERENCES

[1] ANTUS, S., FARKAS, L., GOTTSEGEN, Á., NÓGRÁDI, M., PFLIEGEL, T.: Acta Chim. Acad. Sci. Hung. **98,** 225 (1978)
[2] FARKAS, L., NÓGRÁDI, M.: Hung. Pat. 161.162 (1970)
[3] FARKAS, L., NÓGRÁDI, M., GOTTSEGEN, Á., ANTUS, S.: Hung. Pat. 163.394 (1971)
[4] FARKAS, L., NÓGRÁDI, M., PFLIEGEL, T., GOTTSEGEN, Á., ANTUS, S.: Hung. Pat. 168.495 (1976)
[5] LESPAGNOL, A., LESPAGNOL, C., LESIEUR, C., CAZIN, J. C., CAZIN, M., BEEREUS, H., ROMOND, C.: Chim. Ther. **7,** 365 (1972)

[6] REICHEL, L., STEUDEL, J.: Ann. **553,** 93 (1943)
[7] CHATTAWAY, F. S., CALVET, F.: J. Chem. Soc. **129,** 692 (1927)
[8] ROSENMUND, K. W., SCHNURR, W.: Ann. **460,** 89 (1928)
[9] ZAWADOWSKI, T., MERKEL, M., SZUCHNIK, A., SWIDERSKI, J.: Roczniki Chem. **36,** 895 (1962)
[10] BERHENKE, L. F., BEGIN, L. E., WILLIAMS, B. M., BEMAN, F. L.: J. Am. Chem. Soc. **73** 4458 (1951)
[11] MAUTHNER, N.: J. prakt. Chem. **161,** 284 (1943)
[12] SONN, A., PATSCHKE, E.: Ber. **58,** 1701 (1925)
[13] DICKINSON, R., HEILBRON, I. M., IRVINGS, F.: J. Chem. Soc. 1895 (1927)
[14] KAFAKU, K., ITIKAWA, N.: J. Pharm. Soc. Japan **46,** 35 (1926)
[15] MAHAL, H. S., RAI, H. S., Venkataraman, L.: J. Chem. Soc. 886 (1935)
[16] PERKIN, W. H.: Ann. **148,** 24 (1868)
[17] ELKAN, T.: Ber. **19,** 3041 (1886)
[18] MAUTHNER, F.: J. prakt. Chem. **85,** 567 (1912)

Sándor ANTUS
Loránd FARKAS
Ágnes GOTTSEGEN
Mihály NÓGRÁDI
János STRELISKY
H-1521 Budapest,

Tódor PFLIEGEL H-1325 Budapest, P.O.B. 110.

*Acta Chimica Academiae Scientiarum Hungaricae, Tomus 98 (2), pp. 241—245 (1978)*

# SYNTHESIS OF SOME NATURAL METHYLATED QUERCETIN GLYCOSIDES

K. Székely, B. Vermes, L. Farkas and M. Nógrádi

*(Institute of Organic Chemistry, Technical University, Budapest)*

Received September 20, 1977

Unambiguous syntheses of the 3-*O*-α-L-rhamnoside (**1**) and 3-*O*-β-rutinoside (**6**) of 7-*O*-methylquercetin and of 3',4',7-tri-*O*-methylquercetin-3-*O*-α-L-rhamnoside (**9**) are reported.

There have been at least fourteen different methyl ethers of quercetin reported in the literature [1]; most of them also occur in a glycosylated form [2]. Some years ago, we described the synthesis of some tamarixetin (4'-*O*-methylquercetin) glycosides [3]. As a continuation of this work, we report now the synthesis of three glycosides derived from rhamnetin (7-*O*-methylquercetin) and 3',4',7-tri-*O*-methylquercetin.

The first of these substances, rhamnitrin (7-methoxy-3,3',4',5-tetrahydroxyflavone-3-*O*-α-L-rhamnopyranoside) (**1**), was isolated in 1968 by Clark-Lewis and Dainis from the leaves of *Acacia ixiophylla* [4]. Separation of **1** from quercetin was reported to be difficult and it seemed to us that the wide melting range quoted (179—195 °C) may be an indication for impurity of the sample.

An unequivocal synthesis of rhamnitrin (**1**) required the preparation of a suitably protected aglycone such as **2**, the 4'-benzyl ether of rhamnetin. Compound **2** contains three free hydroxyl groups, but it has been demonstrated repeatedly that the hydroxyls at C-3', and C-5 are less reactive than that at C-3 [3, 5]. 4'-Benzylrhamnetin (**2**) was prepared by selective benzylation of rhamnetin tetraacetate (**3**) [6] followed by saponification. Benzylation at the 4'-position, which could be anticipated considering previous experience [6, 7], was proved by $^1$H-NMR and Uv spectroscopy. $^1$H-NMR indicated one *O*-benzyl group ($\delta$ = 5.05 ppm) and a free hydroxyl at C-5 ($\delta$= 12.4 ppm).

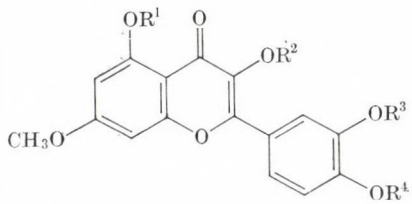
The UV spectrum of the product, either alone or in ($\delta$) the presence of additives was similar to that of 4',7-di-*O*-methylquercetin [7]. Finally, methylation to **4** followed by debenzylation gave the known [8] 4'-hydroxy-3,3',5,7--tetramethoxyflavone (**5**).

Coupling of **2** with 2,3,4-tri-*O*-acetyl-α-L-rhamnopyranosyl bromide [9], saponification of the crude product and chromatography gave the rhamnoside

**6** in a low yield. Debenzylation of **6** gave pure rhamnitrin dihydrate of m. p. 228—233 °C.

The 3-*O*-$\beta$-rutinoside of rhamnetin (**7**) was isolated by MITCHELL and GEISSMAN in 1971 from *Suriana maritima* [10]. Though the substance was claimed to be crystalline, no m. p. has been reported. Coupling of **2** with $\alpha$-acetobromorutinose [11] gave, after saponification, the benzyl-glycoside **8**, which was debenzylated to obtain **7** of m. p. 149—153 °C.

3,5-Dihydroxy-3',4',7-trimethoxyflavone-3-*O*-$\alpha$-L-rhamnoside (**9**) was discovered by TIWARI and YADOVA [12] as a constituent of the flowers of *Cassia javanica*, $\delta$ in 1971. The aglycone (**10**) needed for its synthesis was prepared by controlled methylation of rutin followed by hydrolysis. Compound **10** was coupled with 2,3,4-tri-*O*-acetyl-$\alpha$-L-rhamnopyranosyl bromide to give, after saponification and chromatography, **9**.




**1** : $R^1 = R^3 = R^4 = H$; $R^2 = \alpha$-L-rhamnopyranosyl
**2** : $R^1 = R^2 = R^3 = H$; $R^4 = CH_2Ph$
**3** : $R^1 = R^2 = R^3 = R^4 = CH_3CO$
**4** : $R^1 = R^2 = R^3 = CH_3$; $R^4 = CH_2Ph$
**5** : $R^1 = R^2 = R^3 = CH_3$; $R^4 = H$
**6** : $R^1 = R^3 = H$; $R^2$-$\alpha$-L-rhamnopyranosyl; $R^4 = CH_2Ph$
**7** : $R^1 = R^3 = R^4 = H$; $R^2 = \beta$-rutinosyl
**8** : $R^1 = R^3 = H$; $R^2 = \beta$-rutinosyl; $R^4 = CH_2Ph$
**9** : $R^1 = H$; $R^2 = \alpha$-L-rhamnopyranosyl; $R^3 = R^4 = CH_3$
**10** : $R^1 = R^2 = H$; $R^3 = R^4 = CH_3$.

Coupling of phenols with an acylhalogenorhamnose in pyridine or quinoline in the presence of silver oxide or silver carbonate gives yields in the order of a few per cents [5, 13]. Now, we have found that using benzene as the solvent, silver carbonate as base and removing water by co-distillation with benzene, a method originally devised to prepare glycosides of alcohols [14], gave more acceptable results (10—15%).

Since no authentic samples were available of any of the natural products, the synthetic glycosides have been identified by comparison with the reported physical and spectral data.

## Experimental

M. p.' s. are uncorrected. $^1$H-NMR spectra were taken on a Perkin-Elmer R12 (60 MHz) spectrometer with TMS as internal standard, UV spectra on a Unicam SP-700 spectrometer; CD data were determined on a Jouan dichrograph.

**4'-Benzyloxy-3,3',5'-trihydroxy-7-methoxyflavone (2)**

Rhamnetin tetraacetate [6] (10.0 g), benzyl chloride (3.6 ml), sodium iodide (1.5 g) and dry potassium carbonate (25 g) were refluxed, with stirring, in dry acetone (150 ml) for 10 h, and after the addition of another portion of benzyl chloride (3.6 ml) for 10 h more. After filtration and evaporation, the residual syrup was dissolved in methanol (300 ml), 10% aq. sodium hydroxide (40 ml) was added and the mixture boiled for 10 min. After dilution with 1% hydrochloric acid (1000 ml), the product was separated, extracted by boiling with ethanol (2×50 ml) and recrystalized from ethanol–acetone (1 : 1) to obtain yellow crystals (4.9 g; 58%), m. p. 194–197 °C.

Uv: $\lambda_{max}^{EtOH}$ 255, 295i, 367, $\lambda_{max}^{EtOH+NaOAc}$ 256, 303i, 370;

$\lambda_{max}^{EtOH}$ 263, 299i, 422, $\lambda_{max}^{EtOH+NaOEt}$ 267, 411 nm.

NMR ($CDCl_3$): $\delta$ el = 3.20 (s, OMe), 5.05 (s, $OCH_2$), 6.2–7.7 (m, 10H, aromatic-H), 9.3 and 9.5 (s, 3'- and 3-OH), 12.4 (s, 5-OH).

$C_{23}H_{18}O_7$ (406.4). Calcd. C 67.92; H 4.43. Found C 67.65; H 4.35%.

**4'-Benzyloxy-3,3',5,7-tetramethoxyflavone (4)**

A solution of **2** (100 mg) in dry acetone (3.0 ml) was stirred with dimethyl sulfate (0.1 ml) and potassium carbonate (200 mg) for 2 h. Evaporation, dilution with water, filtration and recrystallization from methanol gave **4** as cream-coloured crystals (90 mg; 81%), m. p. 159–162 °C.

NMR ($CDCl_3$): $\delta$ = 3.95 and 4.02 (s, 6–6H, OMe), 5.18 (s, $OCH_2$), 6.2–6.5 and 7.2–7.8 (m, 12H, aromatic-H).

$C_{26}H_{24}O_7$ (448.5). Calcd. C 69.63; H 5.39. Found C 69.19; H 5.74%.

**4'-Hydroxy-3,3',5,7-tetramethoxyflavone (5)**

Hydrogenation of **4** (40 mg) in hot ethanol in the presence of palladium-on-charcoal catalyst gave after the usual work-up **5** as pale yellow crystals (20 mg; 62%), m. p. 198–201 °C (lit. [8] m. p. 198–201 °C).

**4'-Benzyloxy-3,3',5-trihydroxy-7-methoxyflavone-3-α-L-rhamnopyranoside (6)**

To a boiling solution of **2** (400 mg) in dry benzene (100 ml) silver carbonate (0.5 g) and within 90 min a solution of freshly prepared α-2,3,4-tri-*O*-acetylrhamnopyranosyl bromide [9] (3.3 g) in benzene (100 ml) were added with stirring.

During addition benzene was continuously distilled off. Stirring was continued for 30 min, thereafter the solution was filtered and evaporated. The solution of the residue in methanol was adjusted to pH 12 with 1*N* sodium methoxide and allowed to stand overnight. After acidification and evaporation, the solution was extracted with ethyl acetate and the extract evaporated. Trituration of the residue with ethyl acetate gave the crude product of which some more was obtained by column chromatography of the mother liquor (silica gel, benzene–ethanol 9 : 2). Repeated recrystallization from methanol gave yellow crystals (80 mg; 15%), m. p. 218–221 °C.

$C_{29}H_{28}O_{11}$ (552.6). Calcd. C 63.03; H 5.10. Found C 63.40; H 4.95%.

**3',4'5-Trihydroxy-7-methoxyflavone-3-Q-α-L-rhamnopyranoside, rhamnitrin (1)**

Catalytic hydrogenation of **6** (20 mg) in hot ethanol gave after the usual work-up and recrystallization from methanol **1** (15 mg; 90%), m. p. 228–233 °C (lit. [4] m. p. 179–195 °C).

Uv: $\lambda_{max}^{EtOH}$ 257, 355 (lit. [4] 258, 258, 356);

$\lambda_{max}^{EtOH}$ 259, 355; $\lambda_{max}^{EtOH+NaOAc}$ 275, 375, 400 nm,

CD (EtOH, c = 0.149 mmole/l) 332 (−3.500), 252 (4.450), 213 (−5.513), 206 (2. 185)
$C_{22}H_{22}O_{11} \cdot 2H_2O$ (498.4). Calcd. C 53.01; H 5.26. Found C 53.48; H 5.34%.

### 4'-Benzyloxy-3,3',5-trihydroxy-7-methoxyflavone-3-*O*-(6-*O*-α-L-rhamnopyranosido-β-D-glucopyranoside) (8)

Compound **2** (0.6 g), α-acetobromorutinose 11 (1.0 g), active silver oxide (0.5 g), and anhydrous calcium sulfate (Sikkon, Fluka) (0.8 g) were stirred in freshly distilled quinoline (12.5 ml) for 1.5 h at room temperature. After addition of another partion of α-acetobromorutinose (1.0 g), stirring was continued for 1.5 h, the solution was then diluted with chloroform, filtered washed 6 times with 5% aq. sulfuric acid, dried and the solvent evaporated. After saponification (as described for **6**) the crude glycoside was chromatographed on silica gel (EtOAc–MeOH–$H_2O$ 100 : 16.5 : 13.5). The glycoside fraction gave on recrystallization from 90% ethanol yellow crystals (180 mg; 18%), m. p. 198—203 °C.
$C_{35}H_{38}O_{16}$ (714.4). Calcd. C 58.82; H 5.36. Found C 58.62; H 5.43%.

### 3',4',5-Trihydroxy-7-methoxyflavone-3-*O*-(6-*O*-αr-L-hamnopyranosido-β-D-glucopyranoside) (7)

Catalytic hydrogenation of **8** (300 mg) in hot ethanol gave after the usual work-up and several recrystallizations from 90% ethanol **7** as yellow crystals, m. p. 179—181 °C.

Uv: $\lambda_{max}^{EtOH}$ 259, 290, 360, (lit. [10] 257, 297, 361);

$\lambda_{max}^{EtOH+NaOAc}$ 259, 290, 360;

$\lambda_{max}^{EtOH+AlCl_3}$ 257, 361, 399 nm.

CD (EtOH, c = 0.242 mmole/l) 392 (0.074), 341 (−0.841), 293 (−1.042), 276 (−0.156), 254 (3.490), 228 (−2.819), 206 (1.912) nm.
$C_{28}H_{32}O_{16} \cdot 2H_2O$ (660.6). Calcd. C 50.90; H 5.49. Found C 50.43; H 5.21%.

### 3,5-Dihydroxy-3',4',7-trimethoxyflavone (10)

Rutin (5.0 g), dimethyl sulfate (9.75 ml) and dry potassium carbonate (15.0 g) were stirred in dimethylformamide (35 ml) at 75 °C for 3 h. After having removed the solvent by steam distillation, the solution was acidified with 2*N* HCl and refluxed for 3 h. The precipitated product was crystallized from acetone–methanol to give **10** (2.1 g; 75%), m. p. 183—185 °C (lit. [7] m. p. 183—184 °C).

### 5-Hydroxy-3',4',7-trimethoxyflavone-3-*O*-α-L-rhamnopyranoside (9)

Coupling of **10** (2.0 g) with 2,3,4-tri-*O*-acetyl-α-L-rhamnopyranosyl bromide (5.4 g), following the procedure described for **6**, gave after column chromatography (silica gel, benzene–ethanol 9 : 2) and recrystallization from ethanol yellow needles (120 mg; 10.5%), m. p. 184—186 °C [lit. [12] m. p. 190 °C (d.)].

Uv: $\lambda_{max}^{EtOH}$ 268, 360, (lit. [12] 268, 357);

$\lambda_{max}^{EtOH+NaOAc}$ 268, 362, (lit. [12] 268);

$\lambda_{max}^{EtOH+AlCl_3}$ 276, 304, 360, 415,

CD (EtOH, c = 0.220 mmole/l) 392 (0.074), 341 (−0.841), 310 (0.301), 293 (−1.042), 276 (−0.156), 254 (3.490), 228 (−2.819), 206 (1.912) nm.
$C_{24}H_{26}O_{11}$ (490.3). Calcd. C 58.8; H 5.30. Found C 58.80; H 5.45%.

## REFERENCES

[1] GOTTLIEB, O. R. in "The Flavonoids" (ed. Harborne, J. B., Mabry, T. J., Mabry, H.), p. 324. Chapman and Hall, London, 1975
[2] HARBORNE, J. B., WILLIAMS, A. C.: p. 423 in Ref. [1]
[3] FARKAS, L., VERMES, B., NÓGRÁDI, M.: Acta Chim. (Budapest), **73,** 107 (1972)
[4] CLARK-LEWIS, J. W., DAINIS, I.: Aust. J. Chem. **21,** 425 (1968)
[5] HÖRHAMMER, L., WAGNER, H., ARNDT, H. G., FARKAS, L.: Tetrahedron Letters, **1966,** 567; FARKAS, L., VERMES, B., NÓGRÁDI, M., KÁLMÁN, A.: Phytochemistry **15,** 1184 (1976)
[6] JURD, L.: J. Am. Chem. Soc. **80,** 5531 (1958)
[7] JURD, L.: J. Org. Chem. **27,** 1294 (1962)
[8] RAO, K. V., SESHADRI, T. R.: J. Chem. Soc. **1946,** 771
[9] FISCHER, E., BERGMANN, M., RABE, A.: Ber. Dtsch. Chem. Ges. **53,** 2362 (1920).
[10] MITCHELL, R. E., GEISSMAN, T. J.: Phytochemistry **10,** 1559 (1971)
[11] ZEMPLÉN, G., GERECS, Á.: Ber. Dtsch. Chem. Ges. **70,** 1098 (1937)
[12] TIWARI, R. D., YADOVA, O. P.: Phytochemistry, **10,** 2256 (1971)
[13] HÖRHAMMER, L., WAGNER, H., ARNDT, H. G., DIRSCHEL, R., FARKAS, L.: Chem. Ber. **101,** 450 (1968)
[14] MEYSTRE, C., MIESCHER, K.: Helv. Chim. Acta **27,** 231 (1944)

Krisztina SZÉKELY
Borbála VERMES
Loránd FARKAS
Mihály NÓGRÁDI

H-1521 Budapest

*Acta Chimica Academiae Scientiarum Hungaricae, Tomus 98 (2), pp. 247—249 (1978)*

# THE REACTION OF 2-ETHOXYCARBONYL-1--PHENYL-1,4-DIHYDRO-3(2*H*)-ISOQUINOLINONE WITH AMMONIA YIELDING N-[2--(CARBAMOYLMETHYL) BENZHYDRYL]--ETHYLURETANE

*(SHORT COMMUNICATION)*

E. ZÁRA-KACZIÁN and GY. DEÁK

*(Institute of Experimental Medicine, Hungarian Academy of Sciences, Budapest)*

Received December 1, 1977

For the purpose of biological studies, we attempted the conversion of 1-aryl-1,4-dihydro-3(2*H*)-isoquinolinones **1**, synthetized first by us [1], into the N-carbamoyl derivatives **5**. It was expected that the reaction of the N--ethoxycarbonyl derivative **2** with ammonia would give the desired compound, **5**. When 1-phenyl-1,4-dihydro-3(2*H*)-isoquinolinone (**1**) was allowed to react with ethyl chloroformate the N-ethoxycarbonyl derivative **2** was actually obtained, however, its reaction with ammonia did not yield the expected product (Scheme 1), since cleavage of the lactam ring took place instead of the ammonolysis of the ester group, so the product was N-[2-(carbamoylmethyl)benzhydryl]ethylurethane, **3**. The aminolysis of the ester group could not be achieved even by heating the product with thirty moles of propylamine or piperidine at 80 °C for 8 hrs; the starting material was recovered unchanged.

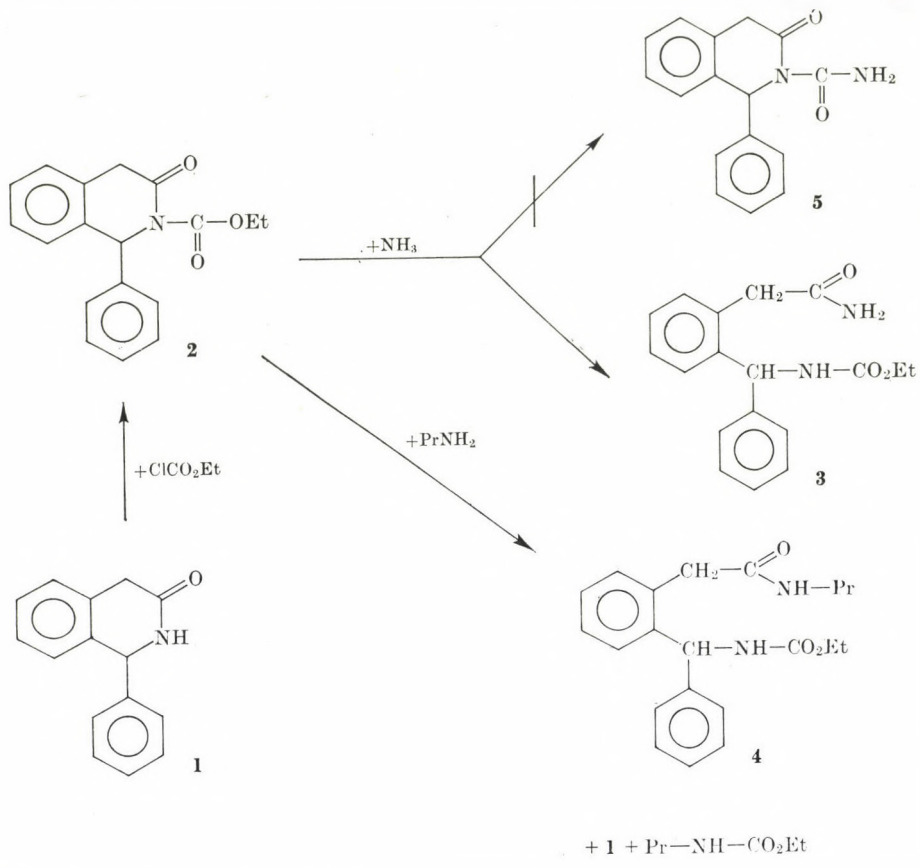
When the reaction was effected with propylamine, by refluxing compound **2** with an excess of propylamine in benzene solution for 4 hrs, the product of ring cleavage **4** was obtained only in 7% yield; the main products were 1-phenyl-1,4-dihydro-3(2*H*)-isoquinolinone and N-propylethylurethane. In chloroform at room temperature, the product of ring cleavage **4** was obtained in 17% yield.

## Experimental

M. p.'s were determined on a Büchi-Tottoli apparatus and are uncorrected. Infrared spectra were recorded in KBr pellets (Perkin-Elmer Model 457). NMR spectra were obtained using a JEOL PS-100 spectrometer; chemical shifts are given in ppm relative to internal tetramethylsilane.

### 2-Ethoxycarbonyl-1-phenyl-1,4-dihydro-3-(2H)isoquinolinone

1-Phenyl-1,4-dihydro-3(2*H*)-isoquinolinone (22.3 g; 0.1 mole) was refluxed in anhydrous benzene (400 ml) with distilled ethyl chloroformate (108 g; 1 mole) for 24 hrs. Benzene and the excess of ethyl chloroformate, were removed in vacuum, the residual brown oil (28 g) was




dissolved in benzene (100 ml) and the solution transferred to a column prepared from Silica gel-40 (90 g) with carbon tetrachloride; elution was effected with benzene (1000 ml). The eluate was evaporated to dryness to leave a yellow oily product (19.2 g; 65%). This was subjected to chromatographic separation as described above and triturated with petroleum ether; in this way a pale yellow powder (12.0 g; 41%) was obtained, m. p. 76–77 °C.

$C_{18}H_{17}NO_3$ (295,343). Calcd. C 73.19; H 5.81; N 4.74. Found C 73.15; H 6.32; N 4.81%.

**N-[2-(Carbamoylmethyl)benzhydryl]ethylurethane**

2-Ethoxycarbonyl-1-phenyl-1,4-dihydro-3(2*H*)-isoquinolinone (4 g; 0.0136 mole) was dissolved at room temperature in methanol (60 ml) saturated with ammonia (22.6 g of $NH_3$ in 100 ml of methanol) and the reaction was allowed to proceed for 3 hrs. The crystals, which separated were filtered off by suction. The crude product (2.0 g; 47.5%) was twice recrystallized from methanol to obtain white needless (1.5 g; 35.5%), m. p. 197 °C.

IR (KBr): $NH_2$ and NH 3400, 3300, 3200; C=O 1680, 1665, 1620, 1540; C–O–C 1245, 1260 $cm^{-1}$.

$^1H$–NMR (in $CDCl_3$): 1.27 (t, 3H) and 4.15 (q, 2H) ($CH_3CH_2O$); 3.58 (s, 2H, $CH_2$–Ph); 5.4 (1H, $NH_2$) and 5.6 (1H, $NH_2$); 6.10 (d, 1H); 6.25 (d, 1H) (CH–NH). $J_{CH-NH}$ 7 Hz; 7.1–7.4 (9H, Ar–H).

$C_{18}H_{20}N_2O_3$ (312,372). Calcd. C 69.20; H 6.4; N 9.0. Found C 68.89; H 6.6; N 8.7%.

**N-[2-(Propylcarbamoylmethyl)benzhydryl]ethylurethane**

2-Ethoxycarbonyl-1-phenyl-1,4-dihydro-3(2*H*)-isoquinolinone (1.5 g; 0.005 mole) was dissolved in dry chloroform containing no alcohol (23 ml) and it was allowed to react with propylamine (0.82 ml; 0.01 mole) at room temperature for 3 days. The reaction mixture was diluted with petroleum ether (300 ml), whereupon a yellow powder separated (1.0 g), m. p. 135—143 °C. This was dissolved in benzene (14 ml) and transferred to a Brockmann II alumina column (24 g), then eluted with a 1 : 1 mixture of benzene and chloroform (50 ml). On evaporation of the eluate to dryness, 0.5 g of the crude product was obtained, m. p. 154—157 °C. This was dissolved in a mixture of benzene (10 ml) and chloroform (5 ml), transferred to a Brockmann II alumina column (20 g) and eluted with a 2 : 1 mixture of benzene and chloroform (100 ml), to obtain white crystals (0.3 g; 17%), m. p. 166 °C.

IR (KBr): NH 3305/3310; C=O 1680, 1650, 1545; C—O—C 1245, 1260 $cm^{-1}$.

$^1H$—NMR (in $CDCl_3$): 1.27 (t, 3H) and 4.15 (q, 2H) ($CH_3CH_2O$); 3.54 (s, 2H, $CH_2$—Ph); 0.84 (t, 3H), 1.46 (sextet, 2H), 3.17 (q, 2H); 6.1 (m, 1H) (PrNH); 6.08 (d, 1H); 5.90 (d, 1H) (CH—NH), $J_{CH-NH}$ 7 Hz; 7.1—7.4 (9H, Ar—H).

$C_{21}H_{26}N_2O_3$ (354,450). Calcd. C 71.16; H 7.39; N 7.9. Found C 70.95; H 7.49; N 7.65%.

*

The authors express their thanks to G. TÓTH for determining the NMR spectra and to Mrs. J. HASKÓ-BREUER for recording the IR spectra.

## REFERENCES

[1] DEÁK, G., GÁLL-ISTÓK, K., HAZAI, L., STERK, L.: Synthesis **1975,** 393

Erzsébet ZÁRA-KACZIÁN
Gyula DEÁK
H-1450 Budapest, P.O. Box 67.

# RECENSIONES

## H. P. Latscha, H. A. Klein, R. Mosebach: *Chemistry for Pharmacists*

Springer Verlag, Berlin—Heidelberg—New York 1977

The book serves as an auxiliary textbook in the GFR for pharmacists preparing for the so-called absorption examination (final examination corresponding to state examination) in the basic subject of chemistry (the questions of examination in the GFR are published). In accordance with this purpose, the authors attempt the summarization of some fundamental chapters of general, inorganic and organic chemistry.

The chapters follow the above sectional order. The part on general chemistry (171 pages) contains, in well-selected sub-chapters, following the organization of the university curriculum, with illustrations and in a concise, clear style, modern knowledge relevant to material structure (atomic structure, periodic system, bond types, states of aggregation, etc.) and to equilibrium systems. The inorganic part (90 pages) tailored to special demands, discusses primarily elements and compounds important from pharmaceutical aspects, mentioning their most important properties, dealing briefly with the mode of preparation, and relatively more extensively, in an up-to-date concept, with structural problems. The organic part of 200 pages covers concisely the main groups of organic compounds (properties, electron structure, preparation, reactions).

The book serves its aim well: it summarizes the most important parts of the fundamental chemistry as a university subject. This task is solved with excellent didactical sence, and good selection. Its individual chapters may serve as a useful text for the post-graduate training of practicing chemists and pharmacists.

Gy. Szász

## William L. Masterton and Emil J. Slowinski: *Chemical Principles*, 3rd edition, Saunders Golden Sunburst Series

W. B. Saunders Co. Philadelphia, London, Toronto. 658 + 40 pp. Appendix + 15 p. Index

The authors of this book are noted for their extensive activities in writing chemical textbooks: they have contributed five other titles on different chemical subjects to the same series. The present work is the 3rd edition in English, and it has been published in 3 Italian and 3 French editions.

As shown by its title, this book has been written for American college students with the aim to provide information on chemical principles for those majoring medicine, biology, engineering, etc., studying chemistry only as a supplementary subject. The authors are of the opinion that, accordingly, these college students are not interested in abstract theories, but are attracted more the practical applicability of chemistry. Therefore, the authors do not discuss in detail, *e. g.* the theory of quantum mechanics, but attempt to emphasize the relationships between theoretical chemistry and practice. This endeavour is furthered also by continuously inserting exercises in the theoretical discussion, which are immediately solved. These examples predominantly concern substances and phenomena well-known from everyday life. Thus, *e. g.* on page 53, after the discussion of the molecule (molecular weight), the student is requested to calculate the mass(in g) of 2.60 mol of baking powder ($NaHCO_3$), and the amount

of 218 g of penicillin ($C_{16}H_{18}O_4N_2S$) in moles. However, if these exercises should prove too difficult for somebody, the detailed solution follows immediately.

The authors thought also of promoting the problem solving ability of the students and at the end of each chapter included problems arranged in two series. Next to each 'problem' of the first series, with numeration in another colour, there is a 'problem' analogous to the original, the answer to which can be found at the end of the volume in Appendix 6. In the reviewers opinion, this system of 'examples', 'solutions', 'problems' and 'answers' provides efficient help in mastering the subject.

The textbook condenses the 'principles' of chemistry into the following chapters:

1. Basic concepts
2. Atoms, molecules and ions
3. Chemical formulas and equations
4. Thermochemistry
5. The physical behaviour of gases
6. The electronic structure of atoms
7. Chemical bonding
8. Physical properties of molecular substances; nature of organic compounds
9. Liquids and solids; changes in state
10. Solutions
11. Water pure and otherwise
12. Spontaneity of reaction; $\Delta G$ and $\Delta S$
13. Chemical equilibrium in gaseous systems
14. Rates of reaction
15. The atmosphere
16. Precipitation reactions
17. Acids and bases
18. Acid-base reactions
19. Complex ions; coordination compounds
20. Oxidation and reduction: electrochemical cells
21. Oxidation-reduction reactions: spontaneity and extent
22. Nuclear reactions
23. An introduction to biochemistry

Appendix 1: Constants, conversion factors and properties of water
Appendix 2: Atomic and ionic radii
Appendix 3: Nomenclature of inorganic compounds
Appendix 4: Exponents and logarithms
Appendix 5: SI units
Appendix 6: Answers to problems

Thus, the authors cover comprehensively, and we may add very clearly, almost the entire subject. They utilize also the possibilities of printing techniques (well-proportioned text in varying type-setting, italics, bold face type, etc.), and several coloured figures illustrate the subject. A feature unusual in Europe is that the subject is occasionally interrupted by comic illustrations, such as *e. g.* on page 301, where a pretty young lady calls out from polluted water: "Thanks, but I think I shall go swimming somewhere else". This picture relaxas the tension of learning in the chapter "Water pure and otherwise". At the end of some chapters a brief historical appraisal is given of persons prominent in the history of chemistry, mentioned in the subject discussed.

The reviewer thinks that the work of Masterton and Slowinsky is a very useful, well-organized and well-written textbook of chemistry, but it is regrettable that the authors sometimes drift away from reality for the sake of didactics. An example for this is the statement on page 173, according to which, the interatomic distance in the fluorine molecule 'exactly equals' the sum of the radii of the two F atoms. This results in a bond length of 1.28 Å for the $F_2$ molecule, while the experimentally measured inter atomic distance is 1.41—1.45 Å (Tables of Interatomic Distances and Configuration in Molecules and Ions. The Chemical Society, London 1958).

It is similarly disturbing and discouraging the student that *e. g.* on page 72 (Table 4.2) a value of —83 kcal/mol is given for the heat of formation of the C—C bond, while at page 195 this value is —150 kcal/mol, in spite of the fact that both values refer to the dissociation energy of the $C_2$ molecule (HERZBERG, G.: Phys. Rev., **70**, 762 (1946)): 83 ± 5 kcal/mol, and DROWART and HONIG: J. Phys. Chem., **61**, 980 (1957), 144 kcal/mol). It is not clear why some of the bond energies given in the same table differ from the data given in the literature (*e. g.* OF: —44

kcal/mol, lit. 56 kcal/mol; OCl: −49 kcal/mol, lit.: 63.31−64.5 kcal/mol; N−N −38 kcal/mol, lit. $H_2N-NH_2$ 60 ±3, $O_2N-NO_2$ 12.8, $N_2$ 225 kcal/mol, etc) (Landolt−Börnstein, I.2).

Similarly as in other American textbooks of chemistry, a rather brief chapter is allotted to organic chemistry within the discussion of general chemistry. In pricniple, this is not objectionable, because general chemical principles are valid likewise for inorganic and organic substances. Nevertheless, after having read this otherwise excellent chapter, the student may overestimate his own knowledge of organic chemistry. It should have been emphasized that this chapter is only a very simplified introduction to organic chemistry.

No doubt, there are minor faults and misprints in this book besides those listed, but in spite of this, it is suitable as a basis of chemical knowledge.

D. SZABÓ

# INDEX

## ANALYTICAL CHEMISTRY

Investigations on the Outer-Sphere Complexes of Tris- (ethylene-diamine)-cobalt(III) and Hexamine-cobalt(III) Cations formed with Orthophosphate and Pyrophosphate Anions, P. HALMOS, J. GAÁL, J. INCZÉDY ..... 141
Some Chemical Reactions of the Electrode Gap and Their Role in Spectrochemical Analysis, XXXI. Behaviour of Metal Oxides in the Arc in an Argon Flow. Role of Burning Time and Current of the Arc with RW 0 Auxiliary Electrodes, Z. L. SZABÓ, H. DOBOLYI-FEJÉRDY ..... 147
Some Chemical Reactions of the Electrode Gap and their Role in Spectrochemical Analysis, XXXII. Behaviour of Metal Oxides in the Arc in an Argon Flow. Role of the Metal Oxide to Carbon Powder Ratio with RW 0 Auxiliary Electrodes, Z. L. SZABÓ, H. DOBOLYI-FEJÉRDY ..... 157

## PHYSICAL AND INORGANIC CHEMISTRY

Force Field Study of Chloroform by Parametric Method, K. RAMASWAMY, S. KARUNANITHI ..... 167
Electrochemical Study of Carbon-Supported Palladium–Copper Catalysts, T. MALLÁT, J. PETRÓ, M. SCHÄFFER ..... 175
On the Interpretation of Precise Data on Vapor Pressures of Molecular Isotopic Isomers, G. JANCSÓ, W. A. VAN HOOK ..... 183
Initiator Combinations for Polymerization, J. BENISKA, E. STAUDNER, G. KYSELA (In (Russian) ..... 193
On the Role of Chemical Factors in the Drawing of Dotted Tungsten Wires, (in German), T. MILLNER ..... 199
Molecular Constants of $ONF_3$, A. NATARAJAN, K. CHOCKALTINGAM ..... 205

## ORGANIC CHEMISTRY

Thermal Transcarboxylation Reactions, XII. Irreversibility of the Thermal Decarboxylation of Alkali Benzoates, J. SZAMMER, L. ÖTVÖS ..... 211
Side Reactions During the Removal of Protecting Groups of N-(Protected Aminoacyl) Urea Derivatives, I. SCHÖN, J. FRISS, L. KISFALUDY ..... 215
Dihydrochalcone Type Sweetening Agents, I. Structure–Taste Relationships, S. ANTUS, L. FARKAS, Á. GOTTSEGEN, M. NÓGRÁDI, T. PFLIEGEL ..... 225
Dihydrochalcone Type Sweetening Agents, II. The Synthesis of Some Dihydrochalcones, S. ANTUS, L. FARKAS, Á. GOTTSEGEN, M. NÓGRÁDI, J. STRELINSKY, T. PFLIEGEL 231
Synthesis of Some Natural Methylated Quercetin Glycosides, K. SZÉKELY, B. VERMES, L. FARKAS, M. NÓGRÁDI ..... 241
The Reaction of 2-ethoxycarbonyl-1-phenyl-1,4-dihydro-3(2*H*)-isoquinolinone with Ammonia Yielding N-[2-(carbamoylmethyl)benzhydry]-ethyllurethane (Short communicaton), E. ZÁRA-KACZIÁN, GY. DEÁK ..... 247

RECENSIONES ..... 251

1828 – 1978
PUBLISHED
IN THE YEAR
OF THE 150th
JUBILEE

*Printed in Hungary*

A kiadásért felel az Akadémiai Kiadó igazgatója. Műszaki szerkesztő: Zacsik Annamária

A kézirat nyomdába érkezett: 1978. IV. 17. — Terjedelem: 10,15 (A/5) ív, 54 ábra

78.5737 Akadémiai Nyomda, Budapest — Felelős vezető: Bernát György

ACTA CHIMICA

ТОМ 98 – ВЫП. 2

РЕЗЮМЕ

## Исследования комплексов типа внешней сферы катионов трис: (этилендиамин)-кобальта(III) и гексаммин-кобальта(III) с ортофосфатнымы и пирофосфатнымы анионами

П. ХАЛМОШ, Й. ГААЛ и И. ИНЦЕДИ

pH-Метрическое титрование было использовано для исследования комплексов, образующихся между комплексными катионами трис-(этилендиамин)-кобальта(III) и гексаммин-кобальта(III) и орто- и пирофосфатными анионами. Логарифмы констант стабильности $Co(en)_3HPO_4^+$, $CO(en)_3PO_4$, $Co(en)_3HP_2O_7$ и $Co(NH_3)_6HPO_4^+$ равны 2,02 ± 0,1, 3,12 ± 0,1, 2,19 ±0,5 и 02,53 ± 0,1, соответственно.

## Некоторые химические реакции в электродной щели и их роль в спектрохимическом анализе, XXXI

### Поведение окислов металлов в дуге с атмосферой проточного аргона. Роль времени горения дуги и силы тока в случае вспомогательного электрода RWO

З. Л. САБО и Х. ДОБОЛИ-ФЕЙЕРДИ

Данные, полученные варьированием времени горения дуги и силы тока с использованием углеродных вспомогательных электродов типа RWO, сравнивались с данными, полученными ранее на углеродных вспомогательных электродах типа RWII. На основе этого было показано, что температурные условия дуги для вспомогательных электродов играют самую важную роль в реакциях, протекающих внутри материала электрода. Природа углеродного порошка, используемого для приготовления порошковой смеси, также не безразлична. На основе полученных результатов было доказано, что те окислительные и восстановительные тенденции электрического характера, которые руководят реакциями, протекающими на поверхности электрода между газовой атмосферой и материалом электрода, не играют, однако, роли в реакциях, протекающих внутри материала.

## Некоторые химические реакции в электродной щели и их роль в спектрохимическом анализе, XXXII

### Поведение окислов металлов в дуге с атмосферой проточного аргона. Роль отношения окись метилла/углеродный порошок в случае вспомогательного электрода RWO

З. Л. САБО и Х. ДОБОЛИ-ФЕЙЕРДИ

Степень протекания химических реакций меньше, а влияние этих реакций на спектры больше в случае электродов с углеродными носителями типа RWO, которые менее разогреваются при возбуждении в дуге и обладают более графитной основой, чем в случае электродов типа RWII, легче разогревающихся и более аморфных. Влияние термохимических реакций двояко. Первое, что известно и в литературе, это то, что освобождающаяся

теплота реакции повышает испарение образца. Второе же заключается в том, что газовые продукты реакции изменяют состав плазмы, что приводит к изменению отношения возбуждения паров металлов в плазме. Этот эффект более сказывается в случае более активных (легче разлагающихся) окислов металлов. Больший избыток углеродного порошка оказался более благоприятным для исследований на порошковых образцах.

## Исследование силового поля хлороформа с помощью параметрического метода

К. РАМАСВАМИ и С. КАРУНАНИТИ

Метод параметрической репрезентации был использован для исследования силового поля хлороформа. Изотопные сдвиги и $C^{13}HCl_3$ $C^{13}HCl^{37}_3$ были использованы для фиксации угловых параметров колебательных частиц $a_1$. Константы Кориолиса и изотопные сдвиги $C^{13}HCl_3$ были использованы для определения угловых параметров колебательных частиц. Были рассчитаны также силовые постоянные, средние амплитуды колебаний и постоянные вращательного искажения.

## Электрохимическое исследование палладиево-медных катализаторов на углеродных носителях

Т. МАЛЛАТ, R. ПЕТРО и М. ШЕФФЕР

Были исследованы палладиево-медные катализаторы на активированном углероде с содержанием палладия 5 вес.% и с содержанием меди, изменяющиеся в интервале 0—40 ат.%. Они были приготовлены с помощью последовательного восстановления. Адсорбция водорода на них, а также типы фазы на поверхности были исследованы с помощью электрохимического метода (потенциодинамическая поляризация). Активность катализаторов была измерена на модели жидкофазного гидрирования циклогексана. Полученные параметры, помимо содержания меди, зависят также в сильной степени и от возраста катализатора.

## Интерпретация точных данных давления паров молекулярных изотопных изомеров

Г. ЯНЧО и В. А. ВАН ХУК

Обсуждается связь между экспериментальными данными давления паров, изотопным эффектом и/или факторами изотопного обогащения при перегонке с уменьшенной суммой состояний для конденсированной фазы. Демонстрируется, что ранее пренебрегаемые влияния изотопных эффектов на поправки для реальных газов на объемную зависимость внутримолекулярного силового поля, на диэлектрические поправки к ИК и Раман частотам конденсированной фазы и на изменения в ангармоничности внутренних вращательных движений оказывают важное влияние при расчете этих эффектов.

## Влияние химических факторов при обработке вольфрамовой проволоки с различными добавками

Т. МИЛЛЬНЕР

Делалась попытка для объяснения различий, обнаруженных при тяжке вольфрамовых проволок, приготовленных а) без добавки и приготовленных б) с добавкой KAl, в) KSi, г) KSiAl (и с добавкой KSiGa). Различия объяснялись присутствием присоединяющихся к атомам Si «гибко» связанных атомов кислорода, которые позволяют скольжения волокон на друг-друге, а не со сведением проблемы к присутствию частиц окиси, или к присутствию стеклообразных пленок на поверхности волокон.

## Молекулярные постоянные молекулы $ONF_3$

А. НАТАРАДЖАН и К. ЧОКАЛИНГАМ

Константы потенциальной энергии окиси трифторамина ($ONF_3$) были рассчитаны на основе общего валентного силового поля. С помощью ЭВМ были рассчитаны среднеквадратичные амплитуды колебаний, обобщенные средне-квадратичные амплитуды колебаний, константы Кориолиса, константы укорачивания связи и константы искажения вращения.

## Реакции термического перекарбоксилирования, XII

### Необратимость термического декарбоксилирования щелочных бензоатов

Я. САММЕР и Л. ЁТВЁШ

Термические превращения щелочных бензоатов были исследованы в атмосфере $C^{14}O_2$. Было установлено, что детектируемое образование бензоата-$C^{14}$ с низким выходом является следствием декарбоксилирования солей дикарбоновых кислот с высоким содержанием $C^{14}$, образующихся в реакции. На основе экспериментальных данных было установлено, что термическое декарбоксилирование щелочных бензоатов является необратимой реакцией.

## Побочные реакции при удалении защищающих групп у производных N-(защищенный аминоацил)-мочевины

И. ШЁН, Й. ФРИШ и Л. КИШФАЛУДИ

Были исследованы побочные реакции при удалении защищающих групп производных N-(Z — или BOC-аминоацил)-мочевины *(I)*. Каталитическое гидрование *I* приводит к образованию *IV* и *V* в интрамолекулярной реакции *II*. Ацидолитическая обработка *I* в протонных растворителях дает в результате амидное производное, а в апротонных средах соли *II*. Была доказана важность нуклеофильности α-аминогруппы в интрамолекулярной реакции.

## Сладкие агенты типа дигидрохалкона, I

### Зависимость структура — вкус

Ш. АНТУШ, Л. ФАРКАШ, А. ГОТЗЕГЕН, М. НОГРАДИ и Т. ПФЛИГЕЛЬ

Систематические исследования зависимости структура — вкус в серии дигидрохалконов привели к получению натриевой соли 1-[2-гидрокси-4-(3-сульфо-1-пропилокси)-фенил]-3-(3-гидрокси-4-метоксифенил)-пропан-1-она (CHINOIN-401) — атоксичного соединения с чистым сладким вкусом, представляющего значительный торговый потенциал.

## Сладкие агенты типа дигидрохалкона, II

### Синтез некоторых дигидрохалконов

Ш. АНТУШ, Л. ФАРКАШ, А. ГОТЗЕГЕН, М. НОГРАДИ, R. ШТРЕЛИСКИ и Т. ПФЛИГЕЛЬ

Приводится получение 33 новых дигидрохалконов путем конденсации ацетофенонов и альдегидов до халконов с последующим гидрированием.

# Синтез некоторых природных метилированных кверцетинглюкозидов

К. СЕКЕЙ, Б. ВЕРМЕШ, Л. ФАРКАШ и М. НОГРАДИ

Приводится однозначный синтез 3-*O*-α-L-рамнозида *(1)* и 3-*O*-β-рутинозида *(6)* 7-*O*-метилкверцетина и 3', 4', 7-три-*O*-метилкверцетин-3-*O*-α-L-рамнозида (9).

Les Acta Chimica paraissent en français, allemand, anglais et russe et publient des mémoires du domaine des sciences chimiques.

Les Acta Chimica sont publiés sous forme de fascicules. Quatre fascicules seront réunis en un volume (4 volumes par an).

On est prié d'envoyer les manuscrits destinés à la rédaction à l'adresse suivante:

*Acta Chimica*
*H-1521 Budapest, Hongrie*

Toute correspondance doit être envoyée à cette même adresse.

La rédaction ne rend pas de manuscript.

Le prix de l'abonnement: $ 36,00 par volume.

Abonnement en Hongrie à l'Akadémiai Kiadó (1363 Budapest, P.O.B, 24. C.C.B. Compte en banque 215 11488 à l'étranger à l'Entreprise Commerce Extérieur «Kultura» (H-1389 Budapest 62, P.O.B. 149 Compte-courant No. 218 10990) ou chez ses représentants à l'étranger.

---

Die Acta Chimica veröffentlichen Abhandlungen aus dem Bereich der chemischen Wissenschaften in deutscher, englischer, französischer und russischer Sprache.

Die Acta Chimica erscheinen in Heften wechselnden Umfanges. Vier Hefte bilden einen Band. Jährlich erscheinen 4 Bände.

Die zur Veröffentlichung bestimmten Manuskripte sind an folgende Adresse zu senden:

*Acta Chimica*
*H-1521 Budapest, Ungarn*

An die gleiche Anschrift ist jede für die Redaktion bestimmte Korrespondenz zu richten.

Manuskripte werden nicht zurückerstattet.

Abonnementspreis pro Band: $ 36,00.

Bestellbar für das Inland bei Akadémiai Kiadó (1363 Budapest, Postfach 24, Bankkonto Nr. 215 11488), für das Ausland bei »Kultura« Außenhandelsunternehmen (H-1389 Budapest 62, P.O.B. 149. Bankkonto Nr. 218 10990) oder seinen Auslandsvertretungen

---

«Acta Chimica» издает статьи по химии на русском, французском, английском и немецком языках.

«Acta Chimica» выходит отдельными выпусками разного объема, 4 выпуска составляют один том и за год выходит 4 тома.

Предназначенные для публикации рукописи следует направлять по адресу:

*Acta Chimica*
*H-1521 Budapest, BHP*

Всякую корреспонденцию в редакцию направляйте по этому же адресу.

Редакция рукописей не возвращает.

Подписная цена — $ 36,00 за том.

Отечественные подписчики направляйте свои заявки по адресу Издательства Академии Наук (1363 Budapest, P.O.B. 24, Текущий счет 215 11488), а иностранные подписчики через организацию по внешней торговле «Kultura» (H-1389 Budapest 62, P.O.B. 149. Текущий счет 218 10990) или через ее заграничные представительства и уполномоченных.

## Reviews of the Hungarian Academy of Sciences are obtainable at the following addresses:

**AUSTRALIA**
C.B.D. LIBRARY AND SUBSCRIPTION SERVICE, Box 4886, G.P.O., *Sydney N.S.W. 2001*
COSMOS BOOKSHOP, 135 Ackland Street, *St. Kilda (Melbourne), Victoria 3182*

**AUSTRIA**
GLOBUS, Höchstädtplatz 3, *1200 Wien XX*

**BELGIUM**
OFFICE INTERNATIONAL DE LIBRAIRIE, 30 Avenue Marnix, *1050 Bruxelles*
LIBRAIRIE DU MONDE ENTIER, 162, Rue du Midi, *1000 Bruxelles*

**BULGARIA**
HEMUS, Bulvar Ruszki 6, *Sofia*

**CANADA**
PANNONIA BOOKS, P.O. Box 1017, Postal Station "B", *Toronto, Ontario M5T 2T8*

**CHINA**
CNPICOR, Periodical Department, P.O. Box 50, *Peking*

**CZECHOSLOVAKIA**
MAD'ARSKÁ KULTURA, Národní třida 22, *115 66 Praha*
PNS DOVOZ TISKU, Vinohradská 66, *Praha 2*
PNS DOVOZ TLAČE, *Bratislava 2*

**DENMARK**
EJNAR MUNKSGAARD, Norregade 6, *1165 Copenhagen*

**FINLAND**
AKATEEMINEN KIRJAKAUPPA, P.O. Box 128, *SF-00101 Helsinki 10*

**FRANCE**
EUROPERIODIQUES S.A., 41 Avenue de Versailles, *78170 La Celle St.-Cloud*
LIBRAIRIE LAVOISIER, 11, rue Lavoisier, *75008 Paris*
OFFICE INTERNATIONAL DE DOCUMENTATION ET LIBRAIRIE, 38, rue Gay-Lussac, *75240 Paris Cedex 05*

**GERMAN DEMOCRATIC REPUBLIC**
HAUS DER UNGARISCHEN KULTUR, Karl-Liebknecht-Strasse 9, *DDR-102 Berlin*
DEUTSCHE POST ZEITUNGSVERTRIEBSAMT, Strasse der Pariser Kommüne 3—4, *DDR-104 Berlin*

**GERMAN FEDERAL REPUBLIC**
KUNST UND WISSEN ERICH BIEBER, Postfach 46, *7000 Stuttgart 1*

**GREAT BRITAIN**
BLACKWELL'S PERIODICALS DIVISION, Hythe Bridge Street, *Oxford OX1 2ET*
BUMPUS, HALDANE AND MAXWELL LTD., Cowper Works, *Olney, Bucks MK46 4BN*
COLLET'S HOLDINGS LTD., Denington Estate, *Wellingborough, Northants NN8 2QT*
W.M. DAWSON AND SONS LTD., Cannon House, *Folkestone, Kent CT19 5EE*
H. K. LEWIS AND CO., 146 Gower Street, *London WC1E 6BS*

**GREECE**
KOSTARAKIS BROTHERS, International Booksellers, 2 Hippokratous Street, *Athens-143*

**HOLLAND**
MEULENHOFF-BRUNA B.V., Beulingstraat 2, *Amsterdam*
MARTINUS NIJHOFF B.V., Lange Voorhout 9—11, *Den Haag*
SWETS SUBSCRIPTION SERVICE, 347b Heereweg, *Lisse*

**INDIA**
ALLIED PUBLISHING PRIVATE LTD., 13/14 Asaf Ali Road, *New Delhi 110001*
150 B-6 Mount Road, *Madras 600002*
INTERNATIONAL BOOK HOUSE PVT. LTD., Madame Cama Road, *Bombay 400039*
THE STATE TRADING CORPORATION OF INDIA LTD., Books Import Division, Chandralok, 36 Janpath, *New Delhi 110001*

**ITALY**
EUGENIO CARLUCCI, P.O. Box 252, *70100 Bari*
INTERSCIENTIA, Via Mazzé 28, *10149 Torino*
LIBRERIA COMMISSIONARIA SANSONI, Via Lamarmora 35, *50121 Firenze*
SANTO VANASIA, Via M. Macchi 58, *20124 Milano*
D.E.A., Via Lima 28, *00198 Roma*

**JAPAN**
KINOKUNIYA BOOK-STORE CO. LTD., 17-7 Shinjuku-ku 3 chome, Shinjuku-ku, *Tokyo 160-91*
MARUZEN COMPANY LTD., Book Department, P.O. Box 5056 Tokyo International, *Tokyo 100-31*
NAUKA LTD., IMPORT DEPARTMENT, 2-30-19 Minami Ikebukuro, Toshima-ku, *Tokyo 171*

**KOREA**
CHULPANMUL, *Phenjan*

**NORWAY**
TANUM-CAMMERMEYER, Karl Johansgatan 41—43, *1000 Oslo*

**POLAND**
WĘGIERSKI INSTYTUT KULTURY, Marszałkowska 80, *Warszawa*
CKP I W ul. Towarowa 28 *00-985 Warsaw*

**ROMANIA**
D. E. P., *Bucureşti*
ROMLIBRI, Str. Biserica Amzei 7, *Bucureşti*

**SOVIET UNION**
SOJUZPETCHATJ — IMPORT, *Moscow*
and the post offices in each town
MEZHDUNARODNAYA KNIGA, *Moscow G-200*

**SPAIN**
DIAZ DE SANTOS, Lagasca 95, *Madrid 6*

**SWEDEN**
ALMQVIST AND WIKSELL, Gamla Brogatan 26, *S-101 20 Stockholm*
GUMPERTS UNIVERSITETSBOKHANDEL AB, Box 436, *401 25 Göteborg 1*

**SWITZERLAND**
KARGER LIBRI AG, Petersgraben 41, *4011 Basel*

**USA**
EBSCO SUBSCRIPTION SERVICES, P.O. Box 1943, *Birmingham, Alabama 35201*
F. W. FAXON COMPANY, INC., 15 Southwest Park, *Westwood, Mass, 02090*
THE MOORE-COTTRELL SUBSCRIPTION AGENCIES, *North Cohocton, N. Y. 14868*
READ-MORE PUBLICATIONS, INC., 130 Cedar Street *New York, N. Y. 10006*
STECHERT-MACMILLAN, INC., 7250 Westfield Avenue, *Pennsauken N. J. 08110*

**VIETNAM**
XUNHASABA, 32, Hai Ba Trung, *Hanoi*

**YUGOSLAVIA**
JUGOSLAVENSKA KNJIGA, Terazije 27, *Beograd*
FORUM, Vojvode Mišića 1, *21000 Novi Sad*

*2. X. 1978* HU ISSN 0001—5407 **Index: 26.007**

# ACTA CHIMICA

## ACADEMIAE SCIENTIARUM HUNGARICAE

ADIUVANTIBUS

M. T. BECK, R. BOGNÁR, V. BRUCKNER,
GY. HARDY, K. LEMPERT, F. MÁRTA,
K. POLINSZKY, E. PUNGOR,
G. SCHAY, Z. G. SZABÓ, P. TÉTÉNYI

REDIGUNT

B. LENGYEL et GY. DEÁK

TOMUS 98 FASCICULUS 3

AKADÉMIAI KIADÓ, BUDAPEST

1978

ACTA CHIM. ACAD. SCI. HUNG. ACASA2 98 (3) 255–365 (1978)

# ACTA CHIMICA

## A MAGYAR TUDOMÁNYOS AKADÉMIA KÉMIAI TUDOMÁNYOK OSZTÁLYÁNAK IDEGEN NYELVŰ KÖZLEMÉNYEI


FŐSZERKESZTŐ

LENGYEL BÉLA

SZERKESZTŐ

DEÁK GYULA

TECHNIKAI SZERKESZTŐ

HARASZTHY-PAPP MELINDA

SZERKESZTŐ BIZOTTSÁG

BECK T. MIHÁLY, BOGNÁR REZSŐ, BRUCKNER GYŐZŐ, HARDY GYULA, LEMPERT KÁROLY, MÁRTA FERENC, POLINSZKY KÁROLY, PUNGOR ERNŐ, SCHAY GÉZA, SZABÓ ZOLTÁN, TÉTÉNYI PÁL



Acta Chimica is a journal for the publication of papers on all aspects of chemistry in English, German, French and Russian.

Acta Chimica is published in 4 volumes per year. Each volume consists of 4 issues of varying size.

Manuscripts should be sent to

*Acta Chimica*
*H-1521 Budapest, Hungary*

Correspondence with the editors should be sent to the same address. Manuscripts are not returned to the authors.

Subscription: $ 36.00 per volume.

Hungarian subscribers should order from Akadémiai Kiadó, 1363 Budapest, P.O. Box 24. Account No. 215 11488.

Orders from other countries are to be sent to "Kultúra" Foreign Trading Company (H-1389 Budapest 62, P.O. Box 149. Account No. 218 10990) or its representatives abroad.

*Acta Chimica Academiae Scientiarum Hungaricae, Tomus 98 (3), pp. 255—260 (1978)*

# CATHODIC BEHAVIOUR OF THE LEAD DIOXIDE ELECTRODE IN SULFURIC ACID SOLUTION

A. M. AZZAM, S. S. ABD EL REHIM and W. H. BOCTOR

*(Chemistry Department, Faculty of Science, Ain Shams University, Cairo, Egypt)*

Received June 4, 1977

The electrochemical reduction of $PbO_2$ electrode at constant current density was investigated in $H_2SO_4$ solutions of different concentration and at different temperatures. The potential *vs.* time curves involve three arrests before hydrogen evolution. The first arrest corresponds to the reduction of $PbO_2$ to $PbSO_4$. The second and third arrests correspond to the reduction of $PbO \cdot PbSO_4$ and $PbSO_4$ to metallic lead. Addition of either $HClO_4$ or $CH_3COOH$ to the solution does not change the general features of the curves.

## Introduction

The process of cathodic reduction of the $PbO_2$ electrode in sulfuric acid solutions has been the subject of considerable interest, especially with reference to the lead battery. According to the double sulfation theory suggested by GLADSTONE and TRIBE [1], upon discharge, $PbO_2$ on the positive plate gives $PbSO_4$. KINOSHITA [2], DANINA *et. al.* [3, 4] and BECK *et al.* [5] gave data in accordance with this theory, although DANINA *et al.* pointed out that on rapid or prolonged discharge, or at low acid concentrations deviations occur, which might be expected in consequence of the exhaustion of acid in the pores of the plate. However, IKARI and YOSHIZAWA [6] have showed that intermediate compounds occur during the discarge of $PbO_2$ electrodes. LANDER [7] assumes that $PbO_2$ is first electrochemically reduced to PbO and the latter then reacts chemically with sulfuric to form $PbSO_4$. RIESENFELD and SASS [8] established the formation of basic lead sulfate during the discharge of the positive plate. RAGHEB *et al.* [9] noticed a further process during cathodic reduction of $PbO_2$ at very low current densities. This process is related to the deposition of Pb from $Pb^{2+}$ ions in the solution.

The present investigation was undertaken in order to throw more light on this problem.

## Experimental

The electric circuit employed consisted of a constant current unit, a recording potentiometer (Speedomax type G, Leeds and Northrop), and a glass electrolytic cell (250 ml). All potentials were recorded against a saturated calomel electrode over a salt bridge containing the test solution to avoid contamination. Platinum wire was used as the counter electrode.

The test electrodes were made of pure Pb rods (99.994%, Johnson Matthey and Co., Ltd.). Each electrode was tightly fitted into a polyvinyl chloride tube, so that only its cross-sectional area (0.54 $cm^2$) was in contact with the solution. The anode surface was always kept in horizontal position.

Prior to measurements, the clean Pb electrode was anodically charged in the test solution at 0.74 $mA/cm^2$ for 60 min. During this period oxygen evolution occurs, indicating that the material formed on the electrode surface is oxidized to $PbO_2$ [10, 11]. At the end of this period, the passivated electrode was withdrawn and dipped into the cell and discharged at 0.74 $mA/cm^2$, and the potential was recorded as a function of time.

Reduction was carried out in pure $H_2SO_4$ acid solutions (0.7—10 *N*) and in 3 *N* $H_2SO_4$ containing 0.1 *N* of either $HClO_4$ or $CH_3COOH$. All baths were made of bidistilled water and analytical grade reagents. The temperature was kept constant at the required value $\pm$ 0.5 °C.

## Results and discussion

The effect of sulfuric acid concentration and temperature on the cathodic potential *vs.* time curves of the $PbO_2$ electrode discharged at 0.74 $mA/cm^2$ is shown in Figs 1 and 2, respectively. All potentials are given on the hydrogen scale. The curves reveal three potential arrests before the hydrogen evolution

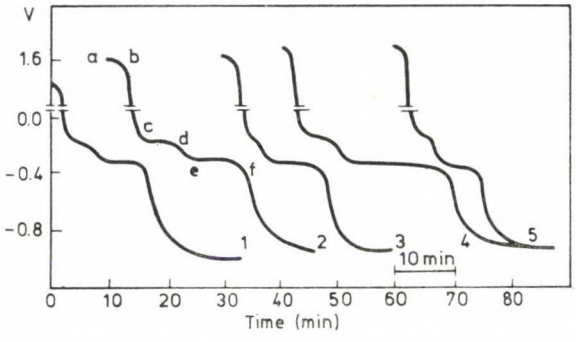



*Fig. 1.* Effect of $H_2SO_4$ concentration on the cathodic potential at 0.74 $mA/cm^2$ and 25 °C. (1) 0.7; (2) 1.0; (3) 3.0; (4) 5.0; (5) 10.0 *N* $H_2SO_4$

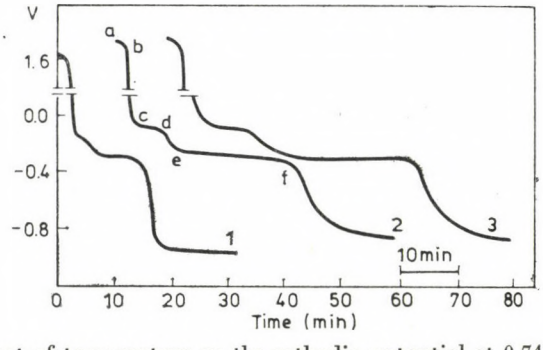



*Fig. 2.* Effect of temperature on the cathodic potential at 0.74 $mA/cm^2$. (1) 15 °C, 3 *N* $H_2SO_4$; (2) 35 °C, 3 *N* $H_2SO_4$; (3) 35 °C, 5 *N* $H_2SO_4$

arrest (c, −0.95 V). The first arrest (a—b) and the third one (e—f) are essentially the same as those found in the literature [12, 13].

The first arrest occuring at about 1.60 V corresponds to the reduction of $PbO_2$ to $PbSO_4$, according to the following reaction:

$$PbO_2 + SO_4^{2-} + 4H^+ + 2e \rightarrow PbSO_4 + 2H_2O$$

At the end of this arrest the electrode surface still retained its brown colour, indicating that the transition from the first to the second arrest occurs before complete reduction of $PbO_2$ to $PbSO_4$.

The second potential arrest (c—d) occurs at about −0.10 V. The possible electrochemical reactions at this potential are:

$$Pb^{2+} + 2e \rightarrow Pb \qquad (A)$$

$$PbO \cdot PbSO_4 + 2H^+ + 4e \rightarrow 2Pb + SO_4^{2-} + H_2O \qquad (B)$$

The thermodynamic potentials of these reactions are −0.12 V [14] and −0.099 V [13].

The third arrest (e—f) occurs at about −0.30 V. At this potential the reduction of $PbSO_4$ to Pb proceeds according to the following reaction [15]:

$$PbSO_4 + 2e^- \rightarrow Pb + SO_4^{2-}$$

In order to decide whether (A) or (B) is the main electrode reaction during the second arrest, the relative duration of this arrest was calculated in per cent of the total duration of the second and third arrests, since both are responsible for the reduction of divalent lead ions to Pb. If the relative duration of the second arrest follows the solubility of $PbSO_4$ in sulfuric acid solution, then reaction (B) could be excluded on the basis that $PbO \cdot PbSO_4$ cannot exit in acidic solutions. However, the data of Fig. 3 show that the relative duration of the second arrest decreases with increasing solubility of $PbSO_4$. It is a minimum in $3N$ $H_2SO_4$, in which the solutbility of $PbSO_4$ is a maximum. Moreover, Fig. 4 shows that at higher temperatures, *i.e.* with increasing solubility of $PbSO_4$, the relative duration of this arrest decreases. In both figures, after VINAL [15], the solubilities of $PbSO_4$ in sulfuric acid solution under similar conditions are shown for comparison. Therefore, it can be concluded that the second arrest corresponds mainly to the reduction of basic lead sulfate to metallic lead.

Basic lead sulfate could exist on the electrode surface under conditions of high local pH values. It is probable that the discharge of the outer $PbO_2$ layer to $PbSO_4$ is accompanied by an increase in volume. The molar volume of

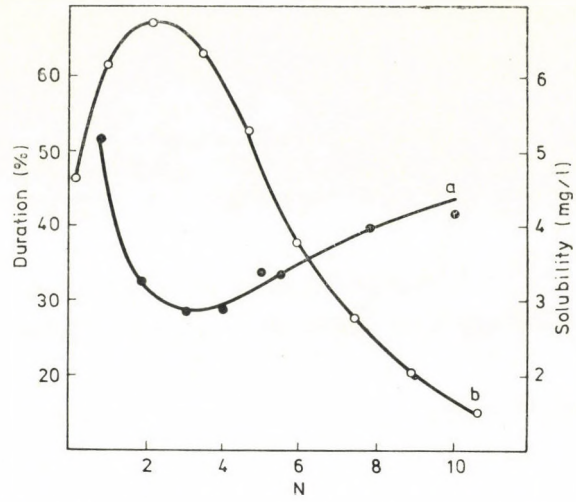



*Fig. 3.* Effect of $H_2SO_4$ concentration on the relative duration of the second arrest at 0.74 mA/cm² and 25 °C. (a) Relative duration; (b) solubility of $PbSO_4$

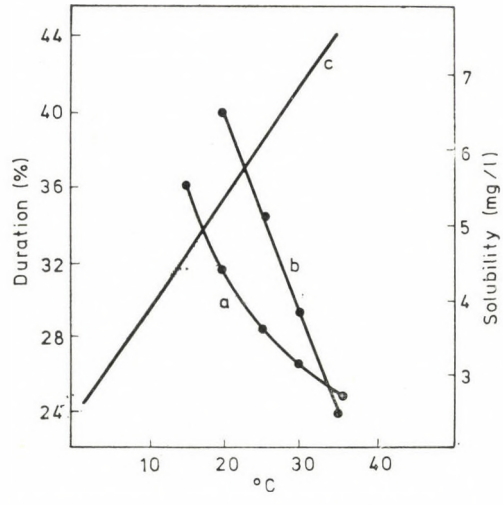



*Fig. 4.* Effect of temperature on the relative duration of the second arrest at 0.74 mA/cm². (a) Relative duration in 3 *N* $H_2SO_4$; (b) relative duration in 5 *N* $H_2SO_4$; (c) solubility of $PbSO_4$

$PbO_2$ and $PbSO_4$ is 25.5 and 48.9 cm³, respectively. Thus, the $PbSO_4$ formed may block the pores and limit the access of sulfate ions. In this case, the reduction of the remaining $PbO_2$ within the pores may proceed according to the following reaction [13]:

$$2PbO_2 + 6H^+ + SO_4^{2-} + 4e \rightarrow PbO\ PbSO_4 + 3H_2O$$

whose thermodynamic potential is 1.44 V. The occurrence of this secondary discharge process under conditions of inhibited ionic diffusion in the interior of the positive plate could be considered as deviation from the double sulfation theory.

The duration of the third arrest depends upon the amount of $PbSO_4$ present on the electrode surface and formed during the first arrest. Conversion of $PbO_2$ to $PbSO_4$ increases if the porosity of the salt formed is sufficient to allow diffusion of sulfate ions in the pores. In turn, the porosity increases with increasing solubility of $PbSO_4$. The data of Fig. 3 reveal that the relative duration of the third arrest is a maximum in solutions which exhibit maximum solubility of $PbSO_4$. This is again verified in Fig. 4 which demonstrates that the relative duration of this arrest increases with increasing temperature.

Similar results were obtained for 3 *N* $H_2SO_4$ containing 0.1 *N* of either $HClO_4$ or $CH_3COOH$, at 0.74 mA/cm$^2$ and 25 °C (Fig. 5). In the presence of either of these acids, the same three potential arrests occur beside the hydrogen evolution potential, and the presence of either additive manifests itself mainly by affecting the relative durations. Both additives increase the duration of the second arrest, indicating that both additives promote the formation of $PbO \cdot PbSO_4$ during the discharge of the $PbO_2$ coating. This may be attributed to the formation of a relatively thicker $PbO_2$ layer during the charging process in the presence of either of these additives; such a thick layer inhibits diffusion during the discharge process.

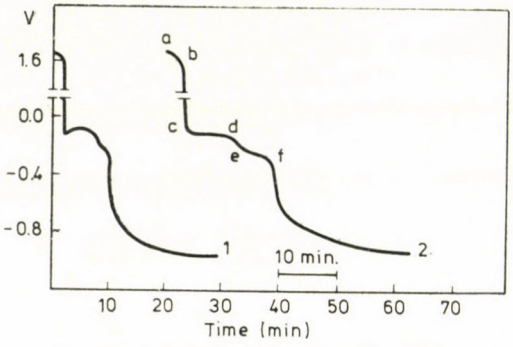



*Fig. 5.* Effect of additives on the cathodic potential in 3 *N* $H_2SO_4$ at 0.74 mA/cm. and 25 °C. (1) 0.1 *N* $HClO_4$; (2) 0.1 *N* $CH_3COOH$

## REFERENCES

[1] Gladstone, J. H., Tribe, A.: Nature, **25,** 221, 481 (1882)
[2] Kinoshita, K.: Bull. Chem. Soc. Japan, **11,** 504 (1936)
[3] Danina, E., Ferrero, G.: Z. Elektrochem., **45,** 314 (1939)
[4] Danina, E., Fornaseri, M.: Z. Elektrochem., **45,** 320 (1939)
[5] Beck, W. H., Wynne-Jones, W. F. K.: Trans. Faraday Soc., **50,** 136 (1954)
[6] Ikari, S., Yoshizawa, S.: J. Electrochem. Soc. Japan, **28,** E 138 (1960)

[7] LANDER, J. J.: J. Amer, Electrochem. Soc., **98,** 220 (1951)
[8] RIESENFELD, E. H., SASS, H.: Z. Elektrochem., **39,** 219 (1933)
[9] RAGHEB, A., MACHU, W., BOCTOR, W. H.: Werkstoffe Korrosion, **16,** 676 (1965)
[10] JONES, P., LIND, R., WYNNE-JONES, W. F. K.: Trans. Faraday Soc., **50,** 972 (1954)
[11] MAEDA, M.: Denki Kagaku, **25,** 195 (1957)
[12] BURBANK, J.: J. Electrochem. Soc., **693,** 104 (1957)
[13] RUETSCHI, P., ANGSTADT, R. T.: J. Electrochem., **1323,** 111 (1964)
[14] LATIMER, W. M.: Oxidation Potentials. Prentice Hall, Inc., New York, 1953
[15] VINAL, G. W.: Storage Batteries, 4th edn. John Wiley and Sons, New York 1962

A. M. AZZAM
S. S. ABD EL REHIM
W. H. BOCTOR

Chemistry Department, Faculty of Science, Ain Shams University, Cairo, Egypt

*Acta Chimica Academiae Scientiarum Hungaricae, Tomus 98 (3), pp. 261—264 (1978)*

# SPECIFIC ADSORPTION OF IODATE IONS AT THE $Hg/KIO_3$ (aq.) INTERFACE AT 25 °C

M. V. RAMANAMURTI, A. QAYUM and R. K. SINGH

*(Department of Chemistry, Faculty of Science, Banaras Hindu University, Varanasi—221005 India)*

Received August 25, 1977

Adsorption of iodate ions at the polarized mercury/$KIO_3$ (aq.) interface was studied by differential capacity measurements at 25 °C. The shift of the potential of zero charge towards more cathodic values with increasing bulk electrolyte activity gave [a qualitative indication of the specific adsorption of iodate], which could be confirmed quantitatively through the plots of charge due to specifically adsorbed anions ($q^1$) *vs*, the electrode charge ($q^M$). For any concentration $q^1$ is greater than $q^M$ ($q^M$, $+ve$), indicating superequivalent adsorption of iodate ions; for a given electrode charge, the magnitude of $q^1$ increases with increasing electrolyte activity.

## Introduction

Specific adsorption of inorganic oxyanions such as nitrate [1] and perchlorate [2] at the mercury-solution interface is more complex than that of the structurally simpler halide ions. GRAHAME and SODERBERG [3] first recognized this aspect through their systematic study of specific adsorption phenomena. The present work is an attempt to investigate the specific adsorption of $IO_3^-$ (which is also an oxyanion) at the $Hg/KIO_3$ (aq.) interface by differential capacity measurements.

## Experimental

Differential capacity measurements were made on an a.c. bridge, similar to the one described by GRAHAME [4, 5], using a dropping mercury electrode (DME) with a thin-walled capillary and giving drop time of about 8 sec at the potential of zero charge ($E_{zc}$) of mercury in 0.10 *m* KCl solution. The frequency of the alternating current was 1 kHz with an amplitude of 5 mV across the cell. An electronically operated magnetic drop detacher was utilized to knock off the drop at about two-thirds of its natural life. The time between two successive knocks was determined by means of a stop watch, accurately [measuring upto time interval to within 0.05 sec.]. The bridge was balanced at the time of drop detachment from the capillary tip. The output signal of the bridge was amplified by a multistage transistor preamplifier (Marconi Type TM6591A) and displayed on a Dumont Oscillograph (Type 274). A large mercury pool electrode and 1NKCl calomel electrode (nce) were used as the auxiliary and reference electrodes, respectively. Direct contact was made between the reference electrode and the test solution by means of a saturated (KCl) salt bridge which minimized the liquid junction potential. The potential applied was measured on a portable potentiometer (Pye-Unicam) with an accuracy of 1 mV. Differential capacities were measured in the potential range of —0.10 to —1.40 V *vs*. nce. The point of zero charge was determined separately, using a stream-

ing mercury electrode [6]. All the measurements were carried out in an air thermostat maintained at (25 ± 0.1) °C.

Mercury was purified by the procedure of TRASSATI [7]. Twice crystallized $KIO_3$ (BDH/AnalaR) was used. Solutions at required molalities were prepared in conductivity water and deoxygenated with purified and presaturated nitrogen gas before carrying out the experiments.

## Results and discussion

The differential capacity of the double layer as a function of the polarization potential are presented in Fig. 1 for eight concentrations of $KIO_3$ in the range 0.025 to 0.500 m. The characteristic capacity hump occurs at anodic polarization with respect to $E_{zc}$, which shifts towards more negative potentials as the bulk electrolyte concentration increases. A clear diffuse layer minimum appears for the 0.025 solution at more cathodic potentials than the $E_{zc}$, due to the effect of superimposed steeply rising inner layer capacity. Complete disappearance of the diffuse layer minimum in the capacity curves as the concentration increases to 0.10 m, gives the first clear indication for some specific adsorption of the anion [8].

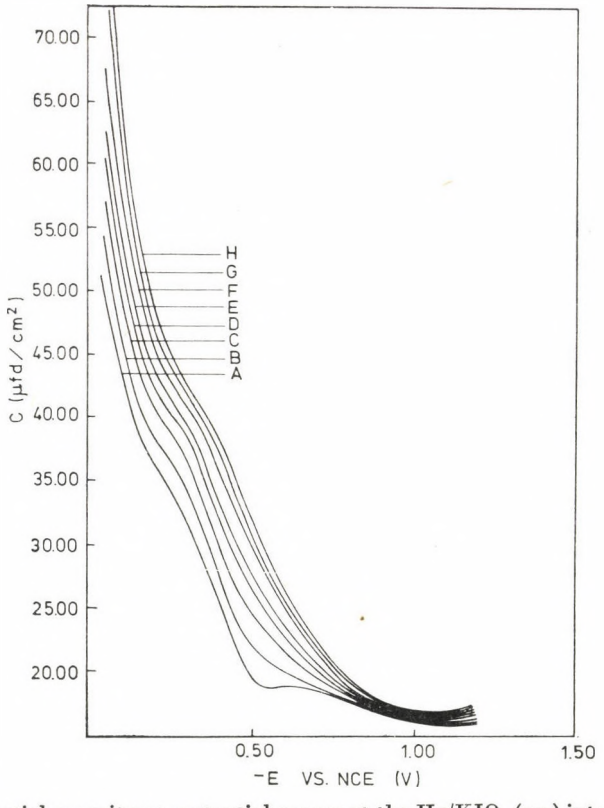



*Fig. 1.* Differential capacity *vs.* potential curves at the Hg/$KIO_3$ (aq.) interface at 25 °C; (A) 0.025, (B) 0.05, (C) 0.10, (D) 0.15, (E) 0.20, (F) 0.30, (G) 0.40, (H) 0.50 m

The shift of $E_{zc}$ from its value of $-0.476$ V *vs.* nce for systems with no specific adsorption, *e.g.* fluoride solution, for the anion under investigation to more cathodic values with increasing bulk-electrolyte activity (Fig. 2), can be taken as a semiquantitative estimate of the extent of specific adsorption: $|\Delta E_{zc}|$ is a direct measure of specific adsorption.

The charge on the electrode surface ($q^M$) has been obtained by numerical integration of the capacity *vs.* potential curves. Knowledge of $E_{zc}$ permits the evaluation of the integration constant. The charge due to specifically adsorbed iodate ions ($q^1$) has been calculated using the equations derived by GRAHAME and SODERBERG [3] from the diffuse layer theory. $q^1$ thus obtained, accurate to $\pm$ 1 $\mu c.\ cm^{-2}$, has been plotted against $q^M$ at four concentrations in the range, 0.05 to 0.40 *m* (Fig. 3). At any concentration, $q^1$ is greater than $q^M$ ($q^M$, + *ve*),

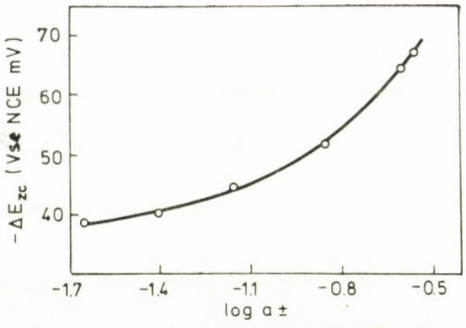



*Fig. 2.* Shift of $E_{zc}$ against the logarithm of bulk electrolyte-activity

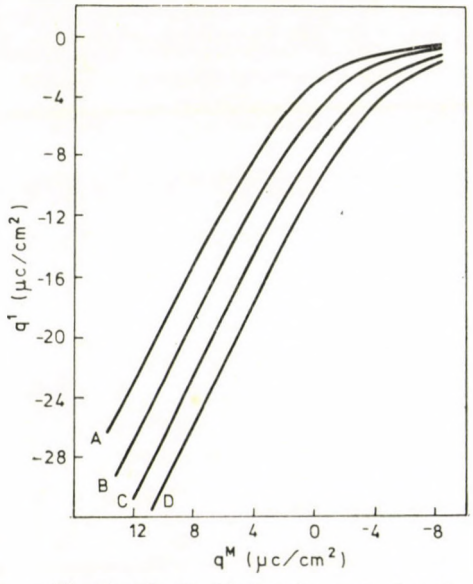



*Fig. 3.* Charge due to specifically adsorbed iodate ions as a function of electrode charge; (A) 0.05, (B) 0.10, (C) 0.20, (D) 0.40 m $KIO_3$

indicating superequivalent adsorption of iodate ions. At the highest concentration studied, there exists a finite value of $q^1$ even at $q^M = -6\,\mu c \cdot \mathrm{cm}^{-2}$, indicating a strong affinity of $IO_3^-$ to the metal. As expected, at any electrode charge, the magnitude of $q^1$ increases with increasing electrolyte activity.

*

Thanks are due to CSIR, Government of India, for financial assistance to one of the authors (RKS).

## REFERENCES

[1] PAYNE, R.: J. Electrochem. Soc., **113,** 999 (1966)
[2] PAYNE, R.: J. Phys. Chem., **70,** 204 (1966)
[3] GRAHAME, D. C., SODERBERG, B.: J. Chem. Phys., **42,** 337 (1965)
[4] GRAHAME, D. C.: J. Amer. Chem. Soc., **63,** 207 (1941)
[5] GRAHAME, D. C.: J. Amer. Chem. Soc., **71,** 2975 (1949)
[6] GRAHAME, D. C., LARSEN, R. P., PATH, M. A.: J. Amer. Chem. Soc. **71,** 2978 (1949)
[7] TRASATTI, S.: J. Electroanal. Chem., **28,** 257 (1970)
[8] PARSONS, R.: in J. O'M. BOCKRIS and B. E. CONWAY, Eds. Modern Aspects of Electrochemistry, p. 103 Col. 1, Butterworths, London 1954

M. V. RAMANAMURTI
A. QAYUM
R. K. SINGH

Department of Chemistry, Faculty of Science,
Banaras Hindu University,
Varanasi — 221005 (India)

*Acta Chimica Academiae Scientiarum Hungaricae, Tomus 98 (3), pp. 265–283 (1978)*

# CHEMICAL SYSTEMS AND SUPERSYSTEMS, III

## MODELS OF SELF-REPRODUCING CHEMICAL SUPERSYSTEMS: THE CHEMOTONS

T. GÁNTI

*(Department of Genetics, L. Eötvös University, Budapest)*

Received August 25, 1977

The coupled functioning of any two or all three of three chemical systems with different properties, a self-reproducing (autocatalytic) chemical cycle, template polymerization and bilayered molecular membrane growth, results in chemical supersystems which display qualitatively new properties of biological nature going beyond chemistry.

The self-reproducing cycle and bilayered molecular membrane growth permit the formation of spheres growing by metabolic means; in a definite phase of the growth, these spontaneously divide into two, *i.e.* they are capable of proliferation.

The coupled functioning of the self-reproducing cycle and template polymerization results in a programe-controlled self-reproducing chemical supersystem.

The coupled functioning of all three chemical systems results in spatially separated, programmed chemical supersystems capable of growth and reproduction: the chemotons. It may be proved that these satisfy all the general criteria characteristic of life, and hence they can be regarded as biological minimal systems.

The present publication discusses the stoichiometric correlations of the functioning of these supersystems. The kinetic description, computer simulation and study of the properties will be dealt with subsequently.

Previous publications gave the stoichiometries of some self-maintaining [1] and self-reproducing [2] chemical systems, and it was pointed out that the aim of the given stoichiometric descriptions was the development of a formalism suitable for the discussion of the functioning of chemical supersystems. Beginning from the present paper in this series, we shall be dealing with chemical supersystems, and it therefore seems necessary here to redefine what we shall understand as chemical systems or supersystems.

Within this series, chemical reactions coupled with one another (the term chemical reaction being taken in a broader sense than usual) are regarded as a chemical system (reaction system). The system is regarded as a system from the aspect of its functioning, it being assumed that the elementary reaction steps (events) comprise a chain or network, where the starting materials of the individual elementary steps may originate only from the sources given in the network, and the reaction products formed may disappear only via the given consumption routes. The system may not contain even a single reaction step which does not have at least one component in common with some other reaction step. In other words, each elementary step is coupled directly to at least one other reaction, and at least indirectly to all of the other elementary

reactions of the system. Thus, a solution in which a number of chemical reactions not involving a common component proceed simultaneously, is not regarded as a chemical system. On the other hand, examples of chemical systems are chain reactions, chemical cycles, chain polymerization, etc., but also included (arbitrarily) is the growth of bilayered molecular membranes ; although in this case the incorporation of the membrane-forming molecules into the membrane does not occur by means of a chemical reaction, but from several aspects the process is analogous to polymerization processes, and it can be described formally with stoichiometric equations.

Chemical supersystems can be obtained by the coupled *i.e.* interdependent functioning of two or more chemical systems (reaction systems) with different properties. Compared to the properties of the chemical systems comprising them, the chemical supersystems possess qualitatively new properties. These arise not directly from the properties of their individual reaction systems, but from the mode of coupling of their functioning, *i.e.* from their organization. Concrete examples of this will be given. In many respects these qualitatively new properties of chemical supersystems are biological in nature (metabolism, growth, spatial multiplication, etc.) [3, 4]. Within the supersystems discussed in the following, one or other chemical system has a governing role as regards the others or the functioning of the supersystem as a whole. Another chemical system possesses the regulating ability necessary for the self-maintenance of the supersystem. To the best of the author's knowledge, the literature does not contain any publications dealing with chemical supersystems, or with their stoichiometric and kinetic investigation.

## Simplified stoichiometric description of self-reproducing chemical systems

The generalized form of the overall equation for self-reproducing chemical reaction cycles in the preceding paper [2] gives the correct quantitative conditions only if

$$\sum_{i=1}^{j} \sum_{k=1}^{l} \alpha_{ik} = \alpha_{1k}$$

*i.e.* if, from among the intermediates of the cyclic process, only the products of the self-reproducing elementary reaction are present at the moment the reaction commences. In the opposite case, in addition to the starting components

$$(2^u - 1) \sum_{i=1}^{j} \sum_{k=1}^{l} \nu_{ik} X_{ik}$$

necessary for regeneration of the self-reproducing component within the $u$-th cycle, the further raw-material demand must be covered that is necessary in

the given cycle for the formation of the components

$$\sum_k \alpha_{2k} A_{2k}, \sum_k \alpha_{3k} A_{3k} \ldots \sum_k \alpha_{lk} A_{lk}$$

from $\sum_k \alpha_{1k} A_{1k}$, *i.e.* from the autocatalytically formed component. The raw-material requirement is therefore expanded by a further additive term relating to the $u$-th cycle:

$$(2^u - 1) \sum_{i=2}^{j} \alpha_i \sum_{z=1}^{i-1} \sum_{k=1}^{l} \nu_{X_{zk}} X_{zk}$$

Accordingly, the quantity of reaction products formed must also be expanded by a term relating to the $u$-th cycle:

$$(2^u - 1) \sum_{i=2}^{j} \alpha_i \sum_{z=1}^{i-1} \sum_{k=1}^{l} \nu_{Y_{zk}} Y_{zk}$$

where

$$z = 1, 2, 3, \ldots, i-1$$

When these expansions too are taken into consideration, the general stoichiometric overall equation of the self-reproducing reaction cycle, summed for the $u$-th cycle, is:

$$\sum_{i=1}^{j} \sum_{k=1}^{l} \nu_{A_{ik}} \alpha_{ik} A_{ik} + (2^u - 1) \left( \sum_{i=1}^{j} \sum_{k=1}^{l} \nu_{X_{ik}} X_{ik} + \right.$$

$$\left. + \sum_{i=2}^{j} \alpha_i \sum_{z=1}^{i-1} \sum_{k=1}^{l} \nu_{X_{zk}} X_{zk} \right) \xrightarrow{\boxed{u}}$$

$$2^u \sum_{i=1}^{j} \sum_{k=1}^{l} \nu_{A_{ik}} \alpha_{ik} A_{ik} +$$

$$+ (2^u - 1) \left( \sum_{i=1}^{j} \sum_{k=1}^{l} \nu_{Y_{ik}} Y_{ik} + \sum_{i=2}^{j} \alpha_i \sum_{z=1}^{i-1} \sum_{k=1}^{l} \nu_{Y_{zk}} Y_{zk} \right) \qquad (1)$$

This equation is already somewhat too complicated for the quantitative correlations of the functioning of supersystems formed by combinations of these to be considered with their help. Accordingly, for the sake of simplification, the following notations are introduced:

$$\sum_{i=1}^{j} \sum_{k=1}^{l} \nu_{X_{ik}} X_{ik} + \sum_{i=2}^{j} \alpha_i \sum_{z=1}^{i-1} \sum_{k=1}^{l} \nu_{X_{zk}} X_{zk} \equiv \mathbf{X}$$

and

$$\sum_{i=1}^{j}\sum_{k=1}^{l} \nu_{Y_{ik}} \mathbf{Y}_{ik} + \sum_{i=2}^{j}\alpha_i \sum_{z=1}^{i-}\sum_{k=1}^{l} \nu_{Y_{zk}} \mathbf{Y}_{zk} \equiv \mathbf{Y}$$

Hence, the simplified form of Eq. (1) is:

$$\sum_{i=1}^{j}\sum_{k=1}^{l} \nu_{A_{ik}} \alpha_{ik} A_{ik} + (2^u - 1)\,\mathbf{X} \xrightarrow{\boxed{u}} \overset{A}{}$$

$$2^u \sum_{i=1}^{j}\sum_{k=1}^{l} \nu_{A_{ik}} A_{ik} + (2^u - )\,\mathbf{Y} \qquad (2)$$

This form is now suitable for use in the derivation of the overall equations of chemical supersystems. In the following, chemical supersystems will be characterized stoichiometrically with the aid of these simplified equations.

## Stoichiometry of a spatially separated chemical supersystem capable of multiplication

It is known that, as a consequence of their surface potentials and charge conditions, in the fluid phase molecular membranes readily form spherical surfaces. It is also known that the diffusion coefficients of electrically charged ions (*e.g.* sugar phosphate ions, organic acids, etc.) passing across bimolecular lipid membranes by means of diffusion are three orders of magnitude smaller than those of molecules of similar size, but which are uncharged (*e.g.* those of the corresponding sugars). A stoichiometric description of the growth of these membranes was given previously [2].

Let us assume that in aqueous solution there is a microscopic bilayered membrane sphere, and that the wall of this sphere is practically impermeable to the substances $A_{ik}$ dissolved in the interior of the sphere and to the substances $I_{ik}$ in its environment, while it is permeable to the substances $X_{ik}$ and $Y_{ik}$ in the interior and in the environment of the sphere. Let us further assume that the substances $A_{ik}$ react with the substances $X_{ik}$ to give rise to a self-reproducing cyclic process in which $A_{ik}$ are formed; examples are the Calvin cycle consisting of sugar phosphates, or the malate cycle consisting of organic acids, described earlier [2]. In this case, two chemical systems with different properties (previously discussed separately), the self-reproducing cyclic process and membrane formation, are connected spatially, *i.e.* they take place in the same microscopic spatial interval of the solution.

For the sake of simplicity, let the self-reproducing cyclic process consist of the following elementary reaction steps:

$$A_1 + X_1 \rightleftarrows A_2 \tag{3a}$$

$$A_2 \rightleftarrows A_3 + Y_2 \tag{3b}$$

$$A_3 \rightleftarrows A_4 + Y_3 \tag{3c}$$

$$A_4 \rightleftarrows 2A_1 \tag{3d}$$

$$\sum_{i=1}^{4} \alpha_i A_i + \mathbf{X} \xrightarrow{\boxed{\pm 1}} 2 \sum_{i=1}^{4} \alpha_i A_i + \mathbf{Y} \tag{3}$$

where $\alpha_i$ are the fictive mole fractions of the $A_i$-s, for which it holds that

$$\sum_{i=1}^{4} \alpha_i = 1$$

The symbol $\xrightarrow{\boxed{\pm 1}}$ is the previously introduced [1] symbol of the cyclic process: the number in the square indicates the number of times the cycle takes place, while the $\pm$ sign demonstrates that the process may function either in the self-reproducing (+) or in the self-consuming (−) mode.

The following elementary steps of the self-reproducing cyclic process were selected so that every characteristic event should feature in the cycle, but only one event should occur in each elementary step. Accordingly, Eq. (3a) represents raw-material utilization, (3b) side-product formation, (3c) similarly side-product formation (but this side-product will subsequently play a special role), and (3d) the self-reproducing step.

The membrane growth is described by the following equation:

$$\boxed{T_n} + T \longrightarrow \boxed{T_{n+1}} \tag{4}$$

where $T$ is the membrane-forming molecule, while $\boxed{T_n}$ is a membrane portion made up of $n$ molecules of $T$, its surface area being proportional to the number of incorporated molecules of $T$.

In itself, the fact that the chemical systems characterized by (3) and (4) are enclosed in the same spatial interval does not mean that they form a chemical supersystem. For this, the two systems must also be coupled functionally in such a way that their functioning becomes interdependent. This is achieved chemically if one of the systems produces the raw materials (or at least some of them) required for the functioning of the other system. In our case, the for-

mally most simple means for this is that, for example:

$$A_3 \rightleftarrows A_4 + Y_3 + T \tag{5}$$

where the membrane is not permeable to $T$.

The functioning of the resulting chemical supersystem is described by Eq. (6), obtained by the combination of Eqs (3), (4) and (5):

$$\sum_{i=1}^{4} \alpha_i A_i + \boxed{T_n} + \mathbf{X} \xrightarrow{A} \boxed{1} \longrightarrow 2 \sum_{i=1}^{4} \alpha_i A_i + \boxed{T_{n+1}} + \mathbf{Y} \tag{6}$$

Thus, as a result of the fact that one of the side-products of one of the chemical systems, the self-reproducing cyclic process, has become identical with a raw material of the other chemical system, membrane growth, the two systems have become coupled, their functionings are interdependent, and they form a supersystem. This can clearly be seen from Eq. (6), which demonstrates that the functioning of the autocatalytic cyclic process has resulted in an increase in the numbers of both the intermediates of the cycle and the molecules incorporated into the membrane. Further, the extent of the surface area of the membrane increases in proportion to the number of molecules incorporated.

For the surface area of the membrane to double, $n$ molecules must proceed through the cycle once:

$$n \sum_{i=1}^{4} \alpha_i A_i + \boxed{T_n} + n\mathbf{X} \xrightarrow{A} \boxed{1} \longrightarrow 2n \sum_{i=1}^{4} \alpha_i A_i + \boxed{T_{2n}} + n\mathbf{Y} \tag{7}$$

With a view to investigating that new qualitative property of this chemical supersystem that cannot be observed in its constituent chemical systems, let us place the membrane sphere in an environment which is an infinite source of constant concentration as regards $X$ and $I$, and is an infinite sink with negligibly low concentration as regards $Y$. If $X$ and $Y$ are assumed to diffuse very rapidly, then because of the microscopic dimensions of the sphere, their concentrations may be taken as being the same inside and outside the membrane sphere. Hence, the osmotic conditions are governed by the osmotic pressure of the compounds $\sum_i A_i$, inside the membrane sphere and by the osmotic pressure of the compounds, $\sum_i I_i$, in the environment, or (assuming an ideal case) by their concentrations $c_A$ and $c_I$, respectively. In the event of osmotic equilibrium under the given conditions:

$$c_A = c_I \tag{8}$$

Naturally, a microsphere of given stoichiometric composition, and hence of given size, can be in osmotic equilibrium only with an environment with a specific external osmotic pressure.

$c_I$ is a fixed constant, but $c_A$ varies, partly because it is itself produced during the process, and partly since the volume ($Q$) too changes because of the increase in the surface area ($F$).

For calculation of its time-dependence, it is necessary to know how the volume and the quantities of the intermediates of the autocatalytic cyclic process vary as functions of time. It was previously [2] shown that the substances of the autocatalytic reaction network increase in accordance with the relation

$$\left(\sum_i \alpha_i A_i\right)_t = \left(\sum_i \alpha_i A_i\right)_0 2^{u_1}, \quad u_1 = \frac{t}{\tau_1} \quad * \tag{9}$$

where $\left(\sum_i \alpha_i A_i\right)_0$ is the quantity of the substances of the cyclic process at zero time, $\left(\sum_i \alpha_i A_i\right)_t$ is the corresponding quantity at time $t$, and $\tau_1$ is the period necessary for the quantity of substances to double. A similar relation was derived [2] in connection with the growth of the membrane surface area:

$$(F)_t = (F)_0 2^{u_2}, \quad u_2 = \frac{t}{\tau_2} \quad * \tag{10}$$

where $(F)_0$ and $(F)_t$ are the membrane surface areas at zero time and at time $t$, and $\tau_2$ is the time required for the membrane surface area to double. In the case of a membrane constituting a spherical surface, the volume of the sphere enclosed by it at time $t$ is:

$$(Q)_t = k(F_0 2^{t/\tau_2})^{3/2} \tag{11}$$

where $k$ = constant = $1/6\sqrt{\pi}$.

If the rate of incorporation of $T$ is greater than the rate of production, then the membrane growth will be limited by the rate of production of $T$, *i.e.* by the rate of the autocatalytic cyclic process, and in this case:

$$\frac{d\left(\sum_i A_i \alpha_i\right)}{dt} = f_T \frac{dF}{dt} \tag{12}$$

where $f_T$ is the surface requirement of $T$: (in mol/unit surface area or molecule/unit surface area).

* The detailed derivations of the relations $u_1 = t/\tau_1$ and $u = t/\tau_2$ will be given in the following publication in this series [6].

Now:

$$\tau_1 = \tau_2 = \tau, \text{ and hence } u_1 = u_2 = u. \tag{13}$$

Thus, the value of $c_A$ at time $t$ is:

$$(c_A)_t = \frac{\left(\sum_i \alpha_i A_i\right)_0 2^{t/\tau}}{k(F_0 2^{t/\tau})^{3/2}} = \frac{(c_A)_0}{2^{t/2\tau}} = \frac{(c_A)_0}{2^{u/2}} \tag{14}$$

That is, the concentration of the internal substances within the sphere decreases progressively during the growth of the system. This decrease of the concentration of the substances within the sphere results in an osmotic vacuum under the given starting conditions, and this leads to deformation of the membrane sphere. On the other hand, as a result of its surface tension and charge conditions, the membrane strives to assume a spherical form, and hence, as a consequence of the opposing forces, the membrane splits into two spheres.

It can be proved that only a single case is possible when the splitting into two spheres leads to an equilibrium state. This is when the newly formed two spheres and the sphere prior to growth are of the same size. This is the only case when the double volume corresponds to the twofold increased surface area, and the tensions arising in the membrane are uniformly distributed (see the Appendix).

If the spatial splitting of the membrane sphere is denoted in the following manner:

$$\boxed{T_{2n}} \longrightarrow 2\boxed{T_n} \tag{15}$$

Eq. (7) can be written as

$$\left[n\sum_{i=1}^{4}\alpha_i A_i + \boxed{T_n}\right] + n\mathbf{X} \xrightarrow{A} \boxed{1} \longrightarrow$$
$$2\left[n\sum_{i=0}^{4}\alpha_i A_i + \boxed{T_n}\right] + n\mathbf{Y} \tag{16}$$

In this equation the square brackets represent the supersystem. It can be seen from the equation that, by virtue of processing the 'nutritive material' $X$, the supersystem increases its own substances continuously and in proportion to one another, in a manner regulated by the cyclic process and controlled by the membrane growth; after a certain limit has been reached, this leads to the spatial division of the system into two. Since each new sphere itself also grows further and then divides, in the event of a source $X$ of infinite and con-

stant concentration and an infinite sink $Y$, the number of membrane spheres at time $t$ is:

$$G_t = G_0 2^{t/\tau} = G_0 2^u \tag{17}$$

where $\tau$ is the period necessary for one cycle, and $u = t/\tau$ = the number of completed cycles.

In accordance with the rules described in the preceding publication, if cyclic process (3) is generalized to a closed reaction network consisting of $i$ reaction steps with optional $k$ reaction components, then:

$$\sum_{i=1}^{j} \sum_{k=1}^{l} \nu_{A_{ik}} \alpha_{ik} A_{ik} + (2^u - 1)\,\mathbf{X} \xrightarrow{\boxed{u}}$$

$$2^u \sum_{i=1}^{j} \sum_{k=1}^{l} \nu_{A_{ik}} \alpha_{ik} A_{ik} + (2^u - 1)\,\mathbf{Y} \tag{18}$$

where $\nu_{A_{ik}}$ are the stoichiometric coefficients of the corresponding components $A_{ik}$, $\alpha_{ik}$ are the fictive mole fractions referred to $\sum_i \sum_k A_{ik}$, for which it holds that

$$\sum_{i=1}^{j} \sum_{k=1}^{l} \alpha_{ik} = 1$$

$u$ is the number of cycles. If the growth of the membrane surface area accompanied by division is represented by Eq. (15), we obtain the general equation of a chemical supersystem dividing in space:

$$\left[ n \sum_{i=1}^{j} \sum_{k=1}^{l} \nu_{A_{ik}} \alpha_{ik} A_{ik} + \boxed{T_n} \right] + (2^u - 1)\, n\mathbf{X}$$

$$\xrightarrow{\boxed{u}} 2^u \left[ n \sum_{i=1}^{j} \sum_{k=1}^{l} \nu_{A_{ik}} \alpha_{ik} A_{ik} + \boxed{T_n} \right] + (2^u - 1)\, n\mathbf{Y} \tag{19}$$

Equation (19) shows that the chemical supersystem produced by the coupling of chemical systems of types (3) and (4) possesses a new qualitative property due to the mode of organization: the ability to multiply. This property is not possessed by the chemical systems themselves which constitute the supersystem. The regulatory and control phenomena appearing within this supersystem will be dealt with in detail in a later publication. It can be proved further that the processes taking place within the system also satisfy the criterion of metabolism taken in the biological sense, if this is not restricted specially to enzymatic reactions [4, 5].

## Supersystems controlled by template polymerization

If the functioning of the self-reproducing cyclic process is coupled not with membrane formation, but with a template polymerization process, a supersystem of new type may be attained. Let us denote the process of the template reaction in the simplest manner described previously [2]:

$$nV + pV_n \longrightarrow 2\,pV_n \tag{20}$$

where $pV_n$ is the template molecule, the degree of polymerization of which is $n$, while $V$ is the monomer. Template polymerization (condensation) is known to proceed by the monomers being specifically bound to units of the polymer matrix (template) by secondary bonds, whereby they come into a spatial situation corresponding to the matrix; following this, they themselves are also connected to one another by covalent bonds, and polymerize into a macromolecule with template properties.

On the analogy of the connection (6) between template polymerization and the self-reproducing cyclic process of equation system (3), it can be arranged that reaction step (3c) should be:

$$A_3 \rightleftarrows A_4 + Y_3 + V \tag{21}$$

*i.e.* by comparison of (21) and overall equation (3) following from the elementary steps of the cyclic process:

$$\sum_{i=1}^{4} \alpha_i A_i + \mathbf{X} \xrightarrow{A} \boxed{1} \longrightarrow 2 \sum_{i=1}^{4} \alpha_i A_i + \mathbf{Y} + V \tag{22}$$

If Eq. (22) is multiplied by $n$ and combined with (20), we obtain:

$$\left[ n \sum_{i=1}^{4} \alpha_i A_i + pV_n \right] + n\mathbf{X} \xrightarrow{A} \boxed{1} \longrightarrow 2 \left[ n \sum_{i=1}^{4} \alpha_i A_i + pV_n \right] + n\mathbf{Y} \tag{23}$$

From this it is seen that the two different chemical systems within the supersystem represented by the square brackets do in fact function in an interconnected manner. It may also be proved that this supersystem too possesses many properties of biological nature [3, 4].

If Eq. (23) is generalized in the previously described (2) manner, we obtain:

$$\left[ n \sum_{i=1}^{j} \sum_{k=1}^{l} \nu_{A_{ik}} \alpha_{ik} A_{ik} + pV_n \right] + (2^u - 1)\, n\mathbf{X}$$

$$\xrightarrow{u} \boxed{u} \longrightarrow 2^u \left[ n \sum_{i=1}^{j} \sum_{k=1}^{l} \nu_{A_{ik}} \alpha_{ik} A_{ik} + pV_n \right] + (2^u - 1)\, n\mathbf{Y} \tag{24}$$

In this system $pV_n$ plays the controlling role, for, if the template polymerization process cannot occur for some reason, the functioning of the cyclic process is inhibited because of the accumulating $V$-s. In a later publication it will be demonstrated in detail that the stable form of the template molecule is double-stranded, and that the template polymerization process is initiated just because of the decomposition of this double-stranded structure at a critical monomer concentration $V^*$ [4, 5]. Therefore, if the polymerization process itself takes place with a sufficiently high rate, then the synthesis of $pV_n$ will be a periodically occurring event, which always arises when the concentration of the $V$-s, produced by the cyclic process attains the critical concentration $V^*$. The course of the events occuring in the period between two $pV_n$ syntheses depends on how much $V$ is utilized from the critical concentration during the polymerization, *i.e.* on the length of $pV_n$. Since, in principle, new macromolecules with the same degree of polymerization are synthesized in the course of the template polymerization, the functioning of these cyclic processes is governed in the same manner, and thus consecutive 'generations' of this supersystem function identically in their time-dependences, as a consequence of the constant length of the template molecule.

$pV_n$ therefore carries inherited information as regards the whole of the supersystem, and this is a new qualitative property not possessed by the individual subsystems. This property will be examined in detail (kinetically too) in subsequent publications; it will also be presented *via* concrete examples with the aid of computer simulation; similarly, the kinetic conditions of the control by $pV_n$ will be given too.

## The chemotons

The supersystem represented by general equation (23) can function only under very restricted conditions, since an appreciable $V$ concentration ($V^*$) is necessary for initiation of the synthesis of $pV_n$. If a single $pV_n$ macromolecule is present in a solution with large volume, its controlling role cannot be manifested because of the great amount of $V$; on the other hand, if there are many $pV_n$ molecules, the problem is the statistical nature of the occurrence of the initiation step. However, in a chemical supersystem in which the self-reproducing cyclic process, template polymerization and membrane formation are coupled and the two former chemical systems are enclosed in the membrane sphere, the role of $pV_n$ in the control and storage of inherited information appears unambiguously. This chemical supersystem is named a chemoton.

For the coupled functioning of the three chemical systems, it is necessary that the self-reproducing cyclic process system should include reactions whereby the raw material ($V$) of the template polymerization is formed, and

others, whereby the membrane-forming molecules ($T$) are produced. In the simplest case the elementary steps of the self-reproducing cyclic process are as follows:

$$\begin{aligned} A_1 + X &\rightleftarrows A_2 \\ A_2 &\rightleftarrows A_3 + Y \\ A_3 &\rightleftarrows A_4 + V \\ A_4 &\rightleftarrows A_5 + T \\ A_5 &\rightleftarrows 2\,A_1 \end{aligned}$$

$$\sum_{i=1}^{5} \alpha_i A_i + \mathbf{X} \xrightarrow{\boxed{\pm 1}} 2 \sum_{i=1}^{5} \alpha_i A_i + \mathbf{Y} + V + T \tag{25}$$

Let us multiply Eqs (3) and (25) by $n$, and combine them with Eqs (11) and (20):

$$\left[ n \sum_{i=1}^{5} \alpha_i A_i + pV_n + \boxed{T_n} \right] + n\mathbf{X} \xrightarrow{\overset{A}{\boxed{1}}}$$

$$2 \left[ n \sum_{i=1}^{5} \alpha_i A_i + pV_n + \boxed{T_n} \right] + n\mathbf{Y} \tag{26}$$

*i.e.* if there is a microscopic bilayered membrane sphere, within which can be found the other two chemical systems shown in square brackets, and if the other conditions connected with self-reproducing spheres also hold, then the sphere will grow and multiply by dividing itself. If Eq. (26) is generalized to a self-reproducing reaction network of optional complexity, for $u$ cycles we have

$$\left[ n \sum_{i=1}^{j} \sum_{k=1}^{l} \nu_{A_{ik}} \alpha_{ik} A_{ik} + pV_n + \boxed{T_n} \right] +$$

$$+ (2^u - 1)\, n\mathbf{X} \xrightarrow{\boxed{u}} 2^u \left[ n \sum_{i=1}^{j} \sum_{k=1}^{l} \nu_{A_{ik}} \alpha_{ik} A_{ik} + pV_n + \boxed{T_n} \right] + (2^u - 1)\, n\mathbf{Y}$$

## Discussion

With the aid of equations connected through the previously described cyclic process symbol [1, 2], a study was made of the stoichiometric correlations of supersystems obtainable by the coupling of three chemical systems with different properties: the self-reproducing cyclic process, template polymerization and bilayered membrane growth.

It was found that enclosure of a cyclic process producing a membrane-forming molecule in a microscopic membrane sphere results in a chemical supersystem; under appropriate external conditions, this latter is capable of metabolism-based growth, *i.e.* growth which produces all of the internal substances of the supersystem in a regulated manner by chemical means, from external 'nutritive materials', via a reaction system consisting of many elementary reactions. If the external conditions are suitable, as a consequence of this growth, the sphere divides into two spheres identical in size to each other and the original sphere; each of the divided spheres is capable of growth and division, and hence this supersystem is capable of true multiplication, *i.e.* of self-reproduction connected with spatial separation. This property originates not from the properties of the constituent chemical systems, but from the manner of organization of the supersystem.

The coupling of the self-reproducing cyclic process and template polymerization results in a chemical supersystem in which the template polymerization plays a controlling role as regards the whole of the supersystem. The program of the control in this supersystem is the length of the template molecule, and since this program replicates itself in the course of template polymerization, it is similarly reproduced during the self-reproduction of the supersystem, and thus has the nature of a genetic program. As spatial separation does not occur in the course of the self-reproduction of this supersystem, the controlling role of the multiplied programs is not manifested sufficiently in this system, or only under very restricted conditions.

The coupling of all three chemical systems in such a way that the self-reproducing cyclic process system and the template molecule too are situated inside a microsopic membrane sphere, and the self-reproducing cyclic process produces both the membrane-forming molecule and the raw material of template polymerization, yields a chemical supersystem known as a chemoton.

Under appropriate environmental conditons, the chemoton utilizes suitable compounds in its environment ('nutritive substances') by transforming these into its own internal materials, by means of chemical reactions, in a regulated manner governed by the template molecule. As a consequence of the transformation, the chemoton grows, and then divides into two identical units, similarly to the self-reproducing sphere, *i.e.* it multiplies. The properties of the chemoton, the quantity of its internal substances, its spatial size, etc. are governed by the length of the template polymer with its hereditary nature. It may be proved that the chemotons satisfy the general criteria regarding the living nature of biological systems [3—5].

It was earlier demonstrated [2] that all three self-reproducing systems discussed, the autocatalytic cyclic process, template polymerization and membrane growth, may be characterized by numbers denoting the periodicity, $u_1$, $u_2$ and $u_3$ (dependent on the doubling time $\tau_1$, $\tau_2$ and $\tau_3$). The coupling

of these systems under the given conditions has the result that these numbers denoting the periodicity become dependent on one another, and the supersystem is characterized by just this mutual dependence, *i.e.* it shows that the chemical system constituting the supersystem can function within the supersystem only in accordance with strict quantitative rules.

As a result of their stoichiometric nature, the equations described here hold whether the letters denoting the components refer to molecules or to molar quantities. If they refer to molecules, they give a description of each individual supersystem as an entity, but then the coefficients $\alpha_i$ are not fictive mole fractions, but mean the quantitative numerical ratios of the individual $A_i$ molecules referred to $\sum_i A_i$. If the letters in the equations relate to molar quantities, then the $\alpha_i$ values are fictive mole fractions, but in this case the equations give the quantitative relations not of each individual supersystem, but of a number of supersystems equal to Avogadro's number.

The kinetics of these chemical supersystems and their functioning, growth, multiplication and inheritance properties will be dealt with in more detail in subsequent publications in this series.

*

The author is grateful to Prof. István GYARMATI for his inspiring interest and valuable advice

## Appendix
## The conditions for a growing microsphere to divide

T. GÁNTI and Cs. GÁSPÁR

According to Eq. (8), the condition of osmotic equilibrium is

$$c_A = c_I$$

where $c_I$ = constant.

Since

$$(c_A)_t = \frac{\left(\sum_i \alpha_i A_i\right)_t}{(Q)_t} \qquad (A.1)$$

where $(c_A)_t$ is the concentration of the internal substances of the microsphere at time $t$; $\left(\sum_i \alpha_i A_i\right)_t$ is the quantity of the internal substances at time $t$; $(Q)_t$ is the volume of the microsphere. On the basis of (12):

$$\left(\sum_i \alpha_i A_i\right)_t = (F)_t f_T \qquad (A.2)$$

and

$$(Q)_t = k(F)_t^{3/2} \tag{A.3}$$

Hence:

$$(c_A)_t = \frac{(F)_t f_T}{(Q)_t} = \frac{(F)_t}{k(F)_t^{3/2}} f_T \tag{A.4}$$

which is in contradiction with (8). Setting out from osmotic equilibrium, during its growth the growing microsphere cannot assume a new osmotic equilibrium state without dividing.

In the event of division:

$$(Q)_t = Q_1 + Q_2 \tag{A.5}$$

and

$$(F)_t = F_1 + F_2 \tag{A.6}$$

For division at $t = \tau$:

$$(F)_t = 2(F)_0 = F_1 + F_2 \tag{A.7}$$

On the basis of (A.4), osmotic equilibrium is established if

$$Q_1 + Q_2 = 2(Q)_0 \tag{A.8}$$

If (A.7) and (A.8) are expressed in terms of the radius of the microsphere, we obtain

$$2r_0^2 = r_1^2 + r_2^2 \tag{A.9}$$

and

$$2r_0^3 = r_1^3 + r_2^3 \tag{A.10}$$

where $r_0$ is the radius of the microsphere prior to the beginning of growth, and $r_1$ and $r_2$ are the radii of the two microspheres produced by division at time $t = \tau$. It can be proved that for $t = \tau$ there is no other osmotically stable solution for division of the microsphere apart from separation into two identical microspheres the same in size as the original one; that is, apart from the trivial solution $r_0 = r_1 = r_2$, Eqs (A.9) and (A.10) have no real positive solution.

## Proof

If there exists a triad $(r_0, r_1, r_2)$ which satisfies (A.9) and (A.10), then they are also satisfied by $(\lambda r_0, \lambda r_1, \lambda r_2)$, where $\lambda$ is an optional real number. Let us state that every real solution of (A.9) and (A.10) exists in the form $(\lambda r_0^*, \lambda r_1^*, \lambda)$, where $\lambda$ is an optional real number, and $r_0^*$ and $r_1^*$ are real solutions of the equation system:

$$2r_0^2 = r_1^2 + 1 \tag{A.11}$$

$$2r_0^3 = r_1^3 + 1 \tag{A.12}$$

If $r_0^*$, $r_1^*$ is a solution of (A.11) and (A.12), then ($r_0^*$, $r_1^*$, 1) is a solution of (A.9) and (A.10), and hence $\lambda r_0$, $\lambda r_1$, $\lambda$ too is a solution of (A.9) and (A.10). Conversely, let ($r_0$, $r_1$, $r_2$) be an optional solution of (A.9) and (A.10). If $r_2 = 0$, then $\sqrt{2}\,|\,r_0\,| = |\,r_1\,|$ and $\sqrt[3]{2}\,|\,r_0\,| = |\,r_1\,|$; this can only be so if $r_0 = r_1 = 0$. In this case, therefore, the choice $\lambda = 0$ is appropriate. If $r_2 \neq 0$, then ($r_0/r_2$, $r_1/r_2$) is a solution of (A.11) and (A.12). In this case, therefore, the choice $\lambda = r_2$ is appropriate.

It is sufficient, therefore, to demonstrate that the only positive solution of the system (A.11) and (A.12) is $r_0^* = r_1^* = 1$. Let us assume that $r_0^*$, $r_1^*$ is a solution of (A.11) and (A.12). If (A.11) is cubed, and (A.12) is squared, and multiplied by 2, we have:

$$r_1^{*6} + 3r_1^{*4} + 3r_1^{*2} + 1 = 2r_1^{*6} + 4r_1^{*3} + 2$$

*i.e.* $r_1^*$ is a root of the polynomial

$$P(r) = r^6 - 3r^4 + 4r^3 - 3r^2 + 1$$

$P(r)$ can be factorized:

$$P(r) = (r-1)^2\,(r^4 + 2r^3 + 2r + 1)$$

It immediately emerges from this that the only positive root of $P(r)$ is $r = 1$. Since $r_1^*$ is a root of $P(r)$, we have $r_1^* = 1$. If this in turn is introduced into (A.12), we have $r^* = 1$. We have proved, therefore, that the only positive solution of (A.11) and (A.12) is $r_0^* = r_1^* = 1$, and hence a positive solution of (A.9) and (A.10) is of necessity

$$r_0 = r_1 = r_2 \tag{A.13}$$

According to (A.13), therefore, under the given environmental conditions it is possible to attain an osmotic equilibrium state only if the grown sphere divides into two identical spheres the same in size as the sphere prior to growth. However, this proof refers only to the case when $t = \tau$, *i.e.* when the substance and surface area of the sphere are exactly twice the initial values. A separate study must be made of what division proportions can lead to an osmotic equilibrium state in the interval between $t = 0$ and $t = \tau$. Mathematically, on analogy with (A.9) and (A.10), the solution of the equation system

$$Kr_0^2 = r_1^2 + r_2^2 \tag{A.14}$$

and

$$Kr_0^3 = r_1^3 + r_2^3 \tag{A.15}$$

in the case of $1 < K < 2$, will yield the pairs of radii $r_1$ and $r_2$ for which osmotic equilibrium may exist.

Let us consider equation system (A.14) and (A.15). As in the case of (A.9) and (A.10), it can readily be seen that every positive solution of (A.14) and (A.15) (and only these solutions) exist in the form $(\lambda r_0^*, \lambda r_1^*, \lambda)$, where $\lambda > 0$ is optional, and $r_1^*$ and $r_0^*$ are positive solutions of the equation system

$$kr_0^2 = r_1^2 + 1 \tag{A.16}$$

$$kr_0^3 = r_1^3 + 1 \tag{A.17}$$

Let us assume that $(r_0^*, r_1^*)$ is a solution of (A.16) and (A.17). Then, on the basis of (A.16), it is certain that $r_0^* \neq 0$. If (A.16) is cubed and (A.17) is squared, and the resulting equations are divided:

$$k = \frac{(r_1^{*2} + 1)^3}{(r_1^{*3} + 1)^2}$$

Since $r_0^* \neq 0$, the division may be performed. Hence:

$$k \frac{(r_1^{*3} + 1)^2}{(r_1^{*2} + 1)^3} = 1$$

*i.e.* $r_1^*$ is a root of the function

$$f(r) := k \frac{(r^3 + 1)^2}{(r^2 + 1)^3} - 1$$

$f$ is clearly continuous in $(0, +\infty)$ [and in $(-\infty, +\infty)$ too].

Since $f(0) = k - 1 > 0$, $f(1) = 1/2\,k - 1 < 0$, $\lim_{+\infty} f = k - 1 > 0$, and therefore $f$ certainly has a root in $(0, 1)$ and in $(1, +\infty)$.

Let us state that $f$ has only one root in both $(0, 1)$ and $(1, +\infty)$.

In fact, if $f$ had more than two roots in $(0, +\infty)$, then at least two extrema would exist in $(0, +\infty)$, since $f$ is continuous. Since $f$ can also be differentiated, $f'$ would disappear in at least two places in $(0, +\infty)$. However:

$$f'(r) = 6kr \frac{r^3 + 1}{(r^2+1)^4} (r - 1)$$

From this it immediately follows that $f'$ has only a single root in $(0, +\infty)$, and that this is 1. Accordingly, $f$ does indeed have only one root in both $(0, 1)$ and $(1, +\infty)$. By simple resubstitution it emerges that both positive roots

of $f$ give in fact solutions of (A.16) and (A.17). If $r_1^* > 0$ is a root of $f$, then unambiguously there exists some $r_0^* > 0$ such that $(r_0^*, r_1^*)$ is a solution of (A.16) and (A.17). This is

$$r_0^* = \sqrt{\frac{r_1^* + 1}{k}}$$

Consequently, two sets of solutions of (A.14) and (A.15) exist:

$$r_0 = \lambda \sqrt{\frac{r^* + 1}{k}}, \quad r_1 = \lambda r^*, \quad r_2 = \lambda$$

where $\lambda > 0$ is optional, while $r^*$ is one of the fixed roots of $f$: $0 < r^* < 1$, or $r^* > 1$.

Since determination of the roots of $f$ would require the solution of an equation of the sixth degree, it is to be expected that the roots of the equation cannot in general be given in an explicit manner.

In the following it will be demonstrated that the two sets of solutions obtained above are 'essentially the same', and a better estimation than the above can be given as regards the situation of the solutions.

Let us select $\lambda$, so that $r_0 = 1$; that is, let us consider all those solutions of (A.14) and (A.15) for which $r_0 = 1$. Then, $r_1$ and $r_2$ satisfy the equation system

$$k = r_1^2 + r_2^2 \tag{A.18}$$

$$k = r_1^3 + r_2^3 \tag{A.19}$$

Since the roles of $r_1$ and $r_2$ can be exchanged, it is obvious that if $(\bar{r}_1, \bar{r}_2)$ is one of the solutions of this, then $(\bar{r}_2, \bar{r}_1)$ is definitely its other solution. This clearly does not coincide with the previous solution, since $\bar{r}_1 = \bar{r}_2$ cannot hold.

Consequently, the two sets of solutions of (A.14) and (A.15) can be obtained from each other by interchange of the roles of $r_1$ and $r_2$, which shows in fact that the two sets of solutions are 'essentially the same'.

Finally, from (A.18) and (A.19):

$$r_1^2 + r_2^2 = r_1^3 + r_2^3 \tag{A.20}$$

from which it follows that if $r_1$ and $r_2$ are positive solutions of (A.18) and (A.19) then either

$$0 < r_1 < 1 < r_2$$

or

$$0 < r_2 < 1 < r_1$$

Thus, $r_1$ and $r_2$ are separated by 1. In the opposite case, the equality in (A.20) cannot hold. Additionally, from (A.19) we have trivially:

$$r_1 \leq \sqrt[3]{k}, \quad r_2 \geq \sqrt[3]{k}$$

Specially, for $k = 3/2$, one of the solutions of (A.18) and (A.19) (approximately calculated) is

$$r_0 = 1$$

$$r_1 = 1.1067777$$

$$r_2 = 0.52444569$$

It can be seen, therefore, that in the case $1 < K < 2$ there is an infinite number of solutions, but only such for which $r_1 \neq r_2$.

In the derivation of spatially separated chemical supersystems capable of multiplication, one of the starting theses was that the limiting surface of the system is a bilayered membrane; it was earlier established that this is a two-dimensional fluid, which behaves as a liquid in the plane of the membrane, but as a solid body perpendicularly to the plane [2]. It follows from this that if the membrane is bent, a tension (denoted by $\sigma$) arises in the plane of the membrane. The magnitude of this tension depends on the extent of the bending, *i.e.* on the radius of curvature of the curvature induced:

$$\sigma = f(r)$$

Corresponding to this, in the course of non-uniform division into spheres, in one and the same membrane tensions of different magnitude, $\sigma_1$ and $\sigma_2$, relating to two different radii of curvature, should arise in the plane of the membrane; this is in contradiction with the fact that the membrane is a liquid in nature in the directions of the plane. Therefore, a division which leads to osmotic equilibrium and at the same time does not contradict the two-dimensional liquid structure of the membrane can occur only at time $t = \tau$. This division is that into two identical spheres, *i.e.* in its continuity it results in the multiplication of the spheres.

## REFERENCES

[1] GÁNTI, T.: Acta Chim. (Budapest), **91**, 357 (1976)
[2] GÁNTI, T.: Acta Chim. (Budapest), **91**, 369 (1976)
[3] GÁNTI, T.: The Principle of Life (in Hungarian). 2nd revised edition, Gondolat, Budapest 1978
[4] GÁNTI, T.: A Theory of Biochemical Supersystems and its Application to Natural and Artificial Biogeneses. Akadémiai Kiadó, Budapest (in press)
[5] GÁNTI, T.: Self-organization and Self-regulation of Macromolecular Supersystems. In "Biological Regulation" (in Hungarian) (Ed.: Gy. Csaba), Medicina, Budapest, 1978

Tibor GÁNTI, H-1445 Budapest 8, Pf 324

*Acta Chimica Academiae Scientiarum Hungaricae, Tomus 98 (3), pp. 285—291 (1978)*

# COMPARISON OF SOLVENT UPTAKE AND ION EXCHANGE PROPERTIES OF DIETHYLAMINOETHYLCELLULOSE (DE-CELLULOSE) AND OF BENZOYLATED DIETHYLAMINOETHYLCELLULOSE (BD-CELLULOSE) IN METHANOL – WATER – HYDROCHLORIC ACID MIXTURES

A. LÁSZTITY and M. NÉMETH

*(Institute of Inorganic and Analytical Chemistry L. Eötvös University, Budapest)*

Received August 17, 1977
In revised form November 12, 1977

The swelling and ion exchange properties of DE- and BD-cellulose in water–methanol–1 *M* hydrochloric acid mixtures have been compared. The benzoylation of the OH groups of DE-cellulose changes the swelling and ion exchange properties of DE-cellulose. In aqueous solution the water uptake of BD-cellulose is much less, while its ability to the sorption of metal ions (Cd(II), Hg(II), Bi(III)) is much better than that of DE-cellulose. Chloride complexes prefer the BD-cellulose phase, which contains less water. In contrast to DE-cellulose selective uptake of water cannot be observed with BD-cellulose in methanol–water–1 *M* HCl mixture. At high methanol contents, the two weakly basic anion exchangers have similar sorption abilities.

## Introduction

The distribution of the components of the solvent mixture between the ion exchanger and the solution phase is important in ion exchange processes taking place in solvent mixtures. For synthetic ion exchangers these data are known, whereas for cellulose-based ion exchangers, which can similarly be used for the separation of metal ions from solvent mixtures, no distribution data are available. Data in the literature concern mainly pure cellulose [1]. The sorption of metal ions from hydrochloric acid and nitric acid solution on the weakly basic diethylaminoethylcellulose (DE-cellulose) was investigated by KURODA *et al.* [2, 3]. However, no data of ion exchange behaviour of benzoylated diethylaminoethylcellulose (BD-cellulose) in this mixtures have been reported.

The aim of the present work was to compare the solvent uptake (distribution of the solvent mixture components between the ion exchanger and the solution phase) and ion exchange properties of DE-cellulose and BD-cellulose in methanol–water–1 *M* HCl mixtures of various composition. Parallel with

this, solvent uptake by the strongly basic anion exchanger Dowex-1 and that by pure cellulose have been measured for comparison. No data for pure cellulose are known for methanol–water–hydrochloric acid mixtures [1].

## Experimental

### Reagents

Dowex—1, a strongly basic anion exchanger in the Cl-form, used in air-dry state. Grain size: 50—100 mesh, capacity: 3.82 meq/g dry resin.

Whatman's cellulose powder.

Whatman DE-cellulose has been used in the Cl-form in air-dry state. Capacity of the dry exchanger on the basis of its chloride content and the titration curve with alkali: 0.97 meq/g.

Benzoylated diethylaminoethylcellulose (BD-cellulose, Macherey Nagel Co.) was first prepared in 1967 by GILLAM *et al.* [4]. Before use, it was washed with 96% ethanol, then with 2 *M* NaCl solution containing 25 v/v % ethanol, and finally with 2 *M* NaCl solution, until the absorbance of the filtrate at 260 nm was less than 0.04 (1 cm cell). Subsequently, it was washed chloride-free with deionized water, dried in air and sieved, and used in this form. For comparison, the infrared spectra of DE-cellulose and BD-cellulose purified in this way were recorded. A strong reduction of the OH band intensity was found in the range of 2.8 to 3.2 $\mu$. At the same time in the spectrum of BD-cellulose, bands characteristic for the aromatic ring introduced into the cellulose skeleton appeared at 6.25, 6.35, 6.70 and 14.3—14.4 $\mu$, reported in the literature for benzoylated cellulose [5]. The capacity of BD-cellulose was 0.25 meq/g on the basis of its chloride content.

### Methods

#### Measurement of weight swelling of ion exchangers and solvent distribution between ion exchanger and the solution phase

0.500 g of ion exchanger was kept at room temperature (22 °C) for 2 days in the solvent mixture of the appropriate composition, under periodic stirring, and changing the liquid phase three times. This time was sufficient to reach equilibrium. The ion exchanger was then brought to a surface-dry state by centrifuging (1500 g for 45 min). Then, the swollen exchanger was divided into two parts. In one part the total weight swelling was measured by drying to constant weight at 105 °C, or the water content of the swollen ion exchanger was determined by Karl-Fischer titration [6]. The other half of the swollen ion exchanger was extracted with a given quantity of distilled water (20 00 $cm^3$), to remove methanol and hydrochloric acid bound by the ion exchanger. In the aqueous solution, the methanol content was determined with dichromate, and hydrochloric acid by titration with alkali. Experimental results are given in $\bar{x}_{MeOH}$ *vs.* $\bar{x}_{MeOH}$ and g solvent *vs.* $x_{MeOH}$ diagrams, where $\bar{x}_{MeOH}$ and $x_{MeOH}$ are the mole fraction of methanol in the ion exchanger and in the solution phase, respectively.

#### Ion exchange investigations

The ion exchange behaviour was studied by the static method. 0.500 g BD-cellulose, 0.500 g DE-cellulose and 0.150 g of DE-cellulose, containing the same quantity of exchanger groups as 0.500 g of BD-cellulose were weighed. 20.00 $cm^3$ of water–methanol–1 *M* hydrochloric acid mixture containing 200.0 $\mu$g of metal ion was added to each. After equilibration, the two phases were separated by filtration, and the quantity of metal ion remaining in the solution was determined in an aliquot of the solution and the per cent sorption was calculated. Cd(II) content was determined by atomic absorption spectroscopy after tenfold dilution on a Perkin-Elmer Model 303 instrument, with an air-acetylene flame, at 228.8 nm and slit 4 (1 mm, 0.7 nm). In the diluted solutions, the concentration of methanol varied between 1 and 9 v/v %. For this reason, two calibration series were prepared in water and in 10 v/v % methanol, both containing 1 *M* HCl. The two calibration curves agreed within experimental

errors. Therefore, it was not necessary to adjust the methanol concentration exactly since this was less than 10% in all cases. Zinc and lead were similarly determined by atomic absorption spectroscopy. The Hg(II) concentration was measured spectrophotometrically with dithizone, for the determination of Ni(II), Co(II), Fe(III) and Bi(III) also the spectrophotometric method was used, while the aluminium content was measured by fluorimetry in the form of aluminium oxinate.

## Results and discussion

The swelling of cellulose was studied mainly in alkaline solutions of metals and in mineral acids [7]. For the separation of the swollen cellulose, centrifugation was found to be the best method [8]. The same holds for the synthetic ion exchangers. Therefore, we used the method developed for the synthetic ion exchangers for the measurement of the weight swelling of cellulose ion exchangers in the mixture of methanol–water–1 *M* hydrochloric acid. The distribution of the solvent between the ion exchanger and the solution phase was measured in methanol–water–1 *M* HCl mixtures in the case of pure cellulose (Whatman cellulose powder), DE-cellulose, BD-cellulose and Dowex 1. Figure 1 shows the solvent distribution for the ion exchangers investigated. In the case of pure cellulose, the selective uptake of water is very high because of the strongly hydrophilic nature of the skeleton. For DE-cellulose, the curve shows a lesser asymmetry due to the diethylaminoethyl groups. The conversion of DE-cellulose into BD-cellulose, *i.e.* the esterification of the OH groups with benzoyl chloride, imparts a hydrophobic character to the cellulose skeleton, which is reflected in the distribution of the solvent. The compositions of the two phases differ but slightly from each other, and no selective water uptake can be observed even in the case of Dowex 1.

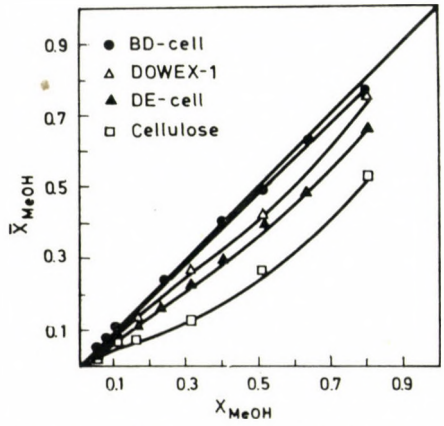



*Fig. 1.* Solvent selectivity: $\bar{x}_{MeOH}$ as a function of $x_{MeOH}$ for ion exchangers in water–methanol–1 *M* HCl mixtures. $\bar{x}_{MeOH}$ and $x_{MeOH}$ are the mole fraction of methanol in the exchanger and in solution, respectively

In the next three figures (Figs. 2, 3, 4) the total weight swelling of the ion exchangers, the quantities of water and methanol sorbed are shown as a function of the mole fraction of methanol in the solution. Figure 2 shows that in the case of pure cellulose and the DE-cellulose, the total swelling

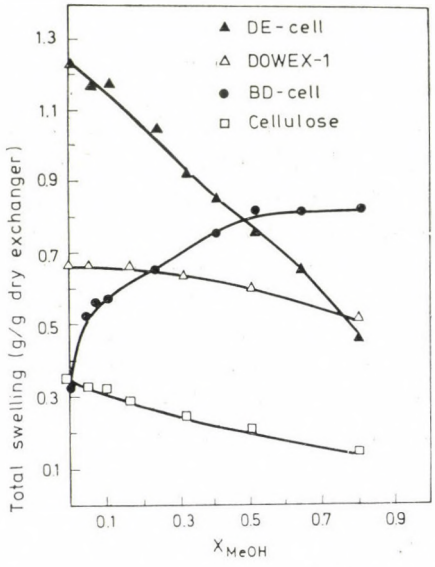



*Fig. 2* Total swelling g solvent/g dry exchanger of different ion exchangers in water–methanol–1 *M* HCl mixtures

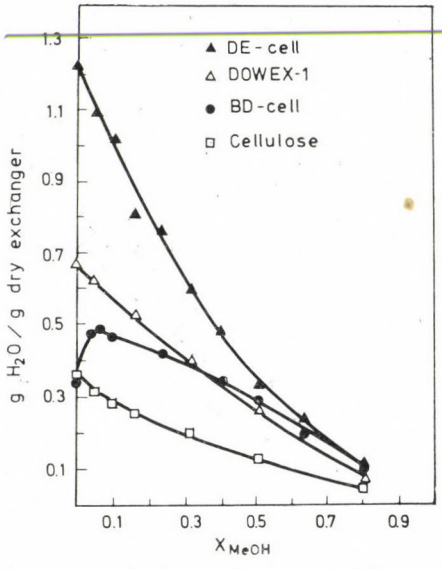



*Fig. 3.* Water uptake g water/g dry exchanger of different ion exchangers in water–methanol–1 *M* HCl mixtures

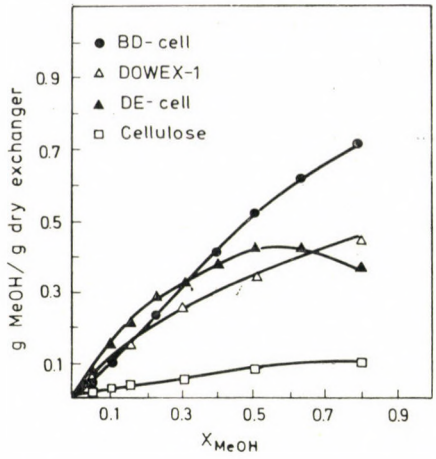



*Fig. 4.* Methanol uptake g methanol/g dry exchanger of different ion exchangers in water–methanol–1 *M* HCl mixtures

decreases considerably with increasing methanol concentration, while for BD-cellulose the opposite effect can be observed, *i.e.* the total swelling increases with increasing methanol concentration. Dowex-1 shows a slight decrease only. The water uptake generally decreases with increasing methanol concentration, as can be seen in Fig. 3. It is of interest to note that the water uptake of BD-cellulose in mixtures of low methanol concentration is higher than in pure water, and gradually decreases with increasing methanol content. A similar behaviour was found for the synthetic ion exchangers, where the addition of a small quantity of water promotes the uptake of acetone and dioxan.

The quantity of hydrochloric acid sorbed was not found to be characteristic for the exchanger groups, since pure cellulose binds about the same amount of hydrochloric acid 0.03 g HCl/g dry exchanger.

As concerns the ion exchange properties of BD- and DE-cellulose, the values obtained for the sorption of Cd(II) and Hg(II) from methanol–water–1 *M* HCl mixtures of various composition are compiled in Table I. The data in the table show that DE-cellulose does not bind Cd(II) from water and mixtures of very low methanol content, while on BD-cellulose the binding is significant. On increasing the methanol concentration, the degree of sorption increases on DE-cellulose. In the case of BD-cellulose, the quantity of Cd(II) bound increases but slightly with increasing methanol concentration and at higher methanol contents a small decrease occurs. The same was observed for Hg(II); BD-cellulose binds more mercury than DE-cellulose in water and at low methanol concentrations.

The sorption of some metal ions (Zn(II), Pb(II), Bi(III)) with a tendency to form chloride complexes has also been investigated. The solution contained

**Table I**

*Per cent sorption of Cd(II) and Hg(II) on DE- and BD-cellulose anion exchangers from methanol–water–1 M HCl mixtures*
(200 $\mu$g metal ion/20.0 cm$^3$ solution)

| xMeOH | Cd(II) | | | Hg(II) | | |
|---|---|---|---|---|---|---|
| | BD | DE | | BD | DE | |
| | 0.50 g | 0.15 g | 0.50 g | 0.50 g | 0.15 g | 0.50 g |
| 0 | 81.0 | no sorption | no sorption | 98.5 | 24.0 | 46.0 |
| 0.05 | 85.0 | no sorption | 12.0 | 99.0 | 24.5 | 49.0 |
| 0.10 | 87.5 | — | — | — | — | — |
| 0.16 | 87.0 | 13.0 | 25.0 | 97.5 | 27.0 | 52.5 |
| 0.23 | 87.5 | — | — | — | — | — |
| 0.31 | 84.0 | 14.0 | 32.5 | 93.0 | 27.5 | 55.5 |
| 0.40 | 80.0 | — | — | — | — | — |
| 0.50 | 75.0 | 24.0 | 52.5 | 88.5 | 40.5 | 68.0 |
| 0.80 | 77.0 | 51.0 | 85.0 | 89.0 | 75.5 | 89.6 |

1 *M* hydrochloric acid. Pb(II) and Zn(II) were found not to be bound either on DE- or BD-cellulose. However, for Bi(III) the BD- and DE-cellulose behaved differently. 29% of 200.0 $\mu$g Bi(III) was bound on 0.500 g DE-cellulose, while the sorption was 91% on the same amount of BD-cellulose. Bi(III) can be said to behave similarly as Cd(II) and Hg(II).

The sorption of a few elements (Ni(II), Cd(II), Cu(II), Fe(III), Al(III)) not bound from 1 *M* hydrochloric acid solution on either weakly or strongly basic anion exchangers has also been studied, using BD-cellulose. No sorption could be observed for any of these elements.

These findings prove that in aqueous solution BD-cellulose behaves in the same way as the strongly basic anion exchangers. The BD-cellulose absorbs only ions that form stable chlorocomplexes under the given conditions.

In water BD-cellulose swells to a considerably smaller degree than DE-cellulose and probably this is the reason for its better sorption ability as compared with DE-cellulose. The chlorocomplexes prefer the ion exchanger phase which contains less water [9].

As organometallic compounds of mercury, cadmium and bismuth are known, they can interact with the benzoyl group and this interaction may lead to a better sorption ability. This effect can be decreased by addition of methanol.

In spite of different solvent uptakes the solvent mixture $x_{MeOH} = 0.8$ and HCl = 1 *M*, BD-cellulose behaves in the same way as DE-cellulose (weakly basic anion exchanger) and not as a strongly basic anion exchangers. It does not bind Co(II) and Cu(II) at all, as was found for DE-cellulose from this mixture [2]. The degree of Fe(III) sorption is very small (10%). However

the sorption of Co(II) and Cu(II) on the strongly basic anion exchanger from the same solvent mixture is about 100% [10].

It would be of interest to study the sorption of other complexes on BD-cellulose from water and water–methanol mixtures.

## REFERENCES

[1] PAPKOV, S. P., FAINBERG, E. Z.: Interaction of cellulose and cellulose materials with water (in Russian). Khimiya, Moscow 1976
[2] KURODA, R., YOSHIKUNI, N.: Talanta, **18,** 1123 (1971)
[3] KURODA, R., KONDO, T., OGUMA, K.: Talanta, **28,** 533 (1972)
[4] GILLAM, I., MILLWARD, S., BLEW, D., TIGERSTROM, M., WIMMER, E., TENER, G. M.: Biochemistry, **6,** 3043 (1967)
[5] O'CONNOR, R. T.: Analysis of Chemically Modified Cotton, in Cellulose and Cellulose Derivates, Part IV, p. 53. N. M. BIKALES and L. SEGAL, Eds. Wiley-Interscience, New York 1971
[6] MARCUS, Y., NAVEH, J.: J. Phys. Chem., **73,** 591 (1969)
[7] WARWICKER, J. O.: Swelling in Cellulose and Cellulose Derivates, Part IV, p. 325. N. M. BIKALES and L. SEGAL, Eds. Wiley-Interscience, New York, 1971
[8] HONOLD, E., GRANT, J. N.: Textile Industries, **133,** 93 (1969)
[9] DIAMOND, R. M., WHITNEY, D. C.: Ion Exchange, Vol. 1, p. 277, J. MARINSKY, Ed., M. Dekker, New York 1966
[10] LÁSZTITY, A., BELYAVSKAYA, T. A.: Proc. 3rd Conference on Analytical Chemistry, Budapest, p. 59. Akadémiai Kiadó, Budapest 1970

Alexandra LÁSZTITY H-1088 Budapest, Múzeum krt. 4/b.
Márta NÉMETH, Tatabányai Szénbányák, Á.V.F. H-2803 Tatabánya 1.

*Acta Chimica Academiae Scientiarum Hungaricae, Tomus 98 (3), pp. 293—295 (1978)*

# PREPARATION AND STUDY OF PENTAFLUOROTHIOPHENOL DERIVATIVES OF In(III), Tl(III) AND Rh(III)

D. M. KAMINARIS and A. G. GALINOS

*(Department of Inorganic Chemistry, University of Patras, Patras, Greece)*

Received July 26, 1977
In revised form January 20, 1978

The reactions of pentafluorothiophenol with nonaqueous solutions of $InBr_3$, $TlCl_3$, and $RhCl_3$ are described together with analytical data, IR spectra and other properties of the new adducts.

The mercaptides of Tl(I), Fe(II), Ni(II), Co(II), In(II) Cd(II), Hg(II), Sn(IV) and Bi(III) were first prepared by CLAESON [1]. The reactions of pentafluorothiophenol with aqueous solutions containing different ions or compounds have been investigated by PEACH [2—3].

Derivatives of transition metals and complex ions such as $M(SC_6F_5)_4^{2-}$ (where $M = Co^{2+}$, $Zn^{2+}$, $Cd^{2+}$, $Hg^{2+}$), $M(SC_6F_5)_2^-$ (where $M = Cu^+$, $Ag^+$, $Au^+$) were been precipitated from aqueous solutions [4], as well as the compound $K(SC_6F_5) \cdot 1.5H_2O$ [5]. Other adducts such as $Ni(SC_6F_5)_2$, $Pb(SC_6F_5)_2$, $Pd(SC_6F_5)_2$, and $Pt(SC_6F_5)_2$ were prepared from the metal acetate in acetone—water solutions in the case of Ni, and in benzene in the case of Pd and Pt [6].

The investigation on the pentafluorothiophenoxide ion ($SC_6F_5^-$) and on the IVa and Va group elements have shown that the ($SC_6F_5^-$) ion is very similar to halide ions [7].

In the present work are reported the direct reactions of indium tribromide, thallium trichloride and rhodium trichloride with pentafluorothiophenol in an inert solvent, where complete replacement of bromide and chloride ions by the pentafluorothiophenoxide ion was found to take place.

## Experimental

Pentafluorothiophenol and anhydrous $InBr_3$, $TlCl_3$ and $RhCl_3$ were commercial products. The solvent *n*-hexane was made absolute just before use.

The reactions were studied by prolonged heating of anhydrous indium tribromide (10 days), thallium trichloride (9 days) and rhodium trichloride (7 days) under reflux and continuous stirring (magnetic stirrer) in absolute *n*-hexane with pentafluorothiophenol salt to ligand (mole ratio 1 : 3) in a

**Table I**

*Physical properties*

| Product | Colour | Melting Point (°C) | Found (%) | | | |
|---|---|---|---|---|---|---|
| | | | M | C | S | F |
| In $(SC_6F_5)_3$ | brown | 208 decomp. | 16.50 | 30.67 | 13.14 | |
| Tl $(SC_6F_5)_3$ | orange | 192 decomp. | 25.93 | 27.40 | 12.12 | |
| Rh $(SC_6F_5)_3$ | brown | 177 decomp. | 14.42 | 30.25 | 14.03 | |
| $(C_6F_5S)_2$ | white | 51—52 | | 36.42 | 15.97 | |

dry nitrogen atmosphere, in an apparatus connected to a vacuum line. Slow elimination of hydrogen halide (chloride or bromide) takes place with the formation of a solid, partially soluble in the solvent. These materials are mixtures with a second product derived from a side reaction of pentafluorothiophenol. On the basis of its infrared spectrum and quantitative analysis, this second material appears to be bis(pentafluorophenyl) disulfide $(C_6F_5S)_2$.

For its purification we used vacuum sublimation at about 65 °C. Under these conditions bis(pentafluorophenyl) disulfide sublimes first, followed later by pure samples of the required compounds, $In(SC_6F_5)_3$, $Tl(SC_6F_5)_3$ and $Rh(SC_6F_5)_3$, which were finally isolated by recrystallization from the same solvent.

The reactions take place in a stepwise manner as evidenced by the variety of colours (see Table I) appearing during reflux. The overall reaction is:

$$MX_3 + 3C_6F_5SH \rightarrow M(SC_6F_5)_3 + 3HX$$

$$(M = In^{3+},\ Tl^{3+},\ Rh^{3+})$$

The new products are crystalline solids with no distinct melting points, decomposing above 180 °C. The compound $In(SC_6F_5)_3$ is air-sensitive but $Tl(SC_6F_5)_3$ and $Rh(SC_6F_5)_3$ are not. They do not behave like Lewis acids towards common Lewis bases such as pyridine or dipyridyl.

The infrared spectra of the prepared compounds were recorded in the range of 4000—225 $cm^{-1}$ on a Perkin-Elmer Model 577 instrument. The samples were used as Nujol mulls.

The observed bands indicate the presence of the coordinated pentafluorophenoxide group and are in good agreement with the data published for the $C_6F_5^-$ [8—9] and $C_6F_5S^-$ groups [2—5], particularly for the shifts in the frequencies of the strong bands at 1098, 987 and 860 $cm^{-1}$.

The metal-ligand bands appear at ca. 300 $cm^{-1}$, *viz.* for the indium compound at 312 $cm^{-1}$, for the thallium compound at 316 $cm^{-1}$, and for the rhodium compound at 320 $cm^{-1}$. Characteristic absorption bands of metal–halogen bonds were not observed in the spectra.

Some physical properties of the new compounds are shown in Table I.

*and analytical data*

| Calculated (%) | | | | Solubility* | Yield (%) |
|---|---|---|---|---|---|
| M | C | S | F | | |
| 16.15 | 30.33 | 13.48 | 40.02 | 4, 5, 8 | 63—68 |
| 25.46 | 26.96 | 11.98 | 35.58 | 2, 3, 4, 7, 8 | 69—72 |
| 14.71 | 30.85 | 13.71 | 40.70 | 2, 5, 8 | 70—74 |
| | 36.18 | 16.08 | 47.73 | 1, 4, 8 | 8—12 |

* Solubilites: 1 = Acetone, 2 = Carbon disulfide, 3 = Carbon tetrachloride, 4 = Chloroform, 5 = Dichloromethane, 6 = Diethyl ether, 7 = Petroleum ether, 8 = *n*-Hexane

*

Microanalyses of metals, carbon, and sulfur were performed in the Microanalytical Laboratory of I.G.M.R. (Institute of Geological and Mining Research), Athens.

## REFERENCES

[1] Claeson, P.: J. Prakt. Chem. **15**, 193 (1877)
[2] Peach, M. E.: Can. J. Chem. **46**, 211 (1968)
[3] Peach, M. E.: Can. J. Chem. **46**, 2699 (1968)
[4] Beck, W., Stetter, K. H., Tadros, S., Schwarzhans, K. E.: Chem. Ber. **100**, 3944 (1967)
[5] Robson, P., Stacey, M., Stephens, R., Tatlow, J. C.: J. Chem. Soc. **1960**, 4754
[6] Nyholm, R. S., Skinner, J. F., Stiddart, M. H. B.: J. Chem. Soc. (A) **1968**, 38
[7] Clark, R. J. H., Kaminaris, D.: Inorg. Chim. Acta, **11**, L7—L8 (1974)
[8] Hyam, I. J., Lippincott, E. R., Bailey, R. T.: Spectrochim. Acta, **22A**, 695 (1966)
[9] Douek, J. A., Spickett, J. T.: J. Inorg. Nucl. Chem. **35**, 511 (1973)

D. M. Kaminaris, A. G. Galinos } Department of Inorganic Chemistry, University of Patras, Patras, Greece.

*Acta Chimica Academiae Scientiarum Hungaricae, Tomus 98 (3), pp. 297—302 (1978)*

# THEORETICAL INVESTIGATIONS OF BARRIERS TO INVERSION

Th. WELLER and R. LOCHMANN

*(Molecular NMR Group, Department of Physics, Karl-Marx-University, 701 Leipzig, G.D.R.)*

Received October 26, 1977
In revised form January 27, 1978

A theoretical study of barriers to inversion for the molecules $NH_3$, $NH_2CH_3$, $NH(CH_3)_2$, $N(CH_3)_3$, $NCl_3$, $NCl(CH_3)_2$, $NClH_2$, $PH_3$, $P(CH_3)_3$ and $PF_3$ was made within the PCILO framework. The results are compared with experimental data and with *ab initio* and CNDO/INDO calculations.

In recent years the PCILO method had great success in the conformational analysis of small and large — especially biological — molecules [1]. Recent publications indicate the feasibility of this quantum-chemical method also for the investigation of the intermolecular interactions of molecules, *e.g.* hydrogen bonded and charge transfer complexes [2].

In this paper a new interesting type of the intramolecular behaviour — barriers to inversion — will be discussed with in the PCILO framework. Whereas a lot of ab initio and semiempirical investigations on this subject can be found in the literature [3—7], analogous PCILO studies are not known. We have investigated the barriers to inversion and the bond angle on the centres N and P, respectively, for the molecules $NH_3$, $NH_2(CH_3)$, $NH(CH_3)_2$, $N(CH_3)_3$, $NCl_3$, $NCl(CH_3)_2$, $NClH_2$, $PH_3$, $P(CH_3)_3$, and $PF_3$. The bond angles were optimized for all these molecules to find the most stable structure in conjunction with the best barrier to inversion. The results will be dealt with briefly.

### Method

We used the PCILO method in its original version [8] with an *sp* basis. The integrals are parametrized as for CNDO/2 [9].

For comparison with other methods a standard geometry was used [10] with bond lengths of 1.09 (C—H), 1.01 (N—H), 1.47 (N—C), 1.42 (P—H), 1.84 (P—C), 1.75 (N—Cl), and 1.57 Å (P—F), respectively.

## Results and discussion

$NH_3$, $NH_2CH_3$, $NH(CH_3)_2$, $N(CH_3)_3$.

Calculations have been made for these molecules, keeping the methyl groups in the staggered conformation as in the to CNDO/2 investigations of COROSINE

*et al.* [11] on similar molecules. They found that for $(CH_3)_3M$ (M = N, P, CH, SiH) compounds the theoretical energy minimum is predicted for the so-called LEM-conformation in which each methyl group is staggered with respect to the two opposite (M–C) bonds. Table I shows a comparison of the PCILO-results with various other quantum-chemical and experimental values. The qualitative prediction of the inversion barriers shows in every case the pyramidal structure as the most stable one in agreement with the experiment. Whereas CNDO-Mislow and INDO barriers are quantitatively in reasonable agreement with experiment, PCILO gives too high barriers (two or three times the experimental values) as does also CNDO/2. INDO gives a more realistic account of the trend in barriers, in going from $NH_3$ to $NH_2(CH_3)$ to $NH(CH_3)_2$ to $N(CH_3)_3$.

For the investigated bond angles a good correspondence between our results and the experimental data for $NH_3$ and $N(CH_3)_3$ can be seen.

$NCl_3$, $NCl(CH_3)_2$, $NCl\,H_2$

Qualitatively the PCILO method indicates again correctly a pyramidal structure of the molecules as the most stable one. Only for $NCl(CH_3)_2$ (methyl groups staggered) an experimental value could be found in the literature, the CNDO-Mislow barrier agrees with this very well (Table I). Our barrier is too high again for this compound, also for the other two compounds, the barriers seem to be too high. Not only our values but also calculations with different sets of parameters I, A and $\beta^\circ$ for the second row atoms within the CNDO-framework (CNDO/A [12] and CNDO/B [13]) and INDO/A [4] (difference to INDO/B [4] in the estimation for the Slater-Condon parameters $F^2$ and $G^1$ for one center exchange integrals) yield quantitatively different barriers. For $NCl_3$ the PCILO bonding angle is somewhat smaller than the experimental one.

$PH_3$, $P(CH_3)_3$, $PF_3$.

The molecules $PH_3$, $PF_3$ have been the subject of several *ab initio* and semiempirical investigations [3—6, 18]. The most detailed *ab initio* investigation of the $PH_3$ inversion gave a barrier of 153.7 kJ/mole, near the experimental value of the free energy of activation for phosphorus inversion in cyclohexyl-methyl-*n*-propylphosphine (149.1 kJ/mole [6], other experimental information is not available).

Our value 219.1 kJ/mole for $PH_3$ lies again above this *ab initio* result as it is the case for CNDO/2, however, our value 443.8 kJ/mole for $PF_3$ is too small in comparison with *ab initio* calculations (Table I). For $PH_3$ only CNDO-

*Explanation*

a) in kJ/mole; b) in degrees; c) Ref. [4]; d) Ref. [14]; e) CNDO/A and CNDO/B from Ref. [12, 13]; f) Ref. [5]; g) Ref. [11]; h) Ref. [6]; i) *ab initio* value [5]; j) INDO/A and INDO/B from Ref. [4]; k) interpolated values (the angles were varied in steps of 2 degrees); l) in part various experimental and quantum-chemical values from the literature are given.

**Table 1**

*Comparison of the calculated inversion barriers (a) and bond angles (b) from PCILO (k) with experimental and other quantum-chemical values (l)*

| Molecule | | exp.[c] | CNDO/2 | CNDO-Mislow[d] | INDO[e] | PCILO |
|---|---|---|---|---|---|---|
| $NH_3$ | a) | 24.3 | 49.4[c] | 13.4 | 20.5 | 56.5 |
| | b) | 107.3 . . . 109.1 | | | 110.0 | 106.8 |
| $NH_2CH_3$ | a) | 20.1 | 54.0[c] | 16.7 | 19.7 | 57.1 |
| | b) | | | | | 106.8 |
| $NH(CH_3)_2$ | a) | 18.4 | 56.9[c] | 21.8 | 18.4 | 59.0 |
| | b) | | | | | 106.8 |
| $N(CH_3)_3$ | a) | 25.1 | 62.8[c] | 27.3 | 21.4 | 53.6 |
| | b) | 108.7 . . . 110.6 | 105.2 . . .105.7[g] | | | 107.5 |
| $NCl_3$ | a) | | 152.0...112.6[e] | 85.0 | 140.3 . . . 101.3[j] | 167.1 |
| | b) | 109.0 | | | | 104.6 |
| $NCl(CH_3)_2$ | a) | 42.3 | 92.1. . .81.2[e] | 41.5 | 54.0. . .43.5[j] | 94.1 |
| | b) | | | | | 105.8 |
| $NClH_2$ | a) | | 72.0 . . . 57.8[e] | 38.1 | 57.4 . . . 46.5[j] | 95.9 |
| | b) | | | | | 104.0 |
| $PH_3$ | a) | 149.1 | 206.8...119.7[e] | 149.9 | 202.6 . . .106.3[j] | 219.1 |
| | b) | | | | | 95.8 |
| $P(CH_3)_3$ | a) | | 171.7 . . . 71.1[e] | 127.3 | 141.9 . . .36.0 | 191.0 |
| | b) | 98.6 . . . 99.1 | | | | 97.2 |
| $PF_3$ | a) | 658.6 . . . 555.6 | | | | 443.8 |
| | b) | | | | | 99.2 |

**Table II**

*Energy partitioning of the PCILO total energies of*

| Energy contribution[a] (I/mole) | $NH_3$ | $NH_2(CH_3)$ | $NH(CH_3)_2$ | $N(CH_3)_3$ |
|---|---|---|---|---|
| Zeroth-order energy $\Delta E_0$ | 74.9 | 62.9 | 47.6 | 30.1 |
| Second-order energy $\Delta E_2$ | — 22.3 | — 9.6 | + 7.8 | 32.2 |
| $\Delta E_0 + \Delta E_2$ | 52.7 | 53.3 | 55.4 | 62.2 |
| Third-order energy $\Delta E_3$ | 0.6 | 3.7 | 0.9 | — 8.8 |
| $\Delta E_0 + \Delta E_2 + \Delta E_3$ | 53.4 | 57.1 | 56.9 | 53.4 |

[a] energy difference
$\Delta E = E_{\text{planar}} - E_{\text{pyramidal}}$

Mislow shows a good agreement with the mentioned experimental and *ab initio* barriers [14].

Our calculated bond angles for $PH_3$ and $P(CH_3)_3$ (methyl groups staggered) are good in comparison with the experimental ones (Table I). A further calculation of the inversion barriers using the cited experimental angles did not influence the height of the barriers essentially (*e.g.*: $PH_3$ with 93.5°: 232.4 kJ/mole).

Table II shows the energy contributions [8] of the barriers to inversion of the individual molecules. It can easily be seen that the most significant contribution is given by the difference in the zeroth-order energies $\Delta E_0$. The CI-perturbation terms ($\Delta E_2$, $\Delta E_3$) of the total energy cannot improve this overestimated barrier considerably.

Investigating the polarities of the bonds and the s-characters we could state that these values are lower for the equilibrium form in comparison with the planar form (as it is revealed by the physical-chemical picture), but they do not seem to influence the bad zeroth-order wave function so strongly as the short basis set.

In comparison with the CNDO/2 results one can see that the CNDO/2 integral parametrization here does not allow the inversion barriers to be predicted quantitatively correctly. The CNDO/2 values lead to barriers to inversion approximately two or three times as large as expected [14] and this is also true for the PCILO values (except $PF_3$).

While CNDO/2 involves the picture of a delocalized molecular orbital basis set, the strong localized basis set of the PCILO method overemphasizes the stable pyramidal structure especially by the energy part $E_0$ in consequence of the bad zeroth-order wave function.

The results of CNDO-Mislow cannot be easily compared with our framework since there an optimization of the parameter set was made (electronegativities, bonding parameters $\beta^{\circ}_{AB}$) in yielding correct inversion barriers.

*the inversion barriers of the investigated molecules*[b)]

| $NCl_3$ | $NCl(CH_3)_2$ | $NClH_2$ | $PH_3$ | $P(CH_3)_3$ | $PF_3$ |
|---|---|---|---|---|---|
| 259.0 | 101.4 | 122.6 | 210.4 | 177.1 | 384.4 |
| — 55.0 | — 4.6 | — 21.6 | 7.6 | 11.3 | 91.3 |
| 203.9 | 96.8 | 101.0 | 218.0 | 188.4 | 475.2 |
| — 38.4 | — 6.1 | — 5.0 | — 1.4 | 2.6 | — 34.2 |
| 165.6 | 90.8 | 95.9 | 216.6 | 191.0 | 440.9 |

[b)] with respect to the corresponding nearest calculated angle to the energy minimum (the angles were varied in 2-degree-steps); here the values are *not* interpolated.

The statement that in the PCILO investigations the configuration interaction terms only have a small influence on the barriers to inversion is also indicated in other quantum-chemical studies. STEVENS [15] performed full CI calculations for the inversion barrier of ammonia, using a near-Hartree-Fock basis set of STO's, and showed that full single and double excitation valence CI reveals only a little energy contribution (less than 2.1 kJ/mole) to the barrier. Similar results were found *e.g.* by DUTTA, KARPLUS [16] and KUTZELNIGG *et al.* [17].

Whereas for intramolecular and intermolecular interactions the PCILO method gives very good qualitative and also quantitative results mainly by the CI-perturbation treatment of the energy, it can be concluded that for the investigation of barriers to inversion only a qualitatively correct result may be expected. For the case of $NH_3$ we have studied the influence of a geometry optimization for the calculated barrier to inversion. This yielded an N–H bond length of 1.07 Å for the planar state; an N–H bond length of 1.08 Å and a bond angle of 104.4° for the pyramidal geometry and a barrier of 78.0 kJ/mole. Thus we could not detect any improvement of the values of the barrier and the corresponding bond angle due to an optimized geometry.

## REFERENCES

[1] PULLMAN, A.: Topics Current Chem. **31,** 45 (1972); PERAHIA D., PULLMAN A.: Chem. Phys. Letters **19,** 73 (1973); WELLER, Th., KLÖPPER, D., KÖHLER, H.-J.: Chem. Phys. Letters **36,** 475 (1975)
[2] SPURLING, Th. H., SNOOK, I. K.: Chem. Phys. Letters **32,** 159 (1975); LOCHMANN, R., WELLER, Th.: Intern. J. Quant. Chem., **10,** 909 (1976); LOCHMANN, R., HOFMANN, H.-J.: Intern. J. Quant. Chem., **11,** 427 (1977)
[3] PETKE, J. D., WHITTEN, J. L.: J. Chem. Phys. 59, 4855 (1973)
[4] STEPHENSON, Ph. E., BURKEY, D. L.: J. Am. Chem. Soc. **96,** 3061 (1974)
[5] AARONS, L. J., GUEST, M. F., HALL, M. B., HILLIER, I. H.: J. Chem. Soc., Faraday Transact. II, **69,** 643 (1973)
[6] LEHN, J. M., MUNSCH, B.: Mol. Phys. **23,** 91 (1972)
[7] KEIL, F., KUTZELNIGG, W.: J. Am. Chem. Soc. **97,** 3623 (1975)

[8] DINER, S., MALRIEU, J. P., JORDAN, F., GILBERT, M.: Theor. chim. Acta **15,** 100 (1969)
[9] POPLE, J. A., BEVERIDGE, D. L.: Approximate molecular orbital theory (McGraw-Hill, New York, 1970)
[10] SUTTON, L. E.: Chem. Soc., Spec. Publ. No. 11 (1958) No. 18 (1965)
[11] COROSINE, M., CRASNIER, F., LABARRE, M. C., LABARRE, J. F., LEIBORICI, C.: Chem. Phys. Letters **20,** 111 (1973)
[12] SANTRY, D. P., SEGAL, G. A.: J. Chem. Phys. **47,** 158 (1967)
[13] SANTRY, D. P.: J. Am. Chem. Soc. **90,** 3309 (1968); SABIN, J. R., SANTRY, D. P., WEISS, K.: J. Am. Chem. Soc. **94,** 6651 (1972)
[14] RAUK, A., ANDOSE, J. D., FRICK, W. G., TANG, R., MISLOW, K.: J. Am. Chem. Soc. **93** 6507 (1971)
[15] STEVENS, R. M.: J. Chem. Phys. **61,** 2086 (1974)
[16] DUTTA, N. C., KARPLUS, M.: Chem. Phys. Letters **31,** 455 (1975)
[17] DRIESSLER, F., AHLRICHS, R., STAEMMLER, V., KUTZELNIGG, W.: Theor. chim. Acta **30,** 315 (1973)
[18] SCOTT, J. M., SUTCLIFFE, B. T.: Theor. chim. Acta **41,** 141 (1976)

T. WELLER
R. LOCHMANN } Karl-Marx Universität 701 Leipzig,

*Acta Chimica Academiae Scientiarum Hungaricae, Tomus 98 (3), pp. 303—313 (1978)*

# AMINOPHTHALAZINONE DERIVATIVES, III

## THE REACTION OF CHLOROPHTHALAZINONE WITH PRIMARY ALKYL-, CYCLOALKYL- AND ARALKYLAMINES STUDY OF THE STERIC EFFECT, I

K. KÖRMENDY

*(Department of Organic Chemistry, Eötvös Loránd University, Budapest)*

Received May 30, 1977

The reactivity between chlorophthalazinone (**1**) and amines is increased in the presence of ethylene glycol because of the formation of reactive transitional glycol adducts (**2** and **4**). The adduct reacts with amines in two ways: the main reaction is aminolysis (**4** → **6**), and the secondary reaction is the conversion **4** → **7** → **8**, leading to the formation of phthalazinone glycol ether. Aminolysis between 130 and 200 °C yields 4-amino-1(2H)-phthalazinone derivates of type **6**, the yield being dependent on the steric structure and basic strength of the amine. The aminolysis of chlorophthalazinone is a reaction particularly sensitive to steric factors. A good yield is to be expected only in the case of amines containing a terminal, sterically free amino group. Two substituents in α position (*e.g.* isopropylamine, 2-aminoheptane) hinder considerably, and three substituents in α position (*e.g. t*-butylamine) may even wholly prevent the reaction, which is then shifted in the secondary direction **4** → **7** → **8**.

According to earlier data in the literature [1—3] chlorophthalazinone (**1**) was found to be resistant to nucleophilic reagents (amines, alkalies). However, as reported in the first part of this series [4], we achieved successful reactions with aminoalcohols, and aminolysis took place even with (diethylamino)—ethylamine in ethylene glycol solution. A hypothetic alcohol adduct (**2**) has been considered as the key substance of the substitution process, because an increased reactivity of the adduct was to be expected on the basis of theoretical considerations [4].

A series of experiments was started to prove experimentally the existence of the reactive alcohol adduct (**2**) and to study the possible generalization of the synthesis. The present communication deals with processes proceeding in ethylene glycol solution between primary alkyl-, cycloalkyl-, aralkylamines and chlorophthalazinone (**1**).

According to our assumption and on the basis of analogies in the literature [5], it is to be expected that the reactive glycol adduct **2** will be formed in an equilibrium reaction in ethylene glycol solution. Though glycol could not be detected by analysis of the chlorophthalazinone precipitating from the solution (which may be due to the high instability of **2**), this does not exclude the existence of the adduct in solution. Similarly to chlorophthalazinone of acid character, the glycol adduct also forms a salt with the amine introduced into the system (**2** → **4**). Salt formation is unquestionably proved, *e.g.*, by

the observation made in the preparation of **6b** showing a rapid initial amine uptake, occurring in the initial stage. This rapid process is reversible (on dilution with water chlorophthalazinone is quantitatively recovered) and cannot be identified with the substitution process, which is slow and irreversible. On the basis of these experiences and considerations, the probability of the conversion **4** → **5** → **6** is suggested (Fig. 1).

Ethylene glycol, besides its role as a reaction catalyst, seems also to be an ideal solvent. Hot ethylene glycol dissolves chlorophthalazinone readily (a solution of about 50% can be prepared at reflux temperature), and owing to its high boiling point, it permits the attaining of the relatively high temperatures (130—200 °C) required for aminolysis without the use of pressure equipment.

Results of aminolysis experiments carried out with 16 primary amines are contained in Table I. It will be noted that the steric structure and the basicity of the amine are the two most important factors determining the yield of the substitution process. For the formation of the aminoalkylated product terminal primary amino groups are the most favourable; alkylamines of this structure give average yields of 60—75%, independently of the chain length. The yield decreases rapidly when the primary amine group is attached to a secondary C(2) atom (two substituents in $\alpha$ position) (compare the yields *e.g.* of **6b** and **6c**, or **6h** and **6i**); a primary amino group attached to a tertiary C-atom (three substituents in $\alpha$ position) results in complete steric shielding against this reaction, thus the formation of alkylaminophthalazinone derivatives becomes virtually impossible. This is the reason why the tertiary butylamino derivative (**6e**) cannot be prepared by the reaction route **1** → **6**.

The effect of the steric factor on the yield can also be clearly seen in the case of cycloalkylamines. While cyclohexylamine gives the derivative **6l** only in a yield of 28—30%, cyclohexylmethylamine having a more favourable steric structure reacts with an excellent yield (**6m**; 85—93%). The poor yield in the aminoalkylation with 2-aminoheptane having almost the same basicity ($pK_b$ 3.52) as that of cyclohexylmethylamine (3.53) proves that the steric factor has the more important role in the conversion **1** → **6**.

In the case of aralkylamines it is more difficult to evaluate the effect of the steric factors because besides the products **6n** and **6p** oily decomposition products are formed in the secondary reaction, their quantity being dependent on the time of heating. In spite of the secondary reaction mentioned, of the three aralkylamino derivatives studied the 2-phenethylamino derivative (**6o**) is formed in the highest yield, while according to expectation, $\alpha$-methylbenzylaminophthalazinone (**6p**) is formed most difficultly.

In addition to reducing the rate of aminolysis, steric shielding of the amine also furthers the reaction of other direction (**4** → **7** → **8**, elimination of

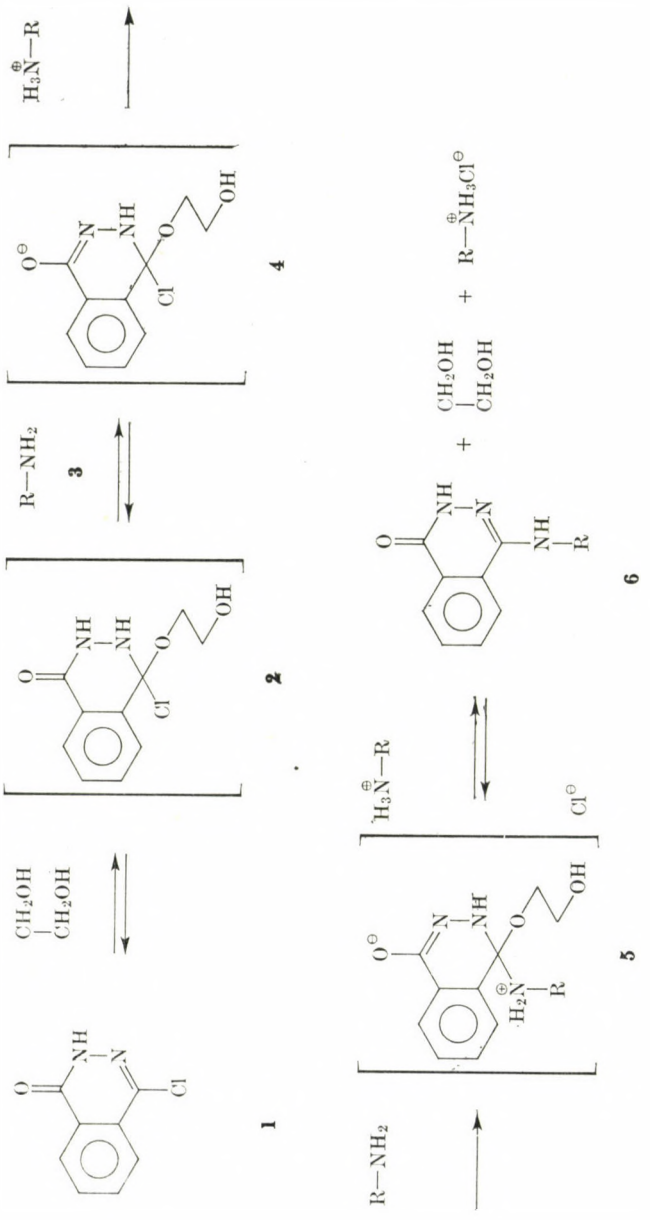


**Table I**

*Effect of the steric structure and basicity of the amine* (**3**) *on the yield of aminoalkylation* (**1** → **6**)

| Product (**6**) | Amine (**3**) | $pK_b$ | Reaction time, hr. | Temperature, °C |
|---|---|---|---|---|
| **a** | $C_2H_5$—$NH_2$ | 3.25 [6] | 30 | 150* |
| **b** | $C_3H_7$—$NH_2$ (n) | 3.41 [6] | 40 | 150—160** |
| **c** | $C_3H_7$—$NH_2$ (i) | 3.37 [6] | 60 | 150—160** |
| **d** | $C_4H_9$—$NH_2$ (n) | 3.39 [6] | 40 | 150—160** |
| **e** | $C_4H_9$—$NH_2$ (tert.) | 3.55 [6] | 60 | 150* |
| **f** | $C_5H_{11}$—$NH_2$ (n) | 3.37 [7] | 20 | 142*** |
| **g** | $C_6H_{13}$—$NH_2$ (n) | 3.36 [7] | 20 | 150*** |
| **h** | $C_7H_{15}$—$NH_2$ (n) | 3.34 [7] | 20 | 156*** |
| **i** | $C_5H_{11}CH(NH_2)CH_3$ | 3.52 [8] | 40<br>60 | 152*** |
| **j** | $C_8H_{17}$—$NH_2$ (n) | 3.35 [7] | 20 | 161*** |
| **k** | $C_{12}H_{25}$—$NH_2$ (n) | 3.37 [7] | 20 | 190*** |
| **l** | $C_6H_{11}$—$NH_2$ | 3.80 [9] | 20<br>40 | 155*** |
| **m** | $C_6H_{11}$—$CH_2$—$NH_2$ | 3.53 [10] | 10<br>20 | 158*** |
| **n** | Ph—$CH_2$—$NH_2$ | 4.70 [6] | 20 | 180*** |
| **o** | Ph—$(CH_2)_2$—$NH_2$ | 4.17 [6] | 10<br>20 | 195*** |
| **p** | Ph—$CH(NH_2)CH_3$ | 4.53 [10] | 40<br>60 | 180*** |

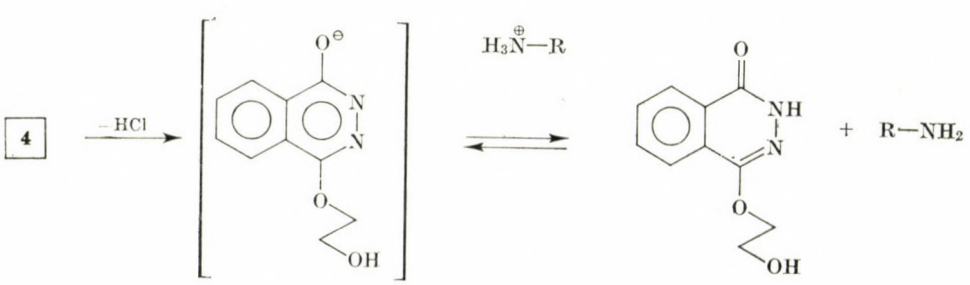
hydrochloric acid), thereby reducing the yield. With increased shielding, the formation of phthalazinone glycol ether (**8**), always accompanying aminoalkylation, gains in prominence, affording at the same time conclusive proof for the doubtless existence of the glycol adduct (**2**) and the adduct salt (**4**).

In the reaction with tertiary butylamine (150 °C, 60 hours) the compound **6e** could not be isolated. As shown by analysis, the crude reaction product consisted of 61.7% glycol ether and 38.3% unchanged chlorophthalazinone (see Table I). Similarly high glycol ether yields were obtained when using other, sterically less shielded amines (2-aminoheptane, cyclohexylamine). However, the high glycol ether yield (50.2%) observed in aminolysis with ethylamine

*Composition of the raw product*, %

| (6) | (1) | (8) | Yield**** of 6 |
|---|---|---|---|
| 45.2 | 4.6 | 50.2 | 37.0 |
| 62.6 | 10.4 | 27.0 | 59.2 |
| 29.3 | 39.0 | 31.7 | 23.8 |
| 79.0 | 5.6 | 15.4 | 60.0 |
| — | 38.3 | 61.7 | — |
| 72.7 | 14.2 | 13.1 | 66.1 |
| 78.0 | 8.6 | 13.4 | 70.3 |
| 79.2 | 8.2 | 12.6 | 74.9 |
| 24.4 | 38.2 | 37.4 | 18.1 |
| 31.5 | 17.1 | 51.4 | 24.3 |
| 73.6 | 5.0 | 21.4 | 57.8 |
| 72.1 | 11.3 | 16.6 | 66.6 |
| 36.0 | 24.3 | 39.7 | 27.8 |
| 45.2 | trace | 54.8 | 29.9 |
| 85.4 | 10.7 | 3.9 | 84.6 |
| 93.9 | trace | 6.1 | 93.3 |
| 52.0 | 37.8 | 10.2 | 36.5 |
| 69.0 | 26.5 | 4.5 | 60.5 |
| 81.4 | 13.5 | 5.1 | 71.4 |
| 44.0 | 32.8 | 23.2 | 34.6 |
| 34.6 | much oil (decomposition product) | | 18.3 |

Note: * in a sealed tube
** with continuous feeding of the amine
*** initial boiling point of the solution containing all the amine
**** for the quantity of the crude product, see Experimental




7 8

cannot result from a steric effect, and must be attributed to the high basicity of ethylamine ($pK_b$ : 3.25).

A halogen-containing substance with sharp melting point (m.p. 219—220 °C), isolated by processing the crude reaction product, is a molecular complex, containing chlorophthalazinone (**1**) and phthalazinone glycol ether (**8**) in equimolar ratio. It can be recrystallized from alcohol or water without decomposition, but crystallization from ethyl acetate causes decomposition into its components.

The most important IR spectral data of the new aminophthalazinone derivatives (**6**) are summarized in Table II.

**Table II**

*Important bands in the IR spectra of the aminophthalazinone derivatives* **6** *(in KBr), $cm^{-1}$*

| | $\nu$NH | $\nu NH_{amide}$ | $\nu CH_2$ | $\nu CH_3$ | $\nu CO_{amide}$ | $\nu$Ar | $\delta$NH | 1,2-di-subst. Ar ring | Mono-subst. Ar ring |
|---|---|---|---|---|---|---|---|---|---|
| **a** | 3375 | 3300—2800 | 2912 | 2960<br>2868 | 1650 | 1588 | 1532 | 782 | — |
| **b** | 3390 | 3300—2800 | 2930 | 2962<br>2875 | 1649 | 1587<br>1471 | 1537<br>1551 | 780 | — |
| **c** | 3388 | 3300—2700 | — | 2972<br>2875 | 1650 | 1580<br>1468 | 1550<br>1532 | 778 | — |
| **d** | 3378 | 3300—2800 | 2930<br>2870 | 2955<br>2870 | 1648 | 1585<br>1475 | 1538 | 782 | — |
| **f** | 3386 | 3300—2800 | 2930<br>2860 | 2960<br>2868 | 1645 | 1584<br>1471 | 1534<br>1550 (sh) | 780 | — |
| **g** | 3380<br>3341 | 3300—3100 | 2929<br>2860 | 2950<br>2864 | 1631 | 1582<br>1479 | 1532<br>1550 (sh) | 780 | — |
| **h** | 3334 | 3280—3130 | 2941<br>2924<br>2851 | 2960<br>2875 | 1642 | 1589<br>1472 | 1538<br>1550 (sh) | 780 | — |
| **i** | 3330 | 3280—3140 | 2931<br>2856 | 2958<br>2870 | 1650 | 1593<br>1474 | 1539<br>1556 (sh) | 782 | — |
| **j** | 3368 | 3325—3130 | 2928<br>2858 | 2952<br>2870 | 1642 | 1590<br>1480 | 1540<br>1552 (sh) | 784 | — |
| **k** | 3340 | 3300—3150 | 2922<br>2851 | 2952<br>2868 | 1642 | 1593<br>1474 | 1538 | 780 | — |
| **l** | 3360 | 3300—2800 | 2928<br>2854 | — | 1645 | 1584<br>1472 | 1530 | 778 | — |
| **m** | 3340 | 3285—3140 | 2925<br>2850 | — | 1645 | 1594<br>1480 | 1552<br>1540 (sh) | 782 | — |
| **n** | * | 3350—2700 | 2925<br>2855 | — | 1642 | 1597<br>1499 | 1539<br>1550 (sh) | 782 | 695<br>732 |
| **o** | 3358 | 3300—2750 | 2915 | — | 1660 | 1591<br>1495 | 1538 | 780 | 682<br>731 |
| **p** | 3308 | 3280—3140 | — | 2970<br>2870 | 1647 | 1596<br>1499 | 1540 | 768 | 708<br>750 |

* merges with the $\nu NH_{amide}$ band

## Experimental

M.p.'s were determined with a Boetius micro melting point apparatus. The IR spectra were recorded in KBr pills with an UR-10 (Zeiss, Jena) spectrophotometer.

### Methods for the separation of the reaction mixture obtained in the aminolysis of chlorophthalazinone

The product obtained by aminolysis contained, besides **6**, more or less unchanged chlorophthalazinone (**1**) and phthalazinone glycol ether (**8**). The quantity of **1** was estimated on the basis of chlorine determination. The three-component mixture was separated on the basis of the different solubilities of the components by methods *A* and *B*. (Solubility in water: **8** > **1** > **6**; in alcohol: **6** > **1** > **8**. The results of separation and the compositions of the raw products are listed in Table I.

**Method A** (Isolation of **6a**, **6c** and **6i**.) The raw product was boiled with ethanol, using 10 ml of the solvent per g. Next day the crystals (**1** and **8**) were filtered off and washed with ethanol. The combined solutions in alcohol were evaporated to dryness on a rotating evaporator, the solid evaporation residue was suspended in a small amount of a 2 : 1 mixture of cold water and ethanol and filtered.

The crude aminophthalazinone derivatives were purified by crystallization from a suitable solvent.

**Method B** (Isolation of the aminophthalazinone derivatives not mentioned above.) An aqueous suspension of the raw product (taking 100 ml of water per g) was boiled and filtered hot with suction. The extraction with hot water was repeated with fresh water, until the sparingly soluble **6**, collected on the filter, gave negative Beilstein test.

### 4-Ethylamino-1(2H)-phthalazinone (6a)

A mixture of 1.80 g (10 mmoles) chlorophthalazinone and 50 ml of anhydrous ethylene glycol, in which previously 4.5 g (0.1 mole) of anhydrous ethylamine had been dissolved, was heated in a sealed tube for 30 hrs at 150 °C. The glycol solution was then distilled at a pressure of 0.1 torr, the solidifying residue suspended in water, slightly acidified with dilute hydrochloric acid, and filtered to give 2.01 g of the crude product. Isolation was effected by Method *A*. Yield: 0.70 g. (37%) The compound is readily soluble in ethanol; colourless crystals, m.p. 222—224 °C (from aqueous ethanol).

$C_{10}H_{11}N_3O$ (189.2) Calcd. N 22.2. Found N 22.4%.

For the IR spectrum see Table II.

### 4-Propylamino-1(2H)-phthalazinone (6b)

In a flask fitted with an efficient (Lansiedel) condenser, dropping funnel and a thermometer reaching down into the liquid, a mixture of 9.00 g (0.05 mole) chlorophthalazinone and 40 ml of anhydrous ethylene glycol was heated to 160 °C, then the slow introduction of *n*-propylamine (8.86 g; 12.32 ml; 0.15 mole) was begun.* After refluxing for 40 hrs, the volume of the solution was made up with water to 750 ml, and after a brief period of standing the solid product (9.60 g) was filtered off.

Isolation: Method *B*. Yield: 6.01 g (59.2%). Colourless prisms from ethyl acetate; m.p. 223—224 °C.

$C_{11}H_{13}N_3O$ (203.2). Calcd. N 20.7. Found N 20.7, 20.8%.

For the IR spectrum see Table II.

* The first portion of about 4 ml (0.05 mole) could be added, owing to salt formation, during 10—15 min. to the suspension. After transitory dissolution the mixture partially crystallized. Consumption of amine was indicated by the slowing down of reflux and by an increase of the internal temperature. The rest of the amine was added at a rate (30—35 hrs), so that at a mild reflux the internal temperature remained between 150 and 160 °C. Dissolution occurred again after boiling for about 25 hrs.

### 4-Isopropylamino-1(2H)-phthalazinone (6c)

In the apparatus used for the preparation of **6b**, isopropylamine (8.86 g; 0.15 mole) was added to a suspension of 9.00 g (0.05 mole) chlorophthalazinone in 40 ml of anhydrous ethylene glycol at 160 °C, ensuring that the internal temperature remained between 150 and 160 °C. After 60 hrs of boiling, the volume of the solution obtained was made up with water to 750 ml, and the precipitated solid product was filtered off (8.36 g). Isolation: Method *A*. Yield: 2.42 g (23.8%). Colourless crystals from ethanol, m.p. 153—155 °C.

$C_{11}H_{13}N_3O$ (203.2). Calcd. N 20.7. Found N 20.8%.

For the IR spectrum see Table II.

### 4-Butylamino-1(2H)-phthalazinone (6d)

Using the procedure described in the preparation of the propylamino derivative (**6b**), 9.62 g of crude **6d** was obtained from chlorophthalazinone (9.00 g; 0.05 mole) and *n*-butylamine (10.96 g; 0.15 mole) in 40 ml of anhydrous ethylene glycol solution at 150—160 °C in 40 hrs. Isolation: Method *B*. Yield: 7.60 g (60.0%). Colourless, well developed prisms from ethyl acetate, colourless plates from water; m.p. 222—223 °C.

$C_{12}H_{15}N_3O$ (217.3). Calcd. N 19.3. Found N 19.2%.

For the IR spectrum see Table II.

### 4-Amylamino-1(2H)-phthalazinone (6f)

In a flask equipped with a reflux condenser, chlorophthalazinone (9.00 g; 0.05 mole), *n*-amylamine (8.70 g; 0.1 mole) and 40 ml of anhydrous ethylene glycol were gently boiled for 20 hrs. The reaction mixture was diluted with water to 750 ml and the crude product (10.50 g) was filtered off. The pure substance was isolated by Method *B*. Yield: 7.64 g (66.1%). Colourless cubes from aqueous ethanol m.p. 159—160 °C.

$C_{13}H_{17}N_3O$ (231.3). Calcd. N 18.2. Found N 18.0, 18.2%.

For the IR spectrum see Table II.

### 4-Hexylamino-1(2H)-phthalazinone (6g)

A mixture of chlorophthalazinone (9.0 g; 0.05 mole), *n*-hexylamine (10.1 g; 0.1 mole) and anhydrous ethylene glycol (40 ml) was refluxed for 20 hrs, and the solution was then diluted to 750 ml. From the crude product (11g) which precipitated, 8.62 g (70.3%) of pure **6g** could be isolated by Method *B*. Colourless needles from ethanol, m.p. 162—164 °C.

$C_{14}H_{19}N_3O$ (245.3). Calcd. N 17.1. Found N 17.0%.

For the IR spectrum see Table II.

### 4-Heptylamino-1(2H)-phthalazinone (6h)

A solution of chlorophthalazinone (9.00 g; 0.05 mole) in ethylene glycol (40 ml) was refluxed with *n*-heptylamine (11.5 g; 0.1 mole) for 20 hrs and the mixture was then diluted with water to 750 ml to obtain 12.24 g of the crude product. Isolation was effected by Method *B*. Yield: 9.69 g (74.9%). Colourless plates from 1 : 1 ethanol–water mixture; m.p. 127—128 °C.

$C_{15}H_{21}N_3O$ (259.4). Calcd. N 16.2. Found N 16.3%.

For the IR spectrum see Table II.

### 4-[(1—Methyl)-hexylamino]-1(2H)-phthalazinone (6i)

A mixture of chlorophthalazinone (9.00 g; 0.05 mole), 2-aminoheptane (11.50 g; 0.1 mole) and anhydrous ethylene glycol (40 ml) was refluxed for 40 and 60 hrs, respectively. The darkening solution was diluted with water 750 ml, and the slowly crystallizing, but still somewhat oily product was filtered off and washed with a cold mixture of ethanol and water (1 : 2, 20 ml) to obtain 10.24 g (40 hrs) and 9.33 g (60 hrs), respectively, of the crude **6i**. Isolation:

Method *A*. Yield: 18.1% and 24.3%, respectively. Colourless plates from dioxane, colourless needless from a chloroform–ether–petroleum ether mixture; m.p. 132—133 °C.

$C_{15}H_{21}N_3O$ (259.4). Calcd. N 16.2. Found 16.3, 16.4%.

For the IR spectrum see Table II.

### 4-Octylamino-1(2H)-phthalazinone (6j)

A mixture of chlorophthalazinone (9.00 g; 0.05 mole) and *n*-octylamine (12.9 g; 0.1 mole), suspended in 40 ml of anhydrous ethylene glycol, was refluxed for 20 hrs. The reaction mixture was diluted with water to 750 ml, and filtered after brief standing to give 10.72 g of the crude product (after washing with 20 ml of a 1 : 2 ethanol–water mixture). Isolation was effected by Method *B*. Yield: 7.9 g (57.8%). Colourless plates from ethyl acetate; m.p. 150—152 °C.

$C_{16}H_{23}N_3O$ (273.4). Calcd N 15.4. Found N 15.5%.

For the IR spectrum see Table II.

### 4-Dodecylamino-1(2H)-phthalazinone (6k)

A mixture of chlorophthalazinone (4.50 g; 25 mmoles) and dodecylamine (11.1 g; 60 mmoles) was refluxed for 20 hrs in 20 ml of anhydrous ethylene glycol. After dilution with water to 300 ml, the product, difficult to filter, was centrifuged and washed with 50% cold ethanol to obtain 7.60 g of the crude product. Crystallization from ethyl acetate gave colourless large plates (5.48 g; 66.6%), m.p. 122—124 °C.

$C_{20}H_{31}N_3O$ (329.5). Calcd. N 12.8. Found N 13.0, 12.9%.

For the IR spectrum see Table II.

### 4-Cyclohexylamino-1(2H)-phthalazinone (6l)

A mixture of chlorophthalazinone (9.00 g; 0.05 mole) and cyclohexylamine (11.88 g; 0.12 mole) was refluxed in 40 ml of anhydrous ethylene glycol for 20 and 40 hrs, respectively. After cooling, the solution was diluted with water (750 ml), and the rapidly solidifying product was filtered off (9.39—9.39 g). Isolation was achieved by Method *B*. to yield 3.38 g (27.8%) and 3.64 g (29.9%), respectively, of colourless needles; m.p.: 216—218 °C (from dioxan).

$C_{14}H_{17}N_3O$ (243.3). Calcd. N 17.3. Found N 17.4, 17.4%.

For the IR spectrum see Table II.

### 4-Cyclohexylmethylamino-1(2H)-phthalazinone (6m)

Chlorophthalazinone (4.50 g; 25 mmoles) and cyclohexane methylamine (5.66 g; 50 mmoles) were refluxed in anhydrous ethylene glycol (20 ml) for 10 and 20 hrs, respectively. On dilution with water (300 ml) a slowly solidifying gum separated. The crude product weighed 6.36 g (10 hrs) and 6.38 g (20 hrs), respectively. Isolation by Method *B* gave 5.43 g (84.6%) and 5.99 g (93.3%), respectively, of colourless prisms, m.p. 194—195 °C from ethanol or from chloroform—ether mixture.

$C_{15}H_{19}N_3O$ (257.3). Calcd. N 16.3. Found N 16.4%.

For the IR spectrum see Table II.

### 4-Benzylamino-1(2H)-phthalazinone (6n)

Chlorophthalazinone (9.00 g; 0.05 mole) and benzylamine (10.7 g; 0.1 mole) were refluxed in anhydrous ethylene glycol (40 ml) for 20 hrs to obtain 8.83 g of the crude product (after washing with 20 ml of 50% aqueous ethanol). Isolation by Method *B* yielded 4.59 g (36.5%) of colourless prisms, m.p. 188—189 °C (from ethanol).

$C_{15}H_{13}N_3O$ (251.3). Calcd. N 16.7. Found N 16.7%.

For the IR spectrum see Table II.

### 4-(2-Phenethylamino)-1(2H)-phthalazinone (6o)

A mixture of chlorophthalazinone (9.00 g; 0.05 mole), β-phenylethylamine (12.1 g; 0.1 mole) and anhydrous ethylene glycol (40 ml) was refluxed for 10 and 20 hrs, respectively. On aqueous dilution (750 ml) a rapidly solidifying oil separated. The crude product weighed 11.62 g (10 hrs) and 11.63 g (20 hrs). Isolation by Method *B* gave 8.02 g (60.5%) and 9.47 g (71.4%), respectively, of large colourless prisms, m.p. 210—212 °C (from chloroform–petroleum ether).

$C_{16}H_{15}N_3O$ (265.3). Calcd. N 15.8. Found N 15.9%.

For the IR spectrum see Table II.

### 4-(α-Methylbenzylamino)-1(2H)-phthalazinone (6p)

A mixture of chlorophthalazinone (4.5 g; 25 mmoles), *dl*-α-methylbenzylamine (6.05 g; 50 mmoles) and anhydrous ethylene glycol (20 ml) was refluxed for 40 and 60 hrs, respectively. The rapidly darkening solution was diluted with 300 ml of water. The sticly crude product was triturated in a mortar with an adequate quantity of cold, 50% aqueous ethanol and filtered. The crude product weighed 5.21 g (40 hrs) and 3.51 g (60 hrs), respectively. Isolation by Method *B* gave 2.29 g (34.6%) and 1.21 g (18.3%) of colourless plates, m.p. 242—243.5 °C (from ethanol).

$C_{16}H_{15}N_3O$ (265.3). Calcd. N 15.8. Found N 15.7%.

For the IR spectrum see Table II.

### 1(2H)-phthalazonyl-4-(2-hydroxyethyl) ether (8) (Phthalazinone glycol ether)

The by-product (a mixture of **1** and **8**) obtained in the isolation (Methods *A* and *B*) of the aminophthalazinone derivatives was repeatedly recrystallized from ethyl acetate until it became free of halogen. Colourless needles from ethyl acetate or water; m.p. 240—242 °C.

$C_{10}H_{10}N_2O_3$ (206.2). Calcd. C 58.3, H 4.9. N 13.6 Found C 58.1, H 4.8, N 13.7%.

IR (in KBr): $\nu$OH 3410, $\nu NH_{amide}$ 3300—2800, $\nu CO_{amide}$ 1660, $\nu$Ar 1596, 1493. $\nu C—O_{ether,\ alcohol}$ 1092, 1078, 1,2-disubst. Ar 776 $cm^{-1}$.

### 1(2H)-phthalazonyl-4-(2-acetoxyethyl) ether

Phthalazinone glycol ether (**8**; 0.18 g) was suspended in dry pyridine (10 ml) containing acetic anhydride (0.8 ml); the substance slowly dissolved at room temperature. After dilution with water, the pyridine was distilled off in vacuum. The colourless product was filtered off (0.17 g). It was very soluble in ethanol. Recrystallization from aqueous ethanol gave colourless prisms, m.p. 150—152 °C. The substance did not change when refluxed for a considerable period in ethanol solution.

$C_{12}H_{12}N_2O_4$ (248.3). Calcd. N 11.3. Found N 11.4%.

IR (in KBr): $\nu NH_{amide}$ 3200—2800, $\nu CO_{ester}$ 1725, $\nu CO_{amide}$ 1660, $\nu$Ar 1622, 1598, 1493, $\nu C—C—O_{ester}$ 1252, 1060, $\nu C—O_{ether}$ 1102, 1,2-disubst. Ar 770 $cm^{-1}$.

### Molecular complex of chlorophthalazinone and phthalazinone glycol ether

(a) The by-product obtained in the isolation methods *A* and *B* (a mixture of **1** and **8**) was repeatedly recrystallized from ethanol, until the melting point remained unchanged at 219—220 °C.

(b) A mixture of chlorophthalazinone (1.81 g; 10 mmoles) and phthalazinone glycol ether (**8**; 2.06 g; 10 mmoles) was dissolved in hot ethanol. Colourless needles separated from the solution (3.60 g; 93%), m.p. 219—220 °C.

The molecular complex could be crystallized from ethanol and water without decomposition. On repeated crystallization from ethyl acetate it was decomposed into its components: from the solution phthalazinone glycol ether precipitated, while chlorophthalazinone remained in the mother liquor.

$C_{18}H_{15}ClN_4O_4$ (386.8). Calcd. Cl 9.2. Found Cl 9.0, 9.1%.

IR (in KBr): The spectrum had the bands characteristic of chlorophthalazinone and phthalazinone glycol ether.

*

Dr. Ferenc RUFF helped in the recording and evaluation of the infrared spectra. The elementary analyses were made in the Microanalytical Laboratory of the Institute (Head: Dr. H. MEDZIHRADSZKY). Starting materials were made available by BRISTOL Laboratories (USA, Syracuse, N. Y.). Our thanks are expressed for these kind cooperations.

## REFERENCES

[1] HAWORTH, R. D., ROBINSON, S.: J. Chem. Soc. **1948,** 777
[2] FLITSCH, W., PETERS, H.: Chem. Ber. **102,** 1304 (1969)
[3] HILL, J. H. M., EHRLICH, J. H.: J. Org. Chem. **36,** 3248 (1971)
[4] KÖRMENDY, K.: Acta Chim. (Budapest) **88,** 129 (1976)
[5] ALBERT, A.: Angew. Chem. **79,** 913 (1967)
[6] LANGE, N. A.: Handbook of Chemistry. (6th Ed.). Handbook Publishers Inc. Sundusky, Ohio, 1946
[7] HOERR, C. W., MCCORKLE, M. R., RALSTON, A. W.: J. Am. Chem. Soc. **65,** 328 (1943)
[8] CHATTEN, L. G., HARRIS, L. E.: Anal. Chem. **34,** 1495 (1962)
[9] WAKSMUNDZKI, A.: Roczniki Chem. **18,** 865, 868 (1938)
[10] VEXLEARSCHI, G., RUMPF, P.: Compt. rend. **236,** 939 (1953)

KÖRMENDY Károly H-1088 Budapest, Múzeum krt. 4/b.

*Acta Chimica Academiae Scientiarum Hungaricae, Tomus 98 (3), pp. 315—319 (1978)*

# INTERNAL α-AMIDOALKYLATION LEADING TO 1,4-DIHYDRO-3(2*H*)-ISOQUINOLINONES

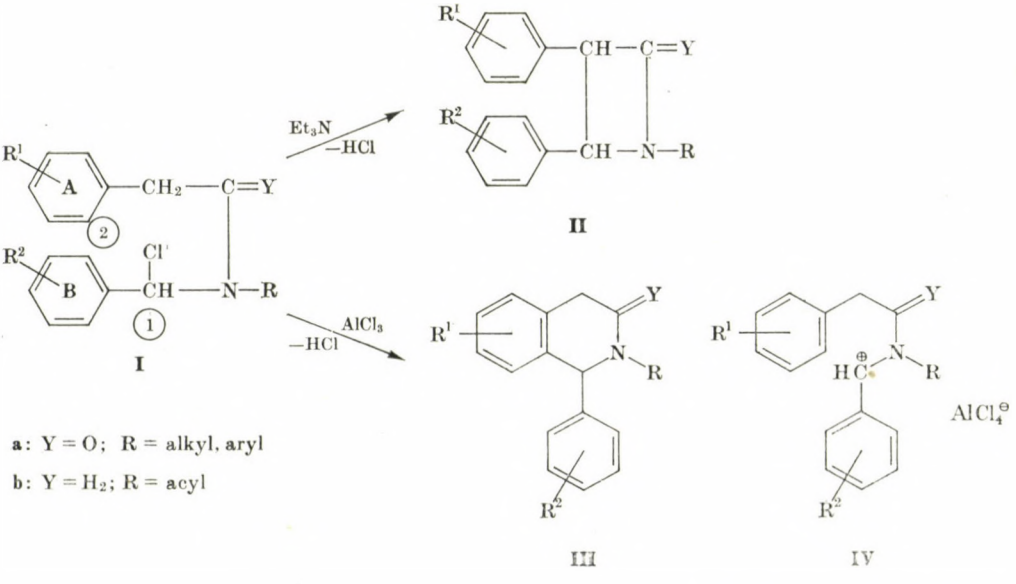
N. M. MOLLOV* and A. P. VENKOV

*(University of Plovdiv, Plovdiv, Bulgaria)*

Received July 26, 1977

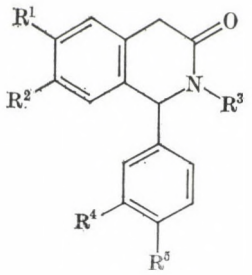
The mechanism and scope of the synthetic use of internal α-amidoalkylation has been investigated. It is shown that the presence of electron-withdrawing substituents in ring B of **Ia** increases the yields of **III**, while electron-releasing groups lower them. Substituents in ring A improve the yields when they increase the electron density in the ring or on the C-2 atom. These results support the assumption that the reaction is an electrophilic substitution passing through an ionic intermediate of the type **IV**.

The adducts of Schiff bases and acyl halides **Ia** may be used for cyclization to 2-azetidinones (**IIa**) and 1,4-dihydro-3(2*H*)-isoquinolinones (**IIIa**), whereas the adducts **Ib** can be readily converted into 1-phenyl-2-acyl-1,2,3,4-tetrahydroisoquinolines (**IIIb**). The reactions leading to **IIIa** and **IIIb** are favourably influenced by Lewis acids [1, 2] and those to **IIa** are catalyzed by basic compounds [3].



*Acta Chim. Acad. Sci. Hung. 98, 1978*

**Table I**




| Product | $R^1$ | $R^2$ | $R^3$ | $R^4$ | $R^5$ | Yield, % | M.p., °C | NMR ($\delta$) | | IR ($cm^{-1}$ $\nu$CO |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | 1—CH | $4-CH_2$ | |
| **1** | H | H | $C_6H_5$ | H | $NO_2$ | 68 | 55—7 (ether) | 6.05 | 3.85 | 1680 |
| **2** | H | H | $CH_3$ | H | $NO_2$ | 52 | 176—7 (ethanol) | 6.15 | 3.71 | 1670 |
| **3** | H | H | $C_6H_5$ | H | Br | 70 | 132—4 (hexane) | 5.87 | 3.84 | 1660 |
| **4** | H | H | $C_6H_5$ | H | Cl | 66 | 118—20 (hexane) | 6.06 | 3.95 | 1660 |
| **5** | H | H | $CH_3$ | H | Cl | 59 | 122—3 (ethanol) | 5.50 | 3.76 | 1660 |
| **6** | H | H | $C_6H_5$ | H | F | 47 | 121—2 (ethanol) | 5.96 | 3.86 | 1670 |
| **7** | H | H | $C_6H_5$ | H | $CH_3$ | 34 | 47—8 (ether) | 5.85 | 3.82 | 1660 |
| **8** | H | H | $C_6H_5$ | $OCH_3$ | $OCH_3$ | 30 | 61—2 (ether–hexane) | 6.00 | 3.95 | 1660 |
| **9** | $CH_3O$ | H | $C_6H_5$ | H | $NO_2$ | 71 | 78—80 (ether) | 5.94 | 3.80 | 1660 |

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| **10** | H | $CH_3O$ | $C_6H_5$ | H | $NO_2$ | 51 | 70—2 (ether–hexane) | 5.94 | 3.82 | 1660 |
| **11** | $CH_3O$ | $CH_3O$ | $C_6H_5$ | H | $NO_2$ | 76 | 183—4 (ether–hexane) | 6.02 | 3.95 | 1680 |
| **12** | $CH_3O$ | $CH_3O$ | $CH_3$ | H | $NO_2$ | 71 | 203—4 (ether–hexane) | 5.98 | 3.90 | 1680 |
| **13** | H | F | $C_6H_5$ | H | $NO_2$ | 55 | 73—5 (ethanol) | 5.95 | 3.80 | 1660 |
| **14** | Cl | H | $C_6H_5$ | H | $NO_2$ | 74 | 175—6 (ethanol) | 5.92 | 3.78 | 1660 |
| **15** | $CH_3O$ | $CH_3O$ | $C_6H_5$ | H | Cl | 76 | 158—60 (methanol) | 5.80 | 3.90 | 1660 |
| **16** | $CH_3O$ | $CH_3O$ | $CH_3$ | H | Cl | 64 | 83—5 (ether–hexane) | 5.35 | 3.67 | 1660 |
| **17** | $CH_3O$ | $CH_3O$ | $C_6H_5$ | $OCH_3$ | $OCH_3$ | 68 | 140—1 (ether–hexane) | 5.75 | 3.75 | 1650 |

In the present work we report the reactivity of some new compounds **Ia**, used as starting materials for the synthesis of **IIIa**. The examples have been selected such as to give more information about the scope of the synthetic use of the reaction as well as about its mechanism.

The starting materials for adducts **Ia** were phenyl-,3,4-dimethoxyphenyl- or 4-nitrophenylacetyl chloride and the azomethines obtained from different aromatic aldehydes and aniline or methylamine. They were prepared in ethylene chloride medium in which compounds **Ia** precipitated. When anhydrous aluminium chloride was added to the reaction mixture, an exothermic reaction took place, whose completion required 8 h stirring at room temperature or 3 h heating at 80 °C. The reaction mixture was then treated with dilute hydrochloric acid and extracted with chloroform. Purification of the compounds followed by recrystallization, or by column chromatography on silica gel. The yields, melting points and some spectral data of the compounds synthesized by this procedure are shown in Table I. Elemental analyses are given in Table II.

The results in Table I show that the presence of electron-withdrawing groups in ring B of **Ia** increases the yields, whereas electron-releasing groups lower them. Substituents in aromatic ring A improve the yields when they increase the electron density in the ring or on the C-2 atom. Since the reaction proceeds in homogeneous medium, the yields can be used to draw some conclusions on the basis of the Hammett equation $lg \frac{k}{k_0} = \sigma\varrho$. The reactivity of the C-1 atom is in good agreement with a positive $\varrho$ value, and that of the C-2 atom with a negative one. The results of our experiments support the assumption that the reaction is an electrophilic substitution passing through an ionic intermediate of type **IV**. In this respect it is worth pointing out Examples 3—6 (*cf.* Table I), which illustrate the influence on the yields of the fluorine, chlorine and bromine atoms in ring B. Fluorine reduces the yield considerably due to its higher resonance interaction with the carbonium ion center in **IV** [4].

## Experimental

M.p.'s were determined on a Kofler hot-stage and are uncorrected. The IR spectra were recorded with a Perkin-Elmer 370 spectrometer, using chloroform or nujol. NMR spectra were obtained with a Jeol JNM-60-S or Tesla BS-487-C spectrometer in $CDCl_3$ or DMSO, using TMS as internal standard.

### 1-(4-Nitrophenyl)-2-Phenyl-1,4-dihydro-3(2H)-isoquinolinone (1)

In a 20-ml round-bottomed two-neck flask 0.465 g (3 mmoles) of phenylacetyl chloride, 0.680 g (3 mmoles) of 4-nitrobenzylideneaniline and 5 ml of anhydrous ethylene chloride were mixed. The flask was connected with a reflux condenser fitted with a calcium chloride tube and during stirring at room temperature, 0.400 g (3 mmoles) of anhydrous aluminium chloride

**Table II**

| Product | Formula | Mol. wt. | Calcd./Found | | |
|---|---|---|---|---|---|
| | | | C% | H% | N% |
| **1** | $C_{21}H_{16}N_2O_3$ | 344.4 | 73.24 | 4.68 | 8.13 |
| | | | 73.56 | 4.19 | 7.61 |
| **2** | $C_{16}H_{14}N_2O_3$ | 282.3 | 68.08 | 5.00 | 9.92 |
| | | | 67.82 | 5.43 | 9.80 |
| **3** | $C_{21}H_{16}BrNO$ | 378.3 | 65.59 | 4.40 | 3.82 |
| | | | 65.20 | 4.26 | 3.68 |
| 4 | $C_{21}H_{16}ClNO$ | 333.8 | 75.56 | 4.83 | 4.20 |
| | | | 75.67 | 5.18 | 4.43 |
| **5** | $C_{16}H_{14}ClNO$ | 272.7 | 70.46 | 5.54 | 5.13 |
| | | | 70.09 | 5.15 | 5.41 |
| **6** | $C_{21}H_{16}FNO$ | 317.4 | 79.16 | 5.07 | 4.41 |
| | | | 78.90 | 4.88 | 4.15 |
| **7** | $C_{22}H_{19}NO$ | 313.4 | 84.31 | 6.11 | 4.47 |
| | | | 84.01 | 5.98 | 4.20 |
| **8** | $C_{23}H_{21}NO_3$ | 359.4 | 76.86 | 5.89 | 3.90 |
| | | | 77.06 | 5.88 | 3.67 |
| **9** | $C_{22}H_{18}N_2O_4$ | 374.4 | 70.58 | 4.85 | 7.48 |
| | | | 70.21 | 4.93 | 7.02 |
| 10 | $C_{22}H_{18}N_2O_4$ | 374.4 | 70.58 | 4.85 | 7.48 |
| | | | 70.28 | 4.39 | 7.14 |
| **11** | $C_{23}H_{20}N_2O_5$ | 404.4 | 68.31 | 4.98 | 6.93 |
| | | | 67.98 | 5.00 | 6.67 |
| **12** | $C_{18}H_{18}N_2O_5$ | 342.4 | 63.15 | 5.30 | 8.18 |
| | | | 63.49 | 5.12 | 7.92 |
| **13** | $C_{21}H_{15}FN_2O_3$ | 362.4 | 69.61 | 4.17 | 7.73 |
| | | | 69.90 | 4.46 | 7.33 |
| **14** | $C_{21}H_{15}ClN_2O_3$ | 378.8 | 66.59 | 3.99 | 7.39 |
| | | | 66.70 | 4.20 | 7.69 |
| **15** | $C_{23}H_{19}ClN_2O_3$ | 353.9 | 70.14 | 5.15 | 3.56 |
| | | | 69.61 | 4.90 | 3.83 |
| **16** | $C_{18}H_{19}ClNO_3$ | 332.8 | 64.96 | 5.12 | 3.56 |
| | | | 65.30 | 5.43 | 3.96 |
| **17** | $C_{25}H_{25}NO_5$ | 419.8 | 71.58 | 6.01 | 3.34 |
| | | | 71.80 | 6.01 | 3.27 |

was added in portions. The reaction mixture was heated 3 h at 80 °C, cooled to room temperature and treated with dilute (1 : 4) hydrochloric acid. The mixture was extracted with chloroform, the extract dried over anhydrous sodium sulfate and the solvent evaporated. A yellowish oil was obtained, which was purified by column chromatography on silica gel 60 (Merck). Petroleum ether and ether were used as eluents.

In several cases the rough products were purified only by recrystallization.

## REFERENCES

[1] MOLLOV, N., VENKOV, A.: Compt. rend. Acad. bulg. sci. **23,** 1055 (1975)
[2] MOLLOV, N., VENKOV, A.: Synthesis, **62,** (1968)
[3] BOSE, A., SPIEGELMAN, G., MANHAS, M.: Tetrahedron Lett. **34,** 3167 (1971)
[4] SWAIN, C., LUPTON, E.: J. Am. Chem. Soc. **90,** 4328 (1968)

Nikola MOLLOV
Atanas VELKOV
Bulgaria 4000, Plovdiv, ul. Zar Asen 24.

*Acta Chimica Academiae Scientiarum Hungaricae, Tomus 98 (3), pp. 321—326 (1978)*

# SYNTHESIS OF 2-AMINO-3-THIO-2-DEOXY-D-MANNOPYRANOSE PENTAACETATE

P. HERCZEGH and R. BOGNÁR

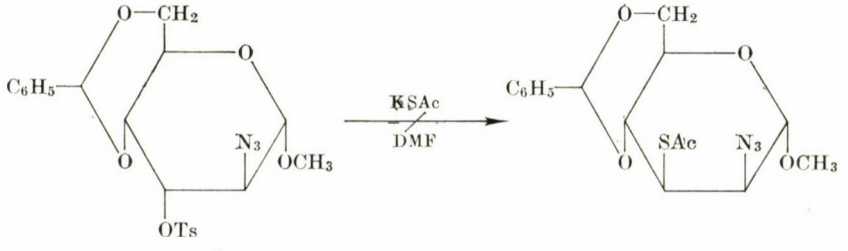
*(Research Group for Chemistry of Antibiotics, Hungarian Academy of Sciences, Debrecen)*

Received February 1, 1977
In revised form, September 20, 1977

Starting with methyl 2-amino-2-deoxy-3-O-*p*-toluenesulfonyl-4,6-O-benzylidene-α-D-altropyranoside (**2**), the *cis*-aminothiol **9** was prepared. Intramolecular nucleophilic substitution of the thioacetamido derivative **5** — obtained from **2** with a new thiacetylation method — resulted in thiazoline **7**, which, on hydrolysis and subsequent acetylation gave the title compound.

In a search for amino sugar derivatives with biological activity, it was necessary to prepare 3-thio-D-mannosamine. A derivative of this compound has been synthesized by BAKER and HOLLAR [1], starting from methyl 2-amino-2-deoxy-4,6-O-benzylidene-α-D-altropyranoside. The preparation of some intermediates in this route was, however, somewhat inconvenient, and yields were not always reproducible. We now report a new convenient method for the preparation of 2-amino-3-thio-2-deoxy-D-mannopyranose pentaacetate.

It has been reported [2] that in the nucleophilic substitution reactions of 2-acylamido-3-O-methanesulfonylaltroside derivatives containing *trans-axial* $C_2$-acetamido- and $C_3$-O-methanesulfonyl groups, a neigbouring group participation strongly predominates, so the products are usually oxazoline or aziridine derivatives. During the azidolysis of the azide derivative **1**, GUTHRIE and MURPHY [3] did not observe such neighbouring group participation; thus we tried the reaction of **1** with potassium thiolacetate. A complex reaction mixture containing numerous components was obtained, therefore this method was not investigated further.



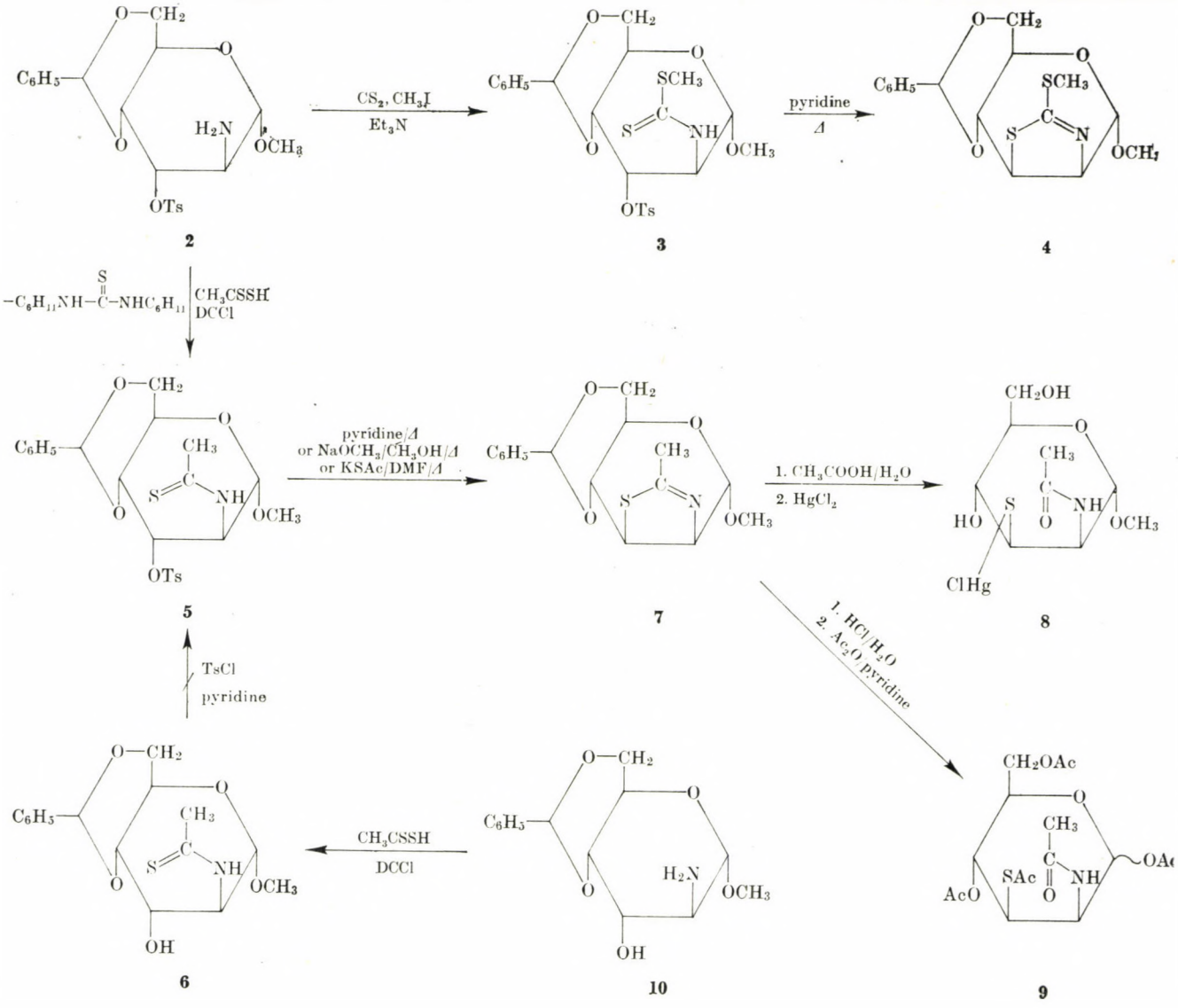

**1**

The application of the method of GOODMAN and CHRISTENSEN [4] or MEYER zu RECKENDORF and BONNER [5], elaborated for the synthesis of *cis*-aminothiols *via* dithiocarbamate derivatives, seemed to be more promising. Thus the reaction of the amino derivative **2** [6] with carbon disulfide and methyl iodide gave methyl 4,6-O-benzylidene-2-methylthiocarbonylamino-3-O-*p*-toluenesulfonyl-2-deoxy-α-D-altropyranoside (**3**) which, on boiling in pyridine, was transformed into 4',6'-O-benzylidene-1'-O-methyl-2-methylthio-α-D-mannopyrano-[2',3' : 4,5]-2-thiazoline (**4**). However, attempted reduction of **4** with aluminium amalgam failed to give a homogeneous product.

It is known [4] that S-methylmercapto thiazolines do not yield aminothiols on acid hydrolysis; therefore it was necessary to synthesize another thiazoline derivative which may be hydrolyzed to the required aminothiol. It has been reported [7] that the hydrolysis of 2-methyl-$\Delta^2$-thiazoline gives *cis*-aminothiol in a good yield. For the preparation of 2-methylthiazoline derivatives of monosaccharides, the corresponding 2-thioacetamido derivatives are first required. Such derivatives of monosaccharides have not yet been reported, probably owing to the instability of the necessary thioacetylating agents, thioacetyl chloride or trithioacetic anhydride.

We succeeded in preparing the thioacetamido derivative **5** in a good yield from **2** and dithioacetic acid in the presence of N,N'-dicyclohexylcarbodiimide. Similarly, thioacetylation of methyl 2-amino-4,6-O-benzylidene-2-deoxy-α-D-altropyranoside (**10**) gave **6**, which was made to react with *p*-toluenesulfonyl chloride. According to TLC examinations, neither the expected **5** nor the thiazoline **7** were formed in this reaction, but some unknown products — possibly arising from the decomposition of the S-tosylated thioamide — could be detected in the dark reaction mixture. This reaction was not further investigated since it had no bearing on our synthetic aim. The thiazoline **7** was finally obtained by boiling **5** in pyridine or by treating it with hot sodium methoxide or potassium thiolacetate in N,N'-dimethylformamide. Treatment of a hot solution of thioamide tosylates of the *trans-diaxial* type with strong bases usually leads to the formation of acyl aziridine derivatives [8] due to the participation of the thioamide group. In our case the electron-donating effect of the methyl group of the thioacetyl substituent may facilitate the formation of the enthiolate ion and the participation of the sulfur atom may become predominant.

Hydrolysis of the thiazoline **7** with aqueous acetic acid gave methyl 2-acetamido-3-thio-2,3-dideoxy-α-D-mannopyranoside, which was isolated in the form of its chloromercurithio derivative **8**. Hydrolysis of **7** with 6 *N* hydrochloric acid, followed by acetylation, resulted in the 3-thio-D-mannosamine pentaacetate **9**. Mass spectrometry of **9** showed a molecular ion peak, *m/e* 405 and an M-$CH_2CO$ fragment, the molecular formula of which was determined to give the expected value of $C_{14}H_{21}NO_8S$.


CS2, CH3I
Et3N
pyridine
Δ
CH3CSSH
DCCl
pyridine/Δ
or NaOCH3/CH3OH/Δ
or KSAc/DMF/Δ
1. CH3COOH/H2O
2. HgCl2
TsCl
pyridine
CH3CSSH
DCCl
1. HCl/H2O
2. Ac2O pyridine

**2** **3** **4**

**5** **7** **8**

**6** **10** **9**

This new thioacetylation method, including the application of dithioacetic acid and N,N'-dicyclohexylcarbodiimide, allows the simple preparation of different N-thioacetyl derivatives of carbohydrates.

The chemical reactions and biological properties of our thioacetamido sugar derivatives are under investigation.

## Experimental

M.p.'s were determined on a Kofler hot-stage apparatus and are uncorrected. IR spectra were obtained with a UNICAM SP 200 spectrophotometer, in KBr discs. NMR spectra were recorded on a JEOL MH-100 (100 MHz) instrument, using TMS as internal standard.

### Methyl 2-amino-4,6-O-benzylidene-3-O-toluenesulfonyl-2-deoxy-α-D-altropyranoside, 2

A stirred solution of **1** (1.9 g) in N,N-dimethylformamide (30 ml) and methanol (15 ml) was treated with sodium borohydride (0.5 g) at room temperature. After 2 hrs the mixture was poured into water and the precipitate was filtered off, washed with water and dried. Recrystallization from ethanol gave 1.5 g (84%) of pure **2**; m.p. 136—137 °C, $[\alpha]_D^{23} + 25°$ ($c = 1$, $CHCl_3$). (GUTHRIE and MURPHY [9] obtained **2** as a syrup by hydrogenation of **1** over Adams catalyst).

$C_{21}H_{25}NO_7S$ (435.484). Calcd. C 57.92; H 5.78; N 3.22. Found C 57.75; H 5.62; N 3.40%.

Acetylation of **2** gave methyl 2-acetamido-4,6-O-benzylidene-2-deoxy-3-O-*p*-toluenesulfonyl-α-D-altropyranoside, m.p. 177 °C, $[\alpha]_D^{18} + 61°$. (Lit. [9] m.p. 174—175 °C; $[\alpha]_D^{18} + 61°$.)

### Methyl 2-amino-4,6-O-benzylidene-2-deoxy-N-dithiocarbomethoxy-3-O-toluenesulfonyl-α-D-altropyranoside, 3

To a solution of **2** (0.7 g; 1.6 mmole) in dry pyridine (10 ml) triethylamine (0.16 g; 1.6 mmole) was added at 0 °C, followed by the dropwise addition of carbon disulfide (0.105 ml; 1.76 mmole). After stirring for 1 hr. the mixture was treated with methyl iodide (0.25 g; 1.76 mmole) for 15 hrs at 5 °C. The mixture was then diluted with water, the solid precipitate was filtered off and recrystallized from 96% ethanol to yield 0.47 g (56%) of **3**, m.p. 152—153 °C, $[\alpha]_D^{23} + 20°$ ($c = 1$, $CHCl_3$).

$C_{23}H_{27}NO_7S_3$ (525.658). Calcd. C 52.54; H 5.14; N 2.66; S. 18.28. Found C 52.57; H 5.43; N 2.69; S 18.20%.

### 4',6'-O-Benzylidene-1'-O-methyl-2-methylthio-α-D-mannopyrano-[2', 3': 4,5]-2-thiazoline, 4

Compound **3** (2.7 g) was refluxed in pyridine (30 ml) under nitrogen atmosphere for 5 hrs. The mixture was poured into ice-water and extracted with chloroform. The organic layer was succesively washed with $NaHCO_3$ solution, $NaHSO_4$ solution and water and dried. On evaporation a chromatographically (TLC: petrolether–acetone 8 : 2) homogeneous foam was obtained. Yield: 1.8 g (82%). $[\alpha]_D^{23} - 184°$ ($c = 2$, $CHCl_3$).

IR: 1555 $cm^{-1}$ (C = N).

NMR ($CDCl_3$) $\delta = 2.48$ (s, 3H, S—$CH_3$); 3.33 (s, 3H, O—$CH_3$); 7.1 ppm (m, 5H, aromatic).

$C_{16}H_{20}NO_4S_2$ (304.458). Calcd. C 54.21; H 5.69; S 18.09. Found C 54.98; H 5.44; N 4.15; S 17.83%.

### Methyl 4,6-O-benzylidene-2-deoxy-2-N-thioacetyl-3-O-*p*-toluenesulfonyl-α-D-altropyranoside

To a solution of **2** (4.8 g; 10 mmoles) and N,N'-dicyclohexylcarbodiimide (3.6 g; 17.6 mmoles) in chloroform (90 ml) dithioacetic acid 10 (1.2 g; 22 mmoles) was added dropwise at 0 °C. The mixture was kept at room temperature for 1 hr. and the crystalline product which

precipitated was filtered off and washed with chloroform, to yield 4.9 g (79%) of 5; m.p. 165—166 °C; $[\alpha]_D^{23} + 31°$ ($c = 0.6$, pyridine).

NMR (DMSO-$d_6$): $\delta = 2{,}7$ (s, 3H, tosyl $CH_3$); 2.85 (s, 3H, thioacetyl); 3.7 ppm (s, 3H, $OCH_3$).

$C_{23}H_{27}NO_7S_2$ (493.588). Calcd. C 55.96; H 5.51; N 2.83; S 12.99. Found C 55.74; H 5.66; N 2.97; S 13.24%.

### 4',6'-0-Benzylidene-1'-0-methyl-2-methyl-α-D-mannopyrano-[2', 3': 4,5]-2-thiazoline, 7

(*A*) Compound **5** (2.0 g) was refluxed in dry pyridine (40 ml) for 4 hrs. The reaction mixture was poured into ice-water and extracted with chlorform. The organic layer was washed with $NaHSO_4$ solution and water, and dried over $Na\ SO_4$. The solvent was evaporated and the residue purified by column chromatography on Silica gel using ether–acetone 9 : 1 for elution, to obtain **7** (1.25 g; 96%) as a solid foam; $[\alpha]_D^{23} - 130°$ ($c = 1$, $CHCl_3$).

IR: 1625 $cm^{-1}$ (C=N).

NMR ($CDCl_3$): $\delta = 2.24$ (d, 2H, $CH_3$); 3.38 ppm (s, 3H, $OCH_3$).

$C_{16}H_{19}NO_4S$ (321.384). Calcd. C 59.79; H 5.96; N 4.36; S 9.98. Found C 59.97; H 5.92; N 4.38; S 9.88%.

(*B*) Compound **5** (0.98 g) was refluxed with 1*N* methanolic sodium methoxide (5 ml) for 4 hrs. After dilution with water, the mixture was extracted with chloroform, the organic layer was dried, and the solvent evaporated to leave 0.4 g (72%) of **7** which, on the basis of IR examination, was identical with the product obtained *via* method (*A*).

(*C*) A solution of **5** (0.69 g) and potassium thiolacetate (0.69 g) in N,N-dimethylformamide (15 ml) was refluxed under nitrogen atmosphere for 1 hr. The mixture was worked up as in method (*B*) to yield 0.5 g of **7**.

### Methyl 4,6-0-benzylidene-2-deoxy-2-N-thioacetyl-α-D-altropyranoside, 6

A solution of methyl 2-amino-4,6-O-benzylidene-2-deoxy-α-D-altropyranoside [11] (1.5 g; 5.3 mmoles) and N,N'-dicyclohexylcarbodiimide (1.25 g; 6 mmoles) in chloroform (22 ml) was prepared and dithioacetic acid (0.57 g; 6 mmoles) was added to it at 0 °C; the reaction mixture was then allowed to stand at room temperature for 6 hrs. The crystalline product which precipitated was filtered off, washed with ether and recrystallized from chloroform to give 0.85 g (47%) of **6**, containing one molecule of chloroform in solvated form; m.p. 110—115 °C; $[\alpha]_D^{23} + 61°$ ($c = 1$, $CHCl_3$).

NMR (DMSO-$d_6$): $\delta = 2.56$ (s, 3H, thioacetyl); 8.34 ppm (s, 1H, $CHCl_3$).

$C_{17}H_{22}NO_5SCl_3$ (458.80). Calcd. C 44.45; H 4.79; N 3.05; S 6.99; Cl 23.22. Found C 45.75; H 5.01; N 3.10; S 7.39; Cl 22.85%.

### Methyl 2-acetamido-3-chloromercurithio-2-deoxy-α-D-mannopyranoside, 8

A solution of **7** (600 mg) in water (2 ml) and acetic acid (5 ml) was heated on a water bath at 100 °C under nitrogen atmosphere for 3 hrs. The reaction mixture was evaporated, then re-evaporated with water; the residue was dissolved in water and treated with mercuric chloride (550 mg). This mixture was evaporated again and the residue was re-evaporated with dry ethanol. The solid foam obtained was purified by column chromatography in Silica gel. Elution was accomplished succesively with chloroform–methanol 8 : 2 and 9 : 1. Yield: 0.49 g (54%).

NMR (DMSO-$d_6$): $\delta = 1.92$ (s, 3H, acetyl); 3.24 ppm (s, 3H, $OCH_3$).

$C_9H_{16}NO_5SHgCl$ (486.37): Calcd. N 2.87. Found N 2.59%.

### 2-Acetamido-3-S-acetyl-1,4,6-tri-O-acetyl-2-deoxy-3-thio-D-mannopyranose, 9

Compound **7** (2.8 g) was hydrolyzed with 6*N* HCl (150 ml) at 120 °C under nitrogen atmosphere for 1 hr. After treatment with decolourizing carbon and filtration through Celite, the mixture was evaporated and extracted with ether. The residue obtained after evaporation was dried in vacuum at 40 °C for 30 min. The syrupy product was acetylated with a mixture of acetic anhydride (10 ml) and pyridine (30 ml) at room temperature for 12 hrs. The reaction mixture was then worked up on the usual way, followed by purification by column chromatog-

raphy on Silica gel using petroleum ether–acetone (1 : 1) as the eluent; 1.2 g of pure **9** (anomeric mixture) was obtained as a solid foam.

MS: *m/e* 405, M; 363, M—CH =C=0, $C_{14}H_{21}NO_8S$.

$C_{16}H_{23}NO_9S$ (405.42). Calcd. C 47.52; H 5.73; N 3.46; S 7.92. Found C 47.56; H 5.77; N 3.25; S 7.96%.

*

The authors' thanks are due to the Hungarian Academy of Sciences for supporting this work. We are indebted to Dr. Gy. BUJTÁS for recording and interpretation of the MS spectrum, to Dr. L. SZILÁGYI and Dr. S. SZABÓ for their helpful discussions in the interpretation of NMR and IR spectra. The technical assistance of Mr. J. TÁLAS is acknowledged.

## REFERENCES

[1] BAKER, B. R., HULLAR, T. L.: J. Org. Chem. **30,** 4038 (1965)
[2] BUSS, D. H., HOUGH, L., RICHARDSON, A. C.: J. Chem. Soc. **1963,** 5295
[3] GUTHRIE, R. D., MURPHY, D.: J. Chem. Soc. **1065,** 6956
[4] GOODMAN, L., CHRISTENSEN, J. E.: J. Am. Chem. Soc. **83,** 3823 (1961)
[5] MEYER zu RECKENDORF, W. M., BONNER, W. A.: Tetrahedron, **19,** 1721 (1963)
[6] ALI, Y., RICHARDSON, A. C.: Carbohyd. Res. **5,** 441 (1967)
[7] HADRICK, G. R., ATKINSON, E. R., GRANCHELLI, F. E., BRUNI, R. J.: J. Med. Chem. **8,** 762 (1965)
[8] GOODMAN, L.: Advan. Carbohyd. Chem. **22,** 109 (1967)
[9] GUTHRIE, R. D., MURPHY, D.: J. Chem. Soc. **1963,** 5288
[10[ HOUBEN, J., POHL, H.: Ber. **40,** 1303 (1907)
[11[ OSAWA, R., WALKER, E., JEANLOZ, R. W.: Fed. Proc., **23,** 379 (1964)

Pál HERCZEGH
Rezső BOGNÁR
H-4010, Debrecen, Hungary

*Acta Chimica Academiae Scientiarum Hungaricae, Tomus 98 (3), pp. 327—333 (1978)*

# SYNTHETIC USES OF MILLON'S REAGENT, I

## SYNTHESIS OF *O*-NITROSOPHENOLS BY MEANS OF MILLON'S REAGENT

J. LÁZÁR, L. MÓD and E. VINKLER

*(Institute of Pharmaceutical Chemistry, Medical University, Szeged)*

Received October 5, 1976
In revised form September 20, 1977

After a thorough literature survey of the *o*-nitrosation of phenols, the use of Millon's reagent is described in the synthesis of *o*-nitrosophenols, based on the authors' earlier results. The *ortho* directing action observed during mercuration in the presence of mercury(II) ions is explained by the conversion of the primary phenol-mercuric complex into a transient *ortho* complex, which is then stabilized as the *ortho* mercuric derivative.

In our earlier work [1, 2] the course of the Millon reaction was examined and the compounds responsible for the development of the colour reaction were isolated. Effecting the colour reaction on preparative scale, subsequent acid decomposition of the reaction mixture gave the *o*-nitroso derivatives of methyl *p*-hydroxybenzoate and *p*-hydroxybenzoic acid in high yields and in pure state, as compared with the other syntheses reported for *o*-nitrosophenols in the literature.

In view of this fact, it seemed reasonable to apply this method to other compounds, and to attempt the development of a preparative method for the synthesis of *o*-nitrosophenols which are relatively difficult to obtain.

When surveying the preparation methods known for nitrosophenols, it is noted that, although variously substituted *p*-nitrosophenols have been synthesized in several ways since the end of the last century [3—41], syntheses of *o*-nitrosophenols were achieved only later, by the application of special methods and the yields were usually low [9, 16, 45—55].

In the nitrosation of aromatic compounds with nitrous acid, the nitroso group enters almost excusively into *p*-position related to the hydroxyl group [4, 7, 14, 16, 19, 21—24, 26—33, 36—41, 63—67]. When the *p*-position is occupied, the nitroso group will, according to the kinetic studies of CHALLIS and LAWSON [68] in perchloric acid medium, enter the *o*-position related to the hydroxyl group, and subsequent oxidation by the ragents leads to the nitro compounds. Derivatives carrying an alkoxyl group in *meta* position are exceptions; here several nitroso isomers are formed [69—78]. *Meta*-dialkylamino derivatives yield *o*-nitrosophenols in satisfactory yields [79, 80].

In the naphthalene series, $\beta$-naphthol and its derivatives are converted into $\alpha$-nitroso-$\beta$-naphthol (*i.e.*, and *o*-nitrosophenol) almost quantitatively [81—89], while $\alpha$-naphthol yields a mixture of 2-nitroso-1-naphthol and 4-nitroso-1-naphthol [90—94].

Similarly to $\beta$-naphthol, 2-hydroxyphenanthrene is converted into 1-nitroso-2-hydroxyphenentrene [95].

In certain phenols carrying carboxyl group, nitrosation is accompanied by decarboxylation and the corresponding nitrosophenols are formed [96—101].

Alkylphenol ethers undergo nitrosation in *para* position [10]. Some phenol ethers yielded *p*-nitrosophenols [102—105].

In nitrosation with nitrous acid esters, the nitroso group again enters the *p*-position [106—111].

GOLDSCHMIDT [9] was the first to prepare the *o*-quinone monoxime tautomeric form of *o*-nitrosophenol. BAEYER and KNORR [17] obtained *o*-nitrosophenol from *o*-nitrosoanisol after cleavage of the ether bond.

Later, BAUDISCH [42—44] prepared *o*-nitrosophenol by reducing *o*-nitrophenol.

The BAUDISCH reaction is another method for the preparation of *o*-nitrosophenols. In this reaction, aromatic hydrocarbons could be converted into *o*-nitrosophenols by simultaneous introduction of the nitroso group and the phenolic hydroxyl group in the presence of hydroxylamine, hydrogen peroxide, sodium pentacyanoamine ferroate or copper(II) salts (copper(II) nitrate or sulfate) [45—52].

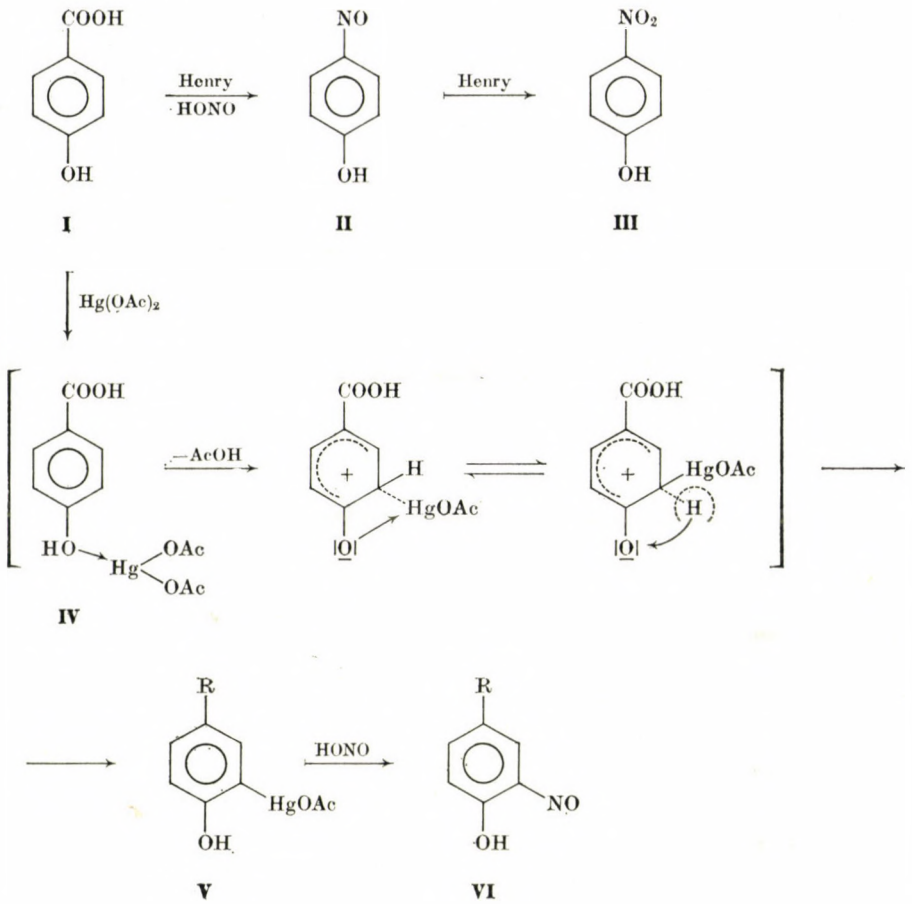
Under the conditions of the BAUDISCH reaction, the nitrosation of phenols in *o*-position could also be realized [45, 50, 52—55].

Both in the BAUDISCH reaction and in nitrosation with nitrous acid in the presence of heavy metal salts [50, 56—62], the fact that *o*-nitrosophenols are formed exclusively can probably be attributed to the *ortho* directing of the chelated complex formed between the phenolic hydroxyl group and the metal ions (*cf.* [112, 113]).

The important role of the transient metal chelate in the occurrence of *o*-substitution in the course of the Millon reaction seems to be confirmed by our experiments on *p*-hydrobenzoic acid, used as a model compound.

Nitrosation and mercuration are electrophilic substitution reactions; in view of this fact, in principle, products substituted at identical positions should be expected. The nitrosation of *p*-hydroxybenzoic acid was studied by HENRY [100]. According to his studies, on treatment with nitrous acid, *p*-hydroxybenzoic acid (**I**) is decarboxylated and converted into *p*-nitrosophenol (**II**). (The product was isolated after oxidation as *p*-nitrophenol (**III**) in a very low yield.) When these experiments were reproduced by us, the amount of *p*-nitrosophenol formed was monitored spectrophotometrically and, after the adjustment of the optimal reaction conditions, it could also be isolated in high yields. Formation of the corresponding *o*-nitrosophenol (**VI**) was not detected even in traces. When, however, the reaction was carried out in the presence of a mercury(II) salt (that is, under the conditions of the Millon reaction) decarboxylation did not take place and, after acid decomposition of the reaction mixture, 3-nitroso-4-hydroxybenzoic acid (**VI**) was obtained in a satisfactory yield.

In the latter case, according to our assumption, the direction of the reaction is determined by the instantaneous complex formation between the phenolic hydroxyl group and mercury(II) ions, (**IV**), instead of nitroso-decarboxylation requiring a considerable time. Presumedly, this complex is converted by the *ortho*-directing action of the substituents and the chelate [112, 113] into the 3-mercury(II)-X-4-hydroxybenzoic acid (**V**) intermediate (X is the anion present, acetate or nitrite) in a relatively rapid reaction, and this product reacts with nitrous acid to give 3-nitroso-4-hydroxybenzoic acid (**VI**) or its mercury complex.




R = $-COOH$; $-COOCH_3$; $-Cl$; $-Br$; $-CH_3$ or the corresponding mercury complex

Two methods have been employed in our experiments for the preparation of *o*-nitrosophenols. In one of them, Millons reagent was prepared from mercury(II) nitrate and potassium nitrite, and a calculated amount of the reagent was heated with an alcoholic solution of the appropriate phenol on a water bath. In the other method, phenol was mercuryted with mercury(II) acetate to obtain the *o*-mercury(II) acetate compound; the mercury compound was isolated and treated in a reaction mixture containing nitrous acid yielding the *o*-nitrosophenol mercury complex. This complex was decomposed with hydrochloric acid, and the *o*-nitrosophenol formed was isolated by extraction with petroleum ether or ether.

The *o*-nitrosophenols were characterized as their silver complexes or potassium salts. Exceptions were the *o*-nitroso derivatives of *p*-hydroxy-

benzoic acid and its methyl ester, which have remarkable stability as compared with other *o*-nitrosophenols and can be stored for a long time in the crystalline state, as well as in petroleum ether or ether solutions without decomposition.

The method seems to be particularly suitable for the *o*-nitrosation of phenols containing a carboxyl group, since, in these cases as described above, other methods of nitrosation are accompanied by simultaneous decarboxylation.

## Experimental

M.p.'s are uncorrected.

**p-Nitrosophenol** (from *p*-hydroxybenzoic acid by "nitrosodecarboxylation")

In this paper, HENRY [100] described the nitrosodecarboxylation of *p*-hydroxybenzoic acid. The product was oxidized and identified as *p*-nitrophenol, the yield being 5.6%.

The low yield seemed to us improbable, thus the experiments of the author were reproduced by us; further, the conditions were altered to attain a higher yield. The amount of *p*-nitrosophenol formed was measured spectrophotometrically. In the repetition of HENRY's experiments, spectrophotometric determination showed 45.52% yield. When the pH of the reaction mixture and the temperature were varied, the yield could be increased to 97.8%. Authentic *p*-nitrosophenol required for the measurement was prepared by the method suggested by BRIDGE [14] and was purified by recrystallization from toluene. The spectrophotometric examinations of both the reaction mixtures and the standard substance were effected in 0.1*N* aqueous sodium hydroxide solution at 401 nm; however, the ultraviolet and visible ranges were also checked in each case to detect the appearance of any decomposition products and to follow decrease in the amount of the starting material (281 nm).

**Procedure:** *p*-Hydroxybenzoic acid (0.138 g; 0.001 mole), sodium nitrite (0.076 g; 0.001 mole + 10%) and glacial acetic acid (0.06 g; 0.001 mole) were heated in water (15 ml) at 60 °C for 30 min. The resulting solution was washed with 0.1*N* NaOH solution into a measuring flask of 100 ml capacity, then 0.50—1.00 ml portions were transferred to measuring flasks of 100 ml capacity and made up to the mark with 0.1*N* aqueous NaOH and the absorbance was measured at 281 nm and 401 nm in 10 mm quartz cells. The concentrations were determined on the basis of the calibration curve recorded in 0.1*N* alkali solutions of standard *p*-nitrosophenol.

**Preparative procedure:** *p*-Hydroxybenzoic acid (1.38 g; 0.01 mole) was, after the addition of glacial acetic acid (0.6 g; 0.01 mole + 10%), heated in water (90 ml) until complete dissolution occurred. Sodium nitrite (0.76 g; 0.01 mole + 10%) was dissolved in water (10 ml) and added in one portion to the reaction mixture cooled to 50—60 °C. The mixture was heated at 50—60 °C under frequent shaking for about 30 min., when the evolution of carbon dioxide ceased. The reaction mixture was allowed to cool, then repeatedly extracted with ether, the combined ethereal solutions were dried ($Na_2SO_4$) and the solvent was evaporated, to obtain greenish-yellow crystals (1.14 g; 92%); m.p.: at 125 °C discolouration (brown), at 148 °C decomposition; identical with the authentic substance; no melting point depression was observed. After recrystallization from benzene the m.p. remained unchanged.

$C_6H_5O_2N$ (123.1). Calcd. C 58.53; H 4.09; N 11.37. Found C 58.66; H 4.19; N 11.25%.

*General procedures for the preparation of o-nitrosophenols*

(1) The appropriate phenol (0.01 mole) was dissolved in ethanol (7 ml) and mixed with a solution of mercury(II) nitrate (1.78 g; 0.0055 mole) and potassium nitrite (0.93 G; 0.011 mole) in water (15 ml). The reaction mixture was gently heated on a water bath for 30 min., with occasional shaking, whereupon a red precipitate separated. This was filtered off and extracted by adding 20% hydrochloric acid in small portions, and shaking and rubbing repeatedly with petroleum ether. (In the case of *p*-hydroxybenzoic acid, ether was used). Addition of hydrochloric acid and extraction with petroleum ether was continued until a hardly coloured extract was obtained. The green extracts in petroleum ether (or in ether) were combined, washed with a saturated solution of sodium chloride, and extracted with 5% NaOH for purification (in the case of methyl *p*-hydroxybenzoate, 5% ammonium hydroxide was used). The dark orange coloured solution was filtered, acidified with dilute sulfuric acid and extracted with petroleum ether (or ether). The extract was washed with saturated sodium chloride solution and dried over $Na_2SO_4$.

The petroleum ether (ether) solution yielded, when concentrated, the corresponding crystalline *o*-nitroso derivative of *p*-hydroxybenzoic acid or its ester. In other cases, the products were not crystalline. The petroleum ether (or ether) solution was then shaken with an aqueous solution of an appropriate heavy metal salt (silver, copper, etc.), whereupon crystalline complexes with metallic lustre appeared. When saturated alkali hydroxide solutions were used, the rusty-red potassium [114] or sodium salts could be precipitated and recrystallized from ethanol. In the preparation of heavy metal complexes, it is advisable to use an aqueous solution of the potassium or sodium salts, or an ammonium hydroxide solution of *o*-nitrosophenol, since the acid formed during the complex formation slightly decomposes the complexes and an equilibrium mixture may be formed. The corresponding *o*-nitrosophenol can be liberated from the complexes or salts with acid and extracted.

(2) The appropriate hydroxy compound (0.01 mole) was dissolved in ethanol (10 ml) and mixed with a solution of mercury(II) acetate (3.2 g; 0.01 mole) and glacial acetic acid (1 ml) in water (25 ml). The reaction mixture was heated on a water bath for 30 min., and the reaction product which separated was filtered off. The yield was nearly 100%.

The mercurated product formed in the above reaction was mixed with methanol (7.5 ml; 0.01 mole) and water (15 ml) and sodium nitrite (0.76 g; 0.011 mole) was added. The reaction mixture was heated on a water bath and glacial acetic acid (0.75 ml) was added in small portions. Most of the methanol evaporated during heating the solution, which turned into dark red, for about 30 min. The solution containing the precipitate was cooled, filtered, and the mercury complex of *o*-nitrosophenol was processed as given above.

Compounds prepared according to the foregoing prescriptions were the following:

**3-Nitroso-4-hydroxybenzoic cid methyl ester** its silver, mercury(I) and mercury (II) complexes, described in a previous paper [2]. Yield: 53%,

**3-Nitroso-4-hydrobenzoic acid and its mercury (II)** complex are disscused in our previous paper [2]. Yield: 57%.

**3-Nitroso-4-methylphenol and its silver complex** $C_7H_6O_2NAg$ (244.0015). Calcd. Ag 41.21. Found Ag 41.46%. Yield: 49%.

**3-Nitroso-4-bromophenol** and its silver complex.

$C_6H_3O_2NBrAg$ (308.7755). Calcd. Ag 34.93. Found Ag 35.38%. Yield: 47.6%.

**3-Nitrosochlorophenol** and its silver complex.

$C_6H_3O_2NClAg$ (264.4195). Calcd. Ag 40.79. Found Ag 41.10%. Yield: 50.8%.

M.p.'s were determined with a Boetius type (Franz Küstner K. G. Dresden) micro melting point determining apparatus. The UV spectra were recorded with a Specord UV-VIS (Carl Zeiss, Jena) instrument.

The authors' thanks are due to Mrs. G. BARTÓK (Institute of Organic Chemistry, Szeged) and Mrs. I. SZABÓ, (Institute of Pharmaceutical Chemistry, Szeged) for the analyses and to Mr. Z. JENEI (Institute of Pharmaceutical Chemistry) for the technical assistance in recording the spectra.

## REFERENCES

[1] LÁZÁR, J., MÓD, L., VINKLER, E.: Kémiai Közlemények **29,** 257 (1968)
[2] LÁZÁR, J., MÓD, L., VINKLER, E.: Acta Chim. Acad. Sci. Hung. **68,** 133 (1971)
[3] BAEYER, A., CARO, H.: Ber. **7,** 809 (1874)
[4] BAEYER, A., CARO, H.: Ber. **7,** 963 (1874)
[5] STENHOUSE, J., GROVES, C. E.: Ann. Chem. Pharm. **188,** 360 (1877)
[6] PATERNO, E., CANZONERI, F.: Gaz. Chim. Ital. (Rome) **8,** 501 (1878)
[7] OLIVERI, V.: Gaz. Chim. Ital. **14,** 459 (1884)
[8] GOLDSCHMIDT, H.: Ber. **16,** 2176 (1883)
[9] GOLDSCHMIDT, H.: Ber. **17,** 213 (1884)
[10] GOLDSCHMIDT, H., SCHMID, H.: Ber. **17,** 2060 (1884)
[11] GOLDSCHMIDT, H., SCHMID, H.: Ber. **18,** 568 (1885)
[12] HENRIQUES, R., ILINSKI, M.: Ber. **18,** 704 (1885)
[13] NIETZKI, R., GUITERMANN, A. L.: Ber. **21,** 428 (1888)
[14] BRIDGE, J. L.: Ann. **277,** 79 (1893)
[15] D. R. P. 48491 (1888) Farbenfabr. Bayer. Frdl. **2,** 221
[16] KLAGES, A.: Ber. **32,** 1518 (1899)
[17] BAEYER, A., KNORR, E.: Ber. **35,** 3034 (1902)
[18] BAMBERGER, E., CZERKIS, M.: J. prakt. Chem. (II) **68,** 473 (1903)
[19] VAN ERP, H.: Rec Trav. Chim. Pays-Bas (Amsterdam) **30,** 276 (1910)

[20] v. Braun, J., Heider, K., Müller, E.: Ber. **51,** 737 (1918)
[21] Schontissen, H. A. J.: Rec. Trav. Chim. Pays-Bas (Amsterdam) **40,** 753 (1921)
[22] Hodgson, H. H., Moore, F. H.: J. Chem. Soc. (London) **123,** 2499 (1923)
[23] Hodgson, H. H., Moore, F. H.: J. Chem. Soc. (London) **127,** 2260 (1925)
[24] Hodgson, H. H., Moore, F. H.: J. Chem. Soc. (London) **1926,** 2036
[25] Hodgson, H. H., Wignol, J. S.: J. Chem. Soc. (London) **1927,** 2216
[26] Hodgson, H. H., Kershaw, A.: J. Chem. Soc. (London) **1929,** 1553
[27] Hodgson, H. H., Clay, H.: J. Chem. Soc. (London) **1929,** 2216
[28] Hodgson, H. H., Kershaw, A.: J. Chem. Soc. (London) **1930,** 1969
[29] Hodgson, H. H.: J. Chem. Soc. (London) **1932,** 866
[30] Anderson, L. C., Geiger, M. B.: J. Am. Chem. Soc. **54,** 3064 (1932)
[31] Tseng, C. L., Hu, M.: J. Chinese Chem. Soc. **1,** 183 (1933); C. A. **28,** 1680 (1934)
[32] Krassnowski, A.: Promysl. org. Chim. **1,** 604 (1936); C. **1936,** II, 3845
[33] Hodgson, H. H., Nicholson, D. E.: J. Chem. Soc. (London) **1939,** 1808
[34] Hodgson, H. H., Nicholson, D. E.: J. Chem. Soc. (London) **1940,** 1268
[35] Munch, R., Tannhauser, G. T., Gottle, D. L.: J. Am. Chem. Soc. **68,** 1297 (1946)
[36] Bonn, W. R.: J. Chem. Soc. (London) **1947,** 307
[37] Kremers, E., Wakeman, N., Hixon, R. M.: Org. Synth. Coll. Vol. I, 511 (1947)
[38] Leonard, N. J., Curry, J. W.: J. Org. Chem. **17,** 1074 (1952)
[39] Kraaieveld, A., Havinga, E.: Rec. Trav. Chim. Pays-Bas (Amsterdam) **73,** 537, 546 (1954)
[40] Ershov, V. V., Zlobina, G. A., Nikoforov, G. A.: Izv. Akad. SSSR **1963,** 1877; C. A. **60,** 2809 (1964)
[41] Niederl. Pat. Anm. 6 415 184 (1964). Hecules Powder Co. C. A. **64,** 647 (1966)
[42] Baudisch, O., Kurzeff, N.: Ber. **45,** 1164 (1912)
[43] Baudisch, O., Rotschild, S.: Ber. **48,** 1660 (1915)
[44] Baudisch, O.: Ber. **51,** 1058 (1918)
[45] Baudisch, O.: Naturwiss. **27,** 768 (1939)
[46] Baudisch, O., Smith, S. H.: Naturwiss. **27,** 769 (1939)
[47] Baudisch, O.: J. Am. Chem. Soc. **63,** 622 (1941)
[48] Baudisch, O.: Arch. Biochemistry **5,** 401 (1944) C. A. **40,** 5323 (1946)
[49] Cronheim, G.: J. Org. Chem. **12,** 1 (1947)
[50] Cronheim, G.: J. Org. Chem. **12,** 7 (1947)
[51] Cronheim, G.: J. Org. Chem. **12,** 20 (1947)
[52] Marujama, K., Tanamito, J., Goto, R.: Tetrahedron Letters **1966,** 5889; J. Org. Chem. **32,** 2516 (1967)
[53] Ellis, G. H., Thompson, J. F.: Ind. Eng. Chem. Anal. **17,** 254 (1945)
[54] Tanamito, J.: Bull. Chem. Soc. Japan **43,** 139 (1970)
[55] Tanamito, J.: Bull. Chem. Soc. Japan **43,** 1182 (1970)
[56] Dienel, H.: Ber. **39,** 926 (1906)
[57] Bevillard, P., Choucrouh, J.: Bull. Soc. Chim. France **1957,** 337
[58] Chrétien, A., Longi, Y.: Compt. rend. **220,** 746 (1945)
[59] Bogdanov, S. V., Gorelik, M. V.: Zh. Obshch. Khim. **29,** 136 (1959)
[60] Bogdanov, S. V., Shibryaeva, L. S.: Zh. Obshch. Khim. **30,** 2229 (1960)
[61] Gorelik, M. V., Michailova, T. A.: Z. Vses. Khim. Obshch. **7,** 700 (1962); C. A. **58,** 112939 (1963)
[62] Gorelik, M. V., Michailova, T. A.: Zh. Obshch. Khim. **34,** 1997 (1964)
[63] Weibel, S.: Ber. **63,** 1577 (1930)
[64] Schmidt, H., Muhr, G., Riedl, P.: Monatsh. **97,** 781 (1966)
[65] Morrison, D. A., Turney, T. A.: J. Chem. Soc. (London) **1960,** 4827
[66] Challis, B. C., Lawson, A. J.: J. Chem. Soc. (B) **1971,** 770
[67] Challis, B. C., Lawson, A. J.: J. Chem. Soc. Perkin II **1972,** 1831
[68] Challis, B. C., Lawson, A. J.: J. Chem. Soc. Perkin II **1972,** 2365
[69] Kietaibl, C.: Monatsh. **19,** 536 (1898)
[70] Weidel, H., Pollak, J.: Monatsh. **21,** 29 (1900)
[71] Heinrich, F., Rhodius, O.: Ber. **35,** 1475 (1902)
[72] Heinrich, F., Eisenach, H.: J. prakt. Chem. **70,** 332 (1904)
[73] Hodgson, H. H., Wignal, J. S.: J. Chem. Soc. (London) **1928,** 329
[74] Hodgson, H. H., Clay, H.: J. Chem. Soc. (London) **1929,** 2775
[75] Hodgson, H. H., Clay, H.: J. Chem. Soc. (London) **1939,** 963
[76] Hodgson, H. H., Clay, H.: J. Chem. Soc. (London) **1931,** 2097
[77] Hodgson, H. H., Clay, H.: J. Chem. Soc. (London) **1932,** 869
[78] Jahelka, J., Sterba, V., Valter, K.: Coll. Czechoslov. Chem. Commun. **38,** 877 (1973)

[79] MÖHLAU, R.: Ber. **25,** 1055 (1892)
[80] ELSLAGER, E. F., WORTH, D. F.: J. Med. Chem. **13,** 370 (1970)
[81] LAGODZINSKI, K., HARDINE, D.: Ber. **27,** 3075 (1894)
[82] FIERZ-DAVID, H. E., BLANGEY, L.: Grundlegende Operationen der Farbenchemie, Ed. 8, 192. pp. Springer Verlag, Wien, 1952
[83] VOGEL, A. I.: Practical Organic Chemistry, 3rd ed., 958. pp. Longmans. Green **X** Co. London, New York, Toronto, 1956
[84] MARVEL, C. S., PORTER, P. K.: Org Synth. Coll. Vol. I, p. 411 (1956)
[85] KONSTANECKI, S.: Ber. **26,** 2898 (1883)
[86] ULLMANN, F., HEISLER, R.: Ber. **42,** 4266 (1909)
[87] LANTZ, R., MINGASSON, G.: Bull. Soc. Chim. France (4) **49,** 1172 (1931)
[88] GULINOW, W. G.: Ukr. Khim. Zh. **7,** 197 (1932); C. **1933,** II 1434
[89] U. S. Pat. 3 051 750 (1960)
[90] FUCHS, F.: Ber. **8,** 625, 1022 (1875)
[91] WORMS, R.: Ber. **16,** 1816 (1882)
[92] HENRIQUES, R., ILINSKI, M.: Ber. **18,** 706 (1885)
[93] BECKMANN, E., LIESCHE, O.: Ber. **56,** 4 (1923)
[94] HODGSON, H. H., KILNER, E.: J. Chem. Soc. **125,** 809 (1924)
[95] MARCINKIEVICZ, S., GREEN, J.: J. Chromatog. **10,** 366 (1963)
[96] REVERDIN, F., DE LA HARPE, C.: Ber. **26,** 1280 (1893)
[97] NIETZKI, R., GUITERMANN, A. L.: Ber. **20,** 1274 (1887)
[98] HELLER, G.: Ber. **45,** 676 (1912)
[99] NEMODRUK, A. A.: Zhur. Obshch. Khim. **26,** 3283; (1956); C. A. **51,** 9528 (1957)
[100] HENRY, R. A.: J. Org. Chem. **23,** 648 (1958)
[101] IBNE-RASA, K. M.: J. Am. Chem. Soc. **84,** 4962 (1962)
[102] HODGSON, H. H., CROUCH, E. A. C.: J. Chem. Soc. (London) **1943,** 221
[103] KRAUS, A.: Monatsh. **12,** 368 (1891)
[104] MEYER, K. H., LENHARDT, S.: Ann. **398,** 79 (1913)
[105] HODGSON, H. H., CLYA, H.: J. Chem. Soc. (London) **1930,** 1872
[106] BORSCHE, W., BERKHOUT, A. D.: Ann. **330,** 95 (1904)
[107] RUPE, H.: Ber. **30,** 2444 (1897)
[108] HEINRICH, F.: Ber. **35,** 4191 (1902)
[109] TESHIGAWARA, T.: Jap. Pat. 65/13918 (1961); Chem. Abstr. **62,** 7688 (1965)
[110] YOUNG, H. L. (Hercules Inc.): U. S. Pat. 3,285,972 (1962); C. A. **66,** 18584 (1967)
[111] JULIAN P. L., COLE, W., DIENER, G.: J. Am. Chem. Soc. **67,** 1721 (1945)
[112] SZÁNTAY, Cs.: Elméleti szerves kémia, p. 299, Műszaki Könyvkiadó, Budapest, 1975
[113] KETCHMER, R. A., MCCLOSKEY, M. B.: J. Org. Chem. **37,** 1989 (1972)
[114] TAMURA, Z., KIDO, Y.: Chem. Pharm. Bull. **16,** 1909 (1968)

János LÁZÁR
László MÓD
Elemér VINKLER
H-6720 Szeged, Eötvös u. 6.

*Acta Chimica Academiae Scientiarum Hungaricae, Tomus 98 (3), pp. 335—338 (1978)*

# STUDIES ON THE COURSE OF THE MILLON REACTION, II*

J. LÁZÁR, L. MÓD and E. VINKLER

*(Institute of Pharmaceutical Chemistry, Medical University, Szeged)*

Received October 5, 1976
In revised form September 20, 1977

On the basis of the earlier work of the authors [1, 2] and that of Japanese researches [3, 4], the possible interconversion of *o*-nitrosophenol mercury complexes of various types have been investigated; some complex conversions have been confirmed, and the course of the Millon reaction is analyzed in detail; a new reaction path accounting for finer details is suggested.

In our previous papers [1, 2], the complexes, 3-nitroso-4-hydroxybenzoic acid methyl ester mercurate nitrate and bis(3-nitroso-4-hydroxybenzoic acid methyl ester) mercurate(II), were described as compounds playing a part in the Millon reaction. Soon after a lecture** reporting our research papers by TAMURA *et al.* [3, 4] were published, describing the isolation of three coloured compounds from the reaction of *p*-cresol with stoichiometric amounts of the reagent. One of these products was identified as a complex compound (**IV**) of mercurated *p*-cresol (**II**) and 2-nitroso-4-methylphenol (**III**); the other was found to be bis(2-nitroso-4-methylphenol) mercurate (**V**). No formula was given for the third substance, however, 2-nitroso-4-methylphenol (**III**) could be isolated from the reaction mixture after its decomposition. Bis(2-nitroso-4-methylphenol) mercurate (**V**) and the third compound probably have the same structure as 2-nitroso-4-methylphenol mercurate nitrate (**VI**) isolated by us. The analogous compound isolated by us first, the mercurated *p*-cresol 2-nitroso-4-methylphenol complex (**IV**) can be formed, in our opinion, only under conditions when the amount of the mercury(II) and nitrite ions is equal to or less than that of the phenol involved in the reaction. However, under the conditions of the Millon colour reaction in practice, there is always a large excess of mercury(II) and nitrite ions as compared with the small amount of the phenol examined. The Japanese authors prepared the mercury complexes with stoichiometric amounts of the reagents, which, according to our investigations, are converted into the complexes studied by us earlier on the effect of a large excess of the reagent.

* Part I: Acta Chim. Acad. Sci. Hung. **68**, 133 (1971).
** Session of the Organic Chemical Committee of the Hungarian Academy of Sciences, Budapest, March 28, 1967 [1].

In order to confirm the above statements, the complex(**IV**) of mercurated *p*-hydroxybenzoic acid methyl ester (**II**) and 3-nitroso-4-hydroxybenzoic acid methyl ester (**III**) was prepared and the absorption curves of this compound as well as of the complex compounds obtained from it by the addition of mercury(II) nitrate and potassium nitrite, and of the coloured reaction mixtures of different compositions were examined in the UV and visible ranges.

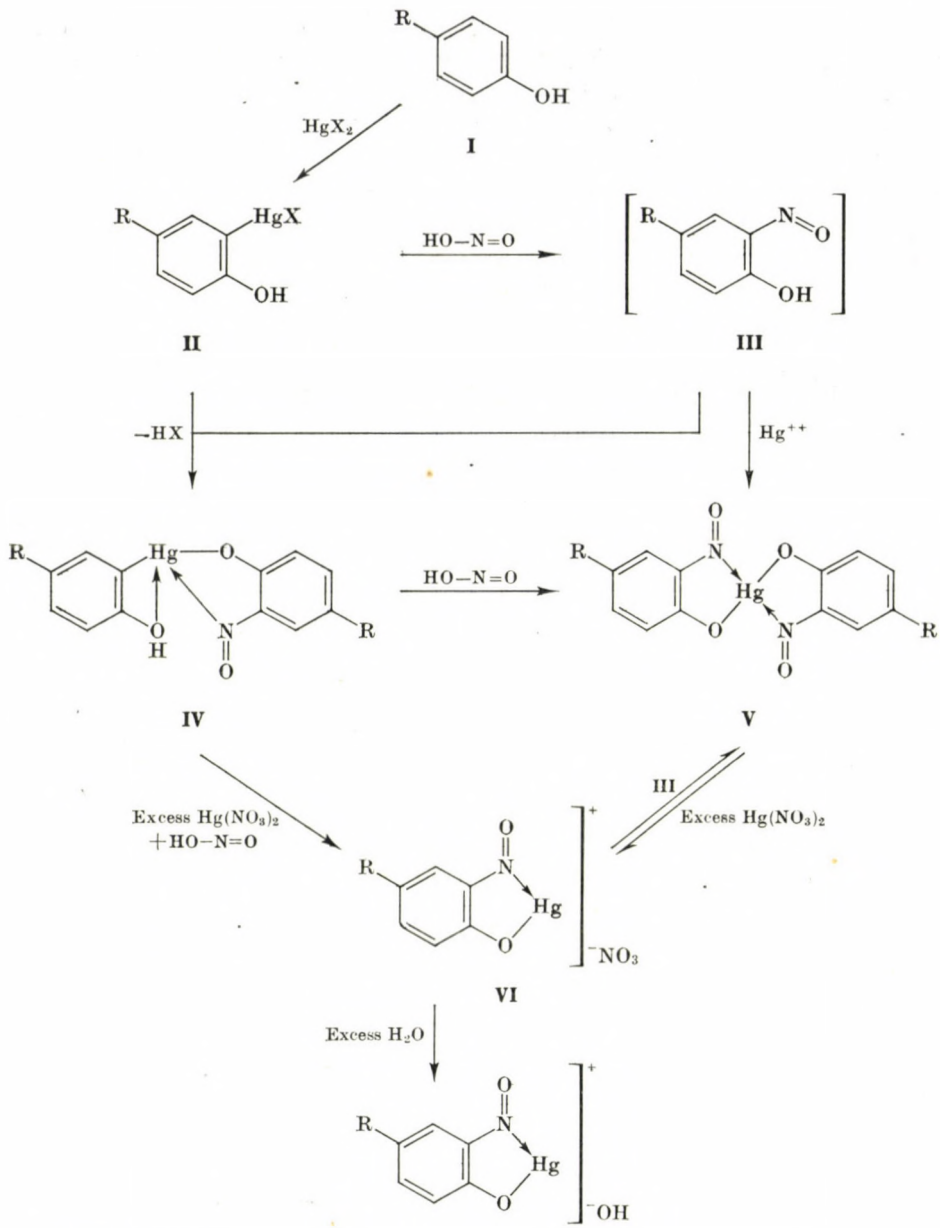
**Table I**

| Compound | Absorption maxima, nm | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| *p*-Hydroxybenzoic acid methyl ester (**I**) | 215 | | | 258 | | | | | | | | |
| 3-Nitroso-4-hydroxybenzoic acid methyl ester (**III**) | | | 247 | | | | | 287 | | | 380 | |
| 3-Mercury(II)-hydroxy-4-hydroxylbenzoic acid methyl ester (**II**) | | 220 | | | 263 | | | | | | | |
| 3-Nitroso-4-hydroxybenzoic acid methyl ester–4-hydroxybenzoic acid methyl ester-3-mercurate (**IV**) | | 220 | | | 263 | | | 341 | | | 490 | |
| Bis(3-nitroso-4-hydroxybenzoic acid methyl ester) mercurate(II) (**V**) | | | | | | 282 | | 341 | | | 490 | |
| Millon reaction mixture, with excess reagent | | * | | | | | | 341 | 349 | | 490—505 | |
| Millon reaction mixture with little reagent | | | | | | | | 341 | | | 490 | |
| **IV** + 40% $Hg(NO_3)_2$ + + $Hg(NO_2)_2$ | | | | | | | | | 349 | | | 505 |
| **IV** + $Hg(NO_2)_2$ | | | | | | | | 341 | | | 490 | |

* Cannot be measured, owing to the high concentration of mercury(II) ions.

Comparison of the maxime of the complex compound in question, of the compound formed from it on treatment with mercury(II) nitrate and nitrite, and of the Millon colour reaction mixtures having different compositions indicated unambiguously that the above complex compound (**IV**) is not present in the usual qualitative Millon colour reaction mixture, or may only appear as a transient intermediate. Its presence should only be taken into account when the concentrations of mercury(II) and nitrite ions are not sufficiently high.

It is considered possible that in the course of the development of a qualitative Millon colour reaction mixture, mercury complexes of different kinds are formed. These compounds may, however, undergo an interconversion, depending on the concentrations of the mercury and nitrite ions. It was described earlier [1, 2] how bis(3-nitroso-4-hydroxybenzoic acid methyl ester)-mercurate(II) (**V**) transforms into 3-nitroso-4-hydroxybenzoic acid methyl ester mercurate(II) nitrate (**VI**). In the present work, the conversion of the




R = $CH_3$, $COOCH_3$

X = $NO_2$, $NO_3$

3-nitroso-4-hydroxybenzoic acid methyl ester-3-mercury(II)-4-hydroxybenzoic acid methyl ester complex (**IV**) into bis(3-nitroso-4-hydroxybenzoic acid methyl ester) mercurate(II) (**V**) and 3-nitroso-4-hydroxybenzoic acid methyl ester mercurate(II) nitrate (**VI**) was proved spectroscopically.

On the basis of the above results, the course of the Millon reaction can be given as shown in Scheme 1, considering all possibilities.

## Experimental

M.p.'s are uncorrected.

### 3-Mercury(II)-4-hydroxybenzoic acid methyl ester complex of 3-nitroso-4-hydroxybenzoic acid methyl ester (IV)

3-Nitroso-4-hydroxybenzoic acid methyl ester [2] was dissolved in anhydrous ethanol to obtain a 5% solution, and finely powdered 3-mercury(II)-hydroxy-4-hydroxybenzoic acid methyl ester was then added in 10% excess. The suspension was shaken until complete reaction of 3-nitroso-4-hydroxybenzoic acid methyl ester had occurred. The excess of 3-mercury(II)-hydroxy-4-hydroxybenzoic acid methyl ester was filtered off from the cherry-red suspension and the alcoholic solution of the complex was diluted with water to twice its volume and allowed to crystallize in a refrigerator. The cherry-red powder was filtered off and dried over phosphorus pentoxide in a vacuum desiccator; m.p. 173 °C; the yield was almost quantitative.

$C_{16}H_{13}NO_7Hg$ (531.87). Calcd. N 2.63; Hg 37.71. Found N 2.32; Hg 37.4%.

The electron spectra were recorded with a Specord UV-VIS (Carl Zeiss, Jena) instrument. The complexes formed from the 3-nitroso-4-hydroxybenzoic acid methyl ester and 3-mercury(II)-4-hydroxybenzoic acid methyl ester complex, as well as the colour reaction mixtures were prepared by means of 40% mercury(II) nitrate and potassium nitrite solutions, applying gentle heating. In the preparation of the sample solutions, 10 mg of the respective compound and 3 ml each of the reagents were used. The Millon resgent was prepared as described earlier [2]. Before the spectroscopic measurement, an equal volume of ethanol (Uvasol®, Merck) was added to the reaction mixture, the salts which separated were filtered off and the measuring concentration was adjusted by the addition of ethanol. Melting points were determined on a Boetius (Franz Küstner K. G. Dresden) micro melting point apparatus.

*

The authors' thanks are due to Mrs. I. SZABÓ for the analyses.

## REFERENCES

[1] LÁZÁR, J., MÓD, L., VINKLER, E.: Kémiai Közlemények **29,** 257 (1968)
[2] LÁZÁR, J., MÓD, L., VINKLER, E.: Acta Chim. Acad. Sci. Hung. **68,** 133 (1971)
[3] TAMURA, Z., KIDO, Y.: Chem. Pharm. Bull. **16,** 1808 (1968)
[4] TAMURA, Z., IITAKA, Y., KIDO, Y.: Chem. Pharm. Bull. **17,** 1767 (1969)

János LÁZÁR
László MÓD
Elemér VINKLER
H-6701 Szeged 1, Eötvös u. 6. P.O.B. 121

*Acta Chimica Academiae Scientiarum Hungaricae, Tomus 98 (3), pp. 339—348 (1978)*

# NITROXIDES, II*

## 1-OXYL-2,2,5,5-TETRAMETHYLPYRROLINE-3-CARBOXYLIC ACID DERIVATIVES

H. O. HANKOVSZKY, K. HIDEG and J. TIGYI

*(Central Laboratory of Chemistry and Biophysical Department, University of Pécs)*

Received October 10, 1977

From 1-oxyl-2,2,5,5-tetramethylpyrroline-3-carboxylic acid esters, a carboxylic acid azide is formed with sodium azide. At room temperature, the acid azide acylates the amino group of aminoalcohols, whereas at higher temperatures it is decomposed into the isocyanate. Some reactions of the isocyanate (with alcohols, thioalcohols and amino derivatives) have been studied.

An important aim of the synthesis of stable nitroxide-free radicals is to prepare free radicals with reactive functional groups that may be attached to nucleophilic groups of biomolecules (mainly to NH, SH, OH) without the loss of the radical character (see reviews [1, 2, 3, 4]). It is important that such couplings should proceed under mild conditions.

Paramagnetic active esters **1** have been prepared from 1-oxyl-2,2,5,5-tetramethylpyrroline-3-carboxylic acid and alcohols bonded to electron-attracting groups, by reaction with dicyclohexylcarbodiimide (DCC), proved satisfactory in peptide synthesis. Some representatives of these radicals (**1a**, **b**) are known [5, 6].

We have extended the domain of these derivatives to thioesters to ensure a larger selection of these acylating agents for biological tests.

By reacting the active esters with hydrazine, carboxylic hydrazide (**3**) has been prepared.

From the carboxylic acid and chloroformic acid ester, GRIFFITH *et al.* [7] prepared mixed anhydride (**2**), and used it mainly for the biological labeling of nucleic acids. The mixed anhydride of phenylcyclopropylcarboxylic acid was first applied by WEINSTOCK for the preparation of acid azide [8]. We used for the synthesis of acid azide both the paramagnetic mixed anhydride (**2**) and active esters (**1**). The azide (**4**) was obtained in good yield from either starting materials.

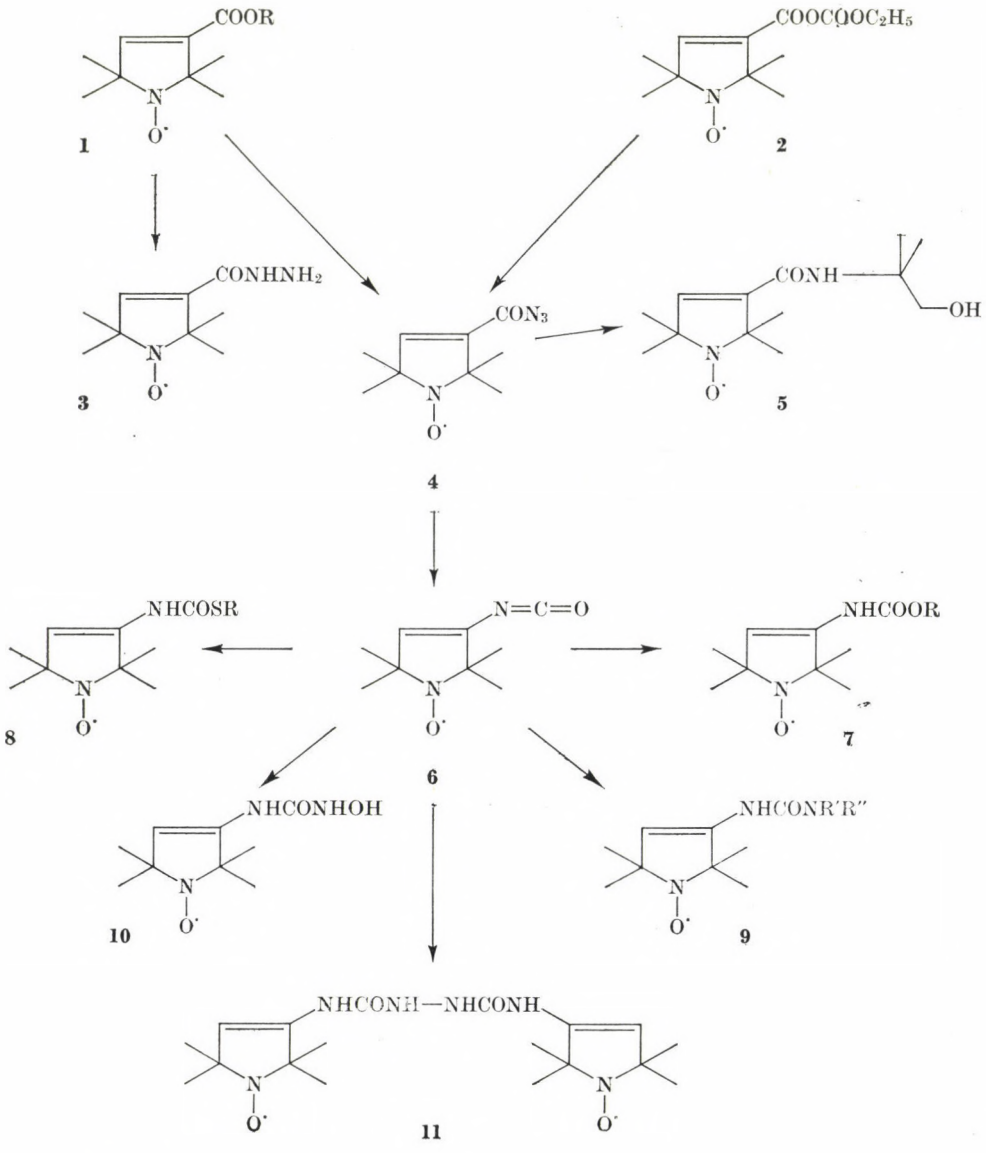
With the carboxylic acid azide, the 2-amino-2-methyl-1-propanol could be acylated under very mild conditions on its amino group to **5**. When heated in inert solvent, the carboxylic acid azide is converted *via* a Curtius type rearrangement into isocyanate **6**.

* Part I: K. HIDEG, O. H. HANKOVSZKY, J. TIGYI: Acta Chim. (Budapest), **92**, 85 (1977).

A paramagnetic isocyanate has previously been prepared from 1-oxyl-3-amino-2,2,5,5-tetramethylpyrrolidine and phosgene [9].

This compound was used without isolation and purification for the labeling of poly-L-lysine. However, this substance did not find wide application, which is probably due to the use of phosgene and to the instability of the non-isolated isocyanate.

We wished also to study the reactions of isocyanate **6** prepared by us:



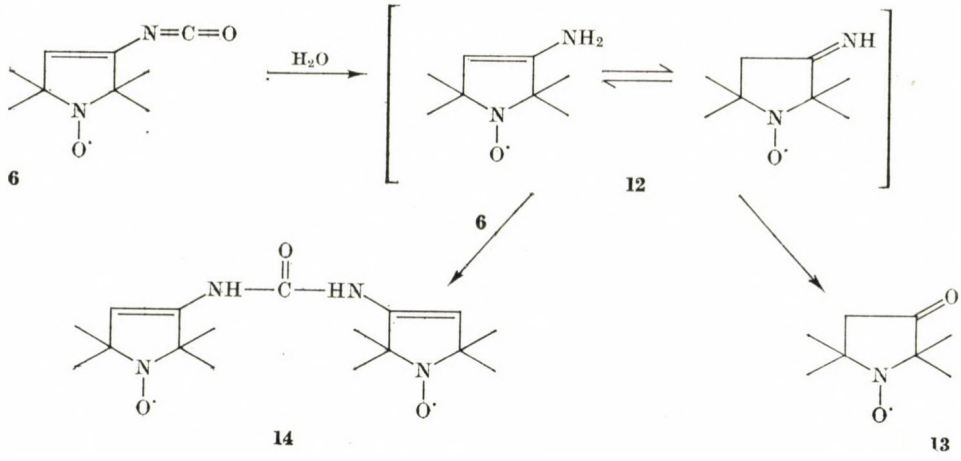
Urethanes **7** were prepared with alcohols and phenols, and thiourethanes **8** with thiophenol and benzyl mercaptan.

With amines, compounds of the urea **9**, with hydroxylamine, those of the hydroxyurea type **10**, and with hydrazine, derivatives of the symmetrical bis(aminoacyl)hydrazine type **11** were formed.

Symbol **R** in Table I includes also the meaning of the R, R′, R″ groups.

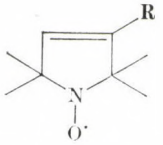
In alkaline aqueous solution the isocyanate **6** is converted, presumably through unstable enamine **12**, into 1-oxyl-2,2,5,5-tetramethylpyrrolidine-3--one (**13**)

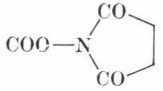
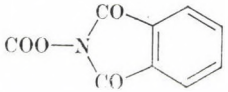
Upon refluxing the acid azide in non-anhydrous benzene or toluene, symmetrical urea **14** was formed. Its biradical structure is supported, beside elemental analysis, by mass-spectrometric analysis and by the 1 : 2 : 3 : 2 : 1 intensity ratio of the five lines in the EPR spectrum.




The compounds prepared are listed in Table I.

**Table I**



| No | R | M.p.(°C) | Method | Yield (%) | Formula (Mol. wt.) | Analysis (%) C | Analysis (%) H | Analysis (%) N | IR[d](cm$^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | | Calcd./Found | | | |
| **1a** | $COOC_6H_4$—4-$NO_2$ | 108—109[a] | **A** | 80 | $C_{15}H_{17}N_2O_5$ (305.32) | | | | 1740 ($\nu$CO) |
| **1b** |  | 179—181[b] | **A** | 82 | $C_{13}H_{17}N_2O_5$ (281.29) | | | | 1765, 1720 ($\nu$CO, $\nu$CON) |
| **1c** |  | 172—173 | **A** | 50 | $C_{17}H_{17}N_2O_5$ (329.34) | 62.00<br>62.24 | 5.20<br>5.44 | 8.50<br>8.67 | 1765, 1730 ($\nu$CO, $\nu$CON) |
| **1d** | $COOC_6H_3$-2,4$(NO_2)_2$ | 162—163 | **A** | 43 | $C_{15}H_{16}N_3O_7$ (350.31) | 51.43<br>51.59 | 4.61<br>5.01 | 11.99<br>11.74 | 1750 ($\nu$CO) |
| **1e** | $COOC_6Cl_5$ | 194—195 | **A** | 48 | $C_{15}H_{13}Cl_5NO_3$ (432.55) | 41.65<br>41.60 | 3.03<br>3.29 | 3.24<br>3.25 | 1740 ($\nu$CO) |
| **1f** | $COSC_6H_5$ | 133—135 | **A** | 72 | $C_{15}H_{18}NO_2S$ (276.38) | 65.19<br>65.29 | 6.56<br>6.88 | 5.07<br>4.94 | 1670 ($\nu$COS) |
| **1g** | $COSCH_2C_6H_5$ | 98—100 | **A** | 83 | $C_{16}H_{20}NO_2S$ (290.41) | 66.18<br>66.38 | 6.94<br>6.65 | 4.82<br>4.69 | 1640 ($\nu$CO) |
| **2** | $COOCOOC_2H_5$ | 63—65[c] | **B** | 90 | $C_{12}H_{18}NO_5$ (256.28) | | | | 1800, 1735 ($\nu$COOCOOEt) |
| **3** | $CONH—NH_2$ | 124—125 | **C** | 90 | $C_9H_{16}N_3O_2$ (198.25) | 54.53<br>54.47 | 8.13<br>7.97 | 21.20<br>20.92 | 3400—3300 ($\nu NHNH_2$)<br>1660 ($\nu$CO) |

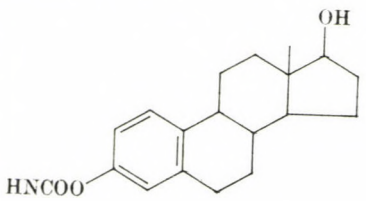
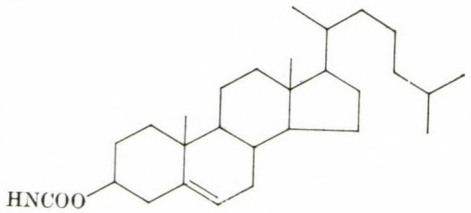
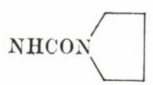
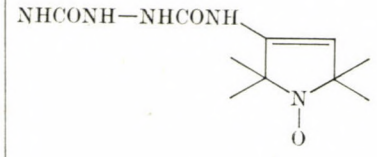
| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| **4** | $CON_3$ | 62—63 | **D** | 93 | $C_9H_{13}N_4O_2$<br>(209.23) | 51.67<br>51.52 | 6.26<br>6.39 | 26.78<br>26.68 | 2150<br>($\nu N_3$)<br>1675<br>($\nu$CO) |
| **5** | $CONHC(CH_3)_2CH_2OH$ | 136—137 | **E** | 62 | $C_{13}H_{23}N_2O_3$<br>(255.33) | 61.15<br>61.38 | 9.08<br>9.12 | 10.97<br>10.71 | 3420, 3260<br>($\nu$OH,NH)<br>1650, 1530<br>($\nu$CONH) |
| **6** | $N = C = O$ | 35—38 | **F** | 97 | $C_9H_{13}N_2O_2$<br>(181.21) | 59.65<br>59.43 | 7.23<br>7.36 | 15.46<br>15.53 | 2260<br>($\nu$NCO) |
| **7a** | $NHCOOC_2H_5$ | 191—192 | **G** | 79 | $C_{11}H_{19}N_2O_3$<br>(227.28) | 58.13<br>58.07 | 8.43<br>8.20 | 12.32<br>12.38 | 3260<br>($\nu$NH)<br>1720<br>($\nu$CO) |
| **7b** | $NHCOOC_6H_4$-4-$NO_2$ | 176—177 | **G** | 68 | $C_{15}H_{18}N_3O_5$<br>(320.33) | 56.25<br>56.02 | 5.66<br>5.80 | 13.12<br>13.43 | 3250<br>($\nu$NH)<br>1720<br>($\nu$CO) |
| **7c** |  | 205—207 | **G** | 78 | $C_{27}H_{37}N_2O_4$<br>(453.60) | 71.49<br>71.48 | 8.22<br>8.32 | 6.18<br>5.75 | 3480, 3230<br>($\nu$OH, $\nu$NH) |
| **7d** |  | 209—210 | **G** | 65 | $C_{36}H_{59}N_2O_3$<br>(567.88) | 76.14<br>76.10 | 10.47<br>10.40 | 4.94<br>4.35 | 3240<br>($\nu$NH)<br>1720<br>($\nu$CO) |
| **8a** | $NHCOSC_6H_5$ | 155—156 | **G** | 85 | $C_{15}H_{19}N_2O_2S$<br>(291.40) | 61.83<br>61.65 | 6.57<br>6.87 | 9.61<br>10.04 | 3230<br>($\nu$NH)<br>1685<br>($\nu$CO) |

**Table I.** (cont.)

| No | R | M.p.(°C) | Method | Yield (%) | Formula (Mol. wt.) | Analysis (%) C | Analysis (%) H | Analysis (%) N | IR[d](cm$^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | | Calcd./ Found | | | |
| **8b** | $NHCOSCH_2C_6H_5$ | 143—144 | **G** | 30 | $C_{16}H_{21}N_3O_2S$ (305.42) | 62.92<br>62.59 | 6.93<br>6.67 | 9.17<br>8.92 | 3250 ($\nu$NH)<br>1690 ($\nu$CO) |
| **9a** |  | 164—165 | **H** | 80 | $C_{11}H_{18}N_3O_2$ (224.28) | 58.90<br>59.11 | 8.09<br>8.02 | 18.74<br>18.94 | 3230 ($\nu$NH)<br>1690 ($\nu$CO) |
| **9b** |  | 146—148 | **H** | 56 | $C_{13}H_{22}N_3O_2$ (252.33) | 61.88<br>61.51 | 8.79<br>8.95 | 16.65<br>16.72 | 3380 ($\nu$NH)<br>1680 ($\nu$CO) |
| **9c** | $NHCONHC(CH_3)_2C{\equiv}CH$ | 211—212 | **H** | 72 | $C_{14}H_{22}N_3O_2$ (264.35) | 63.61<br>63.86 | 8.39<br>8.50 | 15.90<br>15.88 | 3295, 3210 ($\nu$NH)<br>1670, 1650 ($\nu$CONH) |
| **9d** | $NHCONHC(C_2H_5)_2C{\equiv}CH$ | 200—201 | **H** | 64 | $C_{16}H_{26}N_3O_2$ (292.41) | 65.72<br>65.64 | 8.96<br>8.60 | 14.37<br>14.24 | 3300, 3200 ($\nu$NH)<br>1660, 1640 ($\nu$CONH) |
| **9e** | $NHCONHC_6H_4$-4-$COOC_2H_5$ | 192—193 | **H** | 92 | $C_{18}H_{24}N_3O_4$ (346.41) | 62.41<br>62.62 | 6.98<br>6.66 | 12.13<br>12.12 | 3360—3240 ($\nu$NH)<br>1720, 1705, 1670 ($\nu$COO, $\nu$CONH) |
| **9f** | $NHCONHC_6H_4$-4-$COO(CH_2)_2N(C_2H_5)_2$ | 78—79 | **H** | 36 | $C_{22}H_{33}N_4O_4 \cdot H_2O$ (435.53) | 60.67<br>60.90 | 8.10<br>7.89 | 12.86<br>12.78 | 3480, 3290 ($\nu$NH)<br>1715, 1700, 1690 ($\nu$COO, $\nu$CONH) |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| **10** | NHCONHOH | 131—134 | **H** | 37 | $C_9H_{16}N_3O_3$ (214.25) | 50.46<br>50.59 | 7.53<br>7.28 | 19.61<br>19.38 | 3400—3000 ($\nu$OH, $\nu$NH)<br>1700 ($\nu$CO) |
| **11** |  | 185—186 | **I** | 50 | $C_{18}H_{30}N_6O_4$ (394.46) | 54.81<br>54.84 | 7.67<br>7.84 | 21.30<br>21.26 | 3600—3060 ($\nu$NH)<br>1700, 1680 ($\nu$CONH) |

[a] in Ref. [5]: m.p. 116—118.5 °C; [b]in Ref. [6]: m.p. 185—187 °C; [c]in Ref. [7]: m.p. 65 °C (decomp.)
[d]N—O appears = 1350—1305 $cm^{-}j$

## Experimental

Melting points were determined with a Büchi Model SPM-20 apparatus, and are uncorrected. The IR spectra of suspensions in paraffin oil were recorded on a Zeiss Specord 71 spectrophotometer.

### Preparation of active esters (Method A)

*3-(Phenylthio-carbonyl)-1-oxyl-2,2,5,5-tetramethylpyrroline* (**1f**)

The solution of 1-oxyl-2,2,5,5-tetramethylpyrroline-3-carboxylic acid (1.84 g, 0.01 mole) and of thiophenol (1.10 g, 0.01 mole) in dry ethyl acetate (20 ml) was cooled to 0 °C. Under stirring, a solution of DCC (2.05 g, 0.01 mole) in ethyl acetate (30 ml) was added dropwise (over about 5 min). The mixture was stirred for further 2 hrs at room temperature, filtered, and the filtrate evaporated under vacuum. The residue was crystallized from ether. Yield 2.0 g (72%), m.p. 133—135 °C.

### Preparation of mixed anhydride (Method B)

This mixed anhydride **2** is known [7], from the same starting compounds as under, but without triethylamine. The yield was 59%.

*(Carbonic acid — 1-oxyl-2,2,5,5-tetramethylpyrroline-3-carboxylic acid) anhydride ethyl ester* (**2**)

To a suspension of 1-oxyl-2,2,5,5-tetramethylpyrroline-3-carboxylic acid (9.2 g, 0.05 mole) in ether (100 ml), triethylamine (5.05 g, 0.05 mole) was added, then the mixture was cooled to 0 °C, and under stirring a solution of ethyl chloroformate (5.42 g, 0.05 mole) in ether (50 ml) was added dropwise. After the addition had been completed, stirring was continued for 3 hrs at room temperature. Triethylamine hydrochloride was filtrated off, the filtrate evaporated, the residue was taken up in hexane (50 ml) and allowed to stand in refrigerator. The yellow, needle-shaped crystals separated were filtrated. Yield 11.6 g, 90%, recrystallized from ether–hexane. m.p.: 63—65 °C (lit. [7] m.p.: 65°, decomp.).

### Preparation of acid hydrazide (Method C)

*1-Oxyl-2,2,5,5-tetramethylpyrroline-3-carbonyl hydrazine* (**3**)

A solution of 1-oxyl-2,2,5,5-tetramethylpyrroline-3-carboxylic acid N-hydroxysuccinimide ester (**1a**) (2.81 g, 0.01 mole) in alcohol (10 ml) was stirred with a solution of hydrazine hydrate (1.5 g, 0.03 mole) in water (10 ml) at room temperature for 30 min. The solution was saturated with sodium chloride, extracted with chloroform, dried over $Na_2SO_4$, filtered and evaporated. The residue was dissolved in ether and the crystals separated were filtered. Yield 1.8 g (90%), m.p.: 124—125 °C.

### Preparation of carboxylic acid azide (Method D)

*1-Oxyl-2,2,5,5-tetramethylpyrroline-3-carbonylazide* (**4**)

(a) A solution of **2** (10.25 g, 0.04 mole) in aceton-water (2 : 1, 75 ml), was cooled to 0 °C, solution of sodium azide (3.88 g, 0.06 mole) in water (15 ml) was added and the mixture was stirred for 30 min. On the evaporation of the aceton in vacuum at 0 °C, the azide (**4**) was separated in yellow crystals. Yield 7.8 g (93%), m.p.: 62—63 °C.

(b) 1-Oxyl-2,2,5,5-tetramethylpyrroline-3-carboxylic acid N-hydroxysuccinimide ester (**1b**) was reacted and processed as above (a) with sodium azide. Reaction time 2 hrs, yield 88%. The substance is identical with the product obtained in (a).

### Acylation of an amino alcohol with acid azide (Method E)

*N-(1,1-Dimethyl-2-hydroxyethyl)-1-oxyl-2,2,5,5-tetramethylpyrroline-3-carboxamide* (**5**)

A solution of 2-amino-2-methylpropan-1-ol (0.89 g, 0.01 mole) in ethyl alcohol (20 ml) was stirred with acid azide **4** (2.09 g, 0.01 mole) at 0 °C for 2 hrs. The reaction mixture was diluted with water (50 ml), extracted with chloroform (3×10 ml), dried over sodium sulfate and evaporated to dryness. The residue was crystallized from ether–hexane. Yield 1.58 g (62%), m.p.: 136—137 °C.

### Conversion of acid azide into isocyanate (Method F)

*1-Oxyl-2,2,5,5-tetramethylpyrroline-3-isocyanate* (**6**)

The solution of the acid azide (**4**) (2.09 g, 0.01 mole) in cyclohexane (30 ml) was refluxed for 30 min and the solvent was distilled off in vacuum. The residual odorous oil, isocyanate derivative **6** was crystallized on cooling. When thermal decomposition and evaporation were carried out under complete exclusion of moisture, the crystalline substance proved to be fairly pure. Yield is almost quantitative (97%), m.p.: 35—38 °C.

### Preparation of urethanes and thiourethanes (Method G)

*Ethyl-N-(1-oxyl-2,2,5,5-tetramethylpirrolin-3-yl)-carbamate* (**7a**)

The freshly prepared isocyanate (**6**) (1.81 g, 0.01 mole) was reacted under stirring with anhydrous ethyl alcohol (10 ml). After 30 min, excess alcohol was distilled off. The product was crystallized from chloroform–ether. Yield 1.8 g (79%), m.p.: 191—192 °C.

*Phenyl-N-(1-oxyl-2,2,5,5-tetramethylpyrrolin-3-yl)-thiocarbamate* (**8a**)

To a stirred solution of the freshly prepared isocyanate (**6**) (1.81 g, 0.01 mole) in cyclohexane (30 ml) at 0 °C, a solution of thiophenol (1.10 g, 0.01 mole) in cyclohexane (15 ml) was added. After 1 hr the crystals separated were filtered and washed with ether. The product (2.5 g, 85%) was recrystallized from chloroform–hexane, m.p.: 155—156 °C.

### Preparation of urea derivatives (Method H)

*-Aziridine-N-(1-oxyl-2,2,5,5-tetramethylpyrrolin-3-yl)carboxamide* (**9a**)

The acid azide (**4**) (2.09 g, 0.01 mole) was dissolved in cyclohexane (30 ml), decomposed into the isocyanate by boiling for 30 min, then cooled to 0 °C. Under stirring, the solution was reacted with a solution of ethyleneimine (0.51 g, 0.012 mole) in cyclohexane (10 ml). After 30 min, the product separated was filtered, washed with ether and dried. The substance was crystallized from chloroform–hexane. Yield 1.8 g (80%), m.p.: 164—165 °C.

*

*N-Hydroxy-N'-(1-oxyl-2,2,5,5-tetramethylpyrrolin-3-yl)urea* (**10**)

To a solution of freshly decomposed acid azide (**4**) (1.045 g. 0.05 mole) in ether (20 ml), solution of hydroxylamine hydrochloride (0.345 g, 0.005 mol in water (20 ml), made alkaline with $Na_2CO_3$, was added. It was stirred at room temperature for 2 hrs, then staturated with NaCl. The ether phase was separated, dried over sodium sulfate and evaporated. The residual oil was crystallized from ether-hexane. Yield 0.4 g (37%), m.p.: 131—134 °C.

### Reaction of the isocyanate with hydrazine (Method I)

*N,N'-bis(1-Oxyl-2,2,5,5-tetramethylpyrroline-3-aminocarbonyl)hydrazine* (**11**)

To a solution of the freshly decomposed azide (**4**) (2.09 g, 0.01 mole) in ether (20 ml), a solution of hydrazine hydrate (1.5 g, 0.03 mole) in water (10 ml) was added. The mixture was shaken at room temperature, the product precipitated (about 20 min) was filtered, washed with water, ether, and dried. Yield 1 g, (50%). The analytical sample was recrystallized from chloroform–hexane containing a small amount of dimethyl sulfoxide, m.p.: 185—186 °C.

### Hydrolysis of the isocyanate

*a)* *1-Oxyl-2,2,5,5-tetramethylpyrrolidin-3-one* (**13**)

To a solution of the acid azide (**4**) (2.09 g, 0.01 mole) in alcohol (3 ml) an aqueous NaOH solution (30 ml, 10%) was added and boiled for 3 hrs. The solution was then cooled, saturated with potassium carbonate, extracted with chloroform (3 × 10 ml) and dried over sodium sulfate. The solvent was distilled off, and the residual oil (1 g, 64%) was purified by chromatography on alumina, using a petroleum ether–tetrahydrofuran mixture as eluent. The solvent

was distilled off and the residual oil solidified on cooling. m.p.: 41—43 °C. The substance was identical with the ketone prepared by a different method (lit. [10] m.p.: 41.5—42.5 °C).
$C_8H_{14}NO_2$ (156.21)

| | | | |
|---|---|---|---|
| Calcd. | C 61.51, | H 9.03, | N 8.97; |
| Found | C 61.28, | H 8.82, | N 9.02% |

IR (Nujol), 1750 ($\nu$CO) $cm^{-1}$.

b) *N,N'-bis(1-oxyl-2,2,5,5-tetramethylpyrrolin-3-yl)carboxamide* **(14)**

The acid azide (**4**) (2.09 g, 0.01 mole) was boiled in non-anhydrous (water content is about 0.05%) benzene or toluene (200 ml) for 6 hrs. The solvent was distilled off and the residue suspended in hexane. Yield 0.8 g (47.6%), m.p.: 179—180 °C. Recrystallized from chloroform-hexane, m.p.: 186.5 °C.
$C_{17}H_{28}N_4O_3$ (336.4)

| | | | |
|---|---|---|---|
| Calcd. | C 60.99, | H 8.39, | N 16.65; |
| Found | C 61.06, | H 8.21, | N 16.53%. |

IR(Nujol), 3508, 3325 ($\nu$NH), 1702 ($\nu$CO) $cm^{-1}$. MS: M+336.

*

The authors wish to thank Dr. J. Belágyi (University of Pécs) for the ESR spectrometric, and Dr. Gy. Horváth (Institute for Drug Research) for the mass-spectrometric investigations. Technical assistance was provided by Mrs. M. Ott, Miss T. Huszár and Mrs. L. Lovas. For the financial support of this research, thanks are due to Reanal Factory of Laboratory Chemicals.

## REFERENCES

[1] McConnell, H. M., Gaffney-McFarland, B.: Quart. Rev. Biophys., **3,** 91 (1970)
[2] Likhtensthein, G. I.: Spin Labeling Methods in Molecular Biology (translated by P. S. Shelnitz). Wiley-Interscience, New York 1976
[3] Berliner, L. J. (Ed.): Spin Labeling, Theory and Applications, Academic Press, New York 1976
[4] Smith, I. C. P., Schreier-Muccillo, S., Marsh, D. in Spin Labeling "Free Radicals in Biology" (Ed. W. A. Pryor), pp. 149–197. Academic Press, New York 1976
[5] Berliner, L. J.: Biochemistry, **11,** 2921 (1972)
[6] Hoffman, B. M., Schofield, P., Rich, A.: Biochemistry, **9,** 2525 (1970)
[7] Griffith, O. H., Keana, J. F. W., Noall, D. L., Ivey, J. L.: Biochem. Biophys. Acta, **148,** 683 (1967)
[8] Weinstock, J.: J. Org. Chem., **26,** 3511 (1961)
[9] Stone, T. J., Buchman, T., Nordio, P. L., McConnell, H. M.: Proc. Nat. Acad. Sci. U. S., **54,** 1010 (1965)
[10] Rozantsev, E. G., Krinitzkaya, L. A.: Tetrahedron, **21,** 491 (1965)

Kálmán Hideg
Olga H. Hankovszky
József Tigyi
H-7643 Pécs, P.O.Box 99

*Acta Chimica Academiae Scientiarum Hungaricae, Tomus 98 (3), pp. 349—352 (1978)*

# SYNTHESIS OF PHENYL 4-DEOXY-β-D-GLUCOPYRANOSIDE

L. KISS and P. NÁNÁSI

*(Biochemical Institute, Kossuth Lajos University, Debrecen)*

Received October 18, 1977

A simple synthesis has been elaborated for the preparation of phenyl 4-deoxy-β-D-glucopyranoside (**5**), based on the reduction of phenyl 6-O-benzoyl-2,3-di-O-benzyl-4-O-*p*-toluenesulfonyl-β-D-glucopyranoside (**3**) with $LiAlH_4$, directly to the 4-deoxy derivative (**4**). Elimination of the benzyl groups by catalytic hydrogenation gave **5**. It is shown that the benzoyl group at C-6 is located suitably to form an alkoxyaluminium hydride making possible an intramolecular reduction.

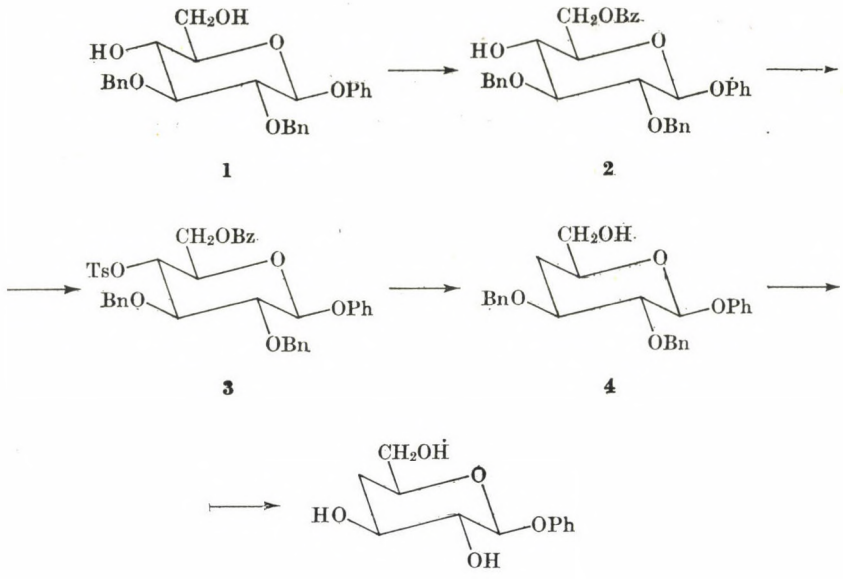
In the course of the work in our laboratory on sweet almond emulsin investigating the formation of the enzym-substrate complex, we needed pheny 4-deoxy-β-D-glucopyranoside.

There are several methods available for obtaining the 4-deoxy function, *e.g.* ,through the epoxide [1, 2] or *via* iodine substitution of a tosyloxy group at $C_4$ followed by hydrogenation [3]. The disadvantages of these methods are poor yield in the first case and tedious and long reaction route in the second.

Therefore, another reaction path was chosen for preparing the title compound. It is known that secondary toluenesulfonyl groups may be reduced to the deoxy stage provided there is a suitably located group which can form an alkoxyaluminium hydride thus allowing an intramolecular reduction [4—7]. Such a group may be a neighbouring hydroxyl or ester group, in *trans* position to the tosyloxy group to be reduced.

It seemed to be of interest to test to what an extent this reaction may be applied to phenyl 2,3-di-O-benzyl-6-O-benzoyl-4-O-*p*-toluenesulfonyl-β-D--glucopyranoside (**3**), where the 6-O-benzoyl group may be suitably located to form an alkoxyaluminium hydride required for the intramolecular reduction.

The reaction route is summarized in Scheme 1. Phenyl 2,3-di-O-benzyl-β--D-glucopyranoside (**1**) [8] was chosen as the starting material, which is a readily available compound. This was benzoylated at 0 °C with 1 molar equivalent of benzoyl chloride in dry pyridine to obtain the 6-O-benzoyl derivative (**2**). The reaction was monitored by TLC, which showed that the benzoylation was complete in two hours. Compound **2** was purified from the contaminating small amount of the di-O-benzoyl derivative and unchanged starting material, detected by TLC, by means of recrystallization from alcohol. Treatment of **2** with




*Scheme* 1

*p*-toluenesulfonyl chloride in dry pyridine gave phenyl 6-O-benzoyl-2,3-di-O--benzyl-4-O-*p*-toluenesulfonyl-β-D-glucopyranoside (**3**) in a good yield (79.7%).

The reaction of **3** with $LiAlH_4$ in boiling anhydrous tetrahydrofuran furnished phenyl 2,3-di-O-benzyl-4-deoxy-β-D-glucopyranoside (**4**) in a good yield (70%) as the main product and a small amount of phenyl 2,3-di-O--benzyl-β-D-glucopyranoside, from which **4** was purified by passing through a short column.

The deoxy function was identified by the NMR signal due to the C-4 *a* and *e* protons. Catalytic hydrogenation of **4** yielded phenyl 4-deoxy-β-D--glucopyranoside (**5**).

The role of the formation of the C-6 alkoxyaluminium hydride derivative was proved by the treatment of phenyl 2,3-di-O-benzyl-4,6-di-O-*p*-toluenesulfonyl-β-D-glucopyranoside with $LiAlH_4$ in the same manner as described above for **3**. In this case at first the 6-deoxy derivative is formed, and because of the lack of formation of the C-6 alkoxyaluminium hydride, O—S fission takes place at C-4; thus, after removal of the benzyl groups, the product is phenyl 6-deoxy-β-D-glucopyranoside.

## Experimental

M.p.'s were determined on a Kofler apparatus and are uncorrected. Optical rotations were measured with a Polamat A Zeiss automatic photoelectric polarimeter. NMR spectra were recorded on a Jeol MH-100 instrument with solutions in $CDCl_3$ and deuterated DMSO,

using TMS internal standard. The reactions were monitored and the purity of products assessed by TLC on Kieselgel G Merck. Kieselgel G was also used for short-column chromatography [9], using benzene: ethyl acetate (9 : 1) mixture.

### Phenyl 2,3-di-O-benzyl-β-D-glucopyranoside (1)

This compound was synthesized according to MICHEEL and KLEMER [8]

### Phenyl 6-O-benzoyl-2,3-di-O-benzyl-β-D-glucopyranoside (2)

Compound **1** (12 g) was dissolved in dry pyridine (60 ml) and stirred while cooling in ice-water. Benzoyl chloride (4,5 ml) was added dropwise and stirring was continued for 2.5 h. The reaction mixture was then poured into ice-water, rubbed to obtain a powder, filtered off and washed free from pyridine. The crude product was crystallized from methanol (180 ml) to yield 12 g (81%) of **2**, m.p. 140 °C; $[\alpha]_D^{20}$ — 23.2° ($c$ = 0.6, $CHCl_3$); $R_f$ 0.55.

$C_{33}H_{32}O_7$, Calcd. C 73.33; H 5.92. Found C 73.16; H 5.88%.

### Phenyl 6-O-benzoyl-2,3-di-O-benzyl-4-O-p-toluenesulfonyl-β-D-glucopyranoside (3)

Compound **2** (13.5 g) was dissolved in dry pyridine (80 ml), tosyl chloride (8.5 g) was added and the mixture was kept at 50 °C for 3 days. After this time the reaction was complete, as shown by TLC, and the reaction mixture was poured into water (600 ml). It was extracted with chloroform (300 ml), the extract was dryed over calcium chloride and evaporated to a syrup, which was then crystallized from alcohol (80 ml) to yield 13 g (79.7%) of **3**, m.p. 113—115 °C; $[\alpha]_D^{20}$ — 15.5° ($c$ = 0.6 $CHCl_3$); $R_f$ 0.9.

$C_{40}H_{38}O_9S$. Calcd. C 69.16; H 5.47. Found C 69.17; H 5.75%.

### Phenyl 2,3-di-O-benzyl-4-deoxy-β-D-glucopyranoside (4)

$LiAlH_4$ (5.44 g; 0.14 mole) was suspended in dry tetrahydrofuran (100 ml) and was stirred and refluxed for 2 h. Then 6.4 g (0.009 mole) of **3** was added, and stirring and refluxing was continued for 20 h. The excess of $LiAlH_4$ was destroyed with ethyl acetate and the reaction mixture was poured into ether (250 ml). The precipitate was filtered off and washed with a 1 : 1 mixture of methanol: acetone. The combined filtrate and washings were washed three times with a 10% solution of Sodium potassium tartrate and then with water, dried over $Na_2SO_4$ and evaporated. The syrupy product was purified by passing through a short column (80 g Silicagel G; solvent system: benzene–ethyl acetate 9 : 1). Recrystallization from ether–hexane gave 2.65 g (68.47%) of **11**, m.p. 86—88 °C; $[\alpha]_D^{20}$ — 27.9° ($c$ = 1; $CHCl_3$).

NMR:$\delta$ 7.3 m, 15H (aromatic protons); 4.9 m, 3H (anomeric proton, 2 benzylic protons); 4.64 s, 2H (benzylic protons); 2 m, 1H (C-4 *equatorial* proton);1.55 m, 1H (C-4 *axial* proton,) 3.59 m, 5H (ring protons). $R_f$ 0.25.

$C_{26}H_{28}O_5$. Calcd. C 74.28; H 6.66. Found C 74.33; H 6.75%.

### Phenyl 4-deoxy-β-D-glucopyranoside (5)

Compound **4** (1 g) was dissolved with stirring in ethyl acetate (30 ml) and it was hydrogenated in the presence of palladium-on-charcoal (200 mg). The reaction was monitored by TLC, which showed that the elimination of the benzyl groups was complete in 4 h. The catalyst was then filtered off and the filtrate evaporated to give crystalline **5** 0.55 g; (96.5%), m.p. 118—120 °C; $[\alpha]_D^{20}$ — 57.9° ($c$ = 1; H O).

$C_{12}H_{12}O_5$. Calcd. C 59.99; H 6.71. Found C. 59.87; H 6.62%.

### Treatment of phenyl 2,3-di-O-benzyl-4,6-di-O-p-toluenesulfonyl-β-D-glucopyranoside with LiAlH

Compound **1** (2 g) was tosylated with 2 g of *p*-toluenesulfonyl chloride in the usual manner to obtain 3 g (88%) of the di-O-tosyl derivative (m.p. 152—154 °C), which was treated in the same manner with $LiAlH_4$ as **3**. After debenzylation by catalytic hydrogenation phenyl 6-deoxy-α-D-glucopyranoside was obtained, m.p. 160—161 °C; $[\alpha]_D^{20}$ — 80 °C. Lit. [9] m.p. 161—162 °C; $[\alpha]_D^{20}$ — 80 °C. $R_f$ 0.32.

## REFERENCES

[1] DAHLGARD, M., CHARTAIN, B. H., RU-JEN LEE HAN: J. Org. Chem. **27,** 929 (1962)
[2] HEDGLEY, E. J., OVEREND, W. E., RENNIE, R. A. C.: J. Chem. Soc. **1963** 4701
[3] SIEWERT, G., WESTPHAL, O.: Ann. **720,** 161 (1968)
[4] REIST, E. J., SPENCER, R. R., BAKER, B. R.: J. Org. Chem. **23,** 1757 (1958); RYAN, K. J. *et al.*: J. Am. Chem. Soc. **86,** 2503, (1964)
[5] HEDGLEY, J., MÉRÉSZ, O., OVEREND, W. G.: J. Chem. Soc. C **1967,** 888
[6] UMEZAWA, S., TSUCHIYA, T., HINENO, H.: Bull. Chem. Soc. Japan **43,** 1212, (1970)
[7] ZOBÁCOVÁ, A., HERMÁNKOVÁ, V., JARY, J.: Coll. Czechoslov. Chem. Commun. **35,** 327, (1970)
[8] MICHEEL, F., KLEMER, A.: Chem. Ber. **91,** 663 (1958)
[9] HELFERICH, B., ROHR, H., GÜNTHER, E. Z. Physiol. Chem. **221,** 90, (1933)

L. KISS
PÁL NÁNÁSI } H-4010 Debrecen

*Acta Chimica Academiae Scientiarum Hungaricae, Tomus 98 (3), pp. 353—356 (1978)*

# QUINOVOSE METHYL ETHERS SYNTHESIS OF 2-O-METHYL, 3-O-METHYL, AND 4-O-METHYL ETHERS OF PHENYL-β-D-QUINOVOSIDE

L. KISS, A. LIPTÁK and P. NÁNÁSI

*(Biochemical Institute, Kossuth Lajos University, Debrecen)*

Received November 18, 1977

Phenyl 2-O-methyl-β-D-quinovoside (**3**), phenyl 3-O-methyl-β-D-quinovoside (**6**), and phenyl 4-O-methyl-β-D-quinovoside (**10**) have been synthesized. Compounds **3** and **6** were obtained from the corresponding partially methylated phenyl 4,6-O-benzylidene-β-D-glucopyranoside after treatment with N-bromosuccinimide (NBS) according to HANESSIAN [3] and reductive elimination of the bromide and benzoyl groups by $LiAlH_4$ in dry ether. The synthesis of compound **10** was effected *via* the 6-O-tosyl derivative of the corresponding partially methylated phenyl-β-D-glucopyranoside derivative. Compound **10** was obtained after treatment with $LiAlH_4$ in dry tetrahydrofuran.

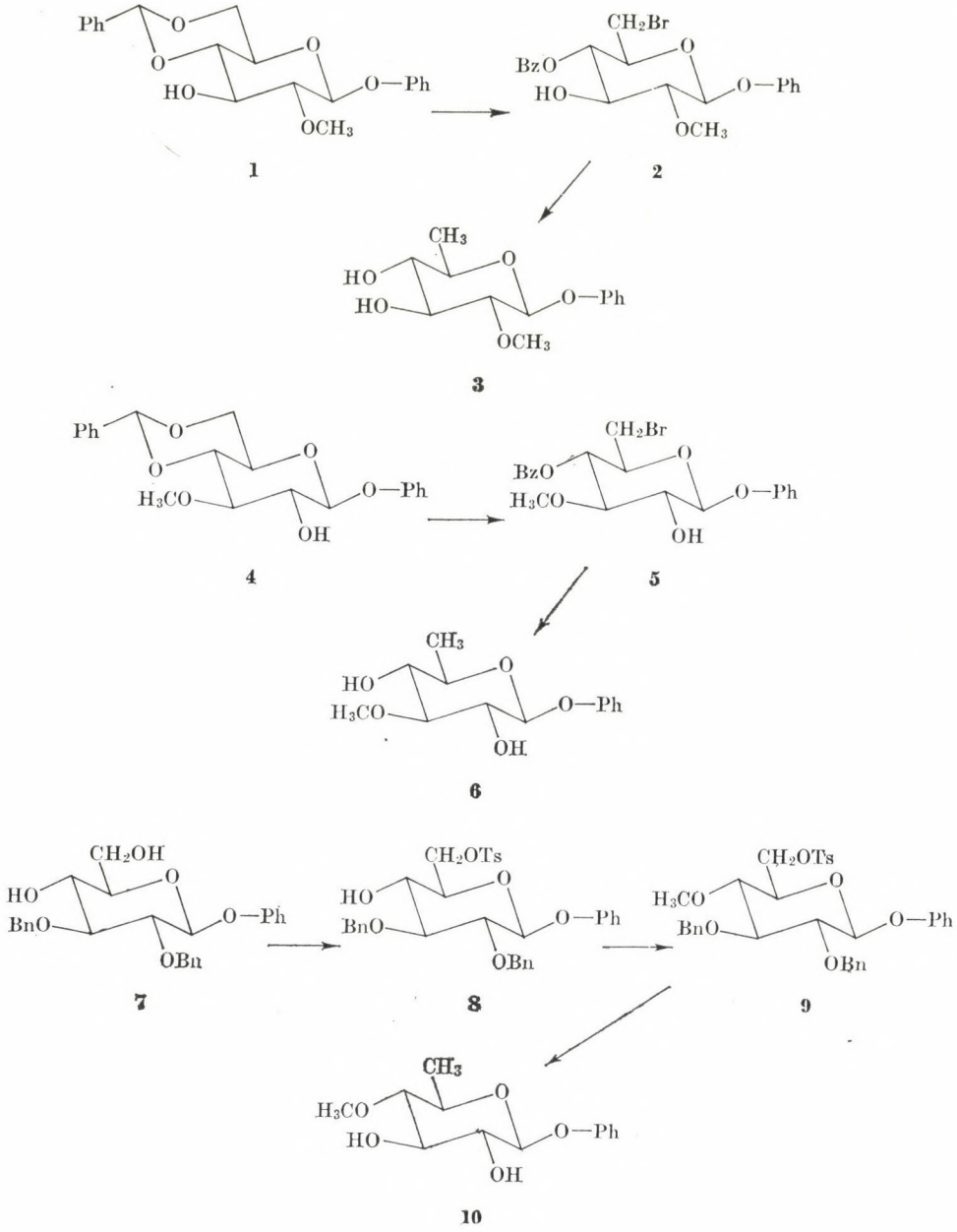
For investigating the mechanism of the action of emulsin, we have prepared partially methylated phenyl 6-deoxy-β-D-glucopyranoside (phenyl-β--D-quinovoside) derivatives. These investigations have shown that the syntheses effected through the β-phenylglycosides are very favourable, owing to the convenient preparation of the intermediates and to the high yield of the individual steps.

Of the three possible mono-O-methyl ethers of phenyl 6-deoxy-β-D--glucopyranoside only the 3-O-methyl derivative has been described so far in the literature [1]. The synthesises of the 2-O-methyl, and 4-O-methyl derivatives are first reported here.

The reaction routes are summarized in Scheme 1. In the synthesis of the 2-O-methyl ether, the starting material was phenyl 4,6-O-benzylidene-2--O-methyl-β-D-glucopyranoside [2] (**1**) which was treated with NBS according to HANESSIAN [3] to give the 6-bromo-6-deoxy derivative (**2**) (yield 82%), which was debrominated and debenzoylated with $LiAlH_4$ in dry ether to yield **3**.

In accordance with the structure of **3**, in the NMR spectrum the doublet due to the C-6 methyl group and the singulet of the 2-O-methyl group appeared at 1.38 and 3.68 ppm, respectively.

3-O-Methyl-D-quinovose (D-thevetose) was first synthesized by REICHSTEIN *et al.* In our laboratory a more favourable synthesis has been devised giving better yields and crystallize intermediates. Phenyl 4,6-O-benzylidene--3-O-methyl-β-D-glucopyranoside (**4**) was treated with NBS according to HANESSIAN [3] to obtain the 6-bromo-6-deoxy derivative 5 in a yield of 71.3%. The bromine atom and benzoyl group were eliminated with $LiAlH_4$




*Scheme* 1

in dry ether to obtain **6**. In accordance with the structure of **6**, in the NMR spectrum the doublet due to the C-6 methyl group and the singulet of the 3-O-methyl group appeared at 1.38 and 3.6 ppm, respectively.

For want of appropriate blocking groups [4], the synthesis of phenyl 4-O-methyl-β-D-quinovoside (**10**) was not carried out through the 6-bromo-6-deoxy derivative, but *via* the 6-O-tosylate. Phenyl 2,3-di-O-benzyl-β-D-glucopyranoside [5] (**7**) was tosylated with 1.1 mole of tosyl chloride in dry pyridine to obtain **8**, which was methylated according to KUHN [6] to give **9**. The latter was treated with $LiAlH_4$ in boiling anhydrous tetrahydrofuran to afford **10**. In its NMR spectrum the doublet at 1.32 ppm due to the C-6-methyl group and the singulet at 3.56 ppm due to the 4-O-methyl group are in accordance with structure **10**.

## Experimental

M.p.'s were determined on a Kofler apparatus and are uncorrected. Optical rotations were measured with a Polamat A Zeiss automatic photoelectric polarimeter. NMR spectra were recorded on a Jeol MH-100 instrument for solutions in $CDCl_3$ and deuterated DMSO, using TMS as the internal standard.

### Phenyl 4-O-benzoyl-6-bromo-6-deoxy-2-O-methyl-β-D-glucopyranoside (2)

Compound **1** (2, 2 g; 5.5 mmoles), was treated with NBS (1.9 g) in dry carbon tetrachloride (160 ml) as described previously [7]; after recrystallization from alcohol (10 ml) 2 g (82%) of **2** was obtained, m.p. 154—157 °C; $[\alpha]_D^{20}$ — 49.02° ($c$ = 0.25, $CHCl_3$).

$C_{20}H_{21}O_6Br$ (437.29). Calcd. C 54.83; H 4.84. Found C 54.90; H 4.80%.

### Phenyl 6-deoxy-2-O-methyl-β-D-glucopyranoside (3)

A solution of 1.1 g (2.5 mmoles) of **2** in dry ether (10 ml) was added to a suspension of $LiAlH_4$ (2 g; 0.057 mole) in dry ether (10 ml). The reaction mixture was stirred overnight at room temperature and then refluxed for 1 h. Ethyl acetate (3 ml) was added to destroy any excess of $LiAlH_4$, followed by the addition of water (2 ml), 15% NaOH solution (2 ml) and water (6 ml) again; the precipitate which separated was filtered off and washed with ethyl acetate (15 ml). The filtrate was evaporated and the crystalline residue recrystallized from ether (40 ml) to yield 400 mg (62.5%) of **3**, m.p. 125—130 °C; $[\alpha]_D^{20}$ — 76.3° ($c$ = 0.25, $CHCl_3$).

NMR: δ7.3 (m, 5H, aromatic protons); 4.9 (d, 1H, anomeric proton, $J_{1,2}$ = 8Hz); 3.68 (s, 1H, 2—O—$CH_3$); 3.38 (m, 4H, skeleton protons); 1.38 (d, 3H, C-6 methyl, $J_{5,6}$ = 6.2Hz).

$C_{13}H_{18}O_5$ (254.27). Calcd. C 61.38; H 7.13. Found C 61.32; H 7.2%.

### Phenyl-4-O-benzoyl-6-bromo-6-deoxy-3-O-methyl-β-D-glucopyranoside (5)

Compound **4** (2 g; 5.5 mmoles) [2] was treated with NBS (1.9 g) in dry carbon tetrachloride (150 ml) as described previously [7]; recrystallization from alcohol (10 ml) gave 1.65 g (71.3%) of **5**, m.p. 128—130 °C; $[\alpha]^{20}$ — 60.3° ($c$ = 0.5, $CHCl_3$).

$C_{20}H_{21}O_6Br$ (437.29). Calcd. C 54.83; H 4.84. Found C 54.82; H 4.80%.

### Phenyl 6-deoxy-3-O-methyl-β-D-glucopyranoside (6)

Compound **5** (1.24 g; 2.8 mmole) was dissolved in dry ether (40 ml) and added to a suspension of $LiAlH_4$ (2.12 g; 0.056 mole) in dry ether (45 ml). The reaction mixture was processed as described above. Recrystallisation from ethyl acetate–ether (1 : 1) (30 ml) gave 520 mg (79%) of **6**, m.p. 146—150 °C; $[\alpha]_D^{20}$ — 63.5° ($c$ = 0.5, $CHCl_3$).

NMR: δ7.3 (m, 5H, aromatic protons); 4.8 (d, 1H, anomeric proton, $J_{1,2}$ = 8Hz); 3.6 (s, 3H, 3-O-methyl); 3.38 (m, 4H, skeleton protons); 1.38 (d, 3H, C-6 methyl, $J_{5,6}$ = 6.2 Hz).

$C_{13}H_{18}O_5$ (254.31). Calcd. C 61.38; H 7.13. Found C 61.54; H 7.11%.

**Phenyl 2,3-di-O-benzyl-6-O-p-tolylsulfonyl-β-D-glucopyranoside (8)**

Compound **7** (5 g) was dissolved in dry pyridine (50 ml) and tosyl chloride (2.1 g) was added; the mixture was then allowed to stand at room temperature for 36 h. It was poured into ice water, extracted with chloroform (3 × 40 ml), the extract was washed with 2N sulfuric acid and water, dried over $Na_2SO_4$ and the solvent evaporated. The crystalline residue was recrystallized from methanol (10 ml) to obtain 2.5 g (37%) of **8**, m.p. 127—129 °C; $[\alpha]_D^{20}$ — 48.6° ($c$ = 0.5, $CHCl_3$).

$C_{33}H_{34}O_8S$ (590.62). Calcd. C 67.12; H 5.76. Found C 66.71; H 5.58%.

**Phenyl 2,3-di-O-benzyl-4-O-methyl-6-O-p-tolylsulfonyl-β-D-glucopyranoside (9)**

Compound **8** (2 g) was methylated according to KUHN [6]. After the usual work-up 1.24 g (60.4%) of **9** was obtained as a syrup; $[\alpha]_D^{20}$ — 48.3° ($c$ = 0.5; $CHCl_3$).

$C_{34}H_{36}O_8S$ (604.64). Calcd. C 67.53; H 5.95. Found C 67.12; H 5.82%.

**Phenyl 6-deoxy-4-O-methyl-β-D-glucopyranoside (10)**

A solution of **9** (1.3 g; 2 mmoles) in dry tetrahydrofuran (20 ml) was added to a suspension of $LiAlH_4$ (1.52 g; 1.40 mmoles) in dry tetrahydrofuran (30 ml). The reaction mixture was stirred and refluxed for 48 h; the excess of $LiAlH_4$ was destroyed with ethyl acetate (5 ml), then water (10 ml) was added. The precipitate was filtered off and washed with ethyl acetate (3 × 10 ml). The filtrate and washings were combined and the solvent evaporated. The residual syrup was crystallized from ether (10 ml) to obtain 220 mg (42.2%) of **10**, m.p. 157—159 °C; $[\alpha]_D^{20}$ — 76.9° ($c$ = 0.13, $CHCl_3$).

NMR: δ7.1 (m, 5H, aromatic protons); 4.7 (m, 1H, anomeric proton); 3.56 (s, 3H, 4-O-methyl); 3.1 (m, 4H, skeletal protons); 1.32 (d, 3H, C-6 methyl protons, $J_{5,6}$ = 6.2 Hz).

$C_{13}H_{18}O_5$ (254.31). Calcd. C 61.38; H 7.13. Found C 61.11, H 7.03%.

## REFERENCES

[1] VISCHER, E., REICHSTEIN, T.: Helv. Chim. Acta **27,** 1332, (1944)
[2] NÁNÁSI, P., LIPTÁK, A.: Acta Chim. Budapest, **84,** 63 (1975)
[3] HANESSIAN, S.: Carbohydr. Res. **2,** 86 (1966)
[4] OKAWARA, M., SATO, H., IMOTO, E.: J. Chem. Soc. Japan **58,** 924 (1955)
[5] MICHAEL, F., KLEMER, A.: Chem. Ber. **91,** 663 (1958)
[6] KUHN, R., TRISCHMANN, H., LÖW, I.: Angew. Chem. **67,** 32 (1955)
[7] KISS, L., LIPTÁK, A., NÁNÁSI, P.: Acta Chim. (Budapest) **83,** 201 (1974)

L. KISS
András LIPTÁK
Pál NÁNÁSI
H-4010 Debrecen

*Acta Chimica Academiae Scientiarum Hungaricae, Tomus 98 (3), pp. 357—360 (1978)*

# CROWN ETHERS INCORPORATING SUGAR UNITS, I

*(PRELIMINARY COMMUNICATION)*

L. Tőke, L. Fenichel, P. Bakó and J. Szejtli*

*(Department of Organic Chemical Technology, Technical University, Budapest, and *Chinoin Pharmaceutical and Chemical Works, Budapest)*

Received March 16, 1978

Macrocyclic polyethers have been shown to form complexes with salts [1], *e.g.* with primary alkylammonium salts [2]. When making use of this ability under *in vivo* conditions, the toxicity characteristics of the crowns should also be satisfactory.

Aiming at the synthesis of crown ethers of this type, protected monosaccharides were first chosen by us for use as one of the building blocks of the synthesis.

Papers dealing with the synthesis of chiral crowns [2] or of crowns with pharmacophore groups [3, 4] have been published and even some derivatives of monosaccharides recommended [5] for the purposes.*

These reports prompted us to summarize our results and the work in progress on this topic; yet it is stressed that this paper is only to be regarded as the first part of outlining our synthetic strategy.

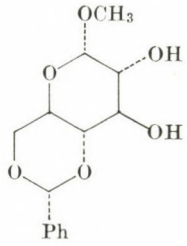
The alkylation of methyl 4,6-O-benzylidene-α-D-glucopyranoside (**1**) was attempted with diethylene glycol derivatives such as **2a**, **2b** and **2c**, under the circumstances suggested for the O-alkylation of this type of compounds [7] (NaH + DMSO or DMF or THF; thallous ethoxide in THF or in DMF etc.). No traces of the desired compound **3** could be detected in TLC (Silica gel G; EtOAc : $CHCl_3$ = 1 : 1; $I_2$) if **2a** was used, but the reaction of **1** with **2b** or **2c** resulted in the formation of two products separable on Silica gel plates or on an $Al_2O_3$ column, the yield being 1—1.5% for each. Analytical and spectroscopic data summarized in Table I have shown that the compound with the higher $R_f$ value has structure **3**, and the other is represented by formula **4**.

On the basis of the data available so far, no decision has been made whether the correct structure of the crown so formed is **3a** or **3b**.**

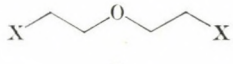
For the separation and purification of compounds **3** and **4** a simple extraction procedure based on the low solubility of **3** has also been worked out besides the chromatographic methods.

* After the completion of this manuscript, Schröder *et al.* [6] published a paper in Tetrahedron Letters on the synthesis of compound, **3**, through in a way different from ours.

** X-Ray studies are in progress.



1

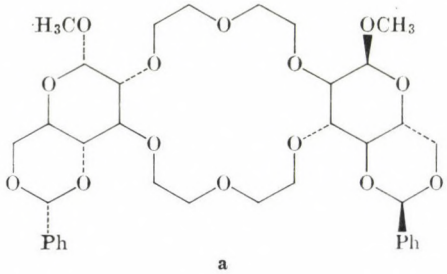


2

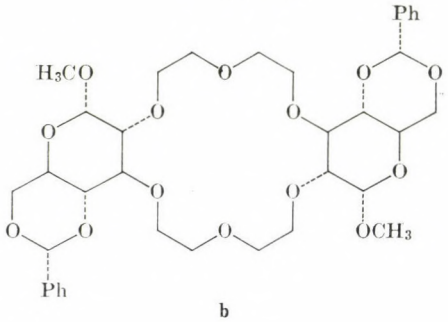
a X = Cl

b X = I

c X = OTs

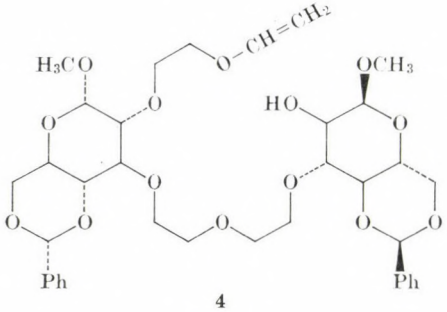


a

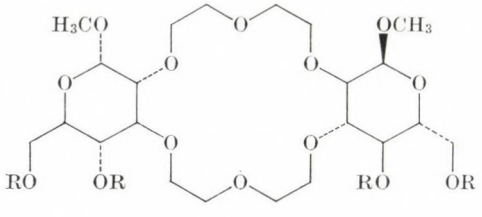


b

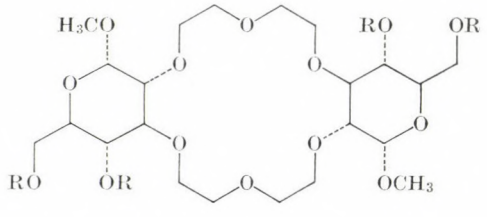
3



4



a



b

5 R = H

6 R = Ac

| Compound | M.p., °C | $[\alpha]_D$ ($CHCl_3$) | C% | | H% | | PMR Spectrum [b] | IR Spectrum, $cm^{-1}$ [c] |
|---|---|---|---|---|---|---|---|---|
| | | | Found | Calcd. | Found | Calcd. | | |
| **3** | 258—61 | 59.3 | 61.40[a] | 61.29 | 6.94 | 6.82 | δ3.3—4.35 (m, 28H)<br>4.82 (d, 2H, J = 3.5 Hz)<br>5.52 (s, 2-benzylidene-H)<br>7.25—7.5 (m, 10H)<br>3.45 (s, 6H) | $\nu_{OH}$ missing<br>$\nu_{C-O-C}$ 1090 (s)<br>$\nu_{Ar}$ 3060<br>mono-substituted benzene: 695, 745 |
| **4** | 136—40 | 65.2 | 61.36[a] | 61.29 | 6.75 | 6.82 | δ3.47 (s, 6H)<br>3.4—4.5 (m, 27H)<br>4.85 (m, 2H)<br>5.55 (s, 2-benzylidene-H)<br>6.5 (dd, J = 8Hz, 1H)<br>7.25—7.7 (m, 10H) | $\nu_{OH}$ 3400 (sharp)<br>$\nu_{C=C}$ 1613 (vinyl)<br>$\nu_{C-O-C}$ 1190<br>mono-substituted benzene: 695, 745 |
| **5** | 132—34 | 115.8 | 50.04 | 50.00 | 7.51 | 7.57 | δ3.3—4.35 (m, 32H)<br>4.82 (d, 2H)<br>3.43 (s, 6H) | $\nu_{OH}$ 3420<br>No aromatic bands |
| **6** | 161—64 | 94.0 | 51.96 | 51.72 | 6.86 | 6.89 | | $\nu_{OH}$ missing<br>$\nu_{C=O}$ 1735 (acetyl)<br>$\nu_{as\ C-O-C}$ 1240 |

[a] MS: 704 ($M^+$)
[b] in $CDCL_3$, 100 MHz NMR, TMS internal standard
[c] in KBr pellets

The complexing ability of **3** toward $K^+$ was measured in $CDCl_3$ using the method suggested by CRAM [8], and the $k_a^-$ value has been found to be $8.81 \cdot 10^4$. (The corresponding values for dibenzo-18-crown-6 in $CH_2Cl_2$ and for 1,3-xylyl-18-crown-5 in $CDCl_3$ are $7 \cdot 10^5$ [9] and $10.9 \cdot 10^4$ [10], respectively.

To obtain a better yield for **3,** liquid-liquid phase transfer catalytic reactions were also applied. Surprisingly, it was found very successful if the reaction of **2c** with **1** was carried out in a mixture consisting of THF and concentrated aueous potassium hydroxide solution. No catalyst was necessary, however, because its role was fully assumed by the crown **3** formed during the reaction. From the mixture which separated into two layers, compound **3** was isolated in a yield of 15% calculated for **1.**

As the procedures of running the reaction and working up the reaction mixture are very simple, the preparation of **3** on a larger scale has become possible.

The benzylidene protecting groups were selectively removed by acetic acid (JEANLOZ's method [11]) to obtain compound **5** in a good yield.

The hydroxyl groups in compound **5** are reactive, so they can readily be acetylated in $Ac_2O$–pyridine. The analytical data of the tetraacetyl compound **6** are also included in Table I.

*

This work was supported by Chinoin Pharmaceutical and Chemical Works; the authors are grateful for this help.

## REFERENCES

[1] PEDERSEN, C. J.: J. Am. Chem. Soc. **89,** 2495 (1967)
[2] CURTIS, W. D., LAIDLER, D. A., STODDART, J. F., JONES, G. H.: J. C. S. Chem. Comm. **1975,** 835
[3] VÖGTLE, F., FRENSCH, K.: Angew. Chem. **88,** 722 (1976)
[4] VÖGTLE, F., JANSEN, B.: Tetrahedron Lett. **1976,** 4895
[5] LAIDLER, D. A., STODDART, J. F.: Carbohydr. Res. **55,** C1 (1977)
[6] HAIN, W., LEHNERT, R., RÖTTELE, H., SCHRÖDER, G.: Tetrahedron Lett. **1978,** 625
[7] GIRODEAU, J.-M., LEHN, J.-M., SAUVAGE, J.-P.: Angew. Chem. **87,** 813 (1975) and publications cited therein
[8] NEWCOMB, M., TIMKO, I. M., WALBA, D. M., CRAM, D. J.: J. Am. Chem. Soc. **99,** 6392 (1977)
[9] PEDERSEN, C. J., FRENSDORFF, H. K.: Angew. Chem. **84,** 16 (1972)
[10] MOORE, S. S., TARNOWSKI, T. L., NEWCOMB, M., CRAM, D. J.: J. Am. Chem. Soc. **99,** 6398 (1977)
[11] WHISTLER, R. L., WOLFROM, M. L.: Methods in Carbohydrate Chemistry, Vol. I. p. 214. Academic Press, New York, 1963

# RECENSIONES

## LYNCH's *Medical Laboratory Technology*. Volume II

pp. 876—1485. Senior Author S. S. RAPHAEL, W. B. SAUNDERS COMPANY, Philadelphia, London, Toronto, 1976

The second volume of the textbook is divided into three sections: Histology by C. F. A. CULLING, Hematology and Blood Bank by M. J. INWOOD and S. THOMSON, Human Cytogenetics by F. SERGEVICH.

The first section deals with conventional histologic and electron-microscopic tissue preparation techniques, the preparation of frozen and cryostat sections, the staining of connective tissue ground substance and fibers, fibrin, amyloid, pigments, tissue deposits and finally of organisms, parasites and fungi in sections. A separate chapter is devoted to the nervous system. Unfortunately, readers interested in applying modern enzyme histochemical methods in pathology have to be satisfied with a meagre description of general concepts and methods for demonstrating only the phosphatases.

In the second section blood cell formation and maturation, basic hematologic techniques, erythrocyte, leucocyte and hemostatic disorders, the principles of immunohematology, blood transfusion therapy and the organization of blood bank are described. Basic cytogenetics, clinical cytogenetics and laboratory cytogenetics are covered in the third section.

Concise explanation of the chemical, biochemical and physiological background helps the understanding of the methods and the evaluation of the results. Alternative methods are given with adequate discussion of their individual merits and disadvantages. The descriptions of the methods are lucid, their reproduction is supported by giving the name and address of suppliers of not widely used substances and equipment.

The black and white illustrations are of high quality. Nevertheless, a few colored pictures would have been of great value, especially for junior readers. This shortcoming is only partly compensated by a supplementary color filmstrip and approximately 300 frames available from the publisher to assist both teachers and students.

The small number of contributors is a distinct advantage of the book. Thus, the individual sections could be written in a uniform didactic concept and style. The result is an excellent book which can be warmly recommended to both laboratory technologists and laboratory physicians.

S. KERPEL-FRONIUS

## H. ENGELHARDT: *Hochdruck-Flüssigkeits-Chromatographie*

Springer-Verlag, Berlin—Heidelberg—New York 1977
(Zweite, überarbeitete und erweiterte Auflage)
257 Seiten, 62 Abbildungen und 18 Tabellen

Die erste Auflage des Buches erschien 1975 (Rezension s. Acta Chimica Hung. **92**, 203, 1977).

Im Verlauf der vergangenen zwei Jahre war in apparativer und methodischer Hinsicht eine derart rasche Entwicklung der Hochdruck-Flüssigkeits-Chromatographie zu verzeichnen,

daß eine Überarbeitung des Werkes bzw. die Einbeziehung der neuer Ergebnisse notwendig erschien.

Dabei blieb die grundlegende Zielsetzung, nämlich einen Überblick über Geräte, Trennungsverfahren und Anwendungsgebiete zu geben, unverändert. Auch die ursprüngliche Struktur des Buches blieb erhalten: es besteht auch weiterhin aus 12 Kapiteln und einem Anhang. Die Behandlung der neuen Ergebnisse wurde teilweise in die früheren Unterabschnitte eingebaut, teilweise wurden neue Unterabschnitte zugefügt.

Kapitel I blieb unverändert; es gibt einen kurzen Überblick über die verschiedenen chromatographischen Trennmethoden.

Kapitel II ist eine Zusammenfassung der theoretischen Grundlagen und praktischen Erfordernisse der chromatographischen Trennung. In einem neuen Unterabschnitt werden, auf den neuesten Ergebnissen basierend, die Zonenverbreiterung und der Einfluß des Teilchendurchmessers ausführlich diskutiert.

In Kapitel III erläutert der Verfasser die Geräte der Hochdruck-Flüssigkeits-Chromatographie. Der Teil über die Trennsäulen wurde wesentlich erweitert; ein neuer Abschnitt behandelt die Charakterisierung und Testung der Säulen.

Kapitel IV befaßt sich mit den in der Hochdruck-Flüssigkeits-Chromatographie angewendeten Detektoren. Die neuentwickelten Detektoren werden in drei neuen Unterabschnitten behandelt.

Kapitel V behandelt die Träger und stationären Phasen. Dieses Kapitel wurde wesentlich erweitert und durch Einbeziehung der neuesten Füllungen auf den letzten Stand gebracht.

Kapitel VI faßt — unter dem Titel Absorptions-Chromatographie — das Wissenswerte über die Füllungen in der Flüssigkeit-Feststoff-Chromatographie und die Probleme ihrer praktischen Anwendung zusammen. Das Kapitel ist in vier Teile gegliedert: 1. Polare stationäre Phasen; 2. Apolare stationäre Phasen; 3. Das Elutionsproblem; 4. Anwendungsgebiete der Adsorptions-Chromatographie. Für den praktizierenden Chemiker, der sich mit Chromatographie befaßt, ist der Teil 2 besonders wichtig, worin die heutzutage allgemein angewendeten "reverse-phase"-Füllungen behandelt werden.

Kapitel VII erläutert die Verteilungs-Chromatographie; dieses Kapitel blieb unverändert.

In dem ebenfalls unverändert gebliebenen Kapitel VIII wird die Ionenaustausch-Chromatographie dargelegt.

In Kapitel IX diskutiert der Verfasser die neuen Verfahren und Füllungen der Gelchromatographie. Dieses Kapitel wurde durch Einbeziehung der neuesten Ergebnisse erweitert.

Kapitel X und XI blieben unverändert; sie befassen sich mit der Wahl des Trennungssystems bzw. mit Spezialvefahren (präparative Trennung, quantitative Analyse, Spurenanalyse).

In Kapitel XII werden Reinigung und Vorbereitung der Lösungsmittel angegeben.

Der Anhang enthält die Bezugsquellen für Apparaturen und Zubehör der Flüssigkeits-Chromatographie, wobei die in den vergangenen zwei Jahren eingetretenen Verändererungen Berücksichtigt wurden.

Zusammenfassend kann festgestellt werden, daß der Leser durch die Überarbeitung des Buches auch über die neuesten Ergebnisse einen guten Überblick erhält. Die Anzahl der Literaturangaben stieg durch die Ergänzung mit den wichtigeren Arbeiten der vergangenen zwei Jahre wesentlich an (von 293 der ersten Auflage auf 454. Der sich mit der Weiterentwicklung von Säulenfüllungen und der Säulenforschung befassende Teil basiert in hohem Maße auf die im Institut des Verfassers erreichten Forschungsergebnisse und enthält Hinweise und Ratschläge für die Praxis.

Das Werk ist ein sehr nützliches Handbuch für jene, die sich mit der Hochdruck-Flüssigkeits-Chromatographie befassen. Darüber hinaus gibt es den in verschiedenen Gebieten arbeitenden Fachleuten einen ausgezeichneten Überblick über die Leistungsfähigkeit und die Anwendungsmöglichkeiten der Hochdruck-Flüssigkeits-Chromatographie.

L. SZEPESY

## *Topics in Current Chemistry*, Vol. 71. 190 pp.

Springer-Verlag, Berlin, Heidelberg, New York, 1977

The last few decades have brought a spectacular advance in the chemistry of metal carbonyls, a class of compounds for a long time regarded as scientific curiosities. This development has largely contributed to the so-called renaissance of inorganic chemistry and is well

justified considering the significance of metal carbonyl catalysts in modern petrochemical processes. Times have long passed when the chemistry of metal carbonyls could be treated in a single book, and there is a great need nowadays for specialised reviews to follow the developments in this field.

This volume of the well-known series contains four such useful chapters dealing with different aspects of metal carbonyl chemistry.

The first chapter written by P. CHINI and B. T. HEATON reviews tetranuclear carbonyl clusters such as $Co_4(CO)_{12}$ and other 90 "not trivially different examples" presently known. Only compounds containing four transition metal atoms are covered, thus definitely excluding those clusters in which atoms of non-transition elements assist the formation of clusters containing a smaller number of transition metal atoms (like $AsCo_3(CO)_9$). The 253 references show the amazing abundance of this seemingly narrow range of complexes.

The second chapter by J. A. CONNOR on thermochemical studies of organotransition compounds gives a long-needed survey of the subject. In the past the complaint was often made that information concerning the thermochemistry of organotransition metal compounds is so meagre as to preclude discussion of bond enthalpies, but this review proves that the state of thermochemical knowledge is in fact not so bad as thought.

S. F. A. KETTLE is the author of the third chapter on vibrational spectra of metal carbonyls, giving a survey of the literature from 1972 till the end of 1975. Largely preparative papers are covered by tabular compilations and discussion is centered on theoretical and principal questions like Raman intensities and the spectra of crystalline materials.

Inorganic applications of X-ray photoelectron spectroscopy are the subject of the last chapter by W. L. JOLLY. Most of the chapter is devoted to methods for systematizing binding energy data and for deducing information about chemical bonding from the spectra.

L. MARKÓ

## F. SOLYMOSI: *Structure and Stability of Salts of Halogen Oxyacids in the Solid Phase*

Akadémiai Kiadó, Budapest, 1977. ISBN 963 05 1030 8 (467 pages). Publishing House of the Hungarian Academy of Sciences. Joint edition with John Wiley and Sons. Printed in Hungary.

To publish monographic treatments of the various domains of chemistry becomes more and more frequent in our time. As a rule, those best informed on the special subjects and also actively engaged in research therein are authors of these monographs. The author of the present one looks back on almost two decades of his activities concerning the chemistry of halogen oxyacids and their salts, and not only is his work known but also acknowledged in the international literature. It is the consequence of the close interrelationship of the author and this field that many important statements of his own, worth general attention, are to be found in this book.

A further characteristic of the monograph before us is the complex way of looking at its subject matter, whereby *e.g.* physical properties and correlations are brought into closest connexion with the chemistry of the substances discussed. A special feature of the treatment is that the points of view of reaction kinetics are kept continuously in mind and are made to serve as a groundwork to interpretations.

The subject matter of this monograph is taken from a field where quick changes occur even today and where the best, the most recent, informations are to be collected mostly through personal contacts and not from the literature with a considerable time lag.

Naturally, each researcher presents his purposes and results from some specific aspect, thus the matter to be reviewed inevitably is quite inhomogeneous. The author of this book made the attempt at a reduction to a uniform pattern, respectively at an adequate accentuation of contradictions. We can state that the author took note of novel results and embodied these in his own researches or adapted his researches accordingly very often and almost at the moment that such results had become accessible, either confirming these or, as it happens quite often, disproving erroneous measurements or interpretations. Considering the volume of this monograph, this kind of, and fully justified, activity of its author is certainly on a level well above the average.

From the total of 820 references about one fifth points to the communications of the author himself.

The book deals with the structures and the characteristics of halogen oxyacids and their salts, in ten chapters. Among these the third deserves special notice: here metal perchlorates are discussed. It is this field in which the author and his co-workers have arrived at the greatest number and the most original results.

In the fourth chapter: that about ammonium perchlorate, AP, perhaps the results most important from a practical point of view are collected; this chapter contains some fundamental, important results obtained by the author and his colleaugues, which correct some errors of earlier workers. Certainly, these statements in correction of some deductions by researchers of repute are of no small service.

AP is a frequently applied oxidant in rocket propellants. Accordingly, this compound was the subject of most of the research. It is of great interest to keep track of the evolution of results, respectively due to research in the Novosibirsk, in English-speaking, and in Hungarian laboratories, especially of the results made possible by the use of scanning electron microscopy, and cinemicrography.

The fifth chapter is an important and necessary complement to the preceding one. The experimental results are useful not only from a practical point of view but are also significant in respect to theoretical considerations.

Chapters 7, and 8 deal with the oxyacids of bromine and with the for a long time problematic existence of perbromic acid and perbromates. Data useful for every inorganic chemist are to be found in these chapters.

We may confidently state that this is an interesting and useful book; owing to the abundance of data in it and, last but not least, thanks to its attractive printing it will be a rather popular, much perused volume in the library of the specialists in this field.

Z. G. SZABÓ

## L. REIMER und G. PFEFFERKORN: *Raster-Elektronenmikroskopie*

Springer-Verlag, Berlin—Heidelberg—New York, 1977. Zweite Auflage, 282 Seiten, 146 Abbildungen

Die Verfasser sind hervorragende Kenner der Elektronenmikroskopie, wovon ihre langjährige umfangreiche Literaturtätigkeit Zeugnis ablegt.

Das Raster-Elektronenmikroskop (im englischen Sprechgebrauch Scanning-Electronenmicroscope) wurde anfänglich weltweit als Gerät mit hohem Auflösungsvermögen zur Untersuchungen Oberlächenstrukturen verwendet. Die Verfasser des Buches erörtern zwei neuere Anwendungsgebiete: die Raster-Transmissions-Elektronenmikroskopie und die Röntgen-Mikroanalyse. Im Rahmen des letzteren Verfahrensbehandeln sie auch die Wellenlängen-bzw. Energiedispersionstechnik als zwei moderne Verfahren der Elementaranalyse.

Ein besonderes Kapitel befaßt sich mit den Auswertungsmethoden der mikroskopischen Aufnahmen und in diesem Zusammenhang mit der Stereometrie und der optischen Transformation.

Im letzten Abschnitt werden die verschiedenen Präpariertechniken behandelt, deren gründliche Kenntnis auch für Biologen und auf anderen Gebieten Arbeitenden von Wichtigkeit sein kann.

Die Literaturangaben sind umfangreich und entsprechen dem neuesten Stand. Das ausführliche Sachregister erleichtert die Orientierung.

Das mit sowohl in didaktischer wie auch in ästhetischer Hinsicht hervorragenden Abbildungen illustrierte Buch kann gleichermaßen von erfahrenen Fachleuten und Anfängern auf dem Gebiet der Elektronenmikroskopie mit Gewinn gelesen werden.

D. SZABÓ

## *Natural Products and the Protection of Plants*

Edited by G. B. MARINI—BETTÒLO (846 pp.). Pontificia Academia Scientiarum. Vatican, and Elsevier, Amsterdam, 1977

No organic chemist, phytochemist or biochemist interested in insect and juvenile hormones, pheromones, natural insecticides, phytoalexins or phytotoxins, uncommon natural amino acids — in short, natural substances of vegetable and insect origin possessing physio-

logical activity — can afford to dismiss this remarkable collection of papers without further study. The volume contains the material of the Study Week held in Vatican, October 18—23, 1976, with the purpose of examining the present state of the basic research on natural products which may afford protection to plants, assessing their possible use in agriculture. The current and too evident problems of environmental pollution, inherent to the use of "artificial" synthetic insecticides, give special emphasis to this approach of investigating the natural protecting agents of the vegetable world, to offer defence against pests and diseases of plants without causing further damage in the eco-systems, making thereby a contribution of chemical science to the solution of social problem, such as food shortage.

Distinguished scientist from all over the world convened to present their most recent researches — and critically discuss one another's — in thirty interesting lectures.

Prof. G. B. MARINI-BETTÒLO's (Italy) initial discourse ("Modern Trends in the Use of Natural Products for Controlling Pests and Plant Diseases") was followed by 11 lectures dealing with products active on plant pests, such as insect hormones and pheromones (Prof. P. KARLSON, FRG), juvenile hormones (Prof. J. B. SIDDALL, USA), protective substances of arthropods and plants (Prof. H. SCHILDKNECHT, FRG), some insect metabolites (Prof. C. CARDANI, Italy), anti-juvenile hormones from plants (Prof. W. S. BOWERS, USA), pyrethrin-based synthetic insecticides (Dr. M. ELLIOTT, UK), insect growth regulators from plants (Prof. K. NAKANISHI, USA), and phytoecdysones (Prof. L. CANONICA, Italy); natural product derivatives in tropical insect and parasite control are discussed by Prof. B. GILBERT (Brasil), the insecticidal endotoxin of *Bacillus thuringiensis* by Prof. H. J. SOMERVILLE (UK), and the use of viruses in plant protection by Prof. A. M. HEIMPEL (USA).

The topic "Arthropoid Control through Natural Products" comprised 7 lectures, dealing again with juvenile hormones (Prof. V. B. WIGGLESWORTH, UK) and their analogues (Prof. G. B. STAAL, USA), anti-juvenile hormones (Prof. C. M. WILLIAMS, USA), pheromones (Prof. H. H. SHOREY, USA), with the impact of natural plant protectants on the environment (Prof. M. JACOBSON, USA), and with natural products from the tropical termite *Macrotermes subhyalinus* (Dr. N. ABO-KHATWA, Kenya).

Under the common title "Products Involved in Plant Parasite Interaction" are listed 6 lectures discussing the chemical aspects of plant disease resistance (Prof. R. L. WAIN, UK), a review of the role of phytoalexins (Prof. I. A. M. CRUICKSHANK, Australia), the possible significance of uncommon natural amino acids (Prof. E. A. BELL, UK), the chemical resistance of plants to insect attack (Prof. R. F. CHAPMAN and Dr. E. H. BERNAYS, UK), and phyto-toxins, their structure and activity (Prof. A. BALLIO, Italy) and new trends in their use (Prof. A. GRANITI, Italy).

The remaining 5 papers are grouped under the common title "Natural Products in the Protection of Plants"; these are concerned with new pest control practices in developing countries (Dr. R. H. GONZALEZ, Italy), with the field use of natural products (Prof. E. ZANINI and F. FRILLI, Italy) and of natural processes for pest control (S.H. RISCO BRICENO and Prof. R. ALVES DE LIMA, Brasil), and the protection of coffee plants against coffee rust (Dr. M. QUIJANO-RICO, Columbia); in conclusion, Dr. E. KNÜSLI (Switzerland) discusses the industrial aspects of the practical use of natural products or derivatives in the protection of crops.

The volume makes vivid, interesting reading, also because of the verbal citation of the discussions following each lecture. In addition, the final chapter contains general discussions evaluating the results of the meeting, reaching the conclusion that natural products provide much promise in the protection of plants; recommendations for future research are forwarded.

A detailed subject index and author index completes the volume.

The editing and the presentation of the book is excellent. Clearly drawn formulae, beautiful photos (several of them in colour) help the reader to enjoy the perusal of the volume.

F. KÁLLAY

# INDEX

## PHYSICAL AND INORGANIC CHEMISTRRY


Cathodic Behaviour of the Lead Dioxide Electrode in Sulfuric Acid Solution, A. M. Azzam, S. S. Abd El Rehim, W. H. Boctor ..... 255

Specific Adsorption of Iodate Ions at the $Hg/KIO_3$ (aq.) Interface AT 25 °C, M. V. Ramanamurti, A. Qayum, R. K. Singh ..... 261

Chemical Systems and Supersystems, III. Models of Self-reproducing Chemical Supersystems: the Chemotons, T. Gánti ..... 265

Comparison of Solvent Uptake and Ion Exchange Properties of Diethylaminoethylcellulose (De-Cellulose) and of Benzoylated Diethylaminoethylcellulose (BD-Cellulose) in Methanol–Water–Hydrochloric Acid Mixtures, A. Lásztity, M. Németh ..... 285

Preparation and Study of Pentafluorothiophenol Derivatives of In(III), Tl(III) and Rh(III), D. M. Kaminaris, A. G. Galinos ..... 293

Theoretical Investigations of Barriers to Inversion, Th. Weller, R. Lochmann ..... 297


## ORGANIC CHEMISTRY


Aminophthalazinone Derivatives, III. The Reaction of Chlorophthalazinone with Primary Alkyl-, Cycloalkyl- and Aralkylamines. Study of the Steric Effect, I, K. Körmendy 303

Internal α-Aminoalkylation Leading to 1,4-Dihydro-3(2*H*)-isoquinolinones, N. M. Mollov, A. P. Venkov ..... 315

Synthesis of 2-Amino-3-thio-2-deoxy-D-mannopyranose pentaacetate, P. Herczegh, R. Bognár ..... 321

Synthetic Uses of Millon's Reagent, I. Synthesis of *o*-Nitrosophenols by means of Millon's Reagent, J. Lázár, L. Mód, E. Vinkler ..... 327

Studies on the Course of the Millon Reaction, II, J. Lázár, L. Mód, E. Vinkler ..... 335

Nitroxides, II. 1-Oxyl-2,2,5,5-tetramethylpyrroline-3-carboxylic Acid Derivatives, H. O. Hankovszky, K. Hideg, J. Tigyi ..... 339

Synthesis of Phenyl 4-deoxy-β-D-glucopyranoside, L. Kiss, P. Nánási ..... 349

Quinovose Methyl Ethers. Synthesis of 2-O-methyl 3-O-methyl, and 4-O-methyl Ethers of Phenyl-β-D-quinovoside, L. Kiss, A. Lipták, P. Nánási ..... 353

Crown Ethers Incorporating Sugar Units, I (Preliminary Communication), L. Tőke, L. Fenichel, P. Bakó, J. Szejtli ..... 357

RECENSIONES ..... 361




*Printed in Hungary*

A kiadásért felel az Akadémiai Kiadó igazgatója — Műszaki szerkesztő: Zacsik Annamária

A kézirat nyomdába érkezett: 1978. V. 17. — Terjedelem: 10,15 (A/5) ív, 32 ábra

78.5884 Akadémiai Nyomda, Budapest — Felelős vezető: Bernát György

ACTA CHIMICA

ТОМ 98—ВЫП. 3

РЕЗЮМЕ

## Катодное поведение электрода двуокиси свинца в растворе серной кислоты

А. М. АЗЗАМ, С. С. АБД-ЭЛЬ РЕХИМ и В. Х. БОКТОР

Электрохимическое востановление электрода $PbO_2$ при постоянных плотностях тока было исследовано в растворе $H_2SO_4$ при различных концентрациях и различных температурах. Результаты указывают на то, что кривые потенциалвремя могут быть разделены на три участка перед выделением водорода. Первый участок соответствует восстановлению $PbO_2$ до $PbSO_4$. Второй и третий участки соответствуют восстановлению PbO. $PbSO_4$ и $PbSO_4$ до металлического свинца. Добавление $HClO_4$ или $CH_3COOH$ к раствору не изменяет основного характера кривых.

## Специфическая адсорбция иодатных ионов на поверхности раздела фаз Hg/$KIO_3$ (aq)

М. В. РАМАНАМУРТИ, А. КВАЙУМ и Р. К. СИНГ

Адсорбция иодатных ионов на поверхности раздела фаз ртуть/$KIO_3$(aq) была исследована измерением дифференциальной емкости при 25°С. Смещение потенциала нулевого заряда в направлении более катодной поляризации с увеличением активности в массе электролита дает качественное доказательство ион-специфической адсорбции, которая количественно может быть подтверждена на основе кривых заряжения за счет специфически адсорбированных анионов ($q^1$) в зависимости от заряда электрода ($q^M$). Для изученных концентраций величина $q^1$ больше, чем $q^M$ ($q^M$, +Ve), что указывает на суперэквивалентную адсорбцию иодатных ионов; для данных зарядов электрода величина $q^1$ увеличивается с увеличением активности электролита.

## Химические системы и суперсистемы, III

### Модели авторепродукционных химических суперсистем: емотоны

Т. ГАНТИ

При связи действия любых двух или всех трех химических систем с различными свойствами: автокеталитического кругового процесса, темплатной полимеризации и роста двухмерной молекулярной мембраны получаем химические суперсистемы, которые обладают качественно новыми свойствами не только с химической, но и с биологической точки зрения.

Автокаталитический круговой процесс и рост мембраны путем обмена веществ открывают возможности образования растущих шаров, которые на определенной стадии роста спонтанно разделяются пополам, т. е. способны к размножению.

Связанное действие автокаталитического кругового процесса с темплатной полимеризацией приводит к автокаталитической химической системе с программированным управлением.

Связанное действие всех трех химических систем приводит к таким, разделенным в пространстве растущим и способным к размножению химическим суперсистемам с программированным управлением, т. е. хемотонам, для которых доказано, что они заранее могут быть охарактеризованы, удовлетворяют всем общим критериям и, таким образом, могут быть рассмотрены как биологические минимальные системы.

В данным сообщении обсуждаются стехиометрические зависимости этих суперсистем, а кинетическое описание их, симуляции с помощью ЭВМ и исследование их свойств приводятся в следующих сообщениях.

## Сравнение поглощения растворителя и ионообменных свойств диэтиламиноэтиловой целлюлозы (ДЭ-целлюлоза) и бензилированной диэтиламиноэтиловой целлюлоза (БД-целлюлоза) в смеси метанол–вода–соляная кислота

А. ЛАСТИТИ и М. НЕМЕТ

Сравниваются набухающие и ионообменные свойства ДЭ- и БД-целюлоз в смесях вода-метанол-1 М соляная кислота. Бензоилирование групп ОН ДЭ-целлюлозы изменяет ее набухающие и ионообменные свойства. В водных растворах поглощение воды БД-целлюлозой гораздо меньше, а сорбция металлических ионов (Cd(II), Hg (II.) и Bi(III)) гораздо лучше, чем в случае ДЭ-целлюлозы. Хлористые комплексы предпочитают фазу БД-целлюлозы, более бедную водой. В противоположность ДЭ-целлюлозе, селективность поглощения воды не наблюдалась на БД-целлюлозе в смеси метанол–вода–1 М HCl. При высоком содержании метанола два слабоосновных анионообменника обладают одинаковой сорбционной способностью.

## Получение и исследование производных пентафтортиофенола с In(III), Tl(III) и Rh(III)

Д. М. КАМИНАРИС и А. Г. ГАЛИНОС

Описываются реакции пентафторфенола с неводными растворами, содержащими $InBr_3$, $TlCl_3$ и $RhCl_3$. Приводятся аналитические данные ИК спектры и другие свойства этих аддуктов.

## Теоретическое исследование барьеров инверсии

Т. ВЕЛЛЕР и Р. ЛОХМАН

Теоретические исследования барьеров инверсии молекул $NH_3$, $NH_2CH_3$, $NH(CH_3)_2$, $N(CH_3)_3$, $NCl(CH_3)_2$, $NClH_2$, $PH_3$, $NCl_3$ $P(CH_3)_3$ и $PF_3$ были проведены в рамках програмы PCILO. Полученные результаты сравниваются с экспериментальными данными и расчетными данными *a b initio* и CNDO/INDO.

## Производные аминофталазинона, III

К. КЁРМЕНДИ

Реакционная способность хлорфталазинона (1) в реакции с аминами возрастает в присутствии этиленгликоля, вследствие образования активного переходного гликольного аддукта (2 и 4). Аддукт реагирует с аминами в двух направлениях: основная реакция — аминоалкилирование (4 → 6) и побочная реакция — превращение 4 → 7 → 8, которое приводит к образованию гликолевого эфира фталазинона. Аминоалкилирование в интер-

вале температур 130—200°С приводит к образованию производных 4-амино-1(2Н)-фталазинона типа *6* с различными выходами в зависимости от стерических условий и основности аминов. Аминолиз хлорфталазинона особенно чувствителен к етерическим факторам. Хороший выход был достигнут лишь в случае аминов, содержащих стерически свободную концевую аминогруппу. Два заместителя в α-положении (напр., изопропиламин, 2-аминогептан) уже сильно затрудняют, а три заместителя в α-положении (*трет*-бутиламин) уже совсем останавливают аминоалкилирование и реакция полностью сдвигается в направлении побочной реакции по пути 4 → 7 → 8.

## Исследование внутреннего α-амидоалкилирования, приводящего к синтезу 1,4-дигидро-3-[2Н]-изохинолинонов

Н. М. МОЛЛОВ и А. П. ВЕНКОВ

Был исследован механизм и синтетические возможности внутреннего α-амидоалкилирования. Было показано, что электроно-акцепторные заместители в кольце В соединения I*a* увеличивают выход соединения III, в то время как электроно-донорные группы уменьшают его выход. Те заместители в кольце А увеличивают выходы, которые повышают электронную плотность в кольце или на углеродном атоме 2. Эти результаты подтверждают то заключение, что реакция представляет собой электрофильное замещение, протекающее через образование промежуточного ионного продукта типа 4.

## Синтез пентаацетата 2-амино-3-тио-2-деокси-D-маннопиранозы

П. ХЕРЦЕГ и Р. БОГНАР

Исходя из метил 2-амино-2-деокси-3-О-п-толуолсульфонил-4,6-О-бензилиден-α-D-альтропиранозида (*2*), был приготовлен *цис*-аминотиол (*9*). Интрамолекулярное нуклеофильное замещение тиоацетамидного производного (*5*), полученного из *2* с помощью нового метода тиоацетилирования, приводит к образованию тиазолина (*7*), гидролиз которого с последующим ацетилированием, дает заглавное соединение.

## Использование реактива Миллона для синтетических целей, I

### Получение о-нитрозофенолов с помощью реактива Миллона

Я. ЛАЗАР, Л. МОД и Э. ВИНКЛЕР

На основе исчерпывающего обзора по о-нитрозованию фенолов с помощью реактива Миллиона были сделаны попытки получения о-нитрозофенолов для препаративных целей. Орто-направляющий эффект, наблюдаемый в присутствии ионов ртути(II), объясняют образованием при меркурировании переходного орто-комплекса из комплекса фенола и трути и стабилизированием первого в виде ортортутного производного.

## Дальнейшие исследования протекания реакции Миллона, II

Я. ЛАЗАР, Л. МОД и Э. ВИНКЛЕР

Авторы на основе своих ранних сообщений [1, 2] ,а также работ японских авторов [3, 4] исследуют возможности превращений друг в друга ртутных комплексов о-нитрозофенола различных типов, доказывают превращения отдельных комплексов, а также подробно анализируют протекание реакции Миллона. В результате предлагается новый механизм реакции, содержащий более тонкие подробности.

## Нитроксиды, II

### Производные 1-оксил-2,2,5,5-тетраметилпирролин-3-карбоновой кислоты

О. Х. ХАНКОВСКИ, К. ХИДЕГ и R. ТЫДЬИ

При взаимодействии эфиров 1-оксил-2,2,5,5-тетраметилпирролин-3-карбоновой кислоты с азидом натрия образуется азид карбоновой кислоты. Последний при комнатной температуре ацилирует аминоспирт по аминогруппе, а при повышенной температуре разлагается до изоцианата. Были исследованы некоторые реакции изоцианата со спиртами, тиоспиртами и аминопроизводными.

## Синтез фанил 4-деокси-$\beta$-D-глюкопиранозида

Л. КИШ и П. НАНАШИ

Был разработая простой синтез фенил 4-деокси-$\beta$-D-глюкопиранозида (*5*). Синтез основан на восстановлении фенил 6-О-бензоил-2,3-ди-О-бензил-4-О-п-толуолсульфонил-$\beta$-D-глюкопиранозида (*3*) $LiAlH_4$-ом непосредственно до 4-деоксипроизводного (*4*). Соединение *5* было получено после элиминации бензильных групп с помощью каталитического гидрирования. Было показано, что бензоильная группа в положении С-6 способна образовывать алкоксилюминийгидрид для дальнейшего интрамолекулярного восстановления.

## Метиловые эфиры хиновозы

### Синтез 2-О-метилового, 3-О-метилового и 4-О-метилового эфиров фенил-$\beta$-D-хиновозида

Л. КИШ, А. ЛИПТАК и П. НАНАШИ

Описывается синтез фенил 2-О-метил-$\beta$-D-хиновозида (*3*), фенил 3-О-метил-$\beta$-D-хиновозида (*6*) и фенил 4-О-метил-$\beta$-D-хиновозида (*10*). Соединения *3* и *6* были получены из соответствующих частично метилированных фенильных 4,6-О-бензилиден -$\beta$-D-глюкопированозидов после обработки N-бромсукцинимидом, согласно Ханессиану [3], и восстановительной элиминации брома и бензоильной группы с помощью $LiAlH_4$ в абсолютном эфире. Синтез соединения *10* был осуществлен через 6—О—тозильное производное соответствующего частично метилированного фенил-$\beta$-D-глюкопиранозида. Соединение *10* было получено после обработки $L_8AlH_4$ в абсолютном тетрагидрофуране.

Les Acta Chimica paraissent en français, allemand, anglais et russe et publient des mémoires du domaine des sciences chimiques.

Les Acta Chimica sont publiés sous forme de fascicules. Quatre fascicules seront réunis en un volume (4 volumes par an).

On est prié d'envoyer les manuscrits destinés à la rédaction à l'adresse suivante:

*Acta Chimica*
*H-1521 Budapest, Hongrie*

Toute correspondance doit être envoyée à cette même adresse.

La rédaction ne rend pas de manuscript.

Le prix de l'abonnement: $ 36,00 par volume.

Abonnement en Hongrie à l'Akadémiai Kiadó (1363 Budapest, P. O. B. 24, C. C. B. 215 11488), à l'étranger à l'Entreprise du Commerce Extérieur « Kultura » (H-1389 Budapest 62, P. O. B. 149 Compte-courant No. 218 10990) ou chez représentants à l'étranger.

---

Die Acta Chimica veröffentlichen Abhandlungen aus dem Bereich der chemischen Wissenschaften in deutscher, englischer, französischer und russischer Sprache.

Die Acta Chimica erscheinen in Heften wechselnden Umfanges. Vier Hefte bilden einen Band. Jährlich erscheinen 4 Bände.

Die zur Veröffentlichung bestimmten Manuskripte sind an folgende Adresse zu senden:

*Acta Chimica*
*H-1521 Budapest, Ungarn*

An die gleiche Anschrift ist jede für die Redaktion bestimmte Korrespondenz zu richten.

Manuskripte werden nicht zurückerstattet.

Abonnementspreis pro Band: $ 36,00.

Bestellbar für das Inland bei Akadémiai Kiadó (1363 Budapest, Postfach 24, Bankkonto Nr. 215 11488), für das Ausland bei »Kultúra« Außenhandelsunternehmen (H-1389 Budapest 62, P. O. B. 149. Bankkonto Nr. 218 10990) oder seinen Auslandsvertretungen.

---

«Acta Chimica» издают статьи по химии на русском, английском, французском и немецком языках.

«Acta Chimica» выходит отдельными выпусками разного объемта, 4 выпуска составляют один том и за год выходят 4 тома.

Предназначенные для публикации рукописи следует направлять по адресу:

*Acta Chimica*
*H-1521 Budapest, BHP*

Всякую корреспонденцию в редакцию направляйте по этому же адресу.

Редакция рукописей не возвращает.

Подписная цена — $ 36,00 за том.

Отечественные подписчики направляйте свои заявки по адресу Издательства Академии Наук (1363 Budapest, P. O. B. 24, Текущий счет 215 11488), а иностранные подписчики через организацию по внешней торговле «Kultúra» (H-1389 Budapest 62, P. O. B. 149. Текущий счет 218 10990) или через ее заграничные представительства и уполномеченных.

## Reviews of the Hungarian Academy of Sciences are obtainable at the following addresses:

**AUSTRALIA**
C.B.D. LIBRARY AND SUBSCRIPTION SERVICE, Box 4886, G.P.O., *Sydney N.S.W. 2001*
COSMOS BOOKSHOP, 145 Ackland Street, *St. Kilda (Melbourne), Victoria 3182*

**AUSTRIA**
GLOBUS, Höchstädtplatz 3, *1200 Wien XX*

**BELGIUM**
OFFICE INTERNATIONAL DE LIBRAIRIE, 30 Avenue Marnix, *1050 Bruxelles*
LIBRAIRE DU MONDE ENTIER, 162 Rue du Midi, *1000 Bruxelles*

**BULGARIA**
HEMUS, Bulvar Ruszki 6, *Sofia*

**CANADA**
PANNONIA BOOKS, P.O. Box 1017, Postal Station "B", *Toronto, Ontario M5T 2T8*

**CHINA**
CNPICOR, Periodical Department, P.O. Box 50, *Peking*

**CZECHOSLOVAKIA**
MAD'ARSKÁ KULTURA, Národní třida 22, *115 66 Praha*
PNS DOVOZ TISKU, Vinohradská 36, *Praha 2*
PNS DOVOZ TLAČE, *Bratislava 2*

**DENMARK**
EJNAR MUNKSGAARD, Norregade 6, *1165 Copenhagen*

**FINLAND**
AKATEEMINEN KIRJAKAUPPA, P.O. Box 128, *SF-00101 Helsinki 10*

**FRANCE**
EUROPERIODIQUES S. A., 31 Avenue de Versailles, *78170 La Celle St. Cloud*
LIBRAIRIE LAVOISIER, 11 rue Lavoisier, *75008 Paris*
OFFICE INTERNATIONAL DE DOCUMENTATION ET LIBRAIRIE, 48 rue Gay-Lussac, *75240 Paris Cedex 05*

**GERMAN DEMOCRATIC REPUBLIC**
HAUS DER UNGARISCHEN KULTUR, Karl-Liebknecht-Strasse 9, *DDR-102 Berlin*
DEUTSCHE POST ZEITUNGSVERTRIEBSAMT, Strasse der Pariser Kommüne 3—4, *DDR-104 Berlin*

**GERMAN FEDERAL REPUBLIC**
KUNST UND WISSEN ERICH BIEBER, Postfach 46, *7000 Stuttgart 1*

**GREAT BRITAIN**
BLACKWELL'S PERIODICALS DIVISION, Hythe Bridge Street, *Oxford OX1 2ET*
BUMPUS, HALDANE AND MAXWELL LTD., Cowper Works, *Olney, Bucks MK43 4BN*
COLLET'S HOLDINGS LTD., Denington Estate, *Wellingborough, Northants NN8 2QT*
WM. DAWSON AND SONS LTD., Cannon House, *Folkes-one, Kent CT19 5EE*
H. K. LEWIS AND CO., 136 Gower Street, *London WC1E 6BS*

**GREECE**
KOSTARAKIS BROTHERS, International Booksellers, 2 Hippokratous Street, *Athens-143*

**HOLLAND**
MEULENHOFF-BRUNA B.V., Beulingstraat 2, *Amsterdam*
MARTINUS NIJHOFF B.V., Lange Voorhout 9—11, *Den Haag*
SWETS SUBSCRIPTION SERVICE, 347b Heereweg, *Lisse*

**INDIA**
ALLIED PUBLISHING PRIVATE LTD., 13,14 Asaf Ali Road, *New Delhi 110001*
150 B-6 Mount Road, *Madras 600002*
INTERNATIONAL BOOK HOUSE PVT. LTD., Madame Cama Road, *Bombay 400069*
THE STATE TRADING CORPORATION OF INDIA LTD., Books Import Division, Chandralok, 36 Janpath, *New Delhi 110001*

**ITALY**
EUGENIO CARLUCCI, P.O. Box 252, *70100 Bari*
INTERSCIENTIA, Via Mazzé 28, *10149 Torino*
LIBRERIA COMMISSIONARIA SANSONI, Via Lamarmora 45, *50121 Firenze*
SANTO VANASIA, Via M. Macchi 58, *20124 Milano*
D. E. A., Via Lima 28, *00198 Roma*

**JAPAN**
KINOKUNIYA BOOK-STORE CO. LTD., 17-7 Shinjuku-ku 3 chome, Shinjuku-ku, *Tokyo 160-91*
MARUZEN COMPANY LTD., Book Department, P.O. Box 5050 Tokyo International, *Tokyo 100-61*
NAUKA LTD., IMPORT DEPARTMENT, 2-30-19 Minami Ikebukuro, Toshima-ku, *Tokyo 171*

**KOREA**
CHULPANMUL, *Phenjan*

**NORWAY**
TANUM-CAMMERMEYER, Karl Johansgatan 41—43, *1000 Oslo*

**POLAND**
WĘGIERSKI INSTYTUT KULTURY, Marszałkowska 80, *Warszawa*
CKP I W ul. Towarowa 28 *00-958 Warsaw*

**ROUMANIA**
D. E. P., *Bucureşti*
ROMLIBRI, Str. Biserica Amzei 7, *Bucureşti*

**SOVIET UNION**
SOJUZPETCHATJ — IMPORT, *Moscow*
and the post offices in each town
MEZHDUNARODNAYA KNIGA, *Moscow G-200*

**SPAIN**
DIAZ DE SANTOS, Lagasca 95, *Madrid 6*

**SWEDEN**
ALMQVIST AND WIKSELL, Gamla Brogatan 26, *101 20 Stockholm*
GUMPERTS UNIVERSITETSBOKHANDEL AB, Box 346, *401 25 Göteborg 1*

**SWITZERLAND**
KARGER LIBRI AG, Petersgraben 31, *4011 Basel*

**USA**
EBSCO SUBSCRIPTION SERVICES, P.O. Box 1943, *Birmingham, Alabama 65201*
F. W. FAXON COMPANY, INC., 15 Southwest Park, *Westwood, Mass, 02090*
THE MOORE-COTTRELL SUBSCRIPTION AGENCIES, *North Cohocton, N. Y. 14868*
READ-MORE PUBLICATIONS, INC., 140 Cedar Street, *New York, N. .Y. 10006*
STECHERT-MACMILLAN, INC., 7250 Westfield Avenue, *Pennsauken* N.J. 08110

**VIETNAM**
XUNHASABA, 32, Hai Ba Trung, *Hanoi*

**YUGOSLAVIA**
JUGOSLAVENSKA KNJIGA, Terazije 27, *Beograd*
FORUM, Vojvode Mišiča 1, *21000 Novi Sad*

*17. XI. 1978* HU ISSN 0001—5407 **Index: 26.007**

# ACTA CHIMICA

## ACADEMIAE SCIENTIARUM HUNGARICAE

ADIUVANTIBUS

M. T. BECK, R. BOGNÁR, V. BRUCKNER,
GY. HARDY, K. LEMPERT, F. MÁRTA,
K. POLINSZKY, E. PUNGOR,
G. SCHAY, Z. G. SZABÓ, P. TÉTÉNYI

REDIGUNT

B. LENGYEL et GY. DEÁK

TOMUS 98 FASCICULUS 4

AKADÉMIAI KIADÓ, BUDAPEST

1978

ACTA CHIM. ACAD. SCI. HUNG. ACASA2 98 (4) 367–499 (1978)

# ACTA CHIMICA

## A MAGYAR TUDOMÁNYOS AKADÉMIA KÉMIAI TUDOMÁNYOK OSZTÁLYÁNAK IDEGEN NYELVŰ KÖZLEMÉNYEI


FŐSZERKESZTŐ

LENGYEL BÉLA

SZERKESZTŐ

DEÁK GYULA

TECHNIKAI SZERKESZTŐ

HARASZTHY-PAPP MELINDA

SZERKESZTŐ BIZOTTSÁG

BECK T. MIHÁLY, BOGNÁR REZSŐ, BRUCKNER GYŐZŐ, HARDY GYULA, LEMPERT KÁROLY, MÁRTA FERENC, POLINSZKY KÁROLY, PUNGOR ERNŐ, SCHAY GÉZA, SZABÓ ZOLTÁN, TÉTÉNYI PÁL



**Acta Chimica is a journal for the publication of papers on all aspects of chemistry in English, German, French and Russian.**

**Acta Chimica is published in 4 volumes per year. Each volume consists of 4 issues of varying size.**

**Manuscripts should be sent to**

***Acta Chimica***
***H-1521 Budapest, Hungary***

**Correspondence with the editors should be sent to the same address. Manuscripts are not returned to the authors.**

**Subscription: $ 36.00 per volume.**

**Hungarian subscribers should order from Akadémiai Kiadó, 1363 Budapest, P.O. Box 24. Account No. 215 11488.**

**Orders from other countries are to be sent to "Kultura" Foreign Trading Company (H-1389 Budapest 62, P.O. Box 149. Account No. 218 10990) or its representatives abroad.**

*Acta Chimica Academiae Scientiarum Hungaricae, Tomus 98 (4), pp. 367–373 (1978)*

# PHOTOMETRIC DETERMINATION OF OXALIC ACID AS IRON(III)-OXALATE COMPLEX IN THE PRESENCE OF ETHYLENE GLYCOL, GLYOXALIC ACID, GLYCOLIC ACID AND GLYOXAL

E. SZETEY, G. INZELT and G. HORÁNYI*

*(Department of Physical Chemistry and Radiology, L. Eötvös University, Budapest, and *Central Research Institute for Chemistry, Hungarian Academy of Sciences)*

Received September 7, 1977
in revised form: December 7, 1977

It was found that oxalic acid can be determined by photometry on the basis of the light absorption properties of its iron(III)-complex in a strongly acidic medium ($[H^+] < 0.1$ mol/dm$^3$) in a perchloric acid and sulphuric acid ground electrolyte. Even great excesses of ethylene glycol, glyoxal, glyoxalic acid and glycolic acid do not interfere with the determination. Consequently, the method can be applied reliably for the quantitative determination of oxalic acid formed during the electrochemical oxidation of these compounds.

In the course of investigations of the electrochemical oxidation of ethylene glycol, glyoxal and glyoxalic acid on a platinum electrode in a sulphuric acid and perchloric acid medium the necessity of the periodical quick determination of oxalic acid as one of the oxidation products emerged in order to follow the progress of the electrolysis. Since several readily oxidizable compounds are present simultaneously a cerimetric or permanganometric determination could not be applied and more lengthy gravimetric procedures did not appear to be suitable either. Then the problem arose whether oxalic acid could be determined by a photometric method in the liquid samples of a few ml volume whose oxalic acid concentration was in the range of $10^{-3}$–$10^{-2}$ mol/dm$^3$. From this aspect our attention was directed to the Fe(III)-oxalate complex whose various properties were already investigated by a number of authors [1–10]. It can be ascertained from the cited literature that in a strongly acidic medium (at $[H^+] \geq 0.1$ mol/dm$^3$) in the presence of an excess of $Fe^{3+}$ ions a yellowish green complex $[Fe(C_2O_4)]^+$ is formed with oxalic acid. Though the light absorption of $Fe^{3+}$ ions and of their complexes formed with various anions is significant in a wide range of wavelengths, the molar extinction coefficients just in case of $Fe(ClO_4)_3$ and $Fe_2(SO_4)_3$ appreciably decrease in the interval of 250–400 nm and 310–400 nm, respectively, as can be seen in Fig. 1 in the curves found in the literature [11].

At the same time it appears from the comparison of the absorption properties of the $[Fe(C_2O_4)]^+$ complex and of $Fe(ClO_4)_3$ that a wavelength interval in fact exists where the light absorption of $Fe(ClO_4)_3$ is negligible in relation to that of the oxalate complex. This is shown in the curves of Fig. 2 found also in the literature [12].

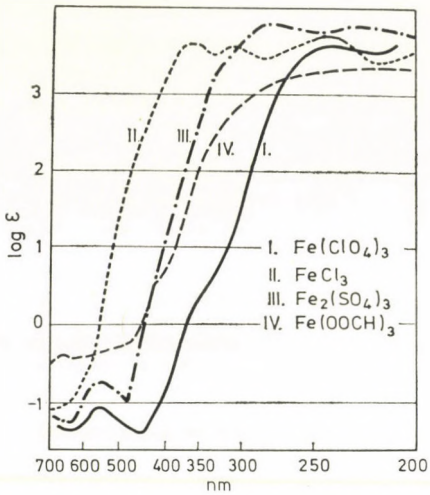



*Fig. 1.* Molar extinction coefficients of various Fe(III) compounds *vs.* wavelengths [11]

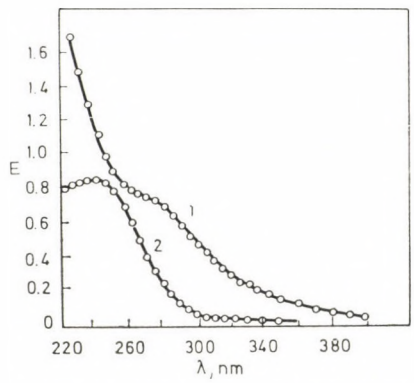



*Fig. 2.* Comparison of the absorption properties of $Fe(ClO_4)_3$ and $[Fe(C_2O_4)]^+$ according to BABKO and DUBOVENKO [2]: 1) $Fe(C_2O_4)^+$, 2) $Fe(ClO_4)_3$

However, it can be found also in literature that the $[Fe(C_2O_4)_3]^{3-}$-complex is applied as a chemical actinometer in the wavelength domain 250–900 nm [6–9], indicating that it is a photosensitive system. The probability of the formation of this complex in a strongly acidic medium and in case of an excess of iron(III) ions in relation to oxalic acid is rather low. Concerning photometric and other investigations carried out under such conditions no mentions can be found of difficulties caused by an eventual photosensitivity in the relevant literature [1–3], [10]. Anyhow, in our present experiments also this problem must be examined and it must be investigated whether the results of the determination are affected by the photosensitivity of the eventually formed $[Fe(C_2O_4)_3]^{3-}$-complex.

On taking into consideration all these aspects it did not appear impossible to determine oxalic acid in perchloric acid and sulphuric acid media on the basis of the light absorption of its iron complex at an adequately chosen wavelength.

## Theoretical fundamentals of the method

Our theoretical considerations will be presented here for perchloric acid as a medium since at a fair approximation the complete dissociation of both $HClO_4$ and $Fe(ClO_4)_3$ can be assumed. At first let us examine the experimental conditions under which we can expect to obtain an unequivocal relationship between the concentration of oxalic acid and the concentration of $[FeC_2O_4]^+$.

Let us examine the equilibria:

$$HOOC—COOH \rightleftharpoons HOOC—COO^- + H^+ \qquad K_1 \qquad (1)$$

$$HOOC—COO^- \rightleftharpoons {}^-OOC—COO^- + H^+ \qquad K_2 \qquad (2)$$

$$[Fe(C_2O_4)]^+ \rightleftharpoons Fe^{3+} + {}^-OOC—COO^- \qquad K_0 \qquad (3)$$

(The formation of complexes containing several (2 or 3) oxalate ions can be neglected because on the one hand, the corresponding equilibrium constants have values higher by several orders of magnitude than those of $K_0$ ($K_0 = 7\times10^{-9}$, $K_{[Fe(C_2O_4)_2]^-} = 1.6\times10^{-6}$, $K_{[Fe(C_2O_4)_3]^{3-}} = 5\times10^{-3}$) [3] and, on the other hand, the concentration of the oxalate ions is low in solutions of high hydrogen ion concentrations.)

Let us denote by $[H_2C_2O_4]_0$ the total concentration of oxalic acid present in various forms, i.e. of oxalic acid weighed in. The equilibrium concentrations in the solution containing also iron will be denoted by: $[H_2C_2O_4]$, $[Fe^{3+}]$, $[HC_2O_4^-]$, $[C_2O_4^{2-}]$, $[FeC_2O_4^+]$. On taking into account the above given denotations and the equilibria, furthermore the material balance the following relationships can be established:

$$[H_2C_2O_4]_0 = [H_2C_2O_4] + [HC_2O_4^-] + [C_2O_4^{2-}] + [FeC_2O_4^+] \qquad (4)$$

$$[C_2O_4^{2-}] = A\,([H_2C_2O_4]_0 - [FeC_2O_4^+]) \qquad (5)$$

$$A = \frac{K_1K_2}{[H^+]^2 + K_1[H^+] + K_1K_2} \qquad (6)$$

On taking into account the equilibrium characterized by equation (3) we obtain the relationship:

$$[FeC_2O_4^+] = \frac{1}{1 + \dfrac{K_0}{A\,[Fe^{3+}]}}\,[H_2C_2O_4]_0 \qquad (7)$$

It can be understood from equation (7) that the requirement

$$[FeC_2O_4^+] \approx [H_2C_2O_4]_0 \tag{8}$$

is fulfilled when

$$\frac{K_0}{A} \frac{1}{[Fe^{3+}]} \ll 1, \quad \text{and resp. } [Fe^{3+}] \gg \frac{K_0}{A} \tag{9}$$

In this case the oxalic acid present initially in the solution will exist practically completely in the form of $[FeC_2O_4^+] \cdot \frac{K_0}{A} = 1.9 \times 10^{-3}$ (if $[H^+] = 1$) and $3 \times 10^{-5}$ (if $[H^+] = 0.1$). It follows unequivocally from equation (9) that even in case of extremely low concentrations of oxalic acid $\left(\frac{K_0}{A} > [H_2C_2O_4]_0\right)$ the concentration of $[Fe^{3+}]$ must be of an order of magnitude of $10^{-2}$ and $10^{-3}$ mol/dm$^3$, respectively, in the hydrogen ion concentration interval of $[H^+] = 1 \div 0.1$, if it is desirable that oxalic present in the solution should be predominantly in the form $[Fe(C_2O_4)]^+$. Thus, in the experimental investigations the concentration of the iron salts weighed-in must be chosen adequately.

## Results

The investigations were carried out on spectrophotometers of Spektromom 361 and Spektromom 201 type.

Curve a) of Fig. 3 represents in case of 1.0 *M* $HClO_4$ as ground solution that part of the absorption spectrum of $[Fe(C_2O_4)]^+$ which is in the wavelength domain corresponding to the visible light. In this domain of wavelength the light absorption of $Fe(ClO_4)_3$ can be practically neglected and this is also confirmed by the fact that no differences in the measured values are observable if the reference solution of 1.0 *M* $HClO_4$ is replaced by a 1.0 *M* solution of $HClO_4$ containing also $Fe(ClO_4)_3$ in the same concentration as the tested solution. When in case of measurements carried out at a wavelength of 380 nm the extinction values were plotted *vs.* the concentration of oxalic acid weighed-in, a straight line was obtained.

In case of sulphuric acid solutions the conditions of equilibrium are more complex than in case of perchlorate serving as a model at the discussion of the theoretical fundamentals of measurement. Namely, on discussing the sulphuric acid system, also the formation of various sulphate complexes should be taken into account. Furthermore, the absorption spectra of the $[Fe(C_2O_4)]^+$ complex and of the sulphate complexes are overlapping already in the visible domain. In spite of this, the increase of extinction occurring on the effect of oxalic acid is well observable also in a sulphuric acid solution in a wide interval

of wavelengths subsequent to the addition of oxalic acid to the system $Fe_2(SO_4)_3 + H_2SO_4$ (curve b) of Fig. 3.

According to experimental experiences at a given wavelength the extinction changes linearly with the concentration of oxalic acid in the same way as in case of perchloric acid as ground solution. For reasons mentioned already in case of perchloric acid, measurements must be carried out also in case of sulphuric acid at high hydrogen ion concentrations, expediently in a ground solution of 1.0 *M* $H_2SO_4$.

On taking into account the above discussion, measurements can be carried out as follows.

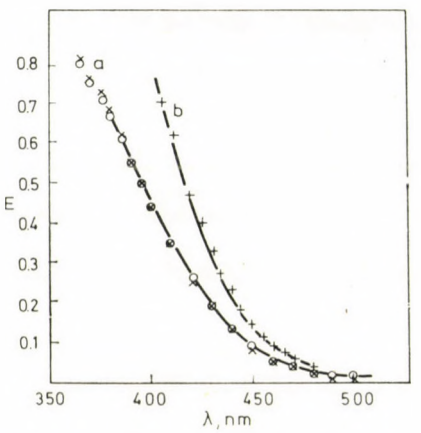



*Fig. 3.* Dependence of extinction on the wavelength: a) in a 1 *M* solution of perchloric acid: $2.5 \times 10^{-2}$ *M* $Fe(ClO_4)_3 + 10^{-2}$ *M* $H_2C_2O_4$. Reference solution: 1 *M* $HClO_4 + 2.5 \times 10^{-2}$ *M* $Fe(ClO_4)_3$ (○); 1 *M* $HClO_4$ (×); b) in a 1 *M* sulphuric acid solution as ground solution: $1.25 \times 10^{-1}$ *M* $Fe_2(SO_4)_3 + 2.5 \times 10^{-2}$ *M* $C_2H_2O_4 + 1$ *M* $H_2SO_4$. Reference solution: $1.25 \times 10^{-1}$ *M* $Fe_2(SO_4)_3 + 1$ *M* $H_2SO_4$

I. In a perchloric acid medium:

Solutions:

1. a solution of $10^{-3}$–$10^{-2}$ mol/dm$^3$ oxalic acid in 1 *M* perchloric acid,

2. a solution of $5 \times 10^{-2}$ mol/dm$^3$ $Fe(ClO_4)_3$ in 1 *M* perchloric acid.

Solutions 1. and 2. are combined in a 1 : 1 volume ratio.

Reference solution: a solution of $2.5 \times 10^{-2}$ $Fe(ClO_4)_3$ in 1 *M* perchloric acid.

Wavelength: 380 nm.

II. In a sulphuric acid medium:

Solutions:

1. a solution of $10^{-3}$–$10^{-2}$ mol/dm$^3$ oxalic acid in 1 *M* sulphuric acid,

2. a solution of $10^{-1}$ mol/dm$^3$ of $Fe_2(SO_4)_3$ in 1 *M* sulphuric acid.

Solutions 1. and 2. are combined in a 1 : 1 volume ratio.

Reference solution: $5 \times 10^{-2}$ mol/dm$^3$ $Fe_2(SO_4)_3$ in 1 *M* sulphuric acid.

Wavelength: 440 nm.

Anions whose complexes and compounds exhibit light absorption of a significant extent at the examined wavelengths (such as $Cl^-$, $HCOO^-$) interfere with the determination. Separate investigations were carried out in order to clear up whether an eventual photosensitivity of the system interferes with the determinations. However, no alterations were observable in the concentrations of oxalic acid of the solutions combined for photometry, even when the samples were previously exposed for two hours to the usual laboratory illumination.

The concentration of oxalic acid was determined by the method described above, in the presence of great excesses of glyoxalic acid, glyoxal, ethylene glycol and glycolic acid. Results of these investigations are summarized in Table I. The data of Table I prove unequivocally that the possibility of determination of oxalic acid is not affected by the above-mentioned components even when their concentrations are higher by one order of magnitude than that of oxalic acid. The sensitivity of the presented method is not too high, it is not suitable for the determination of minute concentrations ($10^{-4}$–$10^{-5}$ mol/dm$^3$) of oxalic acid. Still, the presented method may be significant in that it makes possible the relatively quick determination of the concentration of oxalic acid also in the presence of other organic substances.

**Table I**

| Additive | Ground electrolyte | | | |
|---|---|---|---|---|
| | 1 *M* $HClO_4$ | | 1 *M* $H_2SO_4$ | |
| | Oxalic acid $10^{-2}$ mol/dm$^3$ | | Oxalic acid $10^{-2}$ mol/dm$^3$ | |
| | Weighed-in | Found | Weighed-in | Found |
| 0.1 mol/dm$^3$ glyoxal | 1.0 | 0.975 | 1.0 | 0.975 |
| 0.1 mol/dm$^3$ glyoxalic acid | 1.0 | 1.015 | 1.0 | 1.010 |
| 0.1 mol/dm$^3$ glyoxal + 0.1 mol/dm$^3$ glyoxalic acid | 1.0 | 0.980 | 1.0 | 0.980 |
| 0.1 mol/dm$^3$ glyoxal + 0.1 mol/dm$^3$ glyoxalic acid | | | 0.5 | 0.500 |
| + 0.1 mol/dm$^3$ ethylene glycol | | | 1.0 | 0.980 |
| + 0.1 mol/dm$^3$ glycolic acid | | | 2.0 | 1.980 |

Each value in Table I represents the average of 5—7 measurements.
The relative error of the measurements was ± 0.030.

## REFERENCES

[1] LAMBLING, J.: Bull. Soc. Chim. **1949,** 495
[2] BABKO, A. K., DUBOVENKO, L. I.: Zhurn. Obshtch. Khimii **26,** 660 (1956)
[3] BABKO, A. K., DUBOVENKO, L. I.: Zhurn. Obshtch. Khimii **26,** 996 (1956)
[4] HORNE, R. A.: J. Phys. Chem. **64,** 1512 (1960)

[5] SHEPPARD, J. C., BROWN, L. C.: J. Phys. Chem. **67,** 1025 (1963)
[6] ALLMAND, A. J., WEBB, W. W.: J. Chem. Soc. **1929,** 1518
[7] PARKER, C. A.: Proc. Roy. Soc. (London) **A 220,** 104 (1953)
[8] HATCHARD, C. G., PARKER, C. A.: Proc. Roy. Soc. (London) **A 235,** 518 (1956)
[9] LEE, J., SELIGER, H. H.: J. Chem. Phys. **40,** 519 (1964)
[10] LLOPIS, J., POSEDO, R.: Electrochim. Acta **13,** 1131 (1968)
[11] LANDOLT-BÖRNSTEIN: Zahlenwerte und Funktionen I/3. Springer Verlag, Berlin, 1951
[12] Handbook of Chemistry and Physics. Chem. Rubber Publ. Co., Cleveland, Ohio, 1956

Éva SZETEY
György INZELT } H-1088 Budapest, Puskin u. 11/13.

György HORÁNYI H-1525 Budapest, Pusztaszeri út 57/69.

*Acta Chimica Academiae Scientiarum Hungaricae, Tomus 98 (4), pp. 375–393 (1978)*

# MECHANISM OF THE PYROLYSIS OF PROPANE AND *n*-BUTANE AT LOW (ABOUT 800 K) AND HIGH (ABOUT 1100 K) TEMPERATURES

N. S. NAMETKIN, R. A. KALINENKO, L. V. SHEVELKOVA,* L. ZALOTAI, D. HALÁSZ, T. BÉRCES and F. MÁRTA**

*(*A. V. Topchiev Institute for Oil Chemical Syntheses of the USSR Academy of Sciences, Moscow, U.S.S.R., **Institute of General and Physical Chemistry of the József Attila University, Szeged, and Reaction Kinetics Research Group of the Hungarian Academy of Sciences, Szeged)*

Received 25 July, 1977

On the basis of the product composition as a function of the conversion, three stages of paraffin pyrolysis can be distinguished. They correspond to low, medium and high conversions, respectively.

We studied the self-inhibition processes of the pyrolysis of propane and butane, as well as the effect of olefins on the product distribution in two temperature ranges: at low temperatures (807–833 K) and at high temperatures (973–1113 K). It has been shown that the variation of product composition as a function of the conversion in propane and butane pyrolysis can be interpreted, in the stage of medium conversions, by reactions between hydrogen atom and olefins, in both the low and high temperature ranges. Reactions between alkyl radicals and olefins are the most important secondary processes in the thermal decomposition of *n*-butane, especially at low temperatures, leading to the formation of allyl radicals.

We have elucidated the elementary reactions taking place with the participation of olefins in the low and high temperature pyrolysis of propane and butane, which have basic importance in the process of inhibition.

## Introduction

Pyrolysis of hydrocarbons is one of the most important processes in manufacturing petrochemical products. Owing to this reason, the technology of pyrolysis of various hydrocarbon raw materials has been considerably developed. At the same time, the study of elementary reactions in thermal decomposition is lagging well behind the rapid development of industrial processes. Incomplete knowledge about the mechanism of hydrocarbon pyrolysis may constitute a severe limitation in optimizing the parameters of manufacturing various products.

Research work performed during the last 15–20 years has elucidated the most important questions of the decomposition of paraffinic hydrocarbons at low temperatures (between 700 and 900 K) [1–12]. It has been shown that the process is of radical-chain character, and the decomposition of paraffins at low conversions is well described by the Rice-Herzfeld mechanism.

There are some problems, however, which have remained unsolved so far. Among these the following ones can be mentioned:

(1) the effect of olefins produced during decomposition on the product composition and on the reaction mechanism;

(2) the nature of the reactions responsible for the change of product composition with increasing conversion;

(3) the mechanism of inhibition by olefins in paraffin decomposition;

(4) determination of the rate constants of the various elementary reactions and the dependence of the Arrhenius parameters on the temperature;

(5) elucidation of the regularities of paraffin pyrolysis at higher temperatures (above 1000 K).

The purpose of the present work was to deal with the above questions. Special attention has been paid to the similarities and differences in the decomposition mechanisms observed at lower and higher temperatures. We shall discuss phenomena observed in the pyrolysis of propane and butane.

The stoichiometry of product formation in the pyrolysis of various paraffinic hydrocarbons markedly depends on the conversion. With increasing conversion the concentrations of olefins pass through maxima; the amount of paraffins steadily increases, whereas the concentration of hydrogen approaches a limiting value. These characteristics are illustrated in Figs 1 and 2 for the decomposition of propane [1] and butane [2], up to high conversions.

According to the regularities illustrated by these figures, three stages of the processes can be distinguished. The first one covers the low conversion range up to a few tenth per cent (or maximum up to a few per cent) conversion. Secondary processes are negligible here, and they have practically no influence on the product composition. Rice-Herzfeld kinetics holds.

The second stage covers conversions up to 10–15%. Self-inhibition reactions occur here and the product composition is moderately dependent on the conversion.

High conversions represent the third stage. The main characteristics are here the following: decreasing rates of formation of low olefins, appearance of higher molecular weight products, carbon formation, etc.

The mechanism in the first stage can be regarded as elucidated. The mechanisms operating in the second stage are of the greatest interest from both the theoretical and practical points of view. The present paper will discuss the pyrolysis mechanisms of propane and *n*-butane in the medium conversion range (up to about 20%).

The mechanisms of reactions predominating in the high conversion range are also of considerable scientific interest. They will not, however, be discussed in the present paper.

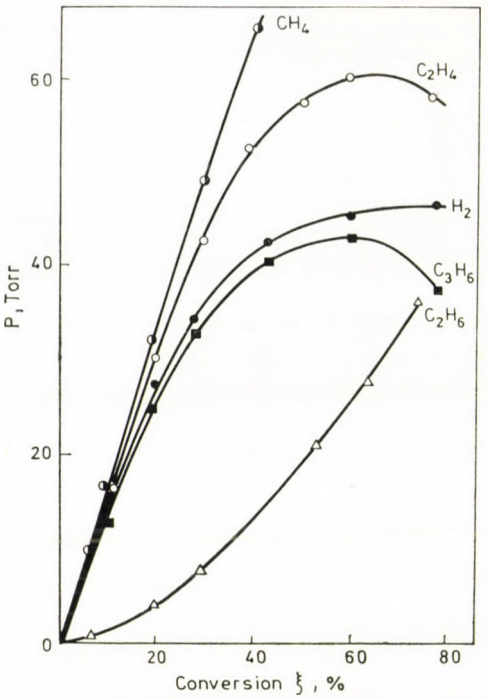



*Fig. 1.* Partial pressures of the decomposition products of propane as a function of the conversion. $T = 863$ K, $[C_3H_8]_0 = 200$ Torr

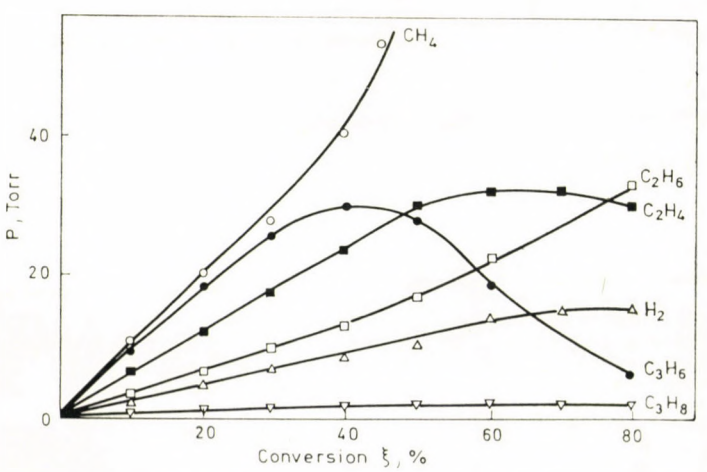



*Fig. 2.* Partial pressures of the decomposition products of *n*-butane as a function of the conversion. $T = 823$ K, $[C_3H_8]_0 = 100$ Torr.

## Experimental

### (a) Low temperature experiments (at about 800 K)

The experiments were carried out in a conventional static vacuum apparatus. The reaction vessel, made of Supremax glass, was placed into an air thermostat. Its volume was 250 $cm^3$ for the experiments with propane and 320 $cm^3$ for *n*-butane; the surface/volume ratio being 1.3 $cm^{-1}$. The accuracy of thermostating was $\pm$ 0.3 K, its reproducibility being $\pm$ 1 K. Mercury- or silicon oil filled U-tube manometers were used as pressure gauges, using glass spiral manometers as null-instruments.

The vessel was evacuated prior to each experiment to $10^{-4}$ Torr; in the cases when the vessel had been in contact with air before the experiment, it was conditioned by pyrolysing a few hydrocarbon samples.

The decompositions were followed by pressure measurements and gas chromatography. For quantitative analysis, the reaction mixture was expanded to an evacuated bulb of 500 $cm^3$ volume; sampling was then carried out by using a Toepler pump.

Gas chromatography was carried out using a Carlo Erba Fractovap Model C and a Perkin Elmer F 11 device, instrument equipped with katharometer and flame ionization detectors, respectively. Analysis of the light hydrocarbons was achieved by thermal conductivity detection, in hydrogen carrier gas (60 $cm^3$ $min^{-1}$) on a 2.5 m, 5 mm i.d. column packed with 60—80 mesh $Al_2O_3$ adsorbent. The hydrogen produced was determined from another sample on a 1.6 m Molecular Sieve 13X adsorbent column with nitrogen carrier gas. The columns were held at 50 °C in both cases.

Higher hydrocarbons were also looked for. By using a 5 m long, 2 mm i.d. column packed with 20% dimethylsulfolane on Chromosorb W, very low amounts of $C_4$–$C_6$ hydrocarbons could be detected. Of these, 1-butene, 2-butene and 1,3-butadiene were identified. The total amount of $C_4$–$C_6$ hydrocarbons in the conversion range studied remained below 1% as compared with the main products. No systematic analysis of the products present in small or trace amounts was attempted.

### (b) High temperature experiments (at about 1100 K)

The experiments were made in a flow type quartz reactor packed with granulated quartz as heat transferring medium. The temperature range was between 1023 and 1123 K. The pressure was maintained at about 100 Torr, the reaction time was between 0.02 and 0.08 s.

The preheater (i.d. 20 mm, length 150 mm) was filled with quartz chips; the reaction zone was of 40 mm i.d. and of 160 mm length. Its total volume was 70 $cm^3$, the average diameter of granulated quartz in it being 0.6 mm.

The starting hydrocarbons were stored in thoroughly de-aerated 40 liter vessels.

The apparatus was evacuated prior to the experiments to a pressure of $10^{-3}$ Torr, and simultaneously heated to the required temperature. Feeding was then begun: the starting material entered the reaction zone *via* the preheater. The feeding rate was measured by a scaled rotameter. After the system had reached steady state conditions, the products were led to a spiral connected downstream to the cooler. When isotopic tracer studies were carried out, it was not necessary to collect considerable amounts of the products. In this case the outflow was led into a trap cooled with liquid nitrogen.

Analyses of the products were made gas chromatographically, using katharometer as detector. Methane and hydrogen were separated at room temperature on a silica gel column (length: 3 m, i.d. 6 mm) in argon carrier gas. $C_2$–$C_5$ hydrocarbons were separated also at room temperature, on a 12 m, 6 mm i.d. diisoamyl phthalate column, using hydrogen carrier gas. Since ethane and ethylene were separated incompletely, an auxiliary column packed with rough silica gel (length 5 m, 6 mm i.d.) has also been applied.

In the tracer studies, the individual components were separated by means of a preparative gas chromatograph equipped with a membrane manometer detector. The columns were packed in this case with silica gel, acetonylacetone, and polybutene.

## Product composition in the pyrolysis of propane and *n*-butane

Product compositions in the pyrolysis of paraffins were characterized by selectivity values. Selectivity is defined as the number of product moles formed when 100 moles of starting material are decomposed.

The main products of propane pyrolysis at 863 K and 100 Torr starting pressure are: methane, hydrogen, ethylene and propylene. The selectivities of these products at conversions close to zero are nearly equal and correspond to about 50 mole/100 mole $C_3H_8$ decomposed (Fig. 3). With increasing conversion, the selectivities for $CH_4$, $C_2H_4$ and $C_2H_6$ increase, those of hydrogen and propylene decrease. An analogous picture was obtained at 1073 K and $P_0 =$ $= 100$ Torr (Fig. 4).

At higher temperatures the selectivities for $H_2$, $CH_4$ and $C_2H_4$ are greater, whereas that for $C_3H_6$ is smaller (compare Figs 3 and 4). In addition, at higher temperatures, butenes, butadiene and very small amounts (0.05–0.10%) of $C_3H_4$ appear.

The variation of product composition with increasing conversion is apparently due to the accumulation of olefinic products in the reaction mixture. In fact, when ethylene (1.6 or 4.5%) is added to the propane, the selectivity of hydrogen at 833 K and 10% conversion is found to be smaller, and that of ethane higher than in the case of pure propane (Table I). Ethylene addition at higher temperatures (1023–1123 K) produces no changes in the product selectivities.

If propylene is added to propane at 833 K, the selectivity of hydrogen decreases and that of methane increases (Table II). If the propylene is added to propane at 1073 K, the selectivities of methane, ethylene, butene and butadiene formation increase considerably, but no marked change can be observed in hydrogen formation (Table III). When propylene is added at a still higher temperature (1123 K) and the reaction mixture is analyzed at 45% conversion, a decreased hydrogen selectivity is observed with the simultaneous increase of all other selectivity values (Table IV).

At high temperatures, propylene labelled at its non-terminal carbon atom by $^{14}C$ isotope ($CH_3—{}^{14}CH=CH_2$) was added to propane and the radioactivity distribution in the product was monitored in order to determine the main reaction pathways. As seen from Table V, about 60% of the labelled molecule gave $^{14}C_2H_4$.

The main products from *n*-butane at 823 K are propylene and methane, found in nearly equal amounts (Fig. 5). There is another, less rapid pathway of pyrolysis leading to ethane, ethylene and hydrogen.

At 973 K, the selectivity of ethane is lower, those of hydrogen and ethylene formation are much higher than at 823 K (Fig. 6). This can be attributed to the consumption of ethyl radicals at lower temperatures in abstraction reac-

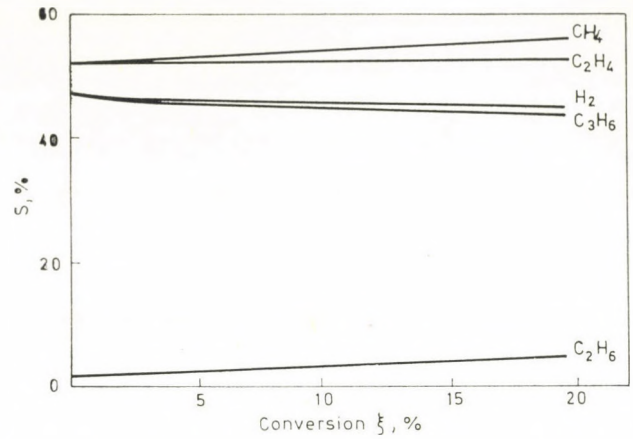



*Fig. 3.* Product composition in propane pyrolysis as a function of the conversion. (Curves fitted by the method of least squares.) $T = 863$ K, $[C_3H_8]_0 = 100$ Torr.

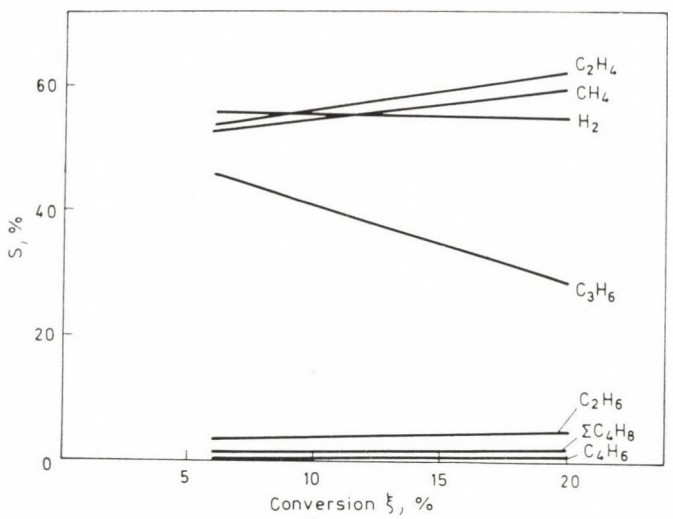



*Fig. 4.* Product composition in propane pyrolysis as a function of the conversion. (Curves fitted by the method of least squares.) $T = 1073$ K, $[C_3H_8]_0 = 100$ Torr.

**Table I**

*Effect of added ethylene on the selectivity of product formation in propane pyrolysis*
Analysis: at 10% conversion. $T = 833$ K; $[C_3H_8]_0 = 103$ Torr

| Additive | $H_2$ | $C_3H_6$ | $CH_4$ | $C_2H_4$ | $C_2H_6$ |
|---|---|---|---|---|---|
| 0 | 47.1 | 46.2 | 52.4 | 49.3 | 4.3 |
| 1.6 Torr $C_2H_4$ | 44.6 | 46.4 | 52.0 | 48.1 | 5.8 |
| 4.5 Torr $C_2H_4$ | 45.3 | 45.3 | 52.4 | 47.1 | 7.8 |

**Table II**

*Effect of added propylene on the selectivity of product formation in propane pyrolysis*
Analysis: at 5% conversion. $T = 833$ K, $[C_3H_8]_0 = 103$ Torr

| Additive | $H_2$ | $C_3H_6$ | $CH_4$ | $C_2H_4$ | $C_2H_6$ |
|---|---|---|---|---|---|
| 0 | 47.7 | 47.2 | 51.6 | 50.1 | 2.8 |
| 1.6 Torr $C_3H_6$ | 47.2 | 45.5 | 56.8 | 49.9 | 2.1 |
| 4.5 Torr $C_3H_6$ | 43.6 | 45.7 | 57.6 | 48.9 | 2.7 |

**Table III**

*Effect of added propylene on the selectivity of product formation in propane pyrolysis*
Analysis: at 10% conversion. $T = 1073$ K, $[C_3H_8]_0 = 100$ Torr

| $C_3H_6$ additive vol. % | $CH_4$ | $C_2H_6$ | $C_2H_4$ | $C_4H_8$ | $C_4H_6$ |
|---|---|---|---|---|---|
| 0 | 56.0 | 4.0 | 56.5 | 1.7 | 0.1 |
| 1.7 | 60.0 | 4.0 | 65.0 | 1.7 | 0.2 |
| 6.4 | 72.5 | 4.0 | 70.0 | 3.6 | 0.3 |

**Table IV**

*Effect of added propylene on the selectivity of product formation in propane pyrolysis*
Analysis: at 45% conversion. $T = 1123$ K, $[C_3H_8]_0 = 100$ Torr

| $C_3H_6$ additive, vol.% | $H_2$ | $CH_4$ | $C_2H_6$ | $C_2H_4$ | $C_4H_8$ | $C_4H_6$ |
|---|---|---|---|---|---|---|
| 0 | 57.0 | 57.5 | 4.2 | 65.0 | 2.5 | 0.8 |
| 1.7 | 55.0 | 60.0 | 4.5 | 67.5 | 2.5 | 0.9 |
| 6,4 | 52.0 | 73.0 | 5.7 | 73.0 | 3.2 | 1.4 |

**Table V**

*Distribution of the radioactivity (counts per minute per cm³) in the pyrolysis products of propane containing 1.7 vol. % of $^{14}C$-propylene inhibitor*
(Radioactivity of propylene in the initial mixture: $A^0_{C_3H_6} = 290$ counts per minute per cm³)

| $T$, K | $\alpha$ | $\xi$, % | $CH_4$ | $C_2H_6$ | $C_2H_4$ | $C_2H_2$ | $C_3H_8$ | $C_3H_6$ | $C_3H_4$ | $C_4H_8$ | $C_4H_6$ | coke | $\alpha\Sigma A_i$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1113 | 1.57 | 50.0 | 1.0 | 0.8 | 59.6 | 2.7 | 1.2 | 92.3 | 2.3 | 8.4 | 2.3 | 0.07 | 268 |
| 1070 | 1.22 | 36.2 | 2.0 | — | 33.7 | — | 0.2 | 151.3 | — | — | — | 0.14 | 228.3 |

$A_i$ — radioactivity of the $i$-th product in the mixture, equal to the specific radioactivity of the given component multiplied by its mole fraction;
$\alpha$ — change of the number of molecules during pyrolysis;
$\alpha\Sigma A_i$ — the sum of radioactivies in the products;
$\xi$ — conversion

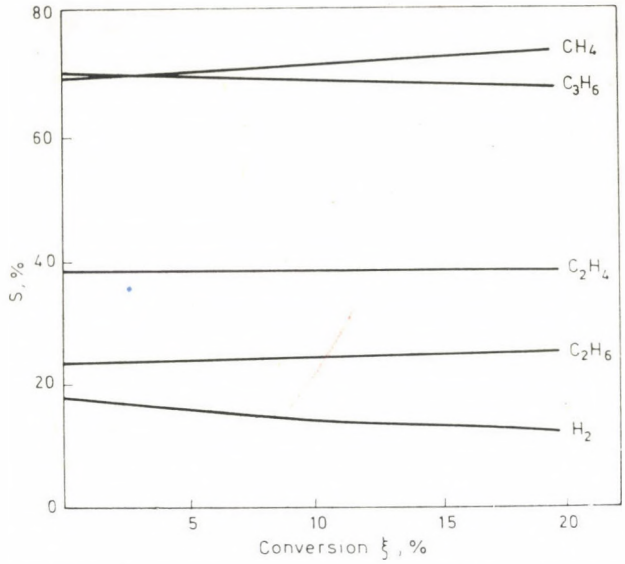



*Fig. 5.* Product composition in *n*-butane pyrolysis as a function of the conversion. (Curves fitted by the method of least squares.) $T = 823$ K, $[C_4H_{10}]_0 = 250$ Torr.

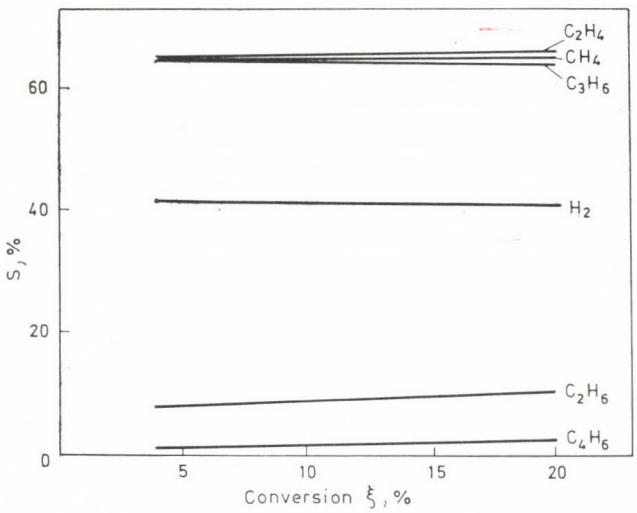



*Fig. 6.* Product composition in *n*-butane pyrolysis as a function of the conversion. (Curves fitted by the method of least squares.) $T = 973$ K, $[C_4H_{10}]_0 = 100$ Torr.

tions giving ethane; at higher temperatures, decomposition to ethylene and hydrogen is more favoured.

In the pyrolysis of *n*-butane, similarly to *n*-propane, the selectivities for hydrogen and propylene formation decrease, those of methane and ethane increase with increasing conversion.

The addition of ethylene to butane at 807 K, leads to enhanced ethane formation and lower hydrogen and propane selectivities (Table VI). Adding propylene to butane at 823 K (Table VII) results in a decrease of the selectivities of hydrogen and ethane formation; at the same time, an increase for ethylene is observed. (Data for 10 and 20% propylene addition have only been included in Table VII for take sake of completeness; the presence of propylene at such high concentrations represents already the third stage of pyrolysis (high conversions). In this range, several secondary processes also take place that are not dealt with in the present study.)

**Table VI**

*Effect of added ethylene on the selectivity of product formation in n-butane pyrolysis*
Analysis: at 20% conversion. $T = 807$ K, $[C_4H_{10}]_0 = 100$ Torr

| Additive | $H_2$ | $C_3H_6$ | $C_3H_8$ | $C_2H_4$ | $C_2H_6$ | $CH_4$ |
|---|---|---|---|---|---|---|
| 0 | 13.8 | 66.1 | 1.8 | 40.0 | 21.6 | 70.2 |
| 2 Torr $C_2H_4$ | 10.1 | 65.4 | 1.6 | 40.0 | 22.1 | 70.9 |
| 10 Torr $C_2H_4$ | 8.4 | 65.0 | 0.8 | 40.0 | 23.2 | 70.6 |

**Table VII**

*Effect of added propylene on the selectivity of product formation in n-butane pyrolysis*
Analysis: at 6.5% conversion. $T = 823$ K, $[C_4H_{10}]_0 = 100$ Torr

| Additive | $H_2$ | $C_3H_6$ | $C_3H_8$ | $C_2H_4$ | $C_2H_6$ | $CH_4$ |
|---|---|---|---|---|---|---|
| 0 | 12.5 | 50.7 | 0.7 | 37.8 | 18.1 | 80.2 |
| 2.5 Torr $C_3H_6$ | 12.0 | 50.9 | 0,7 | 38.3 | 17.7 | 80.4 |
| 5 Torr $C_3H_6$ | 11.7 | 51.0 | 1.6 | 38.7 | 16.3 | 80.7 |
| 10 Torr $C_3H_6$ | 11.1 | 50.6 | 1.8 | 39.1 | 16.8 | 80.7 |
| 20 Torr $C_3H_6$ | 10.1 | 47.2 | 2.3 | 41.9 | 16.4 | 82.1 |

The effect of added ethylene and propylene on product formation selectivity is much lower in the case of *n*-butane than that observed for propane. At higher temperatures, adding of ethylene and up to 6% of propylene exerts practically no effect on the product selectivities. On the other hand, the influence of higher additive concentrations of $C_3H_6$ (20–30%) is practically the same as that of smaller amounts at lower temperature.

## Inhibition phenomena in the decomposition of propane and *n*-butane

Self-inhibition reactions become important at medium conversions in the pyrolysis of paraffinic hydrocarbons. Several scientists have studied the mechanism of such processes at low temperatures [7–17, 20], but the results are somewhat contradictory and lack interpretation from a unified viewpoint. Fewer studies have been published dealing with the characteristics of paraffin decomposition at higher temperatures, and, consequently, much less is known with respect to the mechanism of inhibition reactions. In this context, in the present work special attention has been paid to the comparative study of inhibition reactions occurring in the low (about 800 K) and high (at and above 1000 K) temperature pyrolysis processes of propane and *n*-butane.

Plotting the concentrations of propane ($P_0 = 100$ Torr, $T = 833$ K) and *n*-butane ($P_0 = 100$ Torr, $T = 823$ K) as a function of the reaction time, it can be seen that the experimental points correspond to higher concentrations than the curves calculated from the initial decomposition rates of these hydrocarbons (Figs 7 and 8). This fact points to the inhibition effect of the decomposition products of propane and butane. The experience that adding low amounts

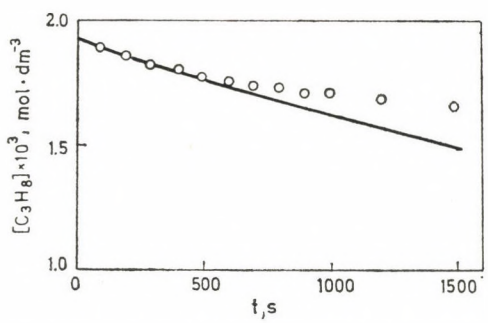



*Fig. 7.* Calculated and experimental propane concentrations. $T = 833$ K, $[C_3H_8]_0 = 100$ Torr.

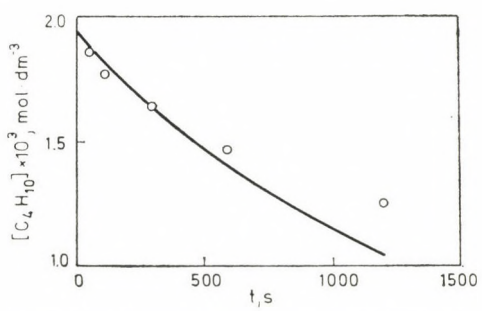



*Fig. 8.* Calculated and experimental concentrations of *n*-butane. $T = 823$ K, $[C_4H_{10}]_0 = 100$ Torr.

of ethylene and propylene to propane at 100 Torr and 833 K decreases the initial rate of decomposition, supports the above statement (Fig. 9). This figure also demonstrates that the inhibiting effect of ethylene is less than that of propylene.

The addition of ethylene to *n*-butane has practically no influence on the rate of *n*-butane decomposition at 807 K and 100 Torr starting pressure; at the same time, propylene additive shows a definite inhibiting effect (Fig. 10). At higher temperatures (1023–1123 K) and 100 Torr initial pressure, ethylene does not inhibit propane decomposition, whereas propylene does, to a considerable extent (Fig. 11).

It should be noted that when the experiments are carried out in a flow system at a constant pressure of 100 Torr, the addition of propylene decreases the concentration of the reacting propane. Therefore, the inhibiting effect of

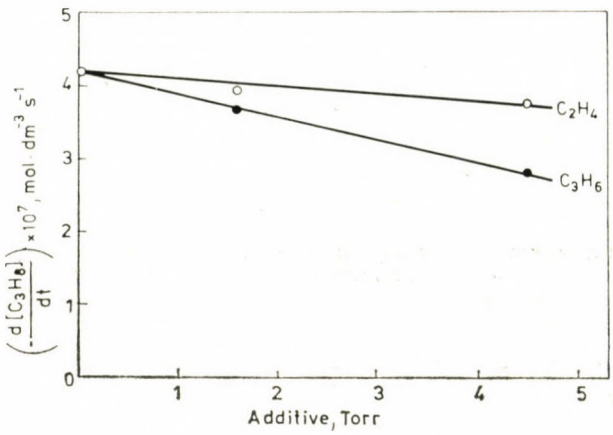



*Fig. 9.* The effect of added olefin on the initial rate of decomposition of propane. $T = 823$ K, $[C_3H_8]_0 = 100$ Torr.

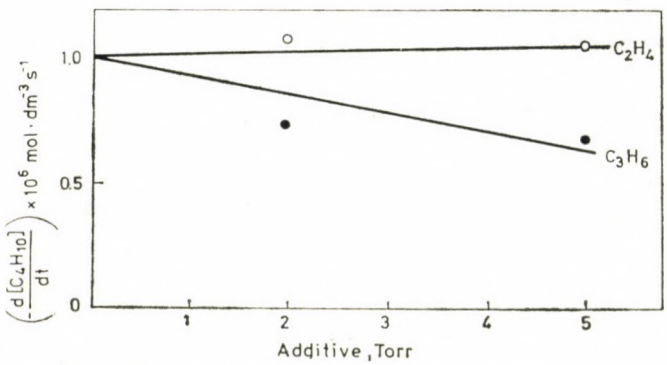



*Fig. 10.* The effect of added olefin on the initial rate of decomposition of *n*-butane. $T = 807$ K, $[C_4H_{10}]_0 = 100$ Torr.

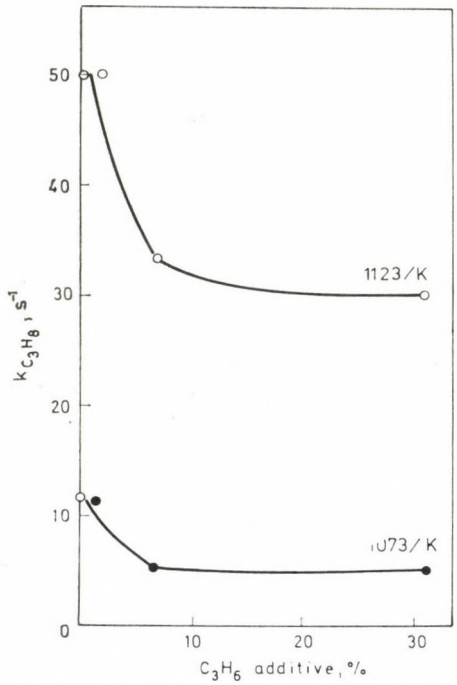



*Fig. 11.* Specific rate of propane decomposition as a function of the concentration of propylene in the initial mixture. P(reactor) = 100 Torr.

propylene on the decomposition of propane has been calculated by means of the following formula:

$$k = [(C_0/\alpha C) - 1]/t$$

where $C_0$ and $C$ denote the propane concentrations in the starting mixture and the products, respectively, $\alpha$ is the change in the number of molecules as a consequence of the pyrolysis, and $t$ is the contact time, which can be defined as the ratio of the reactor volume ($v$) and the volumetric outflow rate ($w$) i.e. $t = v/w$.

The decomposition of propane-propylene mixtures has also been studied by $^{14}C$ isotope labelling, between 1068 and 1113 K. It was shown that propylene inhibited the decomposition of propane; at the same time, propane initiated propylene decomposition (Fig. 12). The figure illustrates that the specific rate of overall propylene decomposition and that of the accumulation of radioactive ethylene both increase when the initial concentration of propane increases.

Thus the use of $^{14}C$-labelled propylene permits to study not only the inhibiting effect of propylene on the decomposition of propane but also the

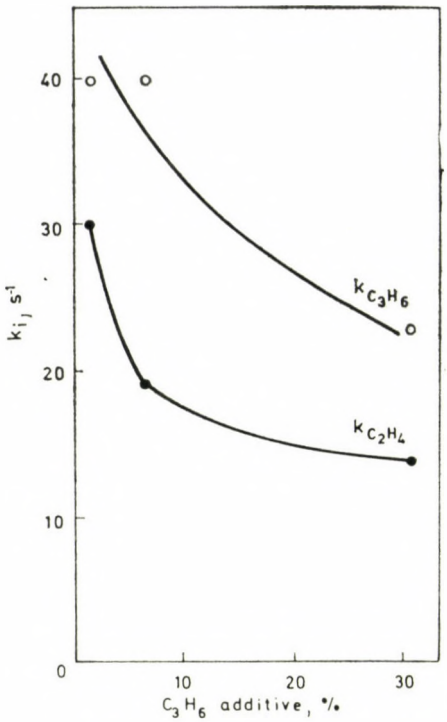



*Fig. 12.* Specific rate of overall decomposition of propylene ($k_{C_3H_6}$) and the specific rate of formation of radioactive ethylene ($k_{C_2H_4}$) as a function of the composition of the starting propane + $^{14}$C-propylene. $T$ = 1123 K, P(reactor) = 100 Torr.

study of the combined decomposition of propylene in the presence of propane. In other words, the effect of propane on propylene decomposition can also be estimated.

## Discussion

Having described the dependence of the product composition in the pyrolysis of propane and *n*-butane as a function of the conversion, as well as the inhibition processes caused by the accumulation of the olefinic products, it can be assumed that both processes can be attributed to the same set of reactions.

The decreasing hydrogen selectivity with increasing conversion or upon the addition of ethylene or propylene can be interpreted in the low temperature range of paraffin decomposition in terms of the following reactions:

$$H + C_2H_4 \rightarrow C_2H_5 \quad (1)$$

$$H + C_3H_6 \rightarrow C_3H_7 \quad (2)$$

The most probable reactions of $C_2H_5$ and $C_3H_7$ radicals are at low temperature those giving ethane and propane, respectively:

$$C_2H_5 + RH \rightarrow C_2H_6 + R \quad (1a)$$

$$C_3H_7 + RH \rightarrow C_3H_8 + R \quad (2a)$$

This results in the enhanced selectivities of these hydrocarbons.

The increase of $CH_4$ selectivity can be attributed to the following process:

$$H + C_3H_6 \rightarrow CH_3 + C_2H_4 \quad (3)$$

As shown by the experimental results at high temperatures, reactions like (1) and (2) are not important in the overall process, since ethylene addition to propane caused no selectivity changes and the adding of $^{14}C$-labelled propylene did not lead to the formation of detectable amounts of propane-[$^{14}C$], either (Table V). This indicates that the rate of decomposition of ethyl and propyl radicals at higher temperatures is much higher than the rate of their formation in Reactions (1) and (2).

On the contrary, Reaction (3) has an important role in the mechanism of the conversion of paraffins at higher temperatures. This is supported by the decrease of hydrogen selectivity together with an increase of the methane and ethylene selectivities with propylene addition to propane, and also by the fact that $CH_3—^{14}C=CH_2$ is decomposed to give mainly $^{14}C_2H_4$ ($\sim$60%).

Several recent publications have pointed out the role of Reaction (3) in the mechanism of the decomposition of hydrocarbons [13–15]. The mechanism of this reaction has been studied in detail with a mixture of ethane and [$^{14}C$]-propylene as a model reactant between 1073 and 1150 K, at 100 Torr starting pressure [21]. In ethane pyrolysis, the only practical possibility of chain formation involves the participation of hydrogen atoms, since methyl radicals are formed in chain initiation only and their concentration is negligibly small. Under such conditions, decrease of the selectivity of hydrogen formation and the increase of that of methane formation have been observed. About 90–95% of [$^{14}C$]-labelled propylene decomposed and the products were $^{14}C_2H_4$ or $^{14}CH_4$ (depending on the position of the label in propylene). This can be explained by the much higher rate of Reaction (3) as compared with that of Reaction (4):

$$H + C_3H_6 \rightarrow H_2 + C_3H_5 \quad (4)$$

It should be noted, however, that the exclusive formation of $C_2H_4$ — without any production of allyl radicals — cannot be expected.

Reaction (3) is, by all means, a complex process which can take place according to one of the following pathways:

$$H + C_3H_6 \longrightarrow CH_3CH_2\dot{C}H_2 \longrightarrow CH_3 + C_2H_4 \quad (3a)$$

$$H + C_3H_6 \longrightarrow CH_3\dot{C}HCH_3 \longrightarrow CH_3 + C_2H_4 \quad (3b)$$

$$H + C_3H_6 \longrightarrow CH_3\dot{C}HCH_3 \xrightarrow{+C_3H_6} CH_3CH(CH_3)CH_2\dot{C}HCH_3 \xrightarrow{1,4} \longrightarrow \dot{C}H_2CH(CH_3)CH_2CH_2CH_3 \xrightarrow{-C_3H_6} CH_3CH_2\dot{C}H_2 \longrightarrow CH_3 + C_2H_4 \quad (3c)$$

Addition of a hydrogen atom to propylene according to Markownikoff's rule gives isopropyl radical (3b), whereas an anti-Markownikoff addition leads to *n*-propyl radical (3a). The ratio of the rate constants of Reactions (3b) and (3a) is equal to 2.7 and 1.9 at 850 K and 1300 K, respectively [16].

The *n*-propyl radicals produced decompose to give methyl radical and ethylene. In order to obtain these products from isopropyl radical, the latter must undergo isomerization. Accordingly, the energy of activation of $CH_3$ and $C_2H_4$ formation from isopropyl radical is higher than that of $CH_3$ plus $C_2H_4$ formation from the *n*-propyl radical. At low temperatures, the rate of Reaction (3b) is much lower than that of (3a) but at higher temperatures (3b) should also be considered.

Mechanism (3c) involves the addition of a hydrogen atom followed by addition of the isopropyl radical, 1,4-isomerization and $\beta$-elimination. Its probability decreases rapidly at higher temperatures and lower propylene concentrations.

Consequently, Reaction (3) is one of the most important steps of the thermal decomposition of propane and butane, and the mechanism followed is mainly reaction (3a).

Elementary processes with the participation of olefins and leading to changed selectivities of product formation have a great importance and result at higher conversions in self-inhibition of paraffin decomposition. It must be noted that only those processes can be regarded as self-inhibiting ones which produce radicals participating in chain termination reactions with a higher probability than the original radicals.

The relative role of the various radicals in the inhibition processes can be estimated using their steady state concentrations in the reaction period as well as the rate constants of their reactions with olefins.

Tables VIII and IX show the concentrations of $CH_3$ and $C_2H_5$ radicals relative to that of H atom in propane pyrolysis at 833 K and in butane pyrolysis at 823 K, respectively, calculated on the basis of the initial rates of formation of $H_2$, $CH_4$ and $C_2H_6$ and the rate constants reported in the literature. It can

**Table VIII**

*Relative radical concentrations in the pyrolysis of propane at various conversions* ($\xi$)
$T = 833$ K, $[C_3H_8]_0 = 103$ Torr

| R | $\xi$/% | | |
|---|---|---|---|
| | 0 | 5 | 10 |
| H | 1 | 1 | 1 |
| $CH_3$ | 610 | 690 | 730 |
| $C_2H_5$ | 620 | 880 | 1820 |

**Table IX**

*Relative radical concentrations in the pyrolysis of n-butane at various conversions* ($\xi$)
$T = 823$ K, $[C_4H_{10}]_0 = 100$ Torr

| R | $\xi$/% | | |
|---|---|---|---|
| | 0 | 5 | 10 |
| H | 1 | 1 | 1 |
| $CH_3$ | 2460 | 2750 | 3220 |
| $C_2H_5$ | 5620 | 8220 | 11730 |

be seen that the concentrations of alkyl radicals are higher than those of hydrogen atoms: for propane, the difference is 2 to 3, and for butane, 3 to 4 orders of magnitude. Since the rate constants of reactions between H atoms and olefins are higher by 3 to 3.5 orders of magnitude than those of the reactions between alkyl radicals and olefins, it can be concluded that in the low-temperature pyrolysis of propane the rates of the reactions between hydrogen and olefins are higher than the rates between alkyl radicals and olefins; for butane pyrolysis, the situation is reversed, the processes occurring between alkyl radicals and olefins being more important.

The rate of decomposition of the ethyl radical increases, and its relative concentration decreases, with increasing temperature. The ratio of the relative concentrations of hydrogen atoms and methyl radicals can be estimated as a function of the temperature on the basis of the rates of formation of hydrogen and methane, respectively, because these products are stable at the experimental temperatures. The ratio of methane and hydrogen formation for propane decomposition is near to unity both at lower and higher temperatures (Tables II and IV). For butane pyrolysis, however, the ratio of hydrogen to methane formation is 1 : 6 at lower temperatures (823 K) (cf. Table VII) whereas this value is 1 : 1.5 at 1023 K (Fig. 6). Thus, the relative importance of hydrogen atoms in butane pyrolysis increases with increasing temperatures.

Self-inhibition in the decomposition of propane and butane can be interpreted by the following reactions:

$$H + C_2H_4 \longrightarrow C_2H_5 \xrightarrow{RH} C_2H_6 + R \quad (1)$$

$$H + C_3H_6 \longrightarrow n\text{- or } i\text{-}C_3H_7 \xrightarrow{RH} C_3H_8 + R \quad (2)$$

$$H + C_3H_6 \longrightarrow CH_3 + C_2H_4 \quad (3)$$

$$H + C_3H_6 \longrightarrow H_2 + C_3H_5 \quad (4)$$

$$CH_3 + C_3H_6 \longrightarrow CH_4 + C_3H_5 \quad (5)$$

$$C_2H_5 + C_3H_6 \longrightarrow C_2H_6 + C_3H_5 \quad (6)$$

The above facts make it evident that these reactions play a special role in the self-inhibition of propane and butane decomposition at lower and higher temperatures.

Let us discuss first the mechanism of inhibition in the decomposition of propane. The product distribution of propane decomposed in the presence of added ethylene indicates that Reaction (1) is of importance at lower temperatures only.

The first step in Reactions (2) and (3) is the formation of vibrationally excited $C_3H_7^*$ radical, with an excess energy as high as 40 kcal/mole. The $C_3H_7^*$ radical may lose its excess energy by collisions with other molecules or may decompose:

$$\begin{array}{ccccc} H + C_3H_6 & \longrightarrow & n\text{-}C_3H_7^* & \longrightarrow & CH_3 + C_2H_4 \\ & & \downarrow M & & \\ CH_3 + C_2H_4 & \longleftarrow & n\text{-}C_3H_7 & \xrightarrow{RH} & C_3H_8 \end{array} \quad (7)$$

$$\begin{array}{ccccc} H + C_3H_6 & \rightleftharpoons & i\text{-}C_3H_7^* & \longrightarrow & CH_3 + C_2H_4 \\ & & \downarrow M & & \\ H + C_3H_6 & \longleftarrow & i\text{-}C_3H_7 & \xrightarrow{RH} & C_3H_8 \end{array} \quad (8)$$

The main direction of decomposition of the $i\text{-}C_3H_7^*$ and $i\text{-}C_3H_7$ species gives H and $C_3H_6$, whereas the $n\text{-}C_3H_7^*$ and $n\text{-}C_3H_7$ species transform mainly into $CH_3$ and $C_2H_4$.

The rate of addition of hydrogen atoms to propylene is nearly independent of the temperature, having an activation energy of about 2 kcal/mole.

The ratio of the rates of decomposition and stabilization of the $C_3H_7^*$ radical depends on the pressure; the importance of stabilization increases

with increasing pressure. At lower temperatures, the formation of both $n$-$C_3H_7^*$ and partly that of $i$-$C_3H_7^*$ radicals leads to the inhibition of the decomposition of propane, since a considerable fraction of the $n$-$C_3H_7$ and $i$-$C_3H_7$ radicals react in hydrogen atom abstraction reactions, giving $C_3H_8$. At higher temperatures the rate of formation of $C_3H_8$ from $n$-$C_3H_7$ and $i$-$C_3H_7$ radical is small as compared with the rate of decomposition of these species. If $i$-$C_3H_7^*$ and $i$-$C_3H_7$ radicals give nothing else but H and $C_3H_6$ at higher temperatures, then the formation of $i$-$C_3H_7^*$ causes no inhibition. However, these radicals give also some $CH_3$ and $C_2H_4$ at higher temperatures.

It has been mentioned that the relative amount of $n$-$C_3H_7$ increases, that of $i$-$C_3H_7$ decreases at higher temperatures. Thus, considering Reactions (7) and (8) together, the inhibiting effect of propylene on the decomposition of propane shows no dramatic changes with the temperature.

Discussing the inhibiting effects of propylene on ethane decomposition we showed [21] that the rate of formation of allyl radical (in Reaction (4)) is considerably lower than that of hydrogen atom addition to propylene. Although the concentration of alkyl radicals is considerably higher in the case of propane, the above evaluation has shown that reactions with the participation of H atom have an important role in the inhibition processes of low temperature propane pyrolysis.

The results of detailed experiments carried out at higher temperatures (1068–1113 K) with $^{14}$C-propylene — which aimed at the elucidation of the mechanism of inhibited decomposition of propane — have shown that about 60% of $^{14}$C-propylene reacts in Reaction (3) to give $^{14}C_2H_4$, and the other 40% reacts according to Reaction (5).

The most important secondary processes of the low temperature decomposition of $n$-butane are reactions between olefins and alkyl radicals. Accordingly, Reactions (5) and (6) leading to allyl radicals are predominant in the mechanism of inhibition, whereas Reactions (1), (2) and (3) with the participation of hydrogen atoms are negligible. This is supported also by the lack of inhibition upon adding ethylene to $n$-butane.

At higher temperatures (at and above 973 K) the role of hydrogen atoms increases and, similarly to propane decomposition, Reactions (3) and (4) should also be considered.

The data obtained in the low and high temperature pyrolysis of propane and $n$-butane under the influence of olefins, as well as other results obtained with other hydrocarbons such as neopentane [12] and isobutane [3, 18] draw our attention to the fact that it is not possible to develop a generally valid mechanism for the inhibiting effect of olefins in pyrolysis. The mechanism of inhibition depends on the temperature, on the nature of the inhibitor used, on the distribution of radicals formed and, mainly, on the role of hydrogen atoms in the overall process.

## REFERENCES

[1] ZALOTAI, L., BÉRCES, T., MÁRTA, F.: Magy. Kém. Folyóirat **78,** 335 (1972); **78,** 341 (1972); **78,** 549 (1972); **78,** 556 (1972); Kémiai Közlemények **41,** 237 (1974)
[2] HALÁSZ, D., MÁRTA, F.: Magy. Kém. Folyóirat **81,** 541 (1975); **81,** 547 (1975); **81,** 553 (1975)
[3] SERES, L., MÁRTA, F.: Kémiai Közlemények **41,** 267 (1974)
[4] SZIROVICZA, L., MÁRTA, F.: Reaction Kinetics and Catalysis Letters **1,** 417 (1974); **3,** 9 (1975); **3,** 71 (1975); **3,** 155 (1975); Int. J. Chem. Kinet. **8,** 897 (1976)
[5] LIN, M. C., BACK, M. H.: Can. J. Chem. **44,** 505 (1966); **44,** 2357 (1966)
[6] LEATHARD, D. A., PURNELL, J. H.: Proc. Roy. Soc. (A) **305,** 517 (1968)
[7] PURNELL, J. H., QUINN, C. P.: Proc. Roy. Soc. (A) **270,** 267 (1962)
[8] MARTIN, R., DZIERZYNSKI, M., NICLAUSE, M.: J. Chem. Phys. **61,** 286 (1964)
[9] SAGERT, N. H., LAIDLER, K. J.: Can. J. Chem. **41,** 838 (1963)
[10] KONAR, R. S., MARSHALL, R. M., PURNELL, J. H.: Trans. Faraday Soc. **64,** 405 (1968); **64,** 1319 (1968)
[11] FUSY, J., MARTIN, R., DZIERZYNSKI, M., NICLAUSE, M.: Bull. Soc. Chim. France **12,** 3783 (1960)
[12] BARONNET, F., DZIERZYNSKI, M., MARTIN, R., NICLAUSE, M.: Compt. rend. Acad. Sci., Paris **267C,** 937 (1968)
BARONNET, F., DZIERZYNSKI, M., COME, G. M., MARTIN, R., NICLAUSE, M.: Proc. of the Symposium on Gas Kinetics, Szeged, p. 73 (1969)
[13] ILLÉS, V.: Acta Chim. Acad. Sci. Hung. **59,** 229 (1969)
[14] PACEY, P. D., PURNELL, J. H.: Ind. Eng. Chem. Fundamentals **11,** 233 (1972)
[15] BACH, G., NOWAK, S., KALINENKO, R. A., LAVROVSKII, K. P., SHEVELKOVA, L. V.: Zeitschrift für Chemie **15,** 165 (1975)
[16] KERR, J. A., PARSONAGE, M. J.: "Evaluated Kinetic Data on Gas Phase Addition Reactions", Butterworths, London, 1972
[17] BLAKEMORE, J. E., BARKER, J. E., CORCORAN, W. H.: Ind. Eng. Chem. Fundamentals **12,** 147 (1973)
[18] KONAR, R. S., MARSHALL, R. M., PURNELL, J. H.: Int. J. Chem. Kinet. **5,** 1007 (1973)
[19] HELLER, C. A., GORDON, A. S.: J. Phys. Chem. **62,** 709 (1958); JACKSON, W. M., MCNESBY, J. R.: J. Chem. Phys. **36,** 2272 (1962); BENSON, S. W., O'NEAL, H. E.: "Kinetic Data on Gas Phase Unimolecular Reactions", NSRDS-NBS **21,** Washington, 1970
[20] STEPUKHOVICH, A. D., ULITSKII, V. A.: "Kinetika i termodinamika radikal'nykh reaktsii krekinga", p. 215, Khimiya, Moscow, 1975.
[21] LAVROVSKII, K. P., KALINENKO, R. A., SHEVELKOVA, L. V.: 8th World Petroleum Congress, Moscow 1971, Proceeding, Appl. Sci. Publ. Ltd, London, Vol. 4, p. 357, 1971—1972.

N. S. NAMETKIN
R. A. KALINENKO
L. V. SHEVEL'KOVA
117071 Moscow, Leninskii Prospect 29.

L. ZALOTAI
D. HALÁSZ
T. BÉRCES
F. MÁRTA
H-6701 Szeged, P. O. Box 105.

*Acta Chimica Academiae Scientiarum Hungaricae, Tomus 98 (4), pp. 395—402 (1978)*

# STATIC DIELETRIC PROPERTIES OF POLAR LIQUIDS

J. LISZI

*(Department of Physical Chemistry, University of Chemical Engineering, Veszprém)*

Received, September 29, 1977

An equation is derived for the static dielectric properties of polar liquids, based on the continuum approach to the environment of the molecules. The model applied is basically an extension of ONSAGER's model and involves concentric dielectric continua. The equation based on this model takes into account the fact that the interaction of the molecules with their nearest neighbours is different from their interaction with the bulk of the liquid.

## Introduction

In the ONSAGER theory [1] of polar liquids, the molecule is treated as a point dipole at the center of a spherical cavity immersed in a homogeneous dielectric continuum. The dipole polarizes the environment by its inhomogeneous electric field and a reaction field arises which acts upon the molecule. The intermolecular forces are taken into account by the interaction of the dipole with the reaction field.

However, the properties of the liquids are mostly determined by the interaction between the nearest neighbouring molecules [2]. As far as dielectric properties are considered, the above statement means that the polarization effect of a central molecule on its closest neighbours is different from that exerted on molecules located farther. In the case of ionic solutions, the inhomogeneity in the vicinity of the ions has been investigated extensively [3—9]. However, only a few attempts were made to take into account this inhomogeneity for polar liquids [10, 11, 12].

Taking into consideration the special role of the nearest neighbours of the molecules, the homogeneous dielectric medium postulated in the ONSAGER theory must be replaced by the assumption of a heterogeneous medium. In the simplest model of this kind, the polar molecule is treated as a point dipole at the center of a spherical cavity of radius $a$ and of static permittivity $\varepsilon_i = 1$. The cavity is surrounded by a spherical layer of thickness $(b-a)$ and static permittivity $\varepsilon_l$, immersed in the bulk of the liquid of static permittivity $\varepsilon_0$. Both the layer and the bulk are considered as continuous media. The difference between $\varepsilon_0$ and $\varepsilon_l$ is caused by the inhomogeneous polarization induced by the dipole in its surrounding. On the basis of this 'heterogeneous' model, an equation will be derived for the static dielectric properties of polar liquids.

## Background

The theoretical treatment is based on the method given by BÖTTCHER[13]. The fundamental equation for the dielectric properties of pure polar liquids is

$$\frac{\varepsilon_0 - 1}{4\pi}\mathbf{E} = N\left[\alpha\mathbf{E}_i + \frac{\mu^2}{3kT}\mathbf{E}_d\right], \tag{1}$$

where $\varepsilon_0$ is the static relative permittivity of the bulk of the liquid, $\mathbf{E}$ is the Maxwell field, $N$ is the number of molecules per cm$^3$, $\alpha$ is the polarizability given by the equation

$$\frac{n^2 - 1}{n^2 + 2} = \frac{4\pi}{3}N\alpha, \tag{2}$$

where $n$ is the internal refractive index, $\mu$ is the permanent dipole moment of the molecule, $k$ is Boltzmann's constant, $T$ is the absolute temperature, $\mathbf{E}_i$ is the internal field and $\mathbf{E}_d$ is the directing field.

The directing field for a polarizable point dipole is given by the equation

$$\mathbf{E}_d = \frac{1}{1 - f\alpha}\mathbf{E}_c \tag{3}$$

where $f$ is the reaction field factor, $\mathbf{E}_c$ is the cavity field. The internal field as a function of the cavity field is given by

$$\mathbf{E}_i = \left(1 + \frac{f}{1 - f\alpha}\frac{\mu^2}{3kT}\right)\frac{1}{1 - f\alpha}\mathbf{E}_c\,. \tag{4}$$

In order to obtain the directing field and the internal field as a function of the Maxwell field, the relation between the cavity field and the Maxwell field has to be determined. Upon inserting the two equations relating to the directing and internal fields into the fundamental equation, the static dielectric properties of pure polar liquids can be calculated.

Let us first consider the reaction field factor, which is different from that in ONSAGER's theory. BEVERIDGE and SCHNUELLE [14] investigated the free energy of charge distribution in concentric dielectric continua. Using their result for the model described above, the free energy of the dipole is obtained in the following form

$$F = \frac{1}{2}\left\{\frac{2(1 - \varepsilon_a')}{2\varepsilon_a' + 1}\frac{\mu^2}{a^3} + \frac{2(1 - \varepsilon_b)}{2\varepsilon_b + 1}\left[1 - \frac{1 - \varepsilon_a'}{2\varepsilon_a' + 1}\right]\frac{\mu^2}{b^3}\right\} \tag{5}$$

where

$$\varepsilon_a' = \varepsilon_l \left[ 1 + \frac{2(1-\varepsilon_l)(1-\varepsilon_b)}{2\varepsilon_b + 1} \frac{a^3}{b^3} \right]^{-1} \tag{6}$$

and

$$\varepsilon_b = \varepsilon_0 / \varepsilon_l \tag{7}$$

On the other hand, the free energy of a dipole in the reaction field **R** is [15]

$$F = -\frac{1}{2} \mu \mathbf{R} = -\frac{1}{2} f \mu^2 \tag{8}$$

The reaction field factor is calculated from Eqs (5) and (8)

$$f = \frac{2(\varepsilon_a' - 1)}{(2\varepsilon_a' + 1)\, a^3} + \frac{2(\varepsilon_b - 1)}{(2\varepsilon_b + 1)\, b^3} \left[ 1 - \frac{1 - \varepsilon_a'}{2\varepsilon_a' + 1} \right] \tag{9}$$

The first term in this equation is due to the polarization charge in the local layer, while the second term arises from long-range polarization of the outer region. If $\varepsilon_l = \varepsilon_0$ and $a = b$, then $\varepsilon_b = 1$ and $\varepsilon_a' = \varepsilon_0$, and Eq. (9) simplifies yielding ONSAGER's reaction field factor ($f_{\mathrm{ONS}}$):

$$f_{\mathrm{ONS}} = \frac{2(\varepsilon_0 - 1)}{(2\varepsilon_0 + 1)\, a^3} \tag{10}$$

## Cavity field

Outside the spherical layer the potential satisfies the Laplace equation

$$\Delta \Phi = 0 \tag{11}$$

since there are no charges in the bulk of the liquid except the charges at a great distance required to maintain the external field. The Laplace equation is also valid in the spherical layer and inside the sphere. However, this equation cannot be applied to the surface of the spherical layer because of the apparent surface charge. Therefore, three different functions describe the electric potential $\Phi$: the first is valid outside the spherical layer ($\Phi_0$), the second in the spherical layer ($\Phi_l$) and the third inside the central sphere ($\Phi_i$).

It is useful to take the center of the sphere as the origin of the coordinate system and to choose the $z$-axis in the direction of the uniform external field for the solution of the Laplace equation. Using spherical polar coordinates

$(r, \theta, \varphi)$ and considering the symmetry about the $z$-axis, the general solution of the Laplace equation can be written in the following forms:

outside the spherical layer

$$\Phi_0 = \sum_{n=0}^{\infty} \left( A_n r^n + \frac{B_n}{r^{n+1}} \right) P_n(\cos \theta) \tag{12}$$

in the spherical layer

$$\Phi_l = \sum_{n=0}^{\infty} \left( C_n r^n + \frac{D_n}{r^{n+1}} \right) P_n(\cos \theta) \tag{13}$$

inside the central sphere

$$\Phi_i = \sum_{n=0}^{\infty} \left( F_n r^n + \frac{G_n}{r^{n+1}} \right) P_n(\cos \theta) \tag{14}$$

In these equations $P_n(\cos \theta)$ are Legendre polynomials, coefficients $A_n$, $B_n$, $C_n$, $D_n$, $F_n$ and $G_n$ being determined from the boundary conditions of the problem.

The boundary conditions are the following

$$1. \quad (\text{grad } \Phi_0)_{r \to \infty} = -\mathbf{E}$$

since far enough from the origin, the field approaches **E**.

$$2. \quad (\Phi_0)_{r=b} = (\Phi_l)_{r=b}$$

$$3. \quad (\Phi_l)_{r=a} = (\Phi_i)_{r=a}$$

since $\Phi$ is continuous across the boundaries. The normal component of the dielectric displacement, **D** must be continuous across the surfaces, therefore

$$4. \quad \varepsilon_0 \left( \frac{\partial \Phi_0}{\partial r} \right)_{r=b} = \varepsilon_l \left( \frac{\partial \Phi_l}{\partial r} \right)_{r=b}$$

$$5. \quad \varepsilon_i \left( \frac{\partial \Phi_i}{\partial r} \right)_{r=a} = \varepsilon_l \left( \frac{\partial \Phi_l}{\partial r} \right)_{r=a} .$$

Finally

6. $\Phi_i$ must not have a singularity at the center of the sphere ($r = 0$).

It follows from the first boundary condition and from the fact that the Legendre functions are linearly independent, that all coefficients $A_n$ are

zero, except $A_1 = -E$ and from the last boundary condition every $G_n = 0$. Thus

$$\Phi_0 = \sum_{n=0}^{\infty} \frac{B_n}{r^{n+1}} P_n(\cos\theta) - Er\cos\theta\,, \tag{15}$$

$$\Phi_l = \sum_{n=0}^{\infty} \left(C_n r^n + \frac{D_n}{r^{n+1}}\right) P_n(\cos\theta)\,, \tag{16}$$

$$\Phi_i = \sum_{n=0}^{\infty} F_n r^n P_n(\cos\theta)\,. \tag{17}$$

On account of boundary conditions 2–5, one obtains for any value of $n$ except $n = 1$:

$$\frac{B_n}{b^{n+1}} = C_n b^n + \frac{D_n}{b^{n+1}}, \tag{18}$$

$$C_n a^n + \frac{D_n}{a^{n+1}} = F_n a^n, \tag{19}$$

$$-\varepsilon_0(n+1)\frac{B_n}{b^{n+2}} = \varepsilon_l\left(nC_n b^{n-1} - (n+1)\frac{D_n}{b^{n+2}}\right), \tag{20}$$

$$\varepsilon_i n F_n a^{n-1} = \varepsilon_l\left(nC_n a^{n-1} - (n+1)\frac{D_n}{a^{n+1}}\right), \tag{21}$$

From these last equations: $B_n = C_n = D_n = F_n = 0$, $(n \neq 1)$.

For $n = 1$:

$$\frac{B_1}{b^2} - Eb = C_1 b + \frac{D_1}{b^2}, \tag{22}$$

$$C_1 a + \frac{D_1}{a^2} = F_1 a, \tag{23}$$

$$\varepsilon_0\left(\frac{2B_1}{b^3} + E\right) = \varepsilon_l\left(\frac{2D_1}{b^3} - C_1\right), \tag{24}$$

$$\varepsilon_l F_1 = -\varepsilon_l\left(\frac{2D_1}{a^3} - C_1\right). \tag{25}$$

Hence

$$F_1\left\{\frac{2a^3(\varepsilon_0 - \varepsilon_l)(1 - \varepsilon_l) + (2\varepsilon_0 + \varepsilon_l)b^3}{3b^3\varepsilon_l(2\varepsilon_0 + \varepsilon_l)} + \frac{2}{3}\right\} = -\frac{3\varepsilon_0\varepsilon_l}{\varepsilon_l(2\varepsilon_0 + \varepsilon_l)}E\,. \tag{26}$$

Combining Eqs (6), (7) and (26):

$$F_1 = -\frac{3\varepsilon_a'}{2\varepsilon_a' + 1}\frac{3\varepsilon_b}{2\varepsilon_b + 1}E\,, \tag{27}$$

Thus the potential inside the sphere is

$$\Phi_i = -\frac{3\varepsilon'_a}{2\varepsilon'_a + 1}\frac{3\varepsilon_b}{2\varepsilon_b + 1} zE \tag{28}$$

and the cavity field strength is given by

$$\mathbf{E}_c = -\frac{\partial \Phi_i}{\partial z} = \frac{2\varepsilon'_a}{2\varepsilon'_a + 1}\frac{3\varepsilon_b}{2\varepsilon_b + 1}\mathbf{E}\,. \tag{29}$$

Thus the cavity field is obtained as a function of the Maxwell field for the model described in the introduction. If $\varepsilon_0 = \varepsilon_l$ and $a = b$, then $\varepsilon'_a = \varepsilon_0$ and $\varepsilon_b = 1$, and Eq. (29) simplifies yielding the ONSAGER cavity field ($\mathbf{E}_{c\,\mathrm{ONS}}$):

$$\mathbf{E}_{c\,\mathrm{ONS}} = \frac{3\varepsilon_0}{2\varepsilon_0 + 1}\mathbf{E}. \tag{30}$$

## The complete equation

The directing field is calculated from Eqs (3) and (29) as a function of the Maxwell field:

$$\mathbf{E}_d = \frac{1}{1 - f\alpha}\frac{3\varepsilon'_a}{2\varepsilon'_a + 1}\frac{3\varepsilon_b}{2\varepsilon_b + 1}\mathbf{E} \tag{31}$$

Similarly from Eqs (4) and (29):

$$\mathbf{E}_i = \left(1 + \frac{f}{1 - f\alpha}\frac{\mu^2}{3kT}\right)\frac{1}{1 - f\alpha}\frac{3\varepsilon'_a}{2\varepsilon'_a + 1}\frac{3\varepsilon_b}{2\varepsilon_b + 1}\mathbf{E} \tag{32}$$

Substitution of Eqs (31) and (32) into fundamental equation (1) leads to

$$\frac{\varepsilon_0 - 1}{4\pi N} = \frac{1}{1 - f\alpha}\frac{3\varepsilon'_a}{2\varepsilon'_a + 1}\frac{3\varepsilon_b}{2\varepsilon_b + 1}\left[\alpha + \frac{1}{1 - f\alpha}\frac{\mu^2}{3kT}\right] \tag{33}$$

This equation can be considered as a generalized form of the ONSAGER equation, taking into account that the polarization effect of a polar molecule on its closest neighbours differs from that exerted on molecules located farther. If $\varepsilon_l = \varepsilon_0$ and $a = b$, then $f = f_{\mathrm{ONS}}$, $\varepsilon_b = 1$ and $\varepsilon'_a = \varepsilon_0$, and Eq. (33) simplifies into the ONSAGER equation:

$$\frac{\varepsilon_0 - 1}{4\pi N} = \frac{1}{1 - f\alpha}\frac{3\varepsilon_0}{2\varepsilon_0 + 1}\left[\alpha + \frac{1}{1 - f_{\mathrm{ONS}}\alpha}\frac{\mu^2}{3kT}\right] \tag{34}$$

The generalization of Eq. (33) for multicomponent systems can be performed by the method given by BÖTTCHER [13].

## Examples of application

Equation (33) contains two new parameters, these are the relative permittivity ($\varepsilon_l$) and the radius ($b$) of the local layer. Both of them affect the applicability of the equation.

The value of Kirkwood's $g$ factor [15] may help in the selection of $\varepsilon_l$. Namely, a discussion of Eq. (33) shows that if $g < 1$, then $\varepsilon_l < \varepsilon_0$, if $g > 1$, then $\varepsilon_l > \varepsilon_0$ and if $g = 1$, then $\varepsilon_l = \varepsilon_0$.

Concerning the value of $b$, as a first approximation one can suppose that the local layer consists of the nearest neighbours of the central molecule. Hence the thickness of the layer is equal to the diameter of the molecules and $b = 3a$.

The equation can be checked in the following way: one calculates permanent dipole moment $\mu$ from Eq. (33) using liquid phase data and this $\mu$ is compared with the experimental dipole moment $\mu_g$ determined in the gas phase. The equation is valid to such an extent as the $\mu$ value approximates $\mu_g$.

As a first step calculations have been made for 22 polar liquids with $g < 1$. In the calculations $b = 3a$ and $\varepsilon_l = n^2$ values are used where $n$ is the internal refractivity. Some of the results are given in Table I as examples. In the last column of the Table the dipole moments calculated by Eq. (34) ($\mu_{ONS}$) are given for the sake of comparison. The data needed for the calculations are from Böttcher's book [13].

**Table I**

*Permanent dipole moments*

| Liquid | $\mu_g$(D) | $\mu$(D) | $\mu_{ONS}$ (D) |
|---|---|---|---|
| Chloromethane | 1.84 | 1.87 | 1.74 |
| Bromomethane | 1.81 | 1.66 | 1.55 |
| Cyanomethane | 3.92 | 3.65 | 3.39 |
| Ethanethiol | 1.58 | 1.58 | 1.50 |
| Bromoethane | 2.03 | 1.97 | 1.84 |
| Cyanoethane | 4.02 | 3.63 | 3.36 |
| 1-Chlorobutane | 2.05 | 2.04 | 1.92 |
| 1-Bromobutane | 2.08 | 1.93 | 1.83 |
| Aniline | 1.53 | 1.53 | 1.44 |
| Cyanobenzene | 4.18 | 3.82 | 3.48 |

The square of the standard deviation $\left[\sigma^2 = \frac{1}{22}\sum(\mu - \mu_g)^2\right]$ for the 22 compounds investigated according to Eq. (33): $\sigma^2 = 0.062$. According to the ONSAGER equation [Eq. (34)]: $\sigma^2_{ONS} = 0.128$.

These preliminary results indicate that in the description of the properties of polar liquids, Eq. (33) can be considered as a better approximation than the original ONSAGER equation. However, the determination of the validity of the equation needs further investigation.

## REFERENCES

[1] ONSAGER, L.: J. Am. Chem. Soc., **58,** 1486 (1936)
[2] GUGGENHEIM, E. A.: Mixtures, Calderon Press, Oxford 1952
[3] NOYES, R. M.: J. Am. Chem. Soc., **84,** 513 (1962)
[4] FRANK, H. S., WEN, W. Y.: Discuss. Faraday Soc., **24,** 133 (1957)
[5] GLUEKAUF, E.: Trans. Faraday Soc., **60,** 572 (1964)
[6] BOOTH, F.: J. Chem. Phys. **19,** 391 (1951)
[7] FRIEDMAN, H. L., KRISHNAN, C. V. in "Water — A comprehensive Treatise", F. Franks, Ed., Plenum Press, New York 1973
[8] BEVERIDGE, D. L., SCHNUELLE, G. W.: J. Phys. Chem., **78,** 2064 (1974)
[9] SCHNUELLE, G. W., BEVERIDGE, D. L.: J. Phys. Chem., **79,** 2566 (1975)
[10] OMINI, M.: J. Chem. Phys., **59,** 6478 (1973)
[11] GROSSE, C., GREFFE, J. L.: J. Chim. Phys. **72,** 1297 (1975)
[12] LISZI, J., MÉSZÁROS, L.: Magyar Kém. Foly. **82,** 546 (1976)
[13] BÖTTCHER C. J. F.: Theory of Electric Polarization Revised. by O. C. VAN BELLE, P. BORDEWIJK, A. RIP, Vol. 1. Elsevier 1973
[14] BEVERIDGE, D. L., SCHNUELLE, G. W.: J. Phys. Chem., **79,** 2562 (1975)
[15] FRÖHLICH, H.: Theory of Dielectrics: Oxford University Press, London 1949

János LISZI, H-8201 Veszprém.

*Acta Chimica Academiae Scientiarum Hungaricae, Tomus 98 (4), pp. 403—419 (1978)*

# ELECTROCHEMICAL BEHAVIOUR OF ETHYLENE GLYCOL AND ITS OXIDATION PRODUCTS ON A PLATINUM ELECTRODE, III

## EFFECT OF CHEMISORPTION ON THE KINETICS OF OXIDATION OF GLYOXAL AND GLYOXALIC ACID

G. INZELT and G. HORÁNYI*

*(Department of Physical Chemistry and Radiology, L. Eötvös University, Budapest, and *Central Research Institute for Chemistry of the Hungarian Academy of Sciences, Budapest)*

Received September 29, 1977

An attempt was made to explain the interpretation of the first step observed in the initial setion of polarization curves recorded during the electrochemical oxidation of glyoxal and glyoxalic acid.

As a consequence of the earlier experimental results, two types of reaction were assumed. One is the reaction resulting in $CO_2$, which takes place *via* strongly chemisorbed molecules. It has been demonstrated that the other reaction, which occurs *via* the molecules weakly adsorbed on the sites not occupied by chemisorbed molecules, and which results in glyoxalic acid or oxalic acid, is the main process in the potential interval examined. On the basis of the simplified kinetic correlations written for these two reactions, a good agreement can be observed between the experimental results and the equations obtained for the concentration and potential dependences of the reaction rate. On this basis, it has been concluded that the first step appearing on the polarization curve can be brought into correlation with the inhibition effect, which decreases as a result of the acceleration of the oxidation of the chemisorbed molecules with increasing potential.

An account was given earlier [1] of experimental results connected with the fundamental phenomena occurring in the electrochemical oxidation of glyoxal and glyoxalic acid.

If the main conclusions to be drawn from these are taken into consideration, together with other results [2–4], the following main points may be made:

1. For both compounds the oxidation may proceed by two different routes:

(a) Following the strong chemisorption of the organic molecule, oxidation resulting directly in $CO_2$.

(b) Following presumably weak adsorption, an oxidation possibly occurring in several steps. In this reaction, oxalic acid is formed in both cases (*via* glyoxalic acid as intermediate in the case of glyoxal); depending on the experimental conditions (primarily the electrode potential), the oxalic acid either accumulates in the solution, or undergoes further oxidation to $CO_2$.

2. In the potential interval examined (in a steady state) reaction route 1b generally predominates over route 1a.

The findings in 1 and 2 are in agreement with observations and conclusions made in connection with the behaviours of other compounds. For example, essentially similar results are to be found in the literature with regard to ethylene glycol [2].

It must be noted here that examination of the literature relating to chemisorption also of necessity leads to the conclusion that two parallel reaction routes exist.

As established in our earlier publication, apart from the evolution of a not too significant amount of $CO_2$, glyoxylic acid and oxalic acid are formed from glyoxal. In the event of a coverage less than 0.5 for the chemisorption of hydrated glyoxal molecules, the following equation is regarded as being valid [3]:

$$CH(OH)_2—CH(OH)_2 + 2^* \rightarrow \underset{*}{C}(OH)_2—\underset{*}{C}(OH)_2 + 2H^+ + 2e$$

where * denotes a surface site.

Thus, it is assumed that dehydrogenation occurs on both carbon atoms. The subsequent oxidation presumably proceeds according to the equation

$$\underset{*}{C}(OH)_2—\underset{*}{C}(OH)_2 \rightarrow 2CO_2 + 4H^+ + 4e + 2^*$$

At higher coverages, chemisorption is described by

$$CH(OH)_2—CH(OH)_2 + ^* \rightarrow \underset{*}{C}(OH)_2—CH(OH)_2 + H^+ + e$$

The reaction

$$\underset{*}{C}(OH)_2—CH(OH)_2 \rightarrow 2CO_2 + 5H^+ + 5e + ^*$$

is then assumed for the further transformation of the chemisorbed molecule.

In another conception [4], a surface complex $\underset{*}{CO}$ is formed in the course of the adsorption of glyoxal, and this is converted by further oxidation to $CO_2$.

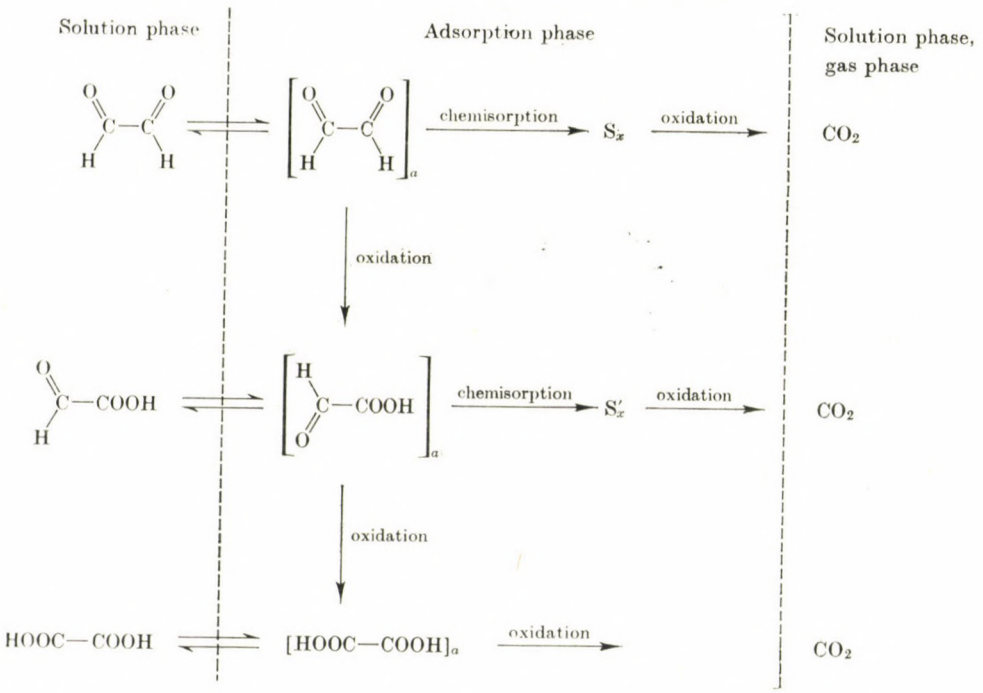
From the aspect of our present considerations it is of no significance which pathway the transformation of the chemisorbed molecule takes. The only essential feature is that experimental data indicate the formation of a strongly chemisorbed species; the rate of desorption of this is practically zero, and its transformation to $CO_2$ occurs without chemisorbed molecule moving from its site, and without any of its oxidation products (with the exception of $CO_2$) passing into the solution.

On this basis, the conclusion may be drawn that the reactions resulting in glyoxalic acid or oxalic acid cannot take place *via* the intensively studied chemisorbed state. Hence, one is compelled to assume two independent reaction paths.

3. Reaction 1b occurs on surface sites not occupied by the chemisorbed molecules. This assumption was made from the phenomena observed in the adsorption of the $Cl^-$ ion in the presence of glyoxal and glyoxalic acid, on the basis of the correlation found between the extent of ion adsorption and the steady oxidation rate.

4. In the case of galvanostatic experimental conditions, potential oscillations develop. Since the phenomenon occurs fairly far from the range of appreciable oxygen adsorption, the interpretation of the periodic phenomenon also requires the assumption of at least two interacting reaction paths, in one of which strongly chemisorbed molecules play a role.

5. Stepwise sections can be observed on the potentiostatic polarization curves, but development of the oxide layer does not result in a decrease in the rate of oxidation. On this basis, in the case of the oxidation of glyoxal we can attempt to give the reaction steps presumably playing a role in the process by means of the following scheme. (This scheme naturally includes the oxida-




Assumed scheme of glyoxal oxidation

tion of glyoxalic acid too.) In the scheme, the products of chemisorption are denoted by $S_x$ or $S'_x$. As we have already mentioned, although the opinion is uniform in the literature that chemisorption proceeds via dehydrogenation, it has not been sufficiently clarified what the composition of the chemisorbed

complex is, or, for example, whether the C–C bond is split or not [3, 4]. Here too it must be stressed that the state and stoichiometry of the chemisorbed molecules are of no relevance as regards our further considerations: the only essential point is that $CO_2$ is formed directly in their oxidation.

It must be assumed that the weakly adsorbed molecules shown in square brackets with the index *a* do exist and are transported from the adsorption phase towards the liquid phase, for both glyoxalic acid and oxalic acid actually appear in the solution. In the case of oxalic acid, direct experimental evidence too is available with regard to the weak reversible adsorption [5].

In the present publication, taking into account the scheme outlined above, we wish to make a more detailed investigation of the kinetics of the oxidation process in the potential interval corresponding to the first steps of the polarization curves presented in the preceding paper, in which the role of chemisorption must definitely be considered. For this, primarily the individual points of the potentiostatic steady-state polarization curves must be recorded more densely than previously (at 10–20 mV intervals), in order that the correlation describing the steps should be obtained as accurately as possible. In addition, it seems indispensable that a detailed study should also be made of the correlation between the rate of the oxidation and the concentration of glyoxal or glyoxalic acid.

## Experimental

The polarization curves were recorded, and investigations connected with the concentration dependence of the rate of oxidation were made, by the method given earlier [1] and with the experimental apparatus described there. A platinized platinum electrode with a geometrical surface area of 10 $cm^2$ and a roughness factor of ca. 1000 was employed.

## Results

### 1. *Study of potential dependence*

Polarization curves recorded at a given concentration in the potential interval corresponding to the first step, and their derived curves, are shown in Figs 1a and 1b.

The nature of the polarization curves essentially does not depend on the concentration of the organic substance, with the exception of glyoxalic acid below the concentration of 0.06 mol $dm^{-3}$, where a small maximum can be observed at around 570–580 mV. At a given concentration the measured currents frequently depend on the history of the electrode (*e.g.* the duration of the anodic-cathodic regeneration), but in the nature of the curves there is even then no appreciable change in the positions of the sections. With the aim of eliminating the various chance effects, possible changes in the magnitude

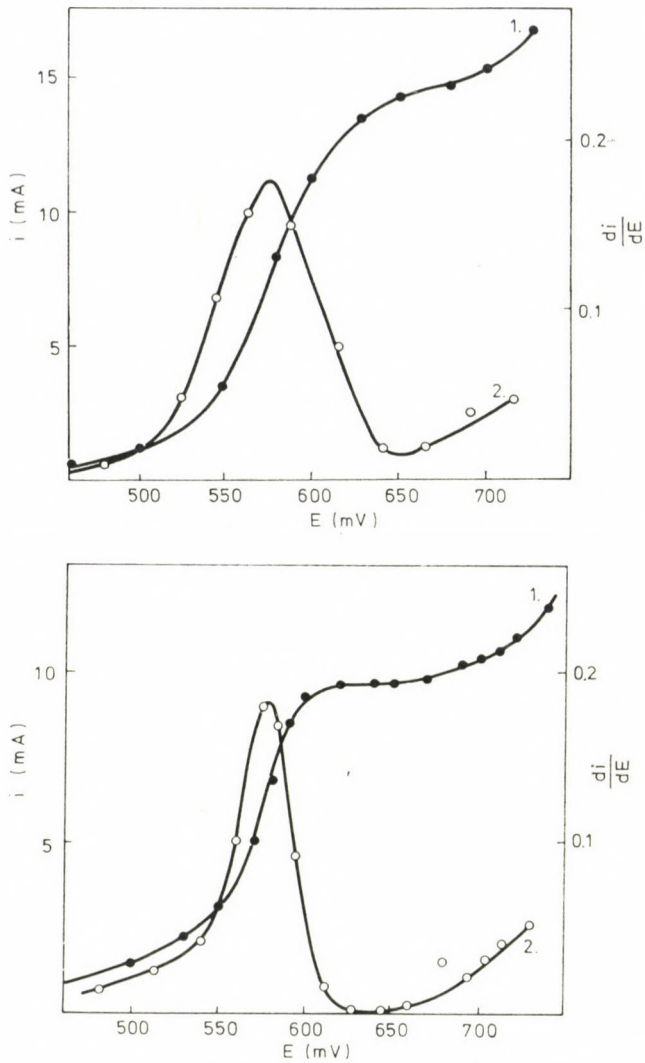



*Fig. 1. i.vs. E* (1) and *di/dE* (2) curves for (a) 0.3 mol $dm^{-3}$ glyoxal and (b) 0.15 mol $dm^{-3}$ glyoxalic acid

of the actual surface area of the electrode, and slow poisoning, it appeared reasonable to introduce some normalization of the polarization curves. For this purpose it seemed simplest to divide all current values referring to each polarization curve by the current value relating to an arbitrarily selected potential, and to give the polarization curve with these relative values. Thus:

$$i_r = \frac{i}{i(E_r)}$$

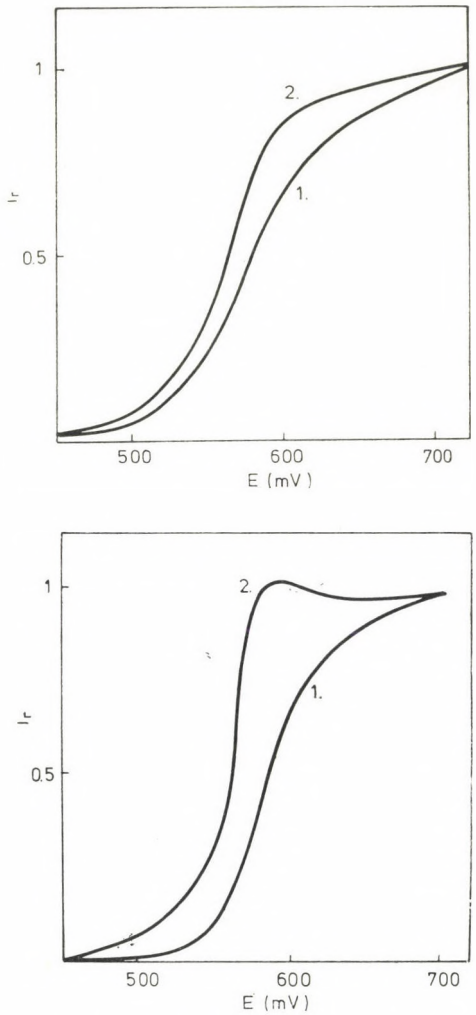



*Fig. 2.* $i_r$ ($i/i(700)$) curves for (a) 0.06 (2) and 0.3 (1) mol dm$^{-3}$ glyoxal, and (b) 0.06 (2) and 0.3 (1) mol dm$^{-3}$ glyoxalic acid

where $i(E_r)$ is the magnitude of the current determined experimentally on the recording of the given polarization curve, referring to an arbitrarily selected potential value $E_r$. The value selected for $E_r$ was 700 mV.

Figure 2 shows polarization curves given with $i_r$ calculated in this way for glyoxalic acid and glyoxal concentrations of both 0.06 and 0.3 mol dm$^{-3}$.

Every $i_r$ *vs.* $E$ curve in the concentration interval of 0.06–0.3 mol dm$^{-3}$ lies between these two limiting curves. As already mentioned, the small maximum to be seen in the Figure in the case of glyoxalic acid appears only at 0.06 mol dm$^{-3}$ or lower concentrations. The Figures reveal that the nature of

the polarization curves does indeed not depend greatly on the concentration, and to a first, rough approximation the reaction rate can be given as the product of a potential-dependent term $F(E)$ and a concentration-dependent term $f(c)$:

$$i \approx F(E)\, f(c) \tag{1}$$

In this conception, the $i_r$ values reported by us can be given approximately by the expression

$$i_r \approx \frac{F(E)}{F(700)} \tag{2}$$

It can be seen clearly from Figs 2a and 2b that only an approximation is involved. $F(E)$ is not completely independent of the concentration: with its increase, the $i_r$ *vs.* $E$ curves are shifted in the direction of higher potentials.

Let us next examine the type of functions with which $F(E)$ and $f(c)$ can be given. On the basis of the curves to be seen in Fig. 1, for $F(E)$ we may assume to a first approximation the validity of a correlation of the type

$$i = \frac{i_m^1\, 10^{b_1(E-E_0^1)}}{1 + 10^{b_1(E-E_0^1)}} \tag{3}$$

in which

$$2\, i_p^1 = i_m^1 \tag{4}$$

$i_p$ is the magnitude of the current relating to the inflection point (to the maximum of the $di/dE$ curve). $E_0^1$ is the position of the inflection point, or the maximum of the $di/dE$ curve. Upon transformation, correlation (1) can be given as

$$\log\left(\frac{i_m^1}{i} - 1\right) = b_1(E - E_0^1) \tag{5}$$

If the log $(i_m^1/i - 1)$ values calculated with the aid of the experimentally determined $i$ values and the $i_m^1$ resulting from the curve are plotted as a function of the potential, a straight line should be obtained if the assumption is correct. As Fig. 3 illustrates, the points calculated in this way do in fact lie to a good approximation on a straight line. $b_1$ can be determined from the slope: its value is $\sim 1/60$ $mV^{-1}$ for glyoxal, and $\sim 1/40$ $mV^{-1}$ for glyoxalic acid.

It must be noted that the maxima appearing at low glyoxalic acid concentrations were not taken into consideration; *i.e.* Eq. (3) can be regarded as valid only at concentrations higher than 0.06 mol $dm^{-3}$ in the case of glyoxalic acid.

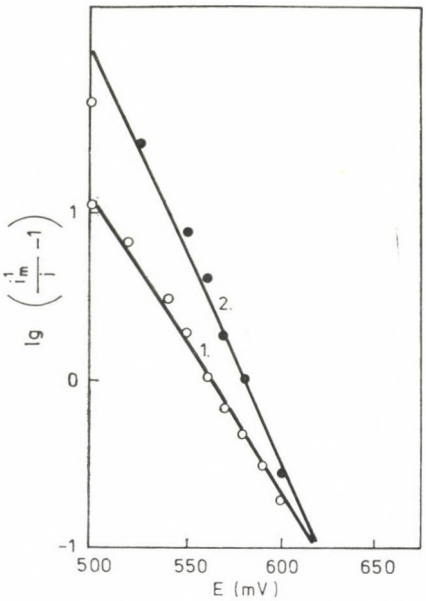



*Fig. 3.* log $(i_m/i-1)$ values as a function of the potential in the case of (1) 0.15 **mol dm$^{-3}$** glyoxal and (2) 0.15 mol dm$^{-3}$ glyoxalic acid

## 2. *Study of concentration dependence*

The concentration dependence of the rate of oxidation was examined by adjusting the potential of the electrode to a given value, and then gradually increasing the concentration of the organic substance; thus, we did not follow the customary procedure wereby complete polarization curves recorded in solutions of different concentrations are compared for determination of the concentration dependence. With the method employed, in essence it proved possible to eliminate the role of those factors which arise as a result of changes that might occur in the state of the electrode in the case of the recording of a complete polarization curve. The increase of the concentration took place without any particular disturbance of the system, and the change in the rate of oxidation could be followed immediately after the addition of the organic substance. Figures 4 and 5 illustrate the changes following the addition of glyoxal and glyoxalic acid at various electrode potentials. The *i vs. c* curves plotted from the experimental data can be seen in Figs 6 and 7. As Figs 8 and 9 show, if $1/i$ is plotted as a function of $1/c$ then to a good approximation straight lines are obtained.

On this basis, the concentration-dependence of the rate can be given in the form

$$i = i_c \frac{\gamma c}{1 + \gamma c} \tag{6}$$

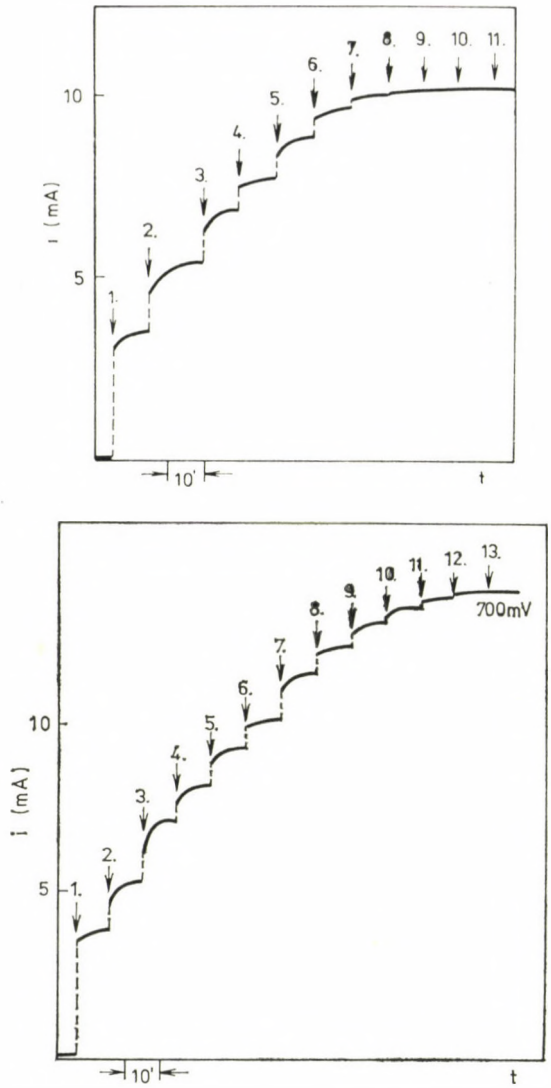



*Fig. 4.* Effect of the increase of concentration on the measured current as a function of time in the case of glyoxal; (a) *1.* 0.012; *2.* 0.024; *3.* 0.036; *4.* 0.048; *5.* 0.06; *6.* 0.072; *7.* 0.084; *8.* 0.096; *9.* 0.102; *10.* 0.12; *11.* 0.15 mol $dm^{-3}$ at 600 mV. (b) *1.* 0.006; *2.* 0.012; *3.* 0.018; *4.* 0.024; *5.* 0.03; *6.* 0.036; *7.* 0.048; *8.* 0.06; *9.* 0.072; *10.* 0.084; *11.* 0.108; *12.* 0.12; *13.* 0.15 mol $dm^{-3}$ at 700 mV

in which $i_c$ and $\gamma$ are constants at a given potential. Equation (6) can be linearized in the known manner:

$$\frac{1}{i} = \frac{1}{i_c} + \frac{1}{i_c \gamma} \frac{1}{c} \tag{7}$$

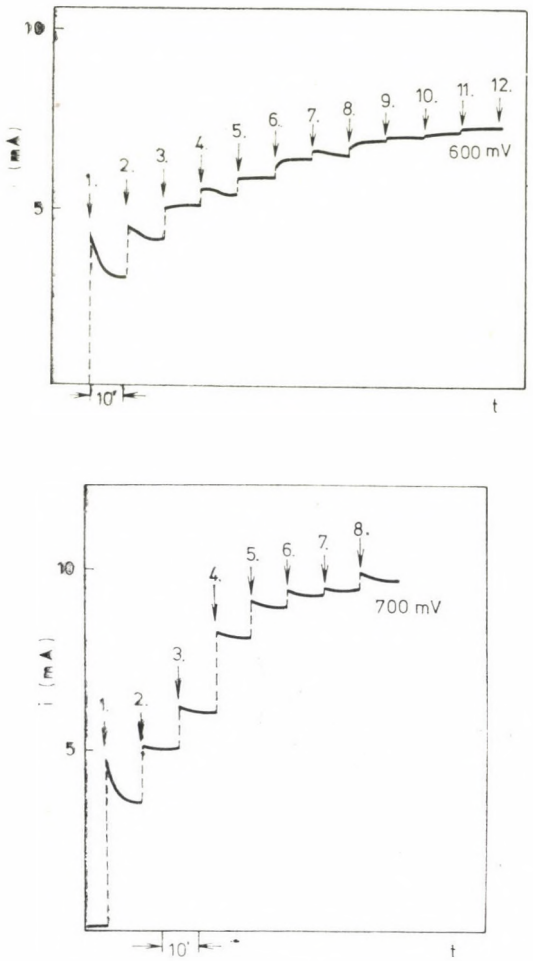



*Fig. 5.* Effect of the increase of concentration on the measured current as a function of time in the case of glyoxalic acid: (a) at 600 mV. *1.* 0.012; *2.* 0.024; *3.* 0.036; *4.* 0.048; *5.* 0.054; *6.* 0.06; *7.* 0.72; *8.* 0.084; *9.* 0.096; *10.* 0.108; *11.* 0.12; *12.* 0.132 mol $dm^{-3}$, (b) at 700 mV. *1.* 0.012; *2.* 0.024; *3.* 0.036; *4.* 0.072; *5.* 0.084; *6.* 0.104; *7.* 0.12; *8.* 0.138 mol $dm^{-3}$

The empirical correlation found for the rate suggests that the adsorbed form of the organic molecule reacts, and a correlation of Langmuir type holds for the adsorption.

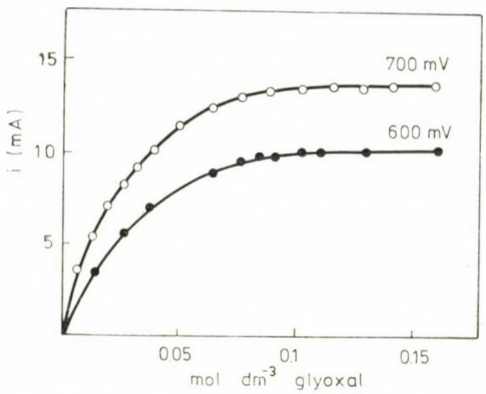



*Fig. 6.* Dependence of the rate of oxidation on the concentration for glyoxal at 600 and 700 mV

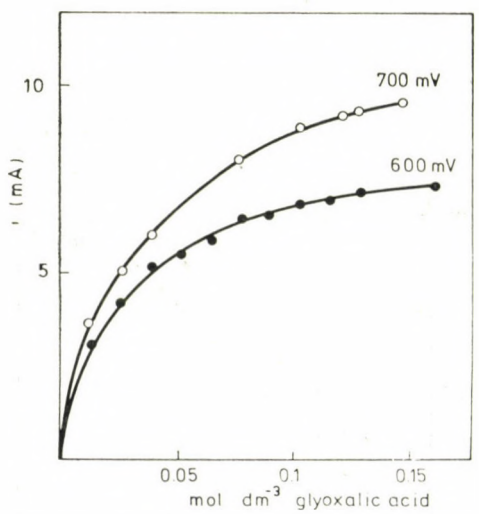



*Fig. 7.* Dependence of the rate of oxidation on the concentration for glyoxalic acid at 600 and 700 mV

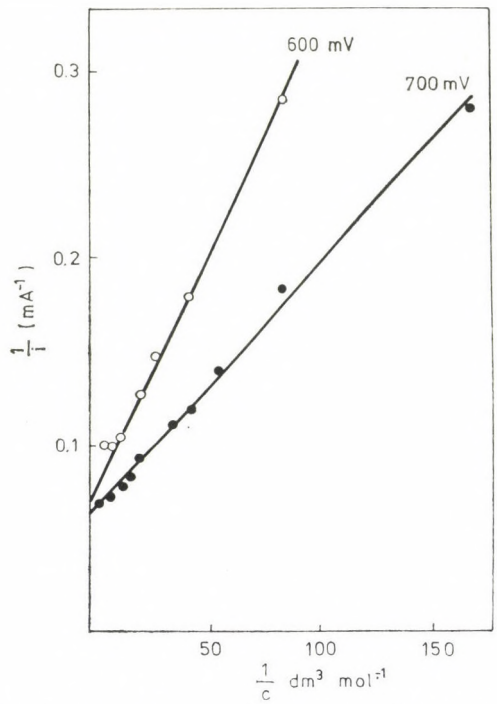



*Fig. 8.* $1/i$ *vs.* $1/c$ curves for glyoxal at 600 and 700 mV

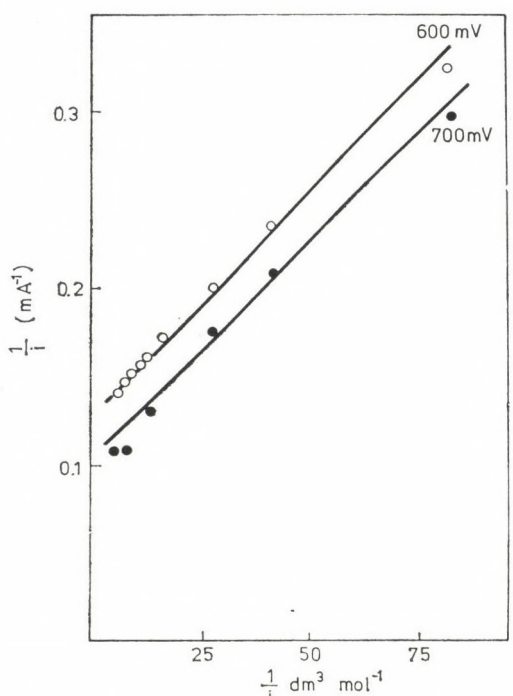



*Fig. 9.* $1/i$ *vs.* $1/c$ curves for glyoxalic acid at 600 and 700 mV

## Discussion

We shall primarily analyse the regularities observed in the oxidation of glyoxalic acid, for the situation is relatively simple in this case. In the potential interval corresponding to the first step, only two reaction paths need be reckoned with. One is oxidation to $CO_2$ via string chemisorption; the other is the reaction path resulting in oxalic acid. The measured current ($i_t$) is therefore composed of two parts:

$$i_t = i_k + i_f$$

where $i_k$ is the current relating to the process occurring *via* chemisorption, and $i_f$ that relating to the reaction resulting in oxalic acid. $i_k$ can essentially be broken down into further two parts:

$$i_k = i'_k + i''_k$$

where $i'_k$ is the current accompanying the chemisorption process, and $i''_k$ that arising from the oxidation of the chemisorbed molecules. From earlier experimental results [1] it follows that $i_k \ll i_f$; in practice, therefore, the current corresponds predominantly to the rate of the reaction resulting in oxalic acid.

For the sake of simplicity, let us assume that the heterogeneity of the electrode surface may be ignored as regards the reactions considered in the scheme, and that adsorption and kinetic correlations may be written which lead to Langmuir isotherms in the case of equilibrium (*i.e.* the Langmuir conditions are fulfilled).

The first step appearing on the polarization curve lies in that potential interval in which the oxidation of the chemisorbed molecules becomes appreciable. At potentials more negative than 450–500 mV the rate of the oxidation is practically zero as, because of the chemisorption, there is no free site on which the weak adsorption and the subsequent oxidation step can occur. The appearance of free sites can be reckoned with only at potentials where the oxidation of the chemisorbed molecules already becomes appreciable.

The rate of weak adsorption is

$$w_a^1 = k_a^1 c(1 - \theta_k - \theta_1) \tag{8}$$

where $\theta_k$ and $\theta_1$ are the coverages referred to the chemisorbed and the weakly bound molecules, respectively, and $c$ is the concentration of the organic substance in the solution.

In principle, the equilibrium coverage of the product (oxalic acid) should also be included in Eq. (8). If we confine ourselves to cases where the concentration of the product in the solution remains low throughout, then the

coverage referred to the product can be neglected, for the rate of desorption of oxalic acid is high [5] and the equilibrium coverage is small in the event of low oxalic acid concentrations in solution.

The rate of desorption of the weakly adsorbed molecules is

$$w_d^1 = k_d^1 \theta_1 \tag{9}$$

The rate of formation of the chemisorbed molecule from the weakly bound one is

$$w_k = k_r \theta_1 \tag{10}$$

The rate of oxidation of the chemisorbed molecule at a given potential is

$$w_0^k = k_0^k \theta_k \tag{11}$$

The rate of oxidation of the weakly bound molecule is

$$w_0^1 = k_0^1 \theta_1 \tag{12}$$

For a steady state, the following equations can be written

$$k_a^1 c(1 - \theta_k - \theta_1) = k_d^1 \theta_0 + k_r \theta_1 + k_0^1 \theta_1 \tag{13}$$

$$k_0^k \theta_k = k_r \theta_1 \tag{14}$$

If it is assumed that an adsorption equilibrium holds for the weakly bound molecules, *i.e.* if

$$k_d^1 \gg k_r + k_0^1$$

then Eq. (13) assumes the following form:

$$k_a^1 c(1 - \theta_k - \theta_1) \approx k_d^1 \theta_1 \tag{15}$$

Further, by making use of the substitution $\theta_k/\theta_1 = p$, we obtain

$$\theta_1 = \frac{k_a^1 c}{k_d^1 + (1 + p) k_a^1 c} \tag{16}$$

If this is taken into account, Eq. (12) can be given in the form

$$w_0^1 = \frac{k_0^1 k_a^1 c}{k_d^1 + (1 + p) k_a^1 c} = A \frac{Bc}{1 + Bc} \tag{17}$$

in which

$$A = \frac{k_0^1}{1 + p} \quad \text{and} \quad B = \frac{(1 + p)\, k_a^1}{k_d^1}$$

It follows from Eq. (17) that the correlation between the rate of oxidation and the concentration is of the same type as that found experimentally. If $1/w$ is plotted against $1/c$ at a given potential, a straight line must be obtained. The situation is somewhat more complex in the study of the potential dependence. In principle, any rate constant may depend on the potential. For the potential dependence of some rate constant $k_i$ we may give the correlation

$$k_i = \exp\,[b_i(E - E_0^i)] \tag{18}$$

The equilibrium constant $k_a^1/k_d^1$ may be written in the form

$$\frac{k_a^1}{k_d^1} = \exp\,[b_k(E - E_0^k)] \tag{19}$$

and $p$, which is equal to $k_r/k_0^k$, in the form

$$p = \exp\,[b_p(E - E_0^p)] \tag{20}$$

This is also valid for $k_0^1$, *i.e.*:

$$k_0^1 = \exp\,[b_v(E - E_0^v)] \tag{21}$$

If this is substituted into Eq. (17), we obtain the correlation

$$w_0^1 = \exp\,[b_v(E - E_0^v)]\,\frac{c\,\exp\,[b_k(E - E_0^k)]}{1 + \exp\,[b_k(E - E_0^k)]\,\{1 + \exp\,[b_p(E - E_0^p)]\}\,c} \tag{22}$$

From this:

$$w_0^1 = \frac{Qc\,\exp\,[(b_v + b_k)E]}{1 + c\,\exp\,[b_k(E - E_0^k)] + Yc\,\exp\,[(b_k + b_p)E]} \tag{23}$$

where

$$Q = \exp\,[-(b_vE_0^v + b_kE_0^k)]$$

and (24)

$$Y = \exp\,[-(b_kE_0^k + b_pE_0^p)]$$

The experimental data indicate that the absolute values of $b_v$ and $b_k$ may be very small compared to the absolute value of $b_p$ in the potential interval corresponding to the first step. If this were not so, then following the change of the potential, when the coverage referred to the chemisorbed molecules does not yet vary appreciably, a significant rate change should be obtained. It is particularly striking that the rate does not vary following the potential change in the case when we proceed from larger, more positive potentials towards lower potentials.

On this basis, it may be assumed to a first approximation that $|b_k| \ll \ll |b_p|$ and $|b_v| \ll |b_p|$ and at the potentials studied $|E| \ll |E_0^k|$.
Equation (23) may then be written in the following form:

$$w_0^1 = \frac{Qc}{1 + Kc + Yc \exp(b_p E)} \tag{25}$$

where $K = \exp[-b_k E_0^k]$
Since $b_p < 0$, and since $\theta_k/\theta_1$ decreases with the increase of the potential, we may write the correlation

$$w_0^1 = \frac{Qc \exp(b_p^1 E)}{(1 + Kc) \exp(b_p^1 E) + Yc} \tag{26}$$

in which $b_p^1 = -b_p$.

It can readily be seen that Eq. (26) may be written in the form

$$w_0^1 = \frac{Qc}{1 + Kc} \frac{\exp[b_p^1(E - E_0^x)]}{1 + \exp[b_p^1(E - E_0^x)]} \tag{27}$$

in which

$$E_0^x = \frac{1}{b_p^1} \ln \frac{Yc}{1 + Kc} \tag{28}$$

Equation (27) agrees formally with correlation (3) suggested on the basis of the experimental data. From a comparison of (3) and (27):

$$i_m^1 = \frac{\alpha Qc}{1 + Kc} \tag{29}$$

where $\alpha$ is the constant serving for the transformation of $w$ to $i$ ($i = \alpha w_0^1$) and $E_0^1 = E_0^x$, and $b_p^1/2.303 = b_1$.

It follows from Eq. (27) that with the increase of the concentration $E_0^x$ is shifted in the direction of higher potentials, and proceeds towards a concentration $E_0$ is shifted in the direction of higher potentials, and proceeds towards a concentration-independent limiting value. This result is also given by the experimental data.

As regards the earlier considerations relating to $i_r$, it can similarly be seen that there is agreement between the experimental results and Eq. (27), although we cannot give an explanation for the maximum appearing at low glyoxalic acid concentrations. If Eq. (27) is compared with Eq. (1), it may be stated that to a first approximation the rate can indeed be given as the product of two functions. One of these functions depends only on the concentration; the other depends primarily on the potential. In the function containing the potential, the concentration dependence is manifested to a certain extent *via* $E_0^x$.

In summary, it must be concluded that the proposed kinetic correlations are in good agreement with the experimental results as regards the fundamental tendencies, and thus to a first approximation they are suitable for the interpretation of the first section in the polarization curves.

## REFERENCES

[1] HORÁNYI, G., INZELT, G., SZETEY, Z.: Acta Chim. Acad. Sci. Hung. 98, 49 (1978)
[2] VIJH, A. K.: Can. J. Chem., **49**, 78 (1971); VIJH, A. K.: Can. J. Chem., **48**, 197 (1970); WEBER, J., VASILEV, Y. B., BAGOTSKII, V. G.: Elektrokhimiya, **2**, 515, 522 (1966)
[3] FORMARO, L., CASTELLI, G.: J. Electroanal. Chem., **28**, 363 (1970); BIANCHI, G., FORMARO, L., TRASATTI, S.: Chim. Ind., **50**, 26 (1968)
[4] SIDHESWARAN, P.: Ind. J. Chem. **12**, 1077 (1974); SIDHESWARAN, P.: J. Electrochem. Soc. India, **24**, 81 (1975)
[5] HORÁNYI, G., HEGEDŰS, D., RIZMAYER, E. M.: J. Electroanal. Chem. **40**, 393 (1972)

György INZELT H-1088 Budapest, Puskin u. 11/13
György HORÁNYI H-1525 Budapest, Pusztaszeri ut 57/69.

*Acta Chimica Academiae Scientiarum Hungaricae, Tomus 98 (4), pp. 421—427 (1978)*

# IONIC POTENTIAL OF MODERATELY HIGHLY CONCENTRATED AQUEOUS SOLUTION OF STRONG ELECTROLYTES

R. DATTA

*(Centre of Advanced Study in Applied Mathematics, Calcutta University, 92, Acharya Prafulla Chandra Road, Calcutta — 700 009)*

and

B. K. SENGUPTA

*(Raja Peary Mohan College, Uttarpara, Hooghly)*

Received September 30, 1977

The paper deals with the thermodynamic properties, particularly activity coefficients of aqueous solutions of strong electrolytes. Here, as in the previous paper (B. K. SENGUPTA and R. DATTA, 1978), DUTTA's distribution formula (M. DUTTA, 1952, 1953) is the starting-point. The resulting Poisson equation is solved by following the method of DUTTA and SENGUPTA (1954) as well as of FUOSS and ONSAGER (1961). The treatment is not restricted to high dilutions.

## Introduction

Here strong electrolytes in aqueous solution are considered. It is well known that long range Coulomb forces as well as short range forces are important in such systems. The repulsive part of the simplest type of short range effects together with the other potentials is hard core potential. We shall take into account the effect of the hard core potential by replacing the Boltzmann distribution by DUTTA's distribution formula (1952, 1953) for charged particles in a dielectric medium. The method of solution of the Poisson equation is more or less similar to that followed by DUTTA and SENGUPTA (1954) for the potential at small distances. At large distances the same equation is solved by the method of FUOSS and ONSAGER (1961) retaining terms up to the third degree in the potential (since $\psi \to 0$ as $r \to \infty$). Integration constants are obtained in a similar fashion as by FUOSS and ONSAGER (1961). Unlike our previous work (B. K. SENGUPTA and R. DATTA, 1978) the simplified assumption for high dilutions, $bn \ll 1$, where $n$ is the average number of ions per unit volume and $b = \frac{4}{3}\pi a^3$, $a$ being the mean distance of approach of positive or negative ions, has been dropped here. Calculations are made retaining $bn$ as it occurs in the Poisson equation.

The solution of the Poisson equation arises in an extremely complicated form. Numerical values of potentials and then activity coefficients are computed for aqueous solutions of different 1 : 1 electrolytes at different concentrations with the help of digital computer. Only the final figures from the computed values have been entered in our results for comparison with experimental datas.

One notable and peculiar feature about the activity coefficient of solutions of strong electrolytes is that in most cases of 1 : 1 electrolytes, the activity coefficient decreases first with increase of concentration of the solute and then increases again with further increase of concentration. This well-known peculiar and important property is clearly manifested by the results of the present investigation.

## Mathematical Calculations

An aqueous solution of a strong electrolyte with dielectric constant $D$ is considered. Complete dissociation of the solutes into ions is assumed and each ion is taken to be surrounded by an ionic cloud.

Other ions are distributed about a central ion according to DUTTA's distribution formula (1952, 1953).

$$n_r^{\pm} = \frac{\dfrac{1}{b_{\pm}}}{\exp\left(\nu_{\pm} + \dfrac{z_{\pm} \pm \varepsilon\psi_r}{kT}\right) + 1}, \tag{1}$$

where $n_r^{\pm}$ = number densities of positive or negative ions at a point $r$ where the electrostatic potential is $\psi$.

$b_{\pm}$ = exclusion volumes of two like ions.

$z_{\pm}$ = valency of positive of negative ions.

$\nu_{\pm}$ = parameters of distribution.

The charge density at any point is given by

$$\varrho_r = \varepsilon(n_r^+ - n_r^-) = \varepsilon\left\{\frac{\dfrac{1}{b_+}}{e^{\nu_+ + \varepsilon\psi/kT} + 1} - \frac{\dfrac{1}{b_-}}{e^{\nu_- - \varepsilon\psi/kT} + 1}\right\}. \tag{2}$$

For simplicity, we assume $|z_{\pm}| = 1$ and $b_+ = b_- = b$ (say), so that $\nu_+ = \nu_- = \nu$ (say).

On approaching the central ion, $\psi \to \infty$ and so the charge density becomes $\varrho \approx -\dfrac{\varepsilon}{b}$. Thus the Poisson equation for ions near to the centre of the cloud is

$$\nabla^2\psi_s = -\frac{4\pi\varrho}{D} = \frac{4\pi\varepsilon}{Db}.$$

One can write

$$\nabla^2\psi_s = \varkappa_1^2 m, \tag{3}$$

where $\varkappa_1^2 = 8\pi n\beta(1 - nb)$ and $m = \frac{kT}{\varepsilon} \cdot \frac{1}{2bn(1 - nb)}$. (3a)

For large distances, on the other hand, $\psi \to 0$, the distribution becomes uniform and one gets

$$e^{\nu} = \frac{1 - nb}{nb},$$

where $n$ = average number of ions per unit volume.

One then obtains the charge density, retaining terms up to cubic in $\psi$,

$$\varrho = -2\varepsilon n(1 - nb)\left\{\frac{\varepsilon\psi}{kT} + \frac{1 - 6bn + 6\,b^2n^2}{6} \cdot \left(\frac{\varepsilon\psi}{kT}\right)^3\right\}. \tag{4}$$

The Poisson equation at long distances is therefore

$$\nabla^2\psi_L = \varkappa_1^2\psi_L + \varkappa_1^2\alpha\psi_L^3 \tag{5}$$

where

$$\alpha = \frac{\varepsilon^2}{k^2T^2} \cdot \frac{1 - 6\,bn + 6\,b^2n^2}{6} \tag{5a}$$

and $\varkappa_1^2$ has the same value as before.

Equation (3) gives on integration (assuming spherical symmetry)

$$\psi_s = \varkappa_1^2 m\left(\frac{r^2}{6} + C + \frac{H}{r}\right) \tag{6}$$

where $C$ and $H$ are integration constants.

The solution of Eq. (5) is (assuming spherical symmetry)

$$\psi_L = A \cdot \frac{e^{-\varkappa_1 r}}{r} - \frac{\varkappa_1^2\alpha\varepsilon^3}{D^3}\left[2 \cdot \frac{e^{\varkappa_1 r}}{r} E_4(r) - \frac{e^{-\varkappa_1 r}}{r} E_2(r)\right] \tag{7}$$

where

$$E_n(r) = \int_{n\varkappa_1 r}^{\infty} \frac{e^{-u}}{u}\,du. \tag{7a}$$

The integration constants $C$, $H$, $A$ can be evaluated from the three following conditions

(i) $$-\varepsilon = \int_a^{\infty} 4\pi\varrho r^2\,dr,$$

(ii) $$\psi_s\left(\frac{\beta}{2}-0\right)=\psi_L\left(\frac{\beta}{2}+0\right),$$

(iii) $$\left(\frac{d\psi_s}{dr}\right)_{(\beta/2)-0}=\left(\frac{d\psi_L}{dr}\right)_{(\beta/2)+0},$$

where

$$\beta=\frac{\varepsilon^2}{DkT}.$$

One then obtains

$$H=\frac{a^3}{3}+\frac{\varepsilon}{D\varkappa_1^2 m}, \tag{8a}$$

and

$$C=-\frac{1}{1+\tau_1}\left[\frac{\beta^2}{12}-\frac{2}{\beta}\left(\frac{a^3}{3}+\frac{\varepsilon}{D\varkappa_1^2 m}\right)\right]-\frac{\beta^2}{24}-\frac{2}{\beta}\left(\frac{a^3}{3}+\frac{\varepsilon}{D\varkappa_1^2 m}\right)-$$
$$-\frac{\beta}{2}\cdot\frac{1}{1+\tau_1}\cdot\frac{1}{\varkappa_1^2 m}\cdot\frac{\varkappa_1^2\alpha\varepsilon^3}{D^3}\cdot\left[8\varkappa_1\cdot\frac{e^{\tau_1}}{\beta}E_4\left(\frac{\beta}{2}\right)-\frac{4}{\beta^2}\cdot e^{-3\tau_1}\right], \tag{8b}$$

where

$$\tau_1=\frac{\varkappa_1\beta}{2}.$$

One then gets the potential on the reference ion of radius '$a$'

$$\psi^*=\varkappa_1^2 m\left[\frac{a^2}{2}-\frac{\beta^2(3+\tau_1)}{24(1+\tau_1)}-\frac{2\,\tau_1}{\beta(1+\tau_1)}\cdot\left(\frac{a^3}{3}+\frac{\varepsilon}{D\varkappa_1^2 m}\right)\right]-$$
$$-\frac{\beta}{2}\cdot\frac{1}{1+\tau_1}\cdot\frac{\varkappa_1^2\alpha\varepsilon^3}{D^3}\cdot\left\{8\varkappa_1\cdot\frac{e^{3\tau_1}}{\beta}\cdot E_4\left(\frac{\beta}{2}\right)-\frac{4}{\beta^2}\cdot e^{-3\tau_1}\right. \tag{9}$$

and

$$\frac{d\psi^*}{dn}=\varkappa_1^2 m\left[\frac{\beta}{12}\cdot\frac{1}{(1+\tau_1)^2}\cdot\frac{d\tau_1}{dn}-\frac{2}{\beta}\cdot\frac{1}{(1+\tau_1)^2}\cdot\frac{d\tau_1}{dn}\cdot\left(\frac{a^3}{3}+\frac{\varepsilon}{D\varkappa_1^2 m}\right)\right]-$$
$$-\frac{\beta}{2}\cdot\frac{\varepsilon^3}{D^3}\cdot\frac{(1+\tau_1)\left\{\frac{d\varkappa_1^2}{dn}\cdot\alpha+\varkappa_1^2\frac{d\alpha}{dn}\right\}-\varkappa_1^2\alpha\frac{d\tau_1}{dn}}{(1+\tau_1)^2}\cdot$$
$$\cdot\left\{8\varkappa_1\cdot\frac{e^{3\tau_1}}{\beta}\cdot E_4\left(\frac{\beta}{2}\right)-\frac{4}{\beta^2}e^{-3\tau_1}\right\}-\frac{\beta}{2}\cdot\frac{1}{1+\tau_1}\cdot\frac{\varkappa_1^2\alpha\varepsilon}{D^3}$$
$$\left[\frac{8}{\beta}\cdot\left\{E_4\left(\frac{\beta}{2}\right)e^{3\tau_1}\cdot\frac{d\varkappa_1}{dn}+3\,E_4\left(\frac{\beta}{2}\right)\varkappa_1\cdot e^{3\tau_1}\frac{d\tau_1}{dn}+\right.\right.$$
$$\left.\left.+\,\varkappa_1\cdot e^{3\tau_1}\left(-\frac{e^{-4\tau_1}}{\varkappa_1}\cdot\frac{d\varkappa_1}{dn}\right)\right\}+\frac{12}{\beta^2}\cdot e^{-3\tau_1}\frac{d\tau_1}{dn}\right]. \tag{10}$$

The electric free energy is given by

$$G_e = \frac{1}{2} \sum_j \varepsilon_j n_j \psi_j^* \ . \tag{11}$$

Then the relation $kT \ln f_j = \frac{\partial Ge}{\partial n_j}$ gives for activity coefficient

$$\ln f_j = \frac{1}{2kT} \cdot \left[ \varepsilon_j \psi_j^* + \varepsilon_j n_j \frac{\partial \psi_j^*}{\partial n_j} \right] ,$$

where $\psi_j^*$ and $\frac{\partial \psi_j^*}{\partial n_j}$ are given by Eqs (9) and (10).

## Numerical Results

Numerical values were computed for the activity coefficients of several 1 : 1 electrolytes in aqueous solution at different concentrations and for different values of $a$ (the mean distance of closest approach of two positive or negative ions) at 25 °C, with $D = 78.6$ and standard values of $k$ and $\varepsilon$. The molar concentrations $c$ are converted to the molalities $m$ by the relation (HARNED and OWEN, 1943)

$$\frac{c}{m} = d_0 - Am + Bm^2; \quad d_0 = 0.9970$$

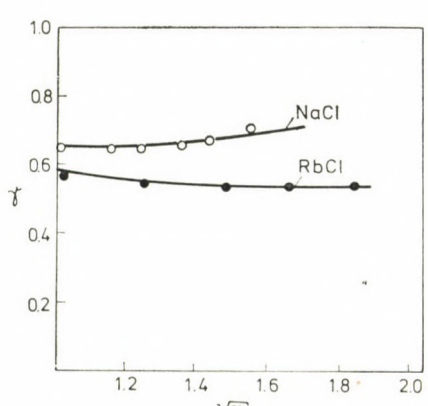



*Fig. 1.* —— The experimental curve for activity coefficient against the square root of molality; ○ —— Computed values of activity coefficient of NaCl with a = 4.5 Å; ● —— Computed values of activity coefficient of RbCl with a = 3.6 Å

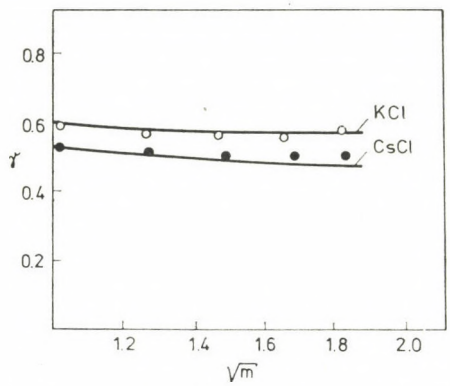



*Fig. 2.* —— The experimental curve for activity coefficient against the square root of molality; ○—— Computed values of activity coefficient of KCl with a = 3.8 Å; ●—— Computed values of activity coefficient of KCl with a = 3.4 Å

where $A$ and $B$ have different numerical values for different electrolytes and the rational activity coefficient $f$ is converted to the molal activity coefficient $\gamma$ by the relation

$$\ln f = \ln \gamma(1 + 0.0360m).$$

Graphical representations of $\gamma$ against the square root of $m$ are given with the most suitable values of $a$. Figs 1 and 2 show the agreement of experimental (HARNED and OWEN, 1943) and theoretical curves for NaCl, RbCl and KCl, CsCl, respectively.

## Conclusion

The results clearly show that an aqueous electrolytic solution can be successfully dealt with, by including short-range interactions represented by a hard core potential over the long range Coulomb potential.

Some kind of exclusion volume of ions has therefore to play a very important part in any investigations of the properties of electrolytic solutions, so that the simple Boltzmann distribution cannot be applied. Instead, DUTTA's distribution function may be applied through which the short range forces of both attractive and repulsive types are taken into consideration. On the other hand the force of interaction between the ions and the solvent molecules is taken into account by the introduction of the dielectric constant of the medium. Good agreement with the experimental results has been achieved.

*

The authors are most grateful to Professor M. DUTTA, Professor-in-charge, S. N. Bose Institute of Physical Sciences, Calcutta University, for his kind help and valuable suggestions in preparing this paper.

## REFERENCES

DUTTA, M.: On Strong Electrolytes in Solutions, Naturwiss., **39,** 108 (1952)
DUTTA, M.: On the Distribution of Ion in Electrolytic Solutions, Naturwiss., **40,** 51 (1953)
DUTTA, M., SENGUPTA, M.: A Theory of Strong Electrolytes in Solution Based on a New Statistics, Proc. Nat. Inst. Sc. Ind., **20,** 1 (1954)
FUOSS, M., ONSAGER, L.: Thermodynamic Potentials of Symmetrical Electrolytes. Proc. Nat. Acad. Sciences, **47,** 818 (1961)
HARNED, H. S., OWEN, B. B.: "The Physical Chemistry of Electrolytic solutions," Reinhold Publishing Corporation, U.S.A. (1943)
SENGUPTA, B. K., DATTA, R.: On Some Correction on Free Energy of an Assembly of Charged Particles due to Hard Core Potential. Ind. J. Phys. **52 B,** 62 (1978)

R. DATTA 92, Acharya Prafulla Chandra Road, Calcutta—700 009
B. K. SENGUPTA Raja Peary Hohan College, Uttarpara, Hooghly

*Acta Chimica Academiae Scientiarum Hungaricae, Tomus 98 (4), pp. 429—437 (1978)*

# INVESTIGATIONS ON THE DISTRIBUTION OF 4-(2-PYRIDILAZO)-RESORCINOL (PAR) IN AQUEOUS SOLUTION–CHLOROFORM AND AQUEOUS SOLUTION–CHLOROFORM SOLUTION OF QUATERNARY AMMONIUM CHLORIDE TWO-PHASE SYSTEMS

E. PAPP and J. INCZÉDY

*(Department of Analytical Chemistry, University of Chemical Engineering, Veszprém)*

Received December 23, 1977

Distribution of 4-(2-pyridilazo)-resorcinol (PAR) was studied in aqueous solution–chloroform and aqueous solution–chloroform–TOMACl systems. The distribution constant of the neutral, $H_2L$ species in the aqueous solution–chloroform system was $\lg d_{H_2L} = 1.25 \pm 0.01$ ($I = 0.1$). In the aqueous solution–chloroform–TOMACl system the $H_2L$ species is associated with TOMACl below pH 4. The association constant in the $4 \cdot 10^{-3}$–$10^{-2}$ *M* TOMACl concentration range was found to be $\lg K_A = 3.84 \pm \pm 0.07$. There is an ion-exchange reaction taking place above pH 7 between the $HL^-$ species of PAR and TOMACl. The value of the exchange-reaction constant is: $\lg K^X = = 2.99 \pm 0.04$.

Results of the distribution experiments carried out with Cu(II) salicylate in aqueous solution–chloroform–trioctylmethyl ammonium chloride (TOMACl) system were presented in a previous paper [1]. The equilibrium ion-exchange constants of a number of inorganic ions and salicylate ion relating to chloride were also presented.

This paper summarizes the results obtained in the course of distribution experiments carried out with a frequently used chelating agent 4-(2 pyridilazo) resorcinol, PAR. The aim of these experiments was to obtain basic data relating to the extraction of metal–PAR complexes with chloroform containing different amounts of a long-chain amine.

The distribution constants of the neutral PAR species ($H_2L$ form) in the chloroform–aqueous solution system was obtained.

The $H_2L$ species, similarly to strong acids [2], was found to be associated with the quaternary ammonium salt in the two-phase aqueous solution–chloroform–TOMACl system. The extent of the association was studied and the value of the association constant was obtained. Ion-exchange was found possible between the charged PAR species ($HL^-$) dissolved in the aqueous phase and the quaternary ammonium chloride species in the chloroform phase. The value of the equilibrium exchange constant of the $HL^-$ species with respect to the chloride ion was determined.

## Experimental

### Chemicals and solutions

Chloroform solution of TOMACl: 50 g TOMACl (Serva, Heidelberg, GFR) was mixed with 680 ml chloroform to obtain a 5% w/w solution. The exact concentration of the solution was determined by shaking it with excess sodium salicylate solution followed by the potentiometric titration of the chloride ion in the aqueous phase.

PAR solution: Monosodium salt of PAR ($C_{11}H_8O_2N_3Na.H_2O$; m.w.: 255.22) was used to prepare the solution (Reanal, Hungary). The paper chromatographic test of POLLARD *et al.* [3] was used to check the purity of PAR. The product proved to be pure by this technique.

Photometric titration at 510 nm and pH 5 with $CuCl_2$ was used to determine the concentration of PAR in the solution. The Cu content of the titrating solution was standardized by complexometric titration using EDTA.

Other chemicals: Reagent grade potassium chloride, sodium acetate, glacial acetic acid, hydrochloric acid, potassium hydroxide and chloroform (all Reanal, Hungary) were used. Deionized water was used for the solutions.

Instruments: A pH meter Type M 25 (Radiometer, Denmark) with a glass-calomel electrode pair, a recording spectrophotometer Type Spekord UV-VIS (Zeiss, Jena, GDR) and a photometer Type Spekol (Zeiss, Jena, GDR) were used.

### Distribution experiments

A number of aqueous PAR solutions of known concentration and pH were shaken with chloroform and chloroform solutions of TOMACl. The optimum contact time was found to be 3 minutes. The phase ratio was 1 : 1. Potassium chloride solution was used to maintain the ionic strength at a constant level. Hydrochloric acid and potassium hydroxide were used to modify the pH of the solutions. The equilibrium PAR concentration of the separated aqueous phase was determined spectrophotometrically after the addition of sodium-acetate buffer solution (pH 5) at 400 nm using a calibration curve. The distribution coefficient of PAR, $D_{PAR}$ was calculated from the known initial and equilibrium aqueous-phase concentrations as

$$D_{PAR} = \frac{g_{PAR}}{c_{PAR}} \tag{1}$$

where $g_{PAR}$ and $c_{PAR}$ denoted the analytical PAR concentrations in the organic and aqueous phases, respectively.

1. Investigations on the distribution of PAR in the aqueous solution–chloroform system.

Solvent series containing initially $8.85 \cdot 10^{-5}$ M and $4.43 \cdot 10^{-4}$ *M* PAR at various pH and constant 0.1 ionic strength values were prepared. The distribution coefficient of PAR, $D_{PAR}$ was obtained and plotted as a function of the pH of the aqueous phase. Results are summarized in Fig. 1 as plot No. 1.

2. Investigations on the distribution of the neutral, $H_2L$ species of PAR in the aqueous solution–chloroform–TOMACl system.

The distribution coefficients of PAR at various equilibrium pH values of the aqueous phase, at various chloride ion concentrations and TOMACl concentrations of the organic phase were studied.

Solvent series of constant and known initial PAR concentrations ($8.85 \cdot 10^{-4}$ *M* and $1.77 \cdot 10^{-3}$ *M*), constant ionic strength (0.1) and varied equilibrium aqueous phase pH (2–9.5) values were prepared. These solutions were shaken with equal volumes of $10^{-2}$ *M* chloroform TOMACl solutions. The distribution coefficient of PAR was obtained as mentioned above.

The lg $D_{PAR}$ *vs* pH relationship is shown in Fig. 1 as plot No. 2. It can be seen by comparing the two curves that the distribution coefficient of PAR is considerably higher in the presence than in the absence of TOMACl.

To determine which PAR species was present in the chloroform TOMACl solution the absorption spectra of the chloroform phase at various equilibrium pH values were recorded. At pH $< 4$ the absorption maximum was — just as in the case of the chloroform extract in absence of TOMACl — at 385 nm. Correspondingly the $H_2L$ species of PAR was present in the organic phase.

The distribution coefficient of PAR as the function of the chloride ion concentration of the aqueous phase was also studied in the 3.7—4.3 pH range. The initial PAR concentration

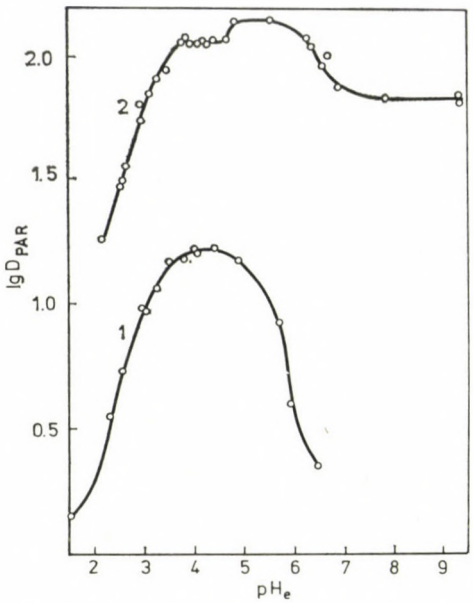



*Fig. 1.* Distribution of PAR as the function of the equilibrium pH of the aqueous phase. 1. Distribution coefficient of PAR in the aqueous solution-chloroform system ($C_{KCl} = 10^{-1}$ *M*). 2. Distribution coefficient of PAR in the aqueous solution–chloroform–TOMACl system ($C_{TOMACl} = 8.3 \cdot 10^{-3}$ *M*; $C^0_{PAR} = 1.77 \cdot 10^{-3}$ *M*, $C_{KCl} = 10^{-1}$ *M*).

was maintained at $1.77 \cdot 10^{-3}$ *M* while the initial chloride ion concentration in the aqueous phase was varied in the $1.5 \cdot 10^{-1}$ *M*–$2.10^{-2}$ *M* range. The TOMACl concentration of the chloroform phase was $10^{-2}$ *M*. The distribution coefficients obtained are shown in Table I. It can be seen that in the pH range studied the distribution coefficient of PAR is practically independent from the chloride ion concentration of the aqueous phase.

**Table I**

*The distribution coefficient of PAR ($D_{PAR}$) at various equilibrium chloride ion concentrations of the aqueous phase*

| $pH_e$ | $C_{Cl}(M)$ | $D_{PAR}$ |
|---|---|---|
| 4.12 | $1.5 \cdot 10^{-1}$ | 111 |
| 4.34 | $10^{-1}$ | 117 |
| 4.16 | $8 \cdot 10^{-2}$ | 111 |
| 3.92 | $6 \cdot 10^{-2}$ | 111 |
| 3.84 | $4 \cdot 10^{-2}$ | 117 |
| 3.74 | $2 \cdot 10^{-2}$ | 111 |

The distribution coefficient of the $H_2L$ species of PAR as a function of the TOMACl concentration of the organic phase was investigated ($c^0_{PAR} = 10^{-3}$ *M*; $c_{Cl} = 10^{-1}$ *M*, $pH_{equ} =$ $= 2.57$ and 3.35). The concentration of TOMACl was varied in the $4 \cdot 10^{-3}$–$10^{-2}$ *M* range. Results are shown in Table II.

**Table II**

*Distribution coefficient of PAR at various TOMACl concentrations in the organic phase*

| $pH_e$ | $10^3 \cdot c_{TOMACl}$ (M) | $\lg D_{PAR}$ |
|---|---|---|
| 2.57 | 3.83 | 1.19 |
| 2.57 | 4.82 | 1.25 |
| 2.57 | 5.81 | 1.32 |
| 2.57 | 9.8 | 1.49 |
| 3.34 | 4 | 1.61 |
| 3.34 | 6 | 1.74 |
| 3.33 | 8 | 1.82 |
| 3.31 | 10 | 1.90 |

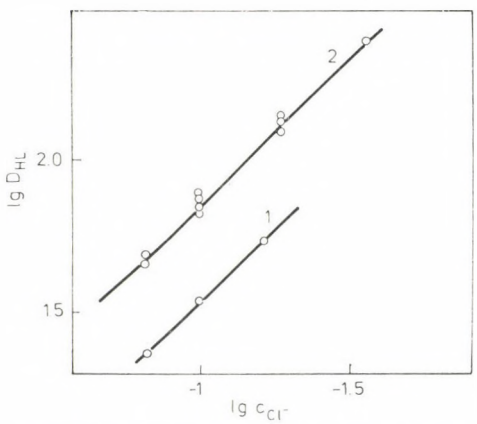



*Fig. 2.* Distribution coefficient of the $HL^-$ species of PAR as the function of the equilibrium chloride ion concentration in the aqueous phase. 1. $C^0_{PAR} = 8.85 \cdot 10^{-4}$ *M*; $C_{TOMACl} = 4.14 \cdot 10^{-3}$ *M*, pH = 9.9–10.3; 2. $C^0_{PAR} = 1.77 \cdot 10^{-3}$ *M*, $C_{TOMACl} = 8.3 \cdot 10^{-3}$ *M*, pH = 6.9–9.5

3. Investigations on the distribution coefficient of PAR in the aqueous solution–chloroform–TOMACl system at pH > 7.

At and above pH 7 PAR is present as $HL^-$ in the aqueous phase. Absorption spectra of the organic phase taken after the extraction step revealed that the absorption maxima were at 400 nm, i.e. the $HL^-$ species of PAR was present in the organic phase as well. The distribution coefficient as a function of the equilibrium chloride ion concentration in the aqueous phase at two different TOMACl concentrations ($4.14 \cdot 10^{-3}$ *M* and $8.3 \cdot 10^{-3}$ *M*) was also determined. Results obtained are shown in Fig. 2. The slopes of both lines were equal to −0.94. Thus, there is a direct proportionality between increasing chloride concentration and decreasing distribution coefficient values.

Changes of the distribution coefficient of PAR above pH 7 as the function of TOMACl concentrations were also studied. The PAR and chloride concentrations of the solutions were constant ($8.85 \cdot 10^{-4}$ *M* and $10^{-1}$ *M*, respectively), the equilibrium pH and the TOMACl concentration in chloroform were varied between 9.8 and 10.2 and $2 \cdot 10^{-3}$ and $10^{-2}$ *M*, respectively. Results are shown in Fig. 3. The slope of the line obtained is 1.0.

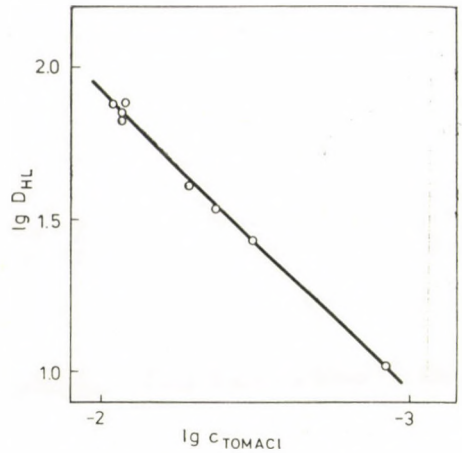



*Fig. 3.* Distribution coefficient of the $HL^-$ species of PAR as the function of the TOMACl concentration of the organic phase. $C^0_{PAR} = 8.85 \cdot 10^{-4}$ M; $C_{KCl} = 10^{-1}$ M; pH = 9.8–10.2

## Discussion

1. Distribution of PAR in the aqueous solution–chloroform system.

In the course of the chloroform extraction step the neutral, $H_2L$ species of PAR is distributed between the two phases. The distribution constant is obtained as

$$d_{H_2L} = \frac{(H_2L)}{[H_2L]} \tag{2}$$

where parentheses and brackets relate to the organic and aqueous phases, respectively.

The side-reaction, the protonation of PAR is accounted for by the so-called $\alpha_{H_2L/H/}$ function as

$$\alpha_{H_2L/H/} = \frac{C_{PAR}}{[H_2L]} = 1 + K_3[H] + \frac{1}{K_2[H]} + \frac{1}{K_1K_2[H]^2} \tag{3}$$

where $K_1$, $K_2$ and $K_3$ are the protonation constants of ligand $L^{2-}$ (lg $K_1 = 11.9$; lg $K_2 = 5.6$; lg $K_3 = 3.1$ [4] and $C_{PAR}$ is the total concentration of PAR in the aqueous phase. Thus, the distribution coefficient of PAR becomes

$$D_{1PAR} = \frac{(H_2L)}{C_{PAR}} = \frac{d_{H_2L}}{\alpha_{H_2L/H/}} \tag{4}$$

or in logarithmic form

$$\lg D_{1PAR} = \lg d_{H_2L} - \lg \alpha_{H_2L/H/} \tag{5}$$

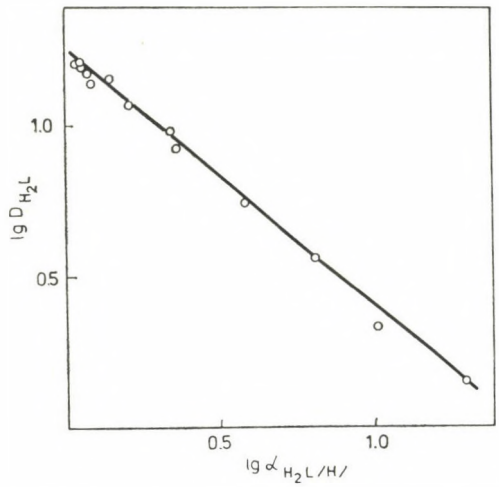



*Fig. 4.* Distribution coefficient of the $H_2L$ species of PAR in the water–chloroform system as the function of $\alpha_{H_2L/H/}$ calculated from the equilibrium pH of the aqueous phase

$\lg D_{1PAR}$ as the function of $\lg \alpha_{H_2L/H/}$ is plotted in Fig. 4. The least square method was used to obtain the intercept yielding the $\lg d_{H_2L} = 1.25 \pm 0.01$ ($I = 0.1$) value.

2. Distribution of PAR in the aqueous solution–chloroform–TOMACl system.

It can be seen from Table II that the distribution coefficient depends on the TOMACl concentration of the organic phase. It can be concluded that in the course of the TOMACl–chloroform extraction step PAR associates with the quaternary ammonium salt as $H_2L$ species. The association reaction assumed to take place is

$$R_4NCl + HCl \rightleftharpoons R_4NCl \cdot H_2L \tag{6}$$

The equilibrium constant of the above association reaction is

$$K_A = \frac{(R_4NCl \cdot H_2L)}{(R_4NCl) \cdot [H_2L]} \tag{7}$$

Thus, the distribution coefficient of PAR becomes

$$D_{PAR} = \frac{(H_2L) + (R_4NCl \cdot H_2L)}{C_{PAR}} = \frac{d_{H_2L}}{\alpha_{H_2L/H/}} + \frac{K_A(R_4NCl)}{\alpha_{H_2L/H/}} = D_{1PAR} + D_{2PAR} \tag{8}$$

The value of D in Eq. (8) can be obtained from the results of the distribution experiments carried out with TOMACl–chloroform. $D_{1PAR}$ is calculated

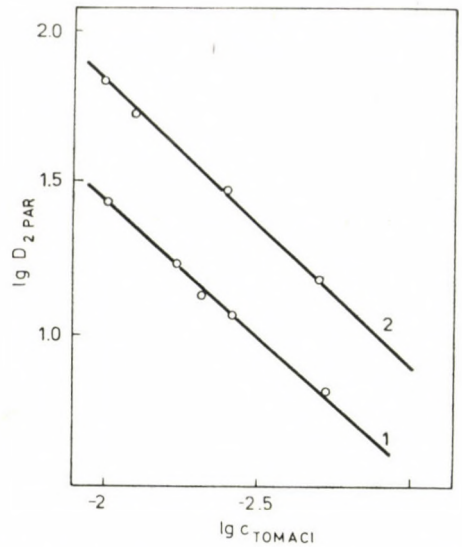



*Fig. 5.* Distribution coefficient of the $H_2L$ species of PAR as the function of the TOMACl concentration of the organic phase. 1. $pH_e = 2.57$; 2. $pH_e = 3.35$; $C^0_{PAR} = 10^{-3}$ *M*, $C_{KCl} = 10^{-1}$ *M*

by Eq. (4) at a given pH from the previously obtained $d_{H_2L}$ value. Once $D_{1PAR}$ is known $D_{2PAR}$ can also be obtained from Eq. (8). The association coefficient, $K_A$ can also be calculated from known $D_{2PAR}$ and TOMACl concentration (in the organic phase) values as

$$K_A = \frac{D_{2PAR} \cdot \alpha_{H_2L/H/}}{(R_4NCl)} \tag{9}$$

To obtain the equilibrium constant of the association reaction calculated $\lg D_{2PAR}$ values were plotted in Fig. 5 as the function of $\lg (R_4NCl)$.

The least square method was used to determine the constants of the linear relationship

$$\lg K'_A = \lg K_A - \lg \alpha_{H_2L/H/} \tag{10}$$

yielding $\lg K_A$. The slope and the intercept values of line 1 in Fig. 5 are $\tan \alpha = 0.88 \pm 0.03$ and $\lg K'_A = 3.18 \pm 0.07$. At equilibrium pH 2.57 one calculates $\lg \alpha_{H_2L/H/} = 0.64$ so $\lg K_A$ becomes $3.82 \pm 0.07$.

The slope and intercept values of Line 2 in Fig. 5 are $0.92 \pm 0.02$ and $3.68 \pm 0.05$ resulting in $\lg K'_A = 3.68 \pm 0.05$ and $\lg \alpha_{H_2L/H/} = 0.19$, which in turn yielded $\lg K_A = 3.87 \pm 0.05$.

3. Distribution of PAR above pH 7 in the aqueous solution–chloroform–TOMACl system.

Experimental results shown above prove that the assumed ion-exchange reaction between the $HL^-$ species of PAR and TOMACl indeed takes place around pH 10 as

$$R_4NCl + HL^- \rightleftharpoons R_4NHL + Cl^- \tag{11}$$

The equilibrium constant of the ion-exchange reaction is

$$K^X = \frac{(R_4NHL)\ [Cl]}{(R_4NCl)\ [HL]} \tag{12}$$

The distribution coefficient, $D_{HL}$ becomes

$$D_{HL} = \frac{(R_4NHL)}{[HL]} \tag{13}$$

The overall concentration of TOMACl ($Q_T$) is

$$Q_T = (R_4NCl) + (R_4NHL) \tag{14}$$

Thus Eq. (12) can be rewritten as

$$K^X = \frac{D_{HL}\ [Cl]}{(R_4NCl)} \tag{15}$$

At constant, $10^{-1}\ M$ chloride ion concentration the term ($\lg K^X - \lg [Cl]$) is constant so the logarithmic form of Eq. (15) rearranged for the distribution coefficient becomes

$$\lg D_{HL} = \lg K^X - \lg [Cl] + \lg (R_4NCl) \tag{16}$$

This means that the intercept of the line plotted in Fig. 2 yields the ($\lg K^X - \lg [Cl]$) value: ($\lg K^X - \lg [Cl]$) $= 3.95 \pm 0.06$ Since $\lg [Cl] = -1$, $\lg K^X = 2.95$.

Results obtained in the experiments changing the chloride concentrations were similarily evaluated and the intercepts of the $\lg D_{HL} - \lg C_{Cl}$ lines were obtained. For Line 1:

$\lg K^X + \lg (R_4NCl) = 0.61 \pm 0.02$
$\lg (R_4NCl) = -2.38$, so
$\lg K^X = 2.99$.

For Line 2:

$\lg K^X + \lg (R_4NCl) = 0.91 \pm 0.04$
$\lg (R_4NCl) = -2.08$ so
$\lg K^X = 2.99$.

## REFERENCES

[1] PAPP, E., INCZÉDY, J.: J. Chromatog. **102,** 225–233 (1974)
[2] TAICHI SATO, HIROSHI WATANABE, SHOJI KIKUCHI: J. appl. Chem. Biotechnol. **25,** 63–72 (1975)
[3] POLLARD, F. H., NICKLESS, G., SAMUELSON, T. J., ANDERSON, R. G.: J. Chromatog., **16,** 233—34 (1964)
[4] FLASCHKA, H. A., BARNARD, A. J.: Chelates in Analytical Chemistry. Vol 4. Marcel Dekker, Inc. (1972)

E. PAPP
János INCZÉDY
H-8201 Veszprém

*Acta Chimica Academiae Scientiarum Hungaricae, Tomus 98. (4), pp. 439—446 (1978)*

# INVESTIGATIONS ON MERCURY(II)-PAN COMPLEXES

## INDIRECT PHOTOMETRIC DETERMINATION OF CHLORIDE ION

Z. PUCHONY and J. INCZÉDY

*(Department of Analytical Chemistry, University of Chemical Engineering, Veszprém)*

Received December 23, 1977

Formation of the Hg(II)-PAN complex was studied by extraction and direct photometric methods in homogeneous phase. The composition of the complex extracted with carbon tetrachloride was found to be $HgL_2$, its extraction equilibrium constant, $\lg K^e = 1.58$.

In 1 : 1 ethanol : water mixtures the composition of the complex formed is 1 : 1 and 1 : 2 at pH $< 4$ and pH $> 6$, respectively. The conditional stability constants of the complexes were also obtained.

The formation of the $HgL^+$ complex is inhibited in the presence of halogenide ions. This phenomenon can be used for the indirect spectrophotometric determination of chloride ions in the $10^{-5}—6 \cdot 10^{-5}$ $MCl^-/l$ concentration range.

Mercury(II)ions and 1-(2-pyridilazo)-2-naphtol (PAN) form an intensive red complex which is insoluble in water but readily soluble in organic solvents such as ethanol, chloroform or carbon tetrachloride. It is known that the complexes formed at pH 6 or above can be readily extracted from aqueous solutions. SHIBATA [1] and LI *et al.* [2] used chloroform to extract the complex at pH 6.0—7.5 and 7.5—11.5 respectively. PÜSCHEL [3] used a 1 : 4 methanol : chloroform mixture to extract the complex from aqueous solutions at pH 10.

According to our experiences a reaction takes place between mercury(II) and PAN in slightly acidic solutions, and under certain conditions the complex can be extracted into the organic phase at pH 6 or even below. According to LI *et al.* [2] the composition of the complex is 1 : 1 at and above pH 6. According to our experiences the composition of the extractable complex is always 1 : 2. In homogeneous phase, depending on the pH of the solution, the composition of the complex can be 1 : 1 and 1 : 2.

The determination of the conditions of the Hg(II)–PAN complex formation and the analytical application of this complex formation for the indirect photometric determination of chloride ions were the aims of this investigation.

Extraction experiments were carried out to determine the composition of the extractable complex. The distribution coefficient of the metal ion as a function of pH at constant reagent concentrations and as a function of reagent concentrations at constant pH were determined.

The effect of pH on the extent of light absorption of the complex was studied in a homogeneous phase, in a 1 : 1 mixture of ethanol and water.

The composition of the complexes formed was determined by simple photometric methods (by the continuous variations and molar ratios methods). The apparent stability constants of the complexes were determined from the photometric data.

## Experimental

Chemicals and solutions. (Chemicals, unless indicated otherwise, were reagent grade.) $10^{-1}$ mole/l stock solution of mercury(II)-nitrate. The stock solution was prepared according to SCHULEK [4] by dissolving pure mercury in nitric acid.

PAN (Reanal, Hungary) was purified by recrystallization from ethanol. No coloured contaminant was found in the recrystallized product by paper chromatography [5]. The melting point of the recrystallized product was 140—141 °C. The effective reagent content of the product determined by photometric titration was 99.2% [6].

$10^{-2}$ and $2 \cdot 10^{-3}$ mole/l ethanol and carbon tetrachloride PAN solutions: 2.513 g and 0.503 g of PAN were dissolved and brought to 1 liter in ethanol and carbon tetrachloride, respectively. Freshly distilled carbon tetrachloride was used.

0.1 mole/l potassium dihydrogen phosphate and 0.05 mole/l borax solution were used to prepare the buffer solutions. Measurements were carried out on a recording spectrophotometer, Type Specord UV-VIS (Zeiss, GDR); a spectrophotometer Type Spektromom 202 (MOM, Hungary) and a pH meter Type pH 25 (Radiometer, Denmark).

### Distribution experiments

Nitric acid was added to the $10^{-4}$ mole/l $Hg(NO_3)_2$ solution to change its pH. Equal volumes of $2 \cdot 10^{-3}$ mole/l PAN solutions in carbon tetrachloride were used to extract for 3 minutes the mercury ion containing solutions.

In another series of experiments 10.0 ml of $5 \cdot 10^{-5}$ mole/l, pH 2.35 $Hg(NO_3)_2$ solutions were extracted for 3 minutes by equal volumes of carbon tetrachloride containing different amounts of PAN.

The phases were separated after centrifugation. Both equilibrium pH and metal ion concentration values were determined in the aqueous phase. Metal ion concentrations were determined spectrophotometrically using dithizone as a photometric reagent [7]. The results are shown in Figs 1 and 2.

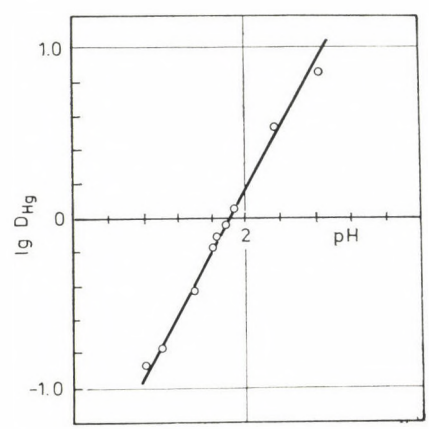



*Fig. 1.* Logarithm of the distribution coefficient of mercury(II) ions as a function of pH (in 1.0—3.0 range) in carbon tetrachloride–water system; $C_{Hg} = 10^{-4}$ *M*; $C^0_{PAN} = 2 \cdot 10^{-3}$ *M*; $I \simeq 0.1$ ($KNO_3$)

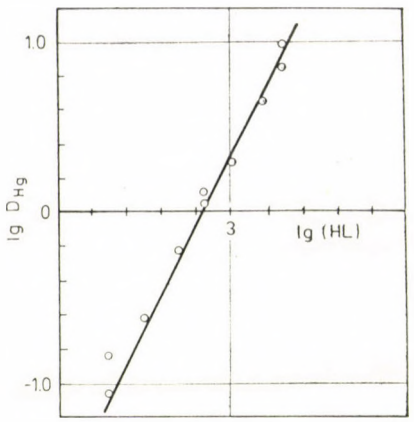



*Fig. 2.* Logarithm of the distribution coefficient of mercury(II) ions as a function of the logarithm of the reagent concentration (in $10^{-2}$—$10^{-4}$ range) in carbon tetrachloride–water system: $C_{Hg} = 5 \cdot 10^{-5}$ *M*; pH = 2.36; I ≃ 0.1 ($KNO_3$)

**The effects of pH on the Hg(II)-PAN complex formation in 1 : 1 ethanol: water mixtures with and without halogenide ions**

1 *M* potassium hydroxide was added from a microburette to 50.0 ml solution containing $5 \cdot 10^{-5}$ *M* $Hg(NO_3)_2$, $10^{-3}$ *M* PAN and $10^{-1}$ *M* $HNO_3$ and 50% v/v ethanol. Light absorption ($A_1$) at 555 nm and the pH of these solutions were determined. In another experimental series the original solution contained chloride, bromide or iodide ions at a concentration of $10^{-4}$ mole/l. A glass–calomel electrode pair calibrated with aqueous buffers was used for the pH measurement.

A potassium nitrate bridge was used to prevent the contamination of the solution with chloride. Changes of the light absorption of the reagent ($A_2$) as a function of pH, but with no metal ion present in the solution were also determined. The difference, $\Delta A = A_1 - A_2$ as a function of pH with and without halogenide ions is plotted in Fig. 3.

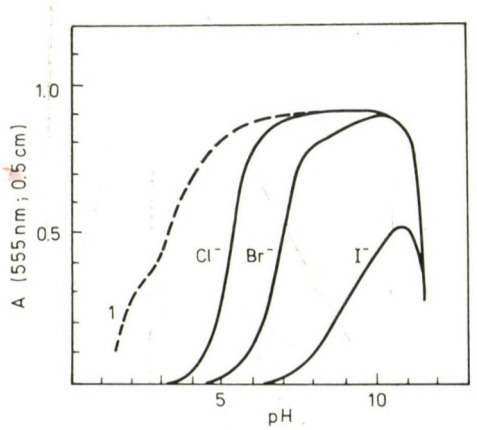



*Fig. 3.* Absorbance of the mercury(II)-PAN complex as a function of pH: $C_{Hg} = 5.10^{-5}$ *M*; $C_{PAN} = 10^{-3}$ *M*, $[Cl^-] = [Br^-] = [I^-] = 10^{-4}$ *M*; (1)---- without halogenide ion

**Investigations on the complex formation by the continuous variations (JOB's) method [8]**

Solutions containing Hg(II) ions and PAN at a $10^{-4}$ mole/l overall concentration level but varying molar ratios were brought to pH 2.35 by adding nitric acid. The solutions contained 50% v/v ethanol as well. The absorption spectra of the solutions in the visible range were taken and the JOB-plots, shown in Fig. 4 were constructed using two wavelengths selected according to the spectra taken. A series of complex containing solutions buffered to pH 9.7 with borax-potassium dihydrogen phosphate were prepared and their spectra taken. The curve shown in Fig. 5 was constructed from these spectra. Spectra of the complexes in basic solutions were taken within 4 minutes after the constituents were mixed, because the complex decomposed relatively rapidly.

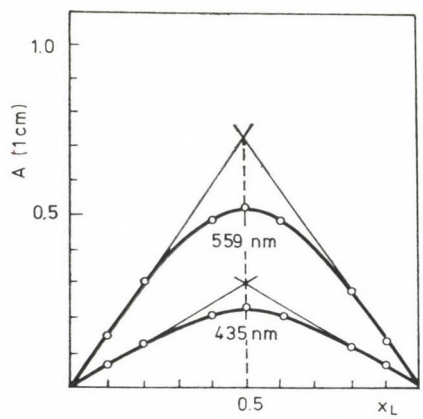



*Fig. 4.* Determination of the composition of the mercury(II)-PAN complex by the continuous variations method in 1 : 1 ethanol–water mixture at pH 2.35; overall concentration: $1 \cdot 10^{-4}$ *M*

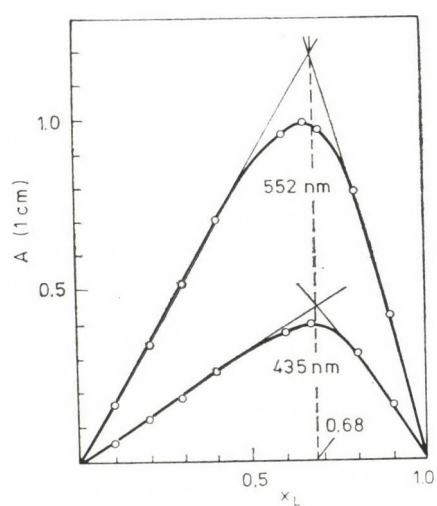



*Fig. 5.* Determination of the composition of the mercury(II)-PAN complex by the continuous variations method in 1 : 1 ethanol–water mixture at pH 9.70; overall concentration: $1 \cdot 10^{-4}$ *M*

**Investigations on the complex formation by the molar-ratio method**

The amount of reactant added to the $10^{-4}$ mole/l Hg(II) solutions containing 50% v/v ethanol was changed. pH was adjusted to 2.30 and 9.5 with nitric acid and borax-phosphate buffer, respectively. Light absorption of the solutions as a function of the ligand : metal ion ratio is plotted in Fig 6.

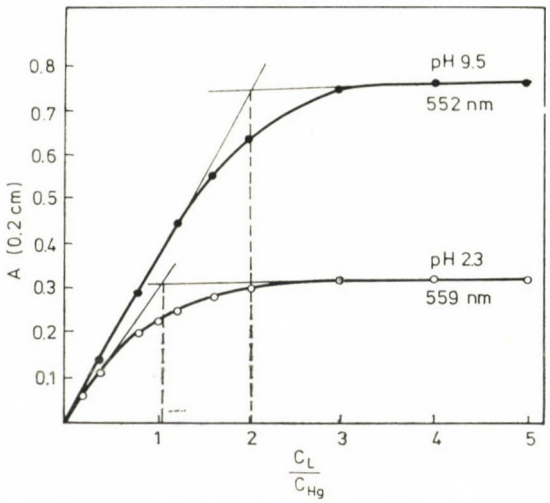



*Fig. 6.* Determination of the composition of the mercury(II)-PAN complex by the molar ratios method in 1 : 1 ethanol–water mixture: $C_{Hg} = 10^{-4}$ *M*

## Discussion

The reaction assumed to take place in the course of the extraction of the Hg(II)–PAN complex with organic solvents is shown below:

$$Hg^{2+}_{aq} + 2HL_{org} \rightleftharpoons HgL_{2org} + 2\,H^{+}_{aq} \qquad (1)$$

where subscripts aq and org refer to the aqueous and organic phase, respectively. This means that the composition of the complex which can be extracted is always 1 : 2. The equilibrium constant of the extraction process can be written as:

$$K^e = \frac{(HgL_2)\,[H^+]^2}{[Hg^{2+}]\,(HL)^2} \qquad (2)$$

where brackets and parentheses denote the concentrations in the aqueous and organic phase, respectively.

The distribution coefficient of the metal ion is

$$\lg D_{Hg} = \lg \frac{(HgL_2)}{[Hg^{2+}]} = \lg K^e + 2 \lg (HL) + 2\,pH \qquad (3)$$

According to Eq. 3 the slopes of both the lg $D_{Hg}$ *vs.* pH and lg $D_{Hg}$ *vs.* lg HL lines are +2. The slopes of the lines shown in Figs 1 and 2 are close to 2 indicating that indeed the reaction shown here takes place. It can be concluded that independently from the equilibrium pH of the aqueous phase between pH 2 and 9 the composition of the complex extracted in the presence of excess reagent is always $HgL_2$. This conclusion is further supported by the fact that the spectrum of the extracted complex is always identical, independently from the pH of the aqueous phase. The absorption maximum occurs at 565 nm (using $CCl_4$ as a solvent).

The extraction equilibrium constant calculated from the experimental data is $\lg K^e = 1.58$ in the case of the carbon tetrachloride–water system.

Experiments carried out in a homogeneous phase using 1 : 1 v/v ethanol : water mixtures demonstrate that the composition of the complex depends on the pH value of the aqueous phase. The composition of the complex is 1 : 1 below pH 4 and 1 : 2 above pH 6. The absorbance of the complex as function of the wavelength is shown by Curve 1 in Figure 3. There is a slight change in the slope of the curve at pH 3 and the absorbance becomes constant in the pH range between 7 and 10.

The spectra of the complexes produced in acidic and basic solutions are dissimilar. The absorption maximum of the complex at pH 2.3 is at 559 nm while at pH 9.7 there are two maxima at 517 and 552 nm.

The number of ligands in the complex can be obtained from the mole fraction of the ligand ($X_L$) at the maximum point of the JOB curves. It was found that the maxima of the curves in the pH 2.5–3.5 range occurred at $X_L = 0.5$, i.e. the composition of the complex formed was 1 : 1 $HgL^+$ while in the pH 9–10 range the maximum was shifted to $X_L = 0.68$ indicating that the $HgL_2$ complex was formed. The same conclusion can be arrived at by the method of mole-ratios, i.e. the composition of the complex being $HgL^+$ and $HgL_2$ in the pH range 2–3 and 9–10, respectively, since the intercepts of the tangents of the linear portions of the curves shown in Fig. 6 are at a mole ratio of 1 : 1 and 1 : 2 metal ion : ligand in solutions of pH 2.3 and 9.5, respectively.

The conditional stability constant of the complex calculated from the JOB curves in 1 : 1 ethanol : water mixtures are:

$$\lg \beta_1' = 5.2 \pm 0.1 \qquad \text{(at pH 2.35)}$$
$$\lg \beta_2' = 10.3 \pm 0.1 \qquad \text{(at pH 9.70)}$$

The formation conditions of the $HgL^+$ complex can be well defined, so the true equilibrium constant can also be obtained. In acidic solutions below pH 3 the hydroxo-complex formation of Hg(II) is negligible ($\alpha_{Hg(OH)} \approx 1$) and the only side reaction to be considered is the protonation of the ligand ($\alpha_{L(H)}$).

The protonation constants of the ligand in 1 : 1 ethanol : water mixtures were obtained spectrophotometrically [8] as $\lg K_1 = 12.3$ and $\lg K_2 = 1.9$. The calculated value of $\lg \alpha_{L(H)}$ at pH 2.35 was 10.2. Thus, according to the relationship

$$\beta_1' = \frac{\beta_1}{\alpha_{L(H)}},$$

the value of the true equilibrium constant at an ionic strength of 0.02 was found to be $\lg \beta_1 = 15.4$.

### Indirect spectrophotometric determination of chloride ions

Experimental results shown in Fig. 3 indicate that in homogeneous phase the composition of the $[Hg(PAN)]^+$ complex at pH 2–3 in the presence of halogenide ions is changed and a more stable halogeno-complex is formed. Formation of $Hg(PAN)_2$ is inhibited in the presence of bromide or iodide ions. According to the experimental results the decrease of the absorbance of the $[Hg(PAN)]^+$ complex at pH 2.0–3.5 caused by halogenide ions can be used to determine the concentration of chloride ions present.

The reagents used were:

$5 \cdot 10^{-3}$ *M* $Hg(NO_3)_2$ solution

$10^{-1}$ *M* $HNO_3$

$10^{-2}$ *M* PAN in ethanol

Ethanol

10 $\mu$g/ml NaCl solution prepared by weighing 0.1649 g freshly heated NaCl and dissolving it in 100 ml water. 10 ml of this solution was successively diluted 100-folds.

The calibration curve:

20.0 ml $5 \cdot 10^{-3}$ *M* $Hg(NO_3)_2$ solution, 25.0 ml $10^{-1}$ *M* nitric acid, 90.0 ml ethanol and 10.00 ml $10^{-2}$ *M* PAN in ethanol were mixed. 15.00 ml of this stock solution were pipetted into 25 ml volumetric flasks and 0–6 ml of the 10 $\mu$g/ml chloride ion stock solution were added. The solutions were diluted to 20–22 ml with deionized water. The flasks were cooled to ambient temperature in about 10 minutes then they were brought to mark (pH 2.20).

The reference solution:

2.5 ml $10^{-1}$ *M* nitric acid, 9.0 ml ethanol, 1.0 ml $10^{-2}$ *M* PAN in ethanol were pipetted into a 25 ml volumetric flask and the mixture was diluted to mark with deionized water. The absorbance of the solutions containing known amounts of chloride was measured at 559 nm against the reference blank solution. The calibration curve is shown in Fig. 7. The colour developed is stable for at least 3 hours.

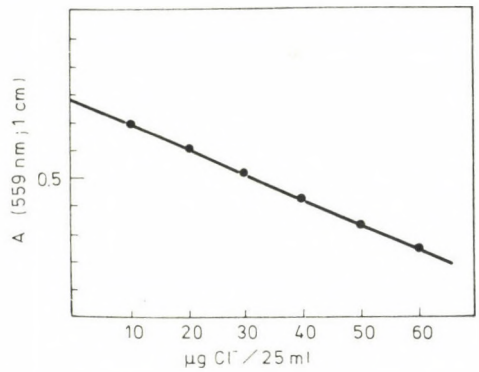



*Fig. 7.* Calibration curve for the spectrophotometric determination of chloride ion: $C_{Hg} = 5 \cdot 10^{-5}$ *M*; $C_{PAN} = 4 \cdot 10^{-4}$ *M*; 40° v/v% ethanol–water; pH = 2.2

The relative error of the determination at intermediate chloride concentrations (40 $\mu$g/25 ml) is $\pm$ 5% providing the pH is controlled to $\pm$ 0.05.

Anions forming stable mercury complexes (bromide, iodide, sulfide, etc.) and Cu(II) ions disturb the determinations. The molar absorbance calculated from the decrease of the absorbance values is $\varepsilon = 7.9 \cdot 10^3$.

This method is more sensitive than the mercury thiocyanate–Fe(III) system, ($\varepsilon = 2 \cdot 10^3$ absorbance units), but is less sensitive than the methylred oxidation method ($\varepsilon = 1.17 \cdot 10^4$) [7]. However, the method presented here is considerably simpler than the methylred one.

## REFERENCES

[1] Püschel, R.: Z. Anal. Chim. 221, 132 (1966)
[2] Shibata, S.: Anal. Chim. Acta **23,** 367 (1960); **25,** 348 (1961)
[3] Li, S. H., Ching, N. K., Ching, S. S., Wu, C.: Chem. Bull. Peking 250, 253 (1965)
[4] Schulek E., Szabó Z.: A kvantitatív analitikai kémia elvi alapjai és módszerei. Tankönyvkiadó, Budapest 1966
[5] Pollard, F. H., Nickless, G., Samuelson, T. J.: J. Chromatog. **16,** 231 (1964)
[6] Pease, B. F., Williams, M. B.: Anal. Chem. **31,** 1044 (1959)
[7] Marczenko, Z.: Spectrophotometric determination of elements. J. Wiley, New York 1976
[8] Inczédy, J.: Analytical Applications of Complex Equilibria. Akadémiai Kiadó, Budapest 1976

Z. Puchony
János Inczédy
} H-8201 Veszprém

*Acta Chimica Academiae Scientiarum Hungaricae, Tomus 98 (4), pp. 447—455 (1978)*

# KINETICS OF THE PERKOW REACTION

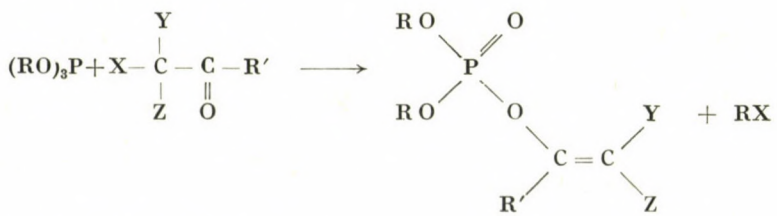
I. PETNEHÁZY, Gy. SZAKÁL, K. RUSZ and L. TŐKE

*(Institute of Organic Chemical Technology, Technical University, Budapest)*

Received July 20, 1977

A rapid, accurate and highly sensitive kinetical investigation method, not applied heretofore, has been developed for the Perkow reaction. The solvent effect and the dependence on the temperature were examined and the enthalpies and entropies activation were calculated. The solution of the Hammett equation indicated nucleophilic substitution reaction by the trivalent phosphorus compound.

The Perkow reaction occurs between α-halogen carbonyl compounds and trialkyl phosphites yielding phosphoric acid dialkyl-vinyl-esters. The general reaction scheme is:



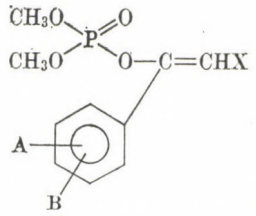
where R = methyl, ethyl, etc.
X = chlorine, bromine, iodine
Y, Z = halogen, H, alkyl, etc.
R′ = alkyl, aryl, etc.

The reaction often takes place concomitant with the process yielding 0,0-dialkyl-β-oxophosphonates, known as Arbuzov reaction. The direction of the reaction is determined by both the nature of the substituents and the reaction conditions [1]. The reactions of α-chloro-acetophenones and α,α-dichloro-acetophenones with trialkyl phosphites results in formation of vinyl phosphates only [2]. In the reaction of α,α-dichloro-acetophenones two geometrical isomers, Z- and E-vinyl-phosphate can be formed.

Kinetics of these reactions have been studied by ARCORIA. He applied classical analytical methods (precipitation titration) and determined reaction kinetical data for the reaction of various α-chloro-acetophenones and triethyl phosphite [3]. GAYDOU examined the kinetics of the Perkow reaction and the catalytic effect of acids and tertiary amine bases in different solvents [4].

**Table I**

*Summary of the preparation of vinyl phosphates*




| No. | Product vinyl phosphates | | | Reaction temp., °C | Solvent | Reaction time, h | Yield, % | Experimental data of the product | |
|---|---|---|---|---|---|---|---|---|---|
| | A | B | X | | | | | B.p., °C/torr | $n_D^{25}$ |
| 1 | H | H | H | 81 | benzene | 1 | 95 | 135—140/0.5 | 1.5110 |
| 2 | 4-Me | H | H | 100 | toluene | 4.5 | 92 | 158—162/0.5—0.6 | 1.5143 |
| 3 | 4-Et | H | H | 100 | toluene | 11 | 85 | 150—156/0.3—0.4 | 1.5130 |
| 4 | 4-Cl | H | H | 81 | benzene | 1 | 83 | 157—163/0.4—0.6 | 1.5270 |
| 5 | 4-Br | H | H | 100 | toluene | 1 | 81 | 142—144/0.2—0.3 | 1.5223 |
| 6 | 4-$NO_2$ | H | H | 40 | benzene | 1 | 93 | 160—162/0.3—0.4 | 1.5175 |
| 7 | 2-Me | 4-Me | H | 81 | benzene | 22.5 | 74.2 | 163—170/0.8—1.3 | 1.5075 |
| 8* | 2-Me | 5-Me | H | 110 | toluene | 14.5 | 95 | 142—150/0.7—0.8 | 1.5064 |
| 9* | 3-Me | 4-Me | H | 110 | toluene | 4.5 | 62 | 182—186/0.8 | 1.5140 |
| 10 | 2-Cl | 4-Cl | H | 80 | benzene | 1 | 84.2 | 155—160/0.5 | 1.5300 |
| 11 | 3-Cl | 4-Cl | H | 80 | benzene | 1 | 82 | 152—156/0.2 | 1.5295 |
| 12 | 2-Cl | 5-Cl | H | 80 | benzene | 1 | 88.4 | 144—156/1.2 | 1.5259 |
| 13 | H | H | Cl | 60 | benzene | 1.5 | 87 | 137/0.7 | 1.5110 |
| 14 | 4-Me | H | Cl | 80 | benzene | 1.5 | 85 | 144/0.1 | 1.5228 |
| 15* | 4-Et | H | Cl | 80 | benzene | 1.5 | 80 | 150—155/0.15 | 1.5210 |
| 16* | 4-Br | H | Cl | 60 | benzene | 1 | 47 | 150—155/0.2 | 1.5300 |
| 17* | 4-Cl | H | Cl | 60 | benzene | 1 | 91 | 138—140/0.25 | — |
| 18* | 4-$NO_2$ | H | Cl | 40 | benzene | 1 | 85 | 195—197/0.2—0.3 | 1.5499 |

Compounds denoted by an asterisk are new ones.

In their studies, UV and NMR methods were employed. Other researchers measured the methyl chloride formed, using photometric methods [5], or the PMR spectrum of the product was utilized for determining the concentration [6].

These studies gave kinetic data for a single model compound only [5], or resulted additional data regarding the nucleophilicities of phosphites [6].

In the present work, the reactions of various α-chloro-acetophenones and α,α-dichloro-acetophenones were examined with trialkyl phosphite reagent. Characteristic data for the model reactions are summarized in Table I.

The reaction was studied by a gas chromatographic method developed for this purpose. The reaction kinetic data were calculated from the concentration of the chloro-acetophenone determined gas chromatographically.

Instantaneous stopping of the reaction was achieved by the decomposition of the non-reacted trialkyl phosphite, that is, by hydrolysis with aqueous hydrochloric acid. Thus, in certain cases, the vinyl phosphate product also decomposed, and this facilitated gas chromatographic analysis.

The reactions were carried out with both an excess (twenty-fold) and with equimolecular amount of trimethyl phosphite. The pseudo-first order rate constants obtained in the first case were transformed into second order constants and these were found to be the same as calculated for the reaction with equimolecular amounts of reactants. The reaction kinetic data are given in Tables II and III.

The reactions of the model compounds were carried out at different temperatures and in aprotic solvents of different dielectric constants. In the graphical representation of the rate equation transformed into the corresponding linear form, the concentration data lied along straight lines, indicating a kinetically second order nature of the reaction and a kinetically first order reaction for α-chloro-acetophenones.

Empirical activation energy values ($E_a$), the activation enthalpies ($\Delta H^*$) and entropies ($\Delta S^*$) were calculated from the temperature dependence of the reaction rate.

It has been found that the rate of the reaction increases with increasing polarity of the solvent. This indicates an intermediate state being more polar than the starting one.

The activation enthalpies (10 – 20 kcal/mole) and the relatively high negative activation entropies (−30 to 50 cal/mole · degree) may be interpreted as indicating a transition state being sterically complex, more ordered and possessing a lower rotational degree of freedom as compared with the starting state. The activation enthalpies of the model compounds vary linearly as a function of the activation entropies, i.e. the transition complex is of the same nature in all cases, the mechanism of the reaction being the same in all model compounds.

**Table II**

*The k values of the ring*

| Model chloro-aceto-phenones | $t$, °C | In toluene | | | In dioxane | | |
|---|---|---|---|---|---|---|---|
| | | $k$ 1/mole · s | $\Delta H^*$ kcal/mole | $\Delta S^*$ cal/deg · mole | $\Delta k$ 1/mole · s | $\Delta H^*$ kcal/mole | $\Delta S^*$ cal/deg · mole |
| α- | 50 | $2.86 \cdot 10^{-5}$ | | | $4.6 \cdot 10^{-5}$ | | |
| | 70 | $1.36 \cdot 10^{-4}$ | 12.6 | — 39.5 | $1.08 \cdot 10^{-4}$ | 10.3 | — 46.9 |
| | 90 | $2.53 \cdot 10^{-4}$ | | | $3.76 \cdot 10^{-4}$ | | |
| 4-Me-α- | 50 | $1.49 \cdot 10^{-5}$ | | | $2.3 \cdot 10^{-5}$ | | |
| | 70 | $8.25 \cdot 10^{-5}$ | 13.05 | — 39.4 | $6.44 \cdot 10^{-5}$ | 9.8 | — 48.9 |
| | 90 | $1.13 \cdot 10^{-4}$ | | | $1.54 \cdot 10^{-4}$ | | |
| 4-Et-α- | 50 | $1.34 \cdot 10^{-5}$ | | | $1.73 \cdot 10^{-5}$ | | |
| | 70 | $6.05 \cdot 10^{-5}$ | 13.05 | — 40.4 | $5.28 \cdot 10^{-5}$ | 10.3 | — 48.3 |
| | 90 | $1.53 \cdot 10^{-4}$ | | | $1.25 \cdot 10^{-4}$ | | |
| 4-Cl-α- | 50 | $8.00 \cdot 10^{-5}$ | | | $1.24 \cdot 10^{-4}$ | | |
| | 70 | $2.97 \cdot 10^{-4}$ | 12.1 | — 38.8 | $2.49 \cdot 10^{-4}$ | 11.65 | — 41.3 |
| | 90 | $8.08 \cdot 10^{-4}$ | | | $1.24 \cdot 10^{-3}$ | | |
| 4-Br-α- | 50 | $7.3 \cdot 10^{-5}$ | | | $7.85 \cdot 10^{-5}$ | | |
| | 70 | $2.8 \cdot 10^{-4}$ | 12.35 | — 39.0 | $2.18 \cdot 10^{-4}$ | 11.65 | — 41.5 |
| | 90 | $1.03 \cdot 10^{-3}$ | | | $7.65 \cdot 10^{-4}$ | | |
| 4-$NO_2$-α- | 30 | $4.36 \cdot 10^{-4}$ | | | $8.05 \cdot 10^{-4}$ | | |
| | 40 | $6.44 \cdot 10^{-4}$ | 8.55 | — 47.8 | $8.06 \cdot 10^{-4}$ | 1.7 | — 67.8 |
| | 50 | $8.00 \cdot 10^{-4}$ | | | $9.65 \cdot 10^{-4}$ | | |
| | 70 | $2.11 \cdot 10^{-3}$ | | | | | |
| 3,4-di-Me-α- | 50 | $1.68 \cdot 10^{-5}$ | | | $2.84 \cdot 10^{-5}$ | | |
| | 70 | $4.45 \cdot 10^{-5}$ | 13.05 | — 40.6 | $3.91 \cdot 10^{-5}$ | 10.75 | — 47.6 |
| | 90 | $1.13 \cdot 10^{-4}$ | | | $1.07 \cdot 10^{-4}$ | | |
| 2,4-di-Me-α- | 80 | $1.37 \cdot 10^{-5}$ | | | $1.53 \cdot 10^{-5}$ | | |
| | 90 | $2.14 \cdot 10^{-5}$ | 14.4 | — 39.5 | $2.81 \cdot 10^{-5}$ | 12.1 | — 48.5 |
| | 100 | $3.67 \cdot 10^{-5}$ | | | $3.26 \cdot 10^{-5}$ | | |
| 2,5-di-Me-α- | 70 | $5.06 \cdot 10^{-6}$ | | | $6.9 \cdot 10^{-6}$ | | |
| | 80 | $1.26 \cdot 10^{-5}$ | 13.7 | — 42.5 | $1.42 \cdot 10^{-5}$ | 12.1 | — 46.9 |
| | 90 | $1.98 \cdot 10^{-5}$ | | | $2.43 \cdot 10^{-5}$ | | |

A further experience is that the increased nucleophilic power of the reagent enhances the reaction rate (Table IV). In the case of tri-*n*-butyl phosphite, the decrease of the reaction rate can be explained by steric reasons. Thus, the order of reaction rates for the reactions examined is: tri-*n*-butyl phosphite < trimethyl phosphite < triethyl phosphite.

Catalytic amounts of acetic acid accelerated the reactions examined (Table V); this can be explained by increased polarization of the oxo group.

Increase of the number of α-halogen atoms caused a significant rise in the reaction rate (Table VI), which can also be explained by increased electrophilic power of the carbon atom in the oxo group.

*substituted chloro-acetophenones*

| In chlorobenzene | | | In nitrobenzene | | | In benzene |
|---|---|---|---|---|---|---|
| $k$ l/mole · s | $\Delta H^*$ kcal/mole | $\Delta S^*$ cal/deg · mole | $k$ l/mole · s | $\Delta H^*$ kcal/mole | $\Delta S^*$ cal/deg · mole | $k$ l/mole · s |
| $6.39 \cdot 10^{-5}$ | | | $8.17 \cdot 10^{-5}$ | | | $3.2 \cdot 10^{-5}$ |
| $2.28 \cdot 10^{-4}$ | 12.1 | — 40.1 | $3.03 \cdot 10^{-4}$ | 12.6 | — 38.4 | $1.37 \cdot 10^{-4}$ |
| $5.94 \cdot 10^{-4}$ | | | $9.00 \cdot 10^{-4}$ | | | — |
| $4.31 \cdot 10^{-5}$ | | | $6.31 \cdot 10^{-5}$ | | | $1.82 \cdot 10^{-5}$ |
| $1.66 \cdot 10^{-4}$ | 12.6 | — 39.8 | $2.21 \cdot 10^{-4}$ | 12.1 | — 39.8 | $7.1 \cdot 10^{-5}$ |
| $2.64 \cdot 10^{-4}$ | | | $4.89 \cdot 10^{-4}$ | | | — |
| $3.11 \cdot 10^{-5}$ | | | $4.03 \cdot 10^{-5}$ | | | $1.53 \cdot 10^{-5}$ |
| $9.25 \cdot 10^{-5}$ | 12.35 | — 41.2 | $1.56 \cdot 10^{-4}$ | 13.05 | — 38.4 | $5.52 \cdot 10^{-5}$ |
| $3.38 \cdot 10^{-4}$ | | | $5.03 \cdot 10^{-4}$ | | | — |
| $2.03 \cdot 10^{-4}$ | | | $2.68 \cdot 10^{-4}$ | | | $1.13 \cdot 10^{-4}$ |
| $5.75 \cdot 10^{-4}$ | 11.9 | — 38.9 | $8.75 \cdot 10^{-4}$ | 11.65 | — 38.8 | $3.25 \cdot 10^{-4}$ |
| $1.71 \cdot 10^{-3}$ | | | $2.53 \cdot 10^{-3}$ | | | — |
| $2.22 \cdot 10^{-4}$ | | | $3.43 \cdot 10^{-4}$ | | | $8.8 \cdot 10^{-5}$ |
| $6.6 \cdot 10^{-4}$ | 11.65 | — 39.3 | $9.1 \cdot 10^{-4}$ | 11.65 | — 39.3 | $2.51 \cdot 10^{-4}$ |
| $2.07 \cdot 10^{-3}$ | | | $3.32 \cdot 10^{-3}$ | | | — |
| $1.09 \cdot 10^{-3}$ | | | $1.24 \cdot 10^{-3}$ | | | $4.67 \cdot 10^{-4}$ |
| $1.76 \cdot 10^{-3}$ | 7.16 | — 46.1 | $2.04 \cdot 10^{-3}$ | 8.55 | — 43.6 | $8.05 \cdot 10^{-4}$ |
| $2.44 \cdot 10^{-3}$ | | | $3.1 \cdot 10^{-3}$ | | | $1.04 \cdot 10^{-3}$ |
| $3.83 \cdot 10^{-5}$ | | | $6.75 \cdot 10^{-5}$ | | | $2.68 \cdot 10^{-5}$ |
| $8.96 \cdot 10^{-5}$ | 12.1 | — 42.1 | $1.4 \cdot 10^{-4}$ | 13.0 | — 38.4 | $4.98 \cdot 10^{-5}$ |
| $2.14 \cdot 10^{-4}$ | | | $4.11 \cdot 10^{-4}$ | | | — |
| $2.4 \cdot 10^{-5}$ | | | $2.78 \cdot 10^{-5}$ | | | $1.25 \cdot 10^{-5}$ |
| $3.42 \cdot 10^{-5}$ | 9.5 | — 52.3 | $7.7 \cdot 10^{-5}$ | 20.8 | — 20.5 | — |
| $6.06 \cdot 10^{-5}$ | | | $1.53 \cdot 10^{-4}$ | | | — |
| $1.23 \cdot 10^{-5}$ | | | $2.48 \cdot 10^{-5}$ | | | $5.75 \cdot 10^{-6}$ |
| $2.34 \cdot 10^{-5}$ | 16.7 | — 33.0 | $5.42 \cdot 10^{-5}$ | 16.25 | — 32.5 | — |
| $6.38 \cdot 10^{-5}$ | | | $1.15 \cdot 10^{-4}$ | | | — |

Finally, a study of the effect of aromatic substituents has shown that the rate of the reaction is strongly dependent on the nature of the substituents in the aromatic ring of chloro-acetophenone. The reaction constants obtained in the graphical solution of the Hammett equation proved to be positive in all solvents and at all temperatures examined. The value of the constant was slightly lowered by increasing the temperature, but it does not change by changing the polarity of the solvent.

One part of the $k$ values in the tables were calculated also by a computer program. The quality of the lines obtained in a log $k$ *vs.* $\varrho_P$ diagram proved to be excellent as shown by the coefficients $r$ (correlation coefficient)

**Table III**

*Kinetic data of di- and trichloro-acetophenones*

Reagent: trimethyl phosphite
solvent: toluene
$k$ = l/mole · s

| Model chloro-aceto phenones | $k$, at 50 °C | $k$, at 70 °C | $k$, at 90 °C | $\Delta H^*$ kcal/mole | $\Delta S^*$ cal/mole · degree |
|---|---|---|---|---|---|
| α, α,-di | $6.54 \cdot 10^{-4}$ | $1.94 \cdot 10^{-3}$ | $3.43 \cdot 10^{-3}$ | 8.75 | — 45.63 |
| 4-Me-α, α-di | $4.89 \cdot 10^{-4}$ | $8.00 \cdot 10^{-4}$ | $2.11 \cdot 10^{-3}$ | 8.28 | — 48.94 |
| 4-Et-α-α-di | $2.97 \cdot 10^{-4}$ | $6.84 \cdot 10^{-4}$ | $1.35 \cdot 10^{-3}$ | 8.22 | — 49.3 |
| 4-Br-α, α-di | $1.13 \cdot 10^{-3}$ | $2.86 \cdot 10^{-3}$ | $4.29 \cdot 10^{-3}$ | 7.0 | — 50.2 |
| 4-Cl-α, α-di | $1.31 \cdot 10^{-3}$ | $3.22 \cdot 10^{-3}$ | $6.27 \cdot 10^{-3}$ | 8.28 | — 44.69 |
| 4-$NO_2$-α, α-di | $5.66 \cdot 10^{-3}$ | $5.86 \cdot 10^{-2}$ | $1.94 \cdot 10^{-1}$ | 5.69 | — 47.82 |
| | $k$, at 50 °C | $k$, at 75 °C | $k$, at 90 °C | | |
| 2,4-diCl-α | $3.8 \cdot 10^{-4}$ | $7.03 \cdot 10^{-4}$ | $1.23 \cdot 10^{-3}$ | 10.17 | — 44.01 |
| 3,4-diCl-α | $4.2 \cdot 10^{-4}$ | $7.66 \cdot 10^{-4}$ | $1.83 \cdot 10^{-3}$ | 11.01 | — 41.43 |
| 2,5-diCl-α | $5.11 \cdot 10^{-4}$ | $1.13 \cdot 10^{-3}$ | $2.05 \cdot 10^{-3}$ | 8.75 | — 47.16 |

**Table IV**

*Dependence of the reaction rate on the nucleophilicity of the reagent*
(In toluene, at 70 °C)

| Model compound | Reagent | $k$ (l/mole · s) |
|---|---|---|
| α-Chloro-acetophenone | trimethyl phosphite | $1.36 \cdot 10^{-4}$ |
| α-Chloro-acetophenone | triethyl phosphite | $2.55 \cdot 10^{-4}$ |
| α-Chloro-acetophenone | tributyl phosphite | $1.19 \cdot 10^{-4}$ |

**Table V**

*Effect of acetic acid on the reaction of trimethyl phosphite and α-chloroacetophenones*
(In toluene at 70 °C, in the presence of 1 mole-% of acetic acid)

| Model compound | $k$ (l/mole · s) |
|---|---|
| α-Chloroacetophenone | $2.72 \cdot 10^{-4}$ |
| 4-Methyl-α-chloroacetophenone | $1.36 \cdot 10^{-4}$ |
| 4-Chloro-α-chloroacetophenone | $4.61 \cdot 10^{-4}$ |
| 4-Bromo-α-chloroacetophenone | $6.26 \cdot 10^{-4}$ |
| 4-Nitro-α-chloroacetophenone | $2.17 \cdot 10^{-3}$ |

**Table VI**

*Dependence of the reaction rate on the number of halogen atoms in α-position*
(In toluene at 50 °C)

| Model compound | $k$ (l/mole · s) |
|---|---|
| α-Chloro-acetophenone | $2.86 \cdot 10^{-5}$ |
| α, α-Dichloro-acetophenone | $6.54 \cdot 10^{-4}$ |
| α, α, α-Trichloro-acetophenone | $3.43 \cdot 10^{-3}$ |

and $s$ (residual error) generally used for the purpose of characterization (Table VII).

These data are not against the mechanism supposed by other researches earlier [7], according to which the nucleophilic attack by the trivalent phosphorus compound takes place at the carbonyl carbon atom in the Perkow reaction, followed by a tricentric rearrangement through a phosphonium alkoxide intermediate yielding vinyl phosphate.

**Table VII**

*The ϱ values of the reaction of ring substituted α-chloro-acetophenones*

| | $\varrho$ | $r$ | $s$ |
|---|---|---|---|
| α-chloro-acetophenones | | | |
| (at 50 °C) | + 1.85 | 0.999 | 0.034 |
| (ar 70 °C) | + 1.62 | 0.997 | 0.047 |
| at acid catalysis (at 70 °C) | + 1.30 | 0.993 | 0.065 |
| α, α-dichloro-acetophenones | | | |
| (at 70 °C) | + 1.97 | 0.987 | 0.126 |

$r$ : correlation coefficient
$s$ : residual error

## Experimental

### Preparation of vinyl phosphates

Trimethyl phosphite (2.0 moles) was added by drops to a solution of the chloro-acetophenone (1.0 mole) in a suitable solvent (400 ml) at 50 °C, at a rate ensuring a not too rapid evolution of methyl chloride. After the addition, the reaction mixture was stirred at reflux temperature until the evolution of methyl chloride ceased. When the reaction was complete, the solvent and excess trimethyl phosphite were evaporated at 20 mm Hg pressure, while the vinyl phosphate was distilled at vacuum of 0,1 – 0,5 mm Hg. The data for the products are given in Table I. The structures of the products were substantiated on the basis of IR and NMR spectra. The IR characteristics of some compounds not reported in the literature are given in Table I/A.

**Table I/A**

*Assignation of the IR bands*

| No. (Vinyl phosphate) | cm$^{-1}$ | | | | | |
|---|---|---|---|---|---|---|
| | $\nu_{C=C}$ | $\nu_{C=O}$ | $\nu_{P=O}$ | $\nu_{P-O-Caliph.}$ | $\nu_{C-Cl}$ | $\nu_{P-O-CH_3}$ |
| 7* | 1645 | — | 1290 | 1180 | — | 990 |
| 8* | 1645 | — | 1280 | 1180 | — | 990 |
| 9* | 1640 | — | 1280 | 1190 | — | 1010 |
| 15* | 1615 | — | 1280 | 1180 | 1040 | 915 |
| 16* | 1630 | — | 1280 | 1175 | 1030 | 915 |
| 18* | 1610 | — | 1280 | 1185 | 1045 | 915 |

### Kinetic studies

A solution of the appropriate acetophenone in the solvent chosen was placed into a drop-shaped, two-necked flask having double walls and equipped with a stop-cock at the bottom, with a reflux condenser carrying a calcium chloride tube, and with a thermometer. The reaction of α-chloro-acetophenone and trialkyl phosphite was examined at molar ratios 1 : 20 and 1 : 1. (The concentration of α-chloro-acetophenone was 0.05 mole/l and 0.3 mole/l, respectively.) In studying the catalytic effect of acetic acid, the concentration of the acid was 1%, i.e. $3 \cdot 10^{-3}$ mole/l.

The reaction mixture was heated to the required temperature in an ultrathermostat and agitated on a shaking machine. After stabilization of the temperature, a required amount of trimethyl phosphite solution of adjusted temperature was added.

Samples were withdrawn periodically from the reaction mixture. The samples were cooled rapidly and the trimethyl phosphite was instantaneously decomposed by the addition of calculated amounts of concentrated hydrochloric acid solution (at 1 : 20 molar ratio) or with dilute aqueous hydrochloric acid solution (at 1 : 1 molar ratio). When concentrated hydrochloric acid solution was used, vinyl phosphate also decomposed.

The amount of unchanged chloro-acetophenone in the organic phase was determined by gas chromatography.

### Gas chromatographic parameters

The analysis was effected with a Packard 802 gas chromatograph. The liquid phase was QF-1 (10%) silicone oil, the carrier was Chromosorb G, and hydrogen carrier gas was used, with a conductivity detector.

Column: 220 °C
Detector: 250 °C
Vaporizer: 240 °C

## REFERENCES

[1] LICHTENTHALER, F. W.: Chem. Rev. **61,** 607 (1961)
[2] PUDOVIK, A. N.: Zhurn. Obshch. Khim. **25,** 2173 (1955)
[3] ARCORIA, A., FISICHELLA, S.: Tetrahedron Letters **1971,** 3347
[4] GAYDOU, E. M., BUONO, G., FREZE, R.: Bull. Soc. Chim. France **1973,** 2284
[5] KONECNY, J., DOUSSE, R., ROSELES, J.: Helv. Chim. Acta **55,** 3048 (1972)
[6] BOROWITZ, I. J., CROUCH, R. K.: Phosphorus **2,** 209 (1973)
[7a] ALLEN, J. F., JOHNSON, O. H.: J. Am. Chem. Soc. **77,** 2871 (1955)
[7b] KHARASCH, M. S., BENGELSDORF, I. S.: J. Org. Chem. **20,** 1356 (1955)

[7c] KREUTZKAMP, N., KAYZER, H.: Chem. Ber. **89,** 1614 (1956)
[7d] BENGELDORF, I. S.: J. Org. Chem. **21**, 475 (1956)
[7e] CHOPARD, P. A., CLARK, V. M., HUDSON, R. F., KIRBY, A. J.: Tetrahedron **21,** 1961 (1965)

Imre PETNEHÁZY
Gyöngyi SZAKÁL
Katalin RUSZ
László TŐKE

H-1521 Budapest, Műegyetem rkp. 3

*Acta Chimica Academiae Scientiarum Hungaricae, Tomus 98 (4), pp. 457—462 (1978)*

# CLEAVAGE OF THE HETEROCYCLIC RING OF ISOFLAVONOIDS BY NUCLEOPHILIC REAGENTS, VII

## REACTIONS OF ISOFLAVONE AND ITS 4-THIONE DERIVATIVE WITH HYDRAZINE AND ITS DERIVATIVES

V. SZABÓ, J. BORDA and V. VÉGH

*(Institute of Applied Chemistry, Lajos Kossuth University, Debrecen)*

Received September 22, 1977

Hydrazine and its methyl and phenyl derivatives attack isoflavone (**I**) at the $C_2$-position, similarly to the nucleophilic reagents examined earlier [1, 2, 10] and pyrazole derivatives are formed.

In contrast with 4-thionflavone, 4-thionisoflavone (**II**) does not give the normal carbonyl derivatives with these reagents either.

Under the usual conditions, isoflavone does not react with carbonyl reagents having a lower nucleophilic power, such as semicarbazide, thiosemicarbazide or 2,4-dinitrophenylhydrazine.

In our previous papers [1, 2] the reaction of isoflavone with hydroxylamine was described. It was found that isoflavone does not give a normal carbonyl reaction with hydroxylamine in solutions also containing a small amount of water; the nucleophilic reagent attacks at the $C_2$-position and the product is an isoxazole derivative.

In the course of our studies on the nucleophilic reactivity of chromonoides, the reactions of isoflavone (**I**) with hydrazine and its methyl and phenyl derivatives were investigated. In the present paper, the results of these experiments are reported.

### Results and evaluation

The reaction of isoflavone (**I**) with hydrazine, a strong nucleophilic agent, was investigated under widely various conditions (alcoholic and aqueous alcoholic solutions, between pH 3 and 11). In these experiments attempts were made at decreasing the nucleophilicity and the concentration of this reagent, and at modifying the pH of the solution so as to prevent cleavage of the $\gamma$-pyrone ring by some other nucleophilic agent (e.g., hydroxide ions.) However, the $\gamma$-pyrone ring of **I** suffered cleavage in all cases, and 3-(2-hydroxyphenyl)-4-phenylpyrazole (**IIIa**) [3, 4] was formed in high yields.

In determining the site of the nucleophilic attack, the experiments with methylhydrazine were very informative.

This nucleophilic reagent used rather rarely, has a basicity higher than

that of hydrazine and, similarly to hydrazine, both of its nitrogen atoms are capable of nucleophilic attack,* although acting in a different way [5].

The reaction of **I** and methylhydrazine was effected under conditions similar to those of the previous experiments (aqueous ethanol; pH 3–11). The reactions yielded two products in all cases, irrespective of the pH, and the ratio of the compounds was also the same ($\sim$ 7 : 1). The products could be separated by preparative layer chromatography. According to elemental analysis, both compounds contain two nitrogen atoms; the IR spectra have a band at 3300 $cm^{-1}$, which can be assigned to a phenolic hydroxyl group; it disappears on acetylation of the substances. Both compounds are very stable and remain unchanged on boiling in 2 *M* sodium hydroxide or 2 *M* hydrochloric acid.

These experimental results point to the formation of pyrazole derivatives. The product formed in higher amount (m.p. 79–80 °C) gives a reddish-brown colour reaction with $FeCl_3$, thus structure **IV** was assigned to this substance. The product of lower amount (m.p. 184–186 °C) which gives no colour reaction with $FeCl_3$ evidently owing to steric reasons, can be represented by structure **IIIb**. The NMR spectra of **IV** and **IIIb** do not exclude the pyrazole structures.

When compound **I** was allowed to react with phenylhydrazine under the conditions similar to the above experiments (aqueous ethanol, pH 3–11, or in anhydrous pyridine), however, only one product was obtained. According to elemental analysis, this substance contains two nitrogen atoms, it is stable to acids and bases, similarly to **IIIb** and **IV** and, since it gives no colour reaction with $FeCl_3$, like **IIIb**, its structure is given by formula **IIIc**.

It is known from the literature that flavone, which is the structural isomer of **I**, yields some of the normal carbonyl derivatives (oxime, hydrazone, phenylhydrazone) only in a round about way, when starting from the more reactive 4-thionflavone [3, 6].

On the basis of these results, in an attempt at preparing the normal carbonyl derivatives, 4-thionisoflavone (**II**) was made to react with hydrazine and its methyl and phenyl derivatives under the conditions given for **I**.

However, the experiments indicated that **II** yielded the same compounds in these reactions as **I** did. Moreover, in the reaction with methylhydrazine, the ratio of the products was also the same.

However, the sulphur analogue reacted more rapidly with the hydrazine derivatives than compound **I**.

The reactions described above show that isoflavone and 4 thionisoflavone, in contrast with flavone and 4-thionflavone, never give the nor-

* Methylhydrazine with 2-hydroxydeoxybenzoin having one nucleophilic centre yields a small amount of the hydrazone giving a violet colour reaction with $FeCl_3$ and, in an addition reaction starting with attack on the $N_1$ atom, a geminal aminoalcohol in an amount significantly higher than that of the hydrazone.

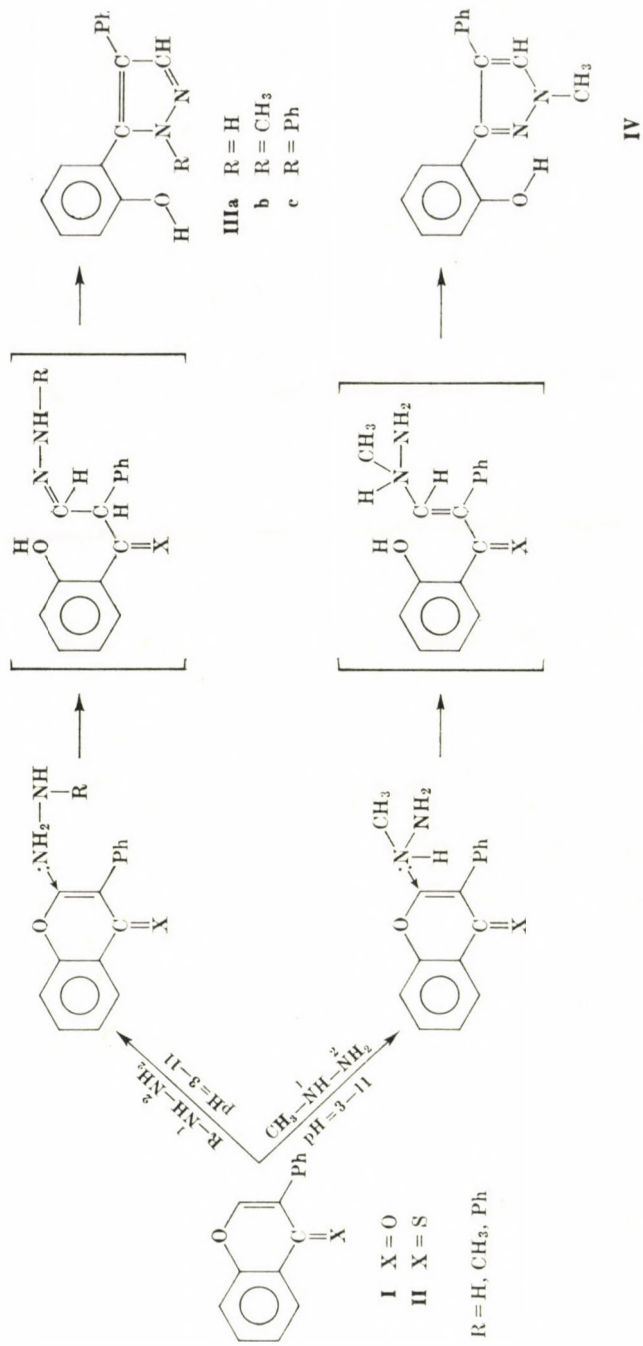

IIIa R = H
b R = CH3
c R = Ph
IV
I X = O
II X = S
R = H, CH3, Ph
pH = 3–11
pH = 3–11

**Table I**

*Comparison of the reactivities of isoflavone and 4-thionisoflavone*

| Reagent | Temperature, °C | Reaction time, h | |
|---|---|---|---|
| | | I | II |
| 1. $NH_2$-$NH_2$ · $H_2O$ (98%) | 25 | 0.4 | 0.15 |
| 2. $CH_3$-NH-$NH_2$ · $H_2O$ (96%) | 25 | 1.0 | 0.15 |
| 3. Ph-NH-$NH_2$ · HCl + equ. NaOAc (pH ~ 6) | 80 | 7.0 | 0.5 |

The end-point of the reactions (disappearance of the starting material from the reaction mixture) was detected by TLC. The error in the measurement of the reaction time is ±10%.

mal carbonyl reactions with hydrazine and its methyl and phenyl derivatives under the usual reaction conditions; moreover, the formation of the pyrazole derivatives isolated cannot be attributed to a secondary transformation of the corresponding hydrazones. Therefore, the first step in the pyrazole formation reaction is considered to be the nucleophilic attack on the $C_2$ atom in all cases.

This can be supported, in addition to the reaction of **I** with hydroxylamine [1, 2], by the following arguments.

Phenylhydrazine can exert a nucleophilic attack only with its $N_2$ atom, owing to steric reasons and the electron density distribution. Since in the above reaction **IIIc** was the sole product and neither the pyrazole isomeric with **IIIc**, nor the phenylhydrazone of **I** (which would evidently give a positive reaction with $FeCl_3$) could be detected in the reaction mixture, initiation of the reaction by attack at $C_2$ seems to be evident.

In methylhydrazine, the $N_1$ atom has a higher nucleophilicity than the $N_2$ atom [5]. In this case the ratio of the products must indicate the site of the attack starting the reaction. Since in the reaction of **I** and methylhydrazine compound **IV** was always obtained in higher amounts, irrespective of the pH, and no addition derivatives indicating $C_4$—$N_1$ or $C_4$—$N_2$ atomic relationships were found in the course of the reaction, furthermore, no methylhydrazone was detected, the attack on the $C_2$ atom is considered to be the primary act in this reaction, too. Primary attack by the $N_1$ atom on $C_4$ would have yielded **IIIb** in higher amounts.

The ratio of the products formed also indicates the ratio of the reactivities of the two nitrogen atoms.

In isoflavone, the O ↑↓ S exchange at $C_4$ increases the nucleophilic reactivity not of the $C_4$ but of the $C_2$ atom, in contrast with the case of flavone, enhancing the nucleophilic sensitivity of the hetero ring, which is shown by the difference in the reaction rates of the conversions of **I** and **II**.

It is to be noted that **I** does not react with 2,4-dinitrophenylhydrazine or thiosemicarbazide under the conditions given for flavone [7, 8, 9]. In media buffered with sodium acetate, no conversion with semicarbazide hydrochloride was observed, either.

Thus these reagents having a relatively lower nucleophilic power are not able to open the $\gamma$-pyrone ring in **I**, and the normal carbonyl reaction does not take place owing to the inactivity of the carbonyl group.

## Experimental

The UV spectra were recorded in ethanol with a UNICAM SP-800 spectrophotometer; the IR spectra were obtained in KBr pellets with a Spectromom 2000 instrument, and a JEOL 100 MHz instrument was used for recording the NMR spectra.

The reactions were monitored by TLC using a DCAluroll Silicagel 254 (Merck) layer. The developing mixture was benzene : ethanol (9 : 1). Melting points are uncorrected.

### 3-(2-Hydroxyphenyl)-4-phenylpyrazole (IIIa)

Isoflavone (**I**) or 4-thionisoflavone (**II**) [3] (1.0 mmole) was dissolved in ethanol (15 $cm^3$), and 98% hydrazine hydrate (3.0 mmole) was added to the solution. The mixture was allowed to stand at room temperature for 10—20 min, then partially evaporated in vacuum. The white substance obtained was crystallized from 80% aqueous ethanol to obtain (**IIIa** in 70 and 90% yield, respectively, m.p. 113–115 °C (lit. [3] m.p. 114—116 °C).

### Reaction of isoflavone and 4-thionisoflavone with methylhydrazine

Compound **I** or **II** (1.0 mmole) was dissolved in ethanol (15 $cm^3$); 96% methylhydrazine (3.0 mmole) was added to the solution, which was then allowed to stand at room temperature for 10—60 min. Then most of the ethanol was evaporated in vacuum, the product was precipitated with water, filtered off and dried. The two-component product obtained in this way was separated on a preparative layer: 100 mg of the substance was applied to a Kieselgel-G 254 layer (20 × 20 cm, 2 mm thick) and treated with 95 : 5 developing agent. The products were eluted with ethanol from the silica gel.

### 1-Methyl-3-(2-hydroxyphenyl)-4-phenylpyrazole (IV)

The product was crystallized from the concentrated ethanolic solution by the addition of water (yield 67 and 72%, respectively; m.p. 79—80 °C).

### [1-Methyl-4-phenyl-5-(2-hydroxyphenyl)pyrazole (IIIb)

After partial evaporation of the ethanol, water was added to crystallize the product (yield 9 and 12%, respectively; m.p. 184—186 °C).

### 1,4-Diphenyl-5-(2-hydroxyphenyl)pyrazole (IIIc)

Compound **I** or **II** (1.0 mmole), phenylhydrazine hydrochloride (3.0 mmole) and crystalline sodium acetate (3.0 mmole) were refluxed in 80% aqueous ethanol (15 $cm^3$) for 7 and 0.5 h, respectively. The solution was then partially evaporated, and the white substance which separated was crystallized from 90% aqueous ethanol to yield 70 and 85%, respectively of **IIIc**, m.p. 200—202 °C.

### Synthesis of diphenyl- and triphenylpyrazoles in aqueous ethanolic solutions of different pH

Compound **I** or **II** (1.0 mmole) was refluxed in the presence of hydrazine, methylhydrazine or phenylhydrazine (3.0 mmoles) in a mixture of ethanol (7 $cm^3$) and a Britton-Robinson buffer of pH 3—11 (7 $cm^3$), or allowed to stand at room temperature until the starting material disappeared from the reaction mixture. The product which separated was processed as described for compounds **IIIa—c** and **IV**.

The most important analytical and spectroscopic data of the pyrazole derivatives prepared are given in Table II.

**Table II**

| Compound | Analysis | UV spectrum | | IR spectrum, $cm^{-1}$ | | | NMR spectrum* | |
|---|---|---|---|---|---|---|---|---|
| | N, % | $\lambda_{max}$ (nm) | log $\varepsilon$ | C = N | N-$CH_3$ | OH | $\delta$ (ppm) $C_3$-, $C_5$-H | OH |
| **IIIa** | C : 11.86 | 254 | 4.08 | 1615 | — | 3350 | 7.60 | 10.00 |
| | F : 11.69 | 261 | 4.05 | | | (OH,NH) | | |
| | | 294 | 3.78 | | | | | |
| **IV** | C : 11.20 | 254 | 3.95 | | | | | |
| | F : 11.38 | 293 | 3.60 | 1620 | 2900 | 3350 | 7.65 | 9.60 |
| **IIIb** | C : 11.20 | 249 | 3.98 | | | | | |
| | F : 11.08 | 266 | 3.70 | 1615 | 2850 | 3300 | 7.55 | 9.55 |
| **IIIc** | C : 8.94 | 241 | 4.25 | | | | | |
| | F : 9.05 | 267 | 4.20 | 1630 | — | 3370 | 7.85 | 9.50 |

C : calculated, F: found

* The NMR spectra were recorded in DMSO-$d_6$, except for **IIIa** ($CDCl_3$).

## REFERENCES

[1] SZABÓ, V., BORDA, J., LOSONCZI, L.: Magyar Kém. Folyóirat **83,** 278 (1977)
[2] SZABÓ, V., BORDA, J., LOSONCZI, L.: Acta Chim. Acad. Sci. Hung. (In the press)
[3] BAKER, W., CLARKE, G. G., HARBORNE, J. B.: J. Chem. Soc. **1954,** 998
[4] SZABÓ, V., BORDA, J.: Topics in Flavonoid Chemistry and Biochemistry, p. 52. and Elsevier, Amsterdam, Ed. L. Farkas, M. Gábor and F. Kállay, Akadémiai Kiadó, Budapest, 1975
[5] VAITKEVICHYUS, A. K., DENIS, G. I., STEPONAVICHYUS, Y. Y.: Zhurn. Org. Khimii, **9,** 2021 (1976)
[6] DE DIESBACH, H., KRAMER, H.: Helv. Chim. Acta **1945,** 1399
[7] KÁLLAY, F., JANZSÓ, G., KOCZOR, I.: Tetrahedron Letters **1968,** 3853
[8] KÁLLAY, F., JANZSÓ, G., KOCZOR, I.: Acta Chim. Acad. Sci. Hung. **58,** 97 (1968)
[9] MOZINGO, R., ADKINS, H.: J. Am. Chem. Soc. **60,** 675 (1938)
[10] SZABÓ, V., ZSUGA, M.: Acta Chim. (Budapest) **85,** 179 (1975)

Vince SZABÓ
Jenő BORDA
Valéria VÉGH
H-4010 Debrecen

*Acta Chimica Academiae Scientiarum Hungaricae, Tomus 98 (4), pp. 463—477 (1978)*

# HETEROCYCLIC ANALOGUES OF PROSTAGLANDINS

## THIAZOLES, II

I. BARTA, G. AMBRUS, Gy. HORVÁTH, M. SÓTI and P. SOHÁR

*(Research Institute for Pharmaceutical Chemistry, Budapest)*

Received October 21, 1977

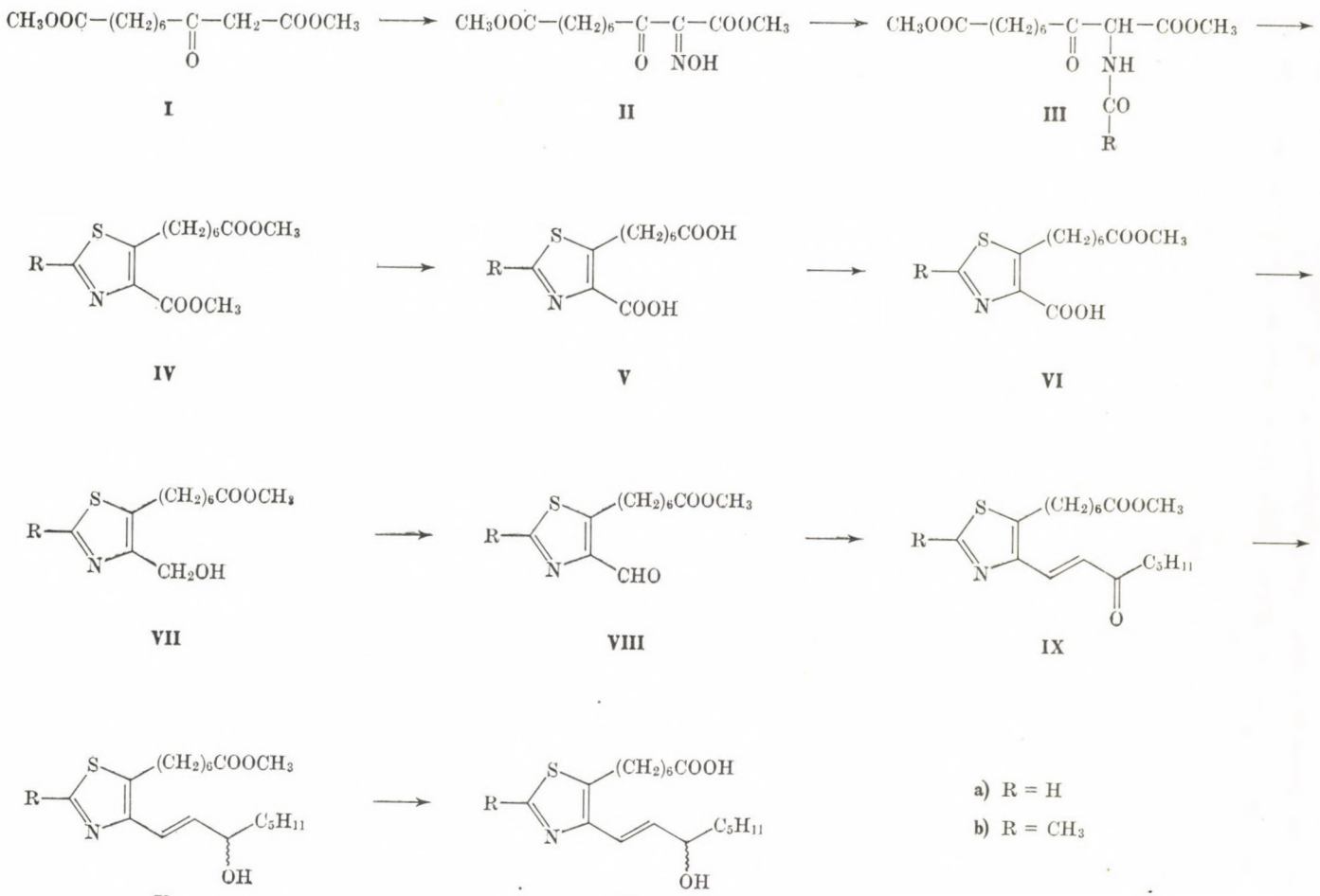
The synthesis of *dl*-4-(3-hydroxy-1-*trans*-octenyl)-5-(6-carboxyhexyl)thiazole and its 2-methyl analogue is described. IR and $^1$H-NMR data and the mass spectral behaviour of the new thiazole derivatives are discussed.

In our previous communications on heterocyclic prostaglandin analogues [1–3] the synthesis of *dl*-4-(6-carboxyhexyl)-5-(3-hydroxy-1-*trans*-octenyl)thiazole and its 2-methyl derivative has been described. In this paper we report on the preparation and properties of the structurally related *dl*-4-(3-hydroxy-1-*trans*-octenyl)-5-(6-carboxyhexyl)thiazole and its 2-methyl derivative. These structural isomers have been synthesized in order to enable a comparison of their spectroscopical and biological data with those of thiazoles described previously, in which side chains characteristic of natural prostaglandins are inversely attached to the ring.

Similarly to the synthetic strategy outlined previously [1, 2] we synthesized first a thiazole derivative which contains the carboxyhexyl side chain in the required position, and the 1-*trans*-octenyl side chain was attached to this intermediate by procedures used in prostaglandin chemistry.

The synthetic route applied for the preparation of the *dl*-4-(3-hydroxy-1-*trans*-octenyl)-5-(6-carboxyhexyl)thiazole and its 2-methyl derivative is shown in Scheme 1.

Reaction of dimethyl 3-oxosebacate (**I**) [1, 2] with sodium nitrite in acetic acid afforded dimethyl 2-oximino-3-oxosebacate (**II**), from which dimethyl 2-formamido-3-oxosebacate (**IIIa**) and dimethyl 2-acetamido-3-oxosebacate (**IIIb**) were prepared. Hydrogenation of compound **II** in methanolic hydrochloric acid in the presence of palladium-charcoal catalyst resulted in the formation of dimethyl 2-amino-3-oxosebacate hydrochloride which was transformed to compound **IIIa** by reaction with a mixture of formic acid and sodium formate at 90 °C. Compound **IIIb** was obtained when hydrogenation of **II** was effected in a mixture of acetic acid and acetic anhydride using palladium-charcoal catalyst. Methyl 5-(6-carbomethoxyhexyl)thiazole-4-carboxylate (**IVa**) and its 2-methyl derivative (**IVb**) were prepared in a reaction of **IIIa** and **IIIb**, respectively, with phosphorus pentasulfide [4]. This reaction was preferably performed in chloroform at reflux temperature.


CH3OOC–(CH2)6–C(=O)–CH2–COOCH3
I
CH3OOC–(CH2)6–C(=O)–C(=NOH)–COOCH3
II
CH3OOC–(CH2)6–C(=O)–CH(NH–CO–R)–COOCH3
III
IV
V
VI
VII
VIII
IX
X
XI
a) R = H
b) R = CH3

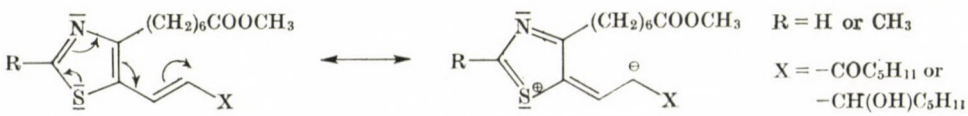
*Scheme 1*

Compound **IVa** was hydrolyzed with ethanolic sodium hydroxide at boiling temperature to afford 5-(6-carboxyhexyl)thiazole-4-carboxylic acid (**Va**). Selective esterification of **Va** in methanol in the presence of toluene-4-sulfonic acid at room temperature gave 5-(6-carbomethoxyhexyl)thiazole-4-carboxylic acid (**VIa**). Reaction of compound **VIa** with ethyl chloroformate in the presence of triethylamine in tetrahydrofuran at −5 °C resulted in the formation of a mixed anhydride [5] which was directly reduced with sodium borohydride to 4-hydroxymethyl-5-(6-carbomethoxyhexyl)thiazole (**VIIa**). Compound **VIIa** was oxidized with chromium trioxide dipyridine complex [6] in dichloromethane to give 4-formyl-5-(6-carbomethoxyhexyl)thiazole (**VIIIa**). Wittig reaction of **VIIIa** with hexanoylmethylene triphenylphosphorane [7] in carbon tetrachloride afforded 4-(3-oxo-1-*trans*-octenyl)-5-(6-carbomethoxyhexyl)thiazole (**IXa**), which was reduced with sodium borohydride in aqueous isopropanol at room temperature into *dl*-4-(3-hydroxy-1-*trans*-octenyl)-5-(6-carbomethoxyhexyl)thiazole (**Xa**). Hydrolysis of **Xa** with potassium carbonate in methanol at room temperature gave *dl*-4-(3-hydroxy-1-*trans*-octenyl)-5-(6-carboxyhexyl)thiazole (**XIa**). Compound **IVb** was transformed into *dl*-2-methyl-4-(3-hydroxy-1-*trans*-octenyl)-5-(6-carboxyhexyl)thiazole (**XIb**) by the same sequence of reactions.

The IR and $^1$H-NMR data of compounds **IVa,b** to **XIa,b** are given in Tables I and II, respectively. In general, the IR spectra of these compounds are closely similar to those of the inversely substituted thiazole isomers discussed previously [3]. Of the $^1$H-NMR data we discuss here those of the olefinic protons of compounds containing 1-*trans*-octenyl side chain.

The olefinic hydrogens of compounds **IXa,b**, **Xa,b** and **XIa,b** show a coupling constant of 15–16 Hz, indicating the *trans*-geometry of this double bond [9]. In the case of **Xa** and **XIa,b** this splitting of the olefinic signals can be observed in $C_6D_6$ since in $CDCl_3$ or in $CCl_4$ the AB part of the *ABX* multiplet is not split owing to an accidental isochrony. The chemical shifts of the olefinic hydrogens of compounds **IXa,b** to **XIa,b** and of their inversely substituted isomers are compared in Table III.

It can be seen from these data that there is a considerable difference between the chemical shifts of protons situated on carbon in $\beta$-position to the ring in the spectra of each isomeric pair. The lower values were found in the case of thiazoles which contain the 1-*trans*-octenyl side chain in position 5 of the ring. This observation can be explained by the fact that the electron density at the $\beta$-carbon atom is higher due to the polarization occurring in these thiazoles, wherein the sulfur atom represents the positive pole while the $\beta$-carbon atom is the negative one (cf. Scheme 2).




*Scheme 2*

## Table I

*IR data of compounds* **IVa,b–XIa,b** *($cm^{-1}$)*

| Compound | νOH band | ν(=CH) band | νC = O bands | | Group vibrations of νC = N and νC = C character of the thiazole ring and the conjugated double bond in the side chain+ | | | γ(=CH) band |
|---|---|---|---|---|---|---|---|---|
| | | | ester | other | | | | |
| **IVa** | — | 3080 *w* | 1730*<br>1715× | — | 1505 | 1435 | | — |
| **IVb** | — | — | 1735*<br>1715× | — | 1500 | 1430 | | — |
| **Va** | 3500–2300×*° | 3080 *m* | — | 1720*° and 1680×° | 1510 | 1445 | | — |
| **Vb** | 3500–2300×*° | — | — | 1710–1700*×° | 1495 | 1455 | | — |
| **VIa** | 3500–2300×° | 3070 *m* | 1735* | 1675×° | 1505 | 1470 | | — |
| **VIb** | 3500–2300×° | — | 1730* | 1690×° | 1495 | 1430 | | — |
| **VIIa** | ∼ 3350×●□ | 3080 *vw* | 1730* | — | 1530 | 1445 | | — |
| **VIIb** | ∼ 3240×●□ | — | 1730* | — | 1545 | 1480 | | — |
| **VIIIa** | — | 3080 *m* | 1730* | 1680×▽ | 1495 | 1430 | | — |
| **VIIIb** | — | — | 1730* | 1685×▽ | 1495 | 1430 | | — |
| **IXa** | — | 3070 *vw* | 1730* | 1680 and 1660×▼ | 1600 1495 | | 1455 | 975× |
| **IXb** | — | — | 1730* | 1680 and 1660×▼ | 1600 1515 | | 1455 | 970× |
| **Xa** | ∼ 3400×●□ | 3070 *vw* | 1730* | — | 1505 | 1455 | | 965× |
| **Xb** | ∼ 3400×●□ | — | 1735* | — | 1520 | 1455 | | 965× |
| **XIa** | 3600–2300°● | 3080 *vw* | — | 1710*° | 1505 | 1455 | | 965× |
| **XIb** | 3600–2300°● | — | — | 1705*° | 1515 | 1450 | | 960× |

\+ The bands at lower frequencies are overlapped by $\beta_s CH_2$ (methylene scissoring) bands of the side chain
× in the side chain or in substituent attached to C-4 of the thiazole ring
* in the side chain attached to C-5 of the thiazole ring
° carboxylic acid
● alcohol
▽ aldehyde
▼ ketone, the νC = O band is split into a doublet, because of the presence of s-*cis* and s-*trans* conformers [8]
□ maximum of a diffuse absorption band
*vs* very strong
*m* medium
*w* weak
*vw* very weak

**Table II**

*$^1H$-NMR data of compounds* **IVa,b–XIa,b** *($\delta TMS = 0$ ppm)*

| Compound | $\delta CH_2$× *t* (3H) | $\delta CH_3$▲ *s* (3H) | $\delta COCH_2$ $t^+$ (2H) | $\delta C_{Ar}CH_2^*$ $t^+$ (2H) | $\delta OCH_3$ *s* (3H) | δ(= CH)△× (1H) | $\delta C_{Ar}$(=CH)× (1H) | δH-2 *s* (1H) | δOH *s* | Other signals |
|---|---|---|---|---|---|---|---|---|---|---|
| **IVa** | — | — | 2.25* | 3.25 | 3.60*<br>3.85× | — | — | 8.55 | — | — |
| **IVb** | — | 2.70 | 2.30* | 3.20 | 3.65*<br>3.90× | — | — | — | — | — |
| **Va** | — | — | 2.30* | 3.35 | — | — | — | 8.95 | 10.1° (2H) | — |
| **Vb** | — | 2.70 | 2.40* | 3.20 | — | — | — | — | 11.0° (2H) | — |
| **VIa** | — | — | 2.35* | 3.35 | 3.70* | — | — | 8.90 | 10.9° (1H) | — |
| **VIb** | — | 2.70 | 2.30* | 3.25 | 3.65* | — | — | — | 8.95° (1H) | — |
| **VIIa** | — | — | 2.20* | 2.85 | 3.60* | — | — | 8.50 | ∼ 4.2• (1H) | 4.55▽× |
| **VIIb** | — | 2.60 | 2.30* | 2.80 | 3.65* | — | — | — | ∼ 4.4• (1H) | 4.60▽× |
| **VIIIa** | — | — | 2.25* | 3.25 | 3.60* | — | — | 8.65 | — | 10.10▼× |
| **VIIIb** | — | 2.65 | 2.25* | 3.15 | 3.60* | — | — | — | — | 9.3▼× |
| **IXa** | 0.90 | — | 2.20*<br>2.50× | 2.90 | 3.60* | 7.00⌀ | 7.35⌀ | 8.50 | — | — |
| **IXb** | 0.90 | 2.65 | 2.30*<br>2.60× | 2.85 | 3.65* | 7.10⌀ | 7.50⌀ | — | — | — |
| **Xa** | 0.85 | — | 2.25* | 2.80 | 3.65* | ∼ 6.5□ | | 8.50 | ∼ 3.0• (1H) | 4.20⊗× |
| **Xb** | 0.90 | 2.60 | 2.20* | 2.75 | 3.60* | 6.50■ | 6.35■ | — | ∼ 2.3• (1H) | 4.15⊗× |
| **XIa** | 0.85 | — | 2.30* | 2.80 | — | ∼ 6.6□# | | 8.60 | ∼ 6.6# | 4.35⊗× |
| **XIb** | 0.95 | 2.75 | 2.40* | 2.85 | — | ∼ 6.8□ | | — | ∼ 8.1°• (2H) | 4.50⊗× |

× in the side chain or in substituent attached to C-4 of the thiazole ring
* in the side chain attached to C-5 of the thiazole ring
\+ $J \approx 7$ Hz
▲ at C-2 of the thiazole ring
△ vicinal to the ketone or to the carbinol group
° carboxylic acid
• alcohol
▽ $\delta CH_2(OH)$, *s* (2H)
▼ aldehyde, *s* (1H)
⌀ *d* (*A* or *B* part of an *AB* multiplet, $J_{AB} = 15$ Hz)
⊗ $\delta CH(OH)$, *m* (1H)
□ in $CCl_4$ a singulet-like *AB* part of an *ABX* multiplet (split in $C_6D_6$: $J_{AB} = 16$ Hz, $J_{AX} < 1$ Hz, $J_{BX} \approx 5$ Hz)
■ *AB* part of an *ABX* multiplet ($J_{AB} = 16$Hz, $J_{BX} \approx 4$ Hz, $J_{AX} < 1$ Hz)
# overlapped signals of 4H intensity
*s* singulet
*d* doublet
*t* triplet
*m* multiplet

**Table III**

*Chemical shifts and shift differences of the olefinic protons in the $^1H$-NMR spectra of compounds* **IX–XI** *and of their isomers (ppm)*

| Structure | | $\delta(=CH_\alpha)$ | $\delta(=CH_\beta)$ | $\delta(=CH_\alpha)$* | $\delta(=CH_\beta)$* | $\Delta\delta_{\alpha,\beta}(=CH)$ | $\Delta\delta_{\alpha,\beta}(=CH)$* |
|---|---|---|---|---|---|---|---|
| **IX** | **a** | 7.35 | 7.00 | 7.54 | 6.30 | 0.35 | 1.24 |
| | **b** | 7.50 | 7.10 | 7.52 | 6.22 | 0.40 | 1.30 |
| **X** | **a** | $\sim 6.5$ | | 6.67 | 5.97 | 0 | 0.70 |
| | **b** | 6.35 | 6.50 | 6.50 | 5.70 | — 0.15 | 0.80 |
| **XI** | **a** | $\sim 6.6$ | | 6.65 | 5.90 | 0 | 0.75 |
| | **b** | $\sim 6.8$ | | 6.55 | 5.78 | 0 | 0.77 |

Indexes $\alpha$ and $\beta$ indicate the protons on carbons 1 and 2 of the octenyl side chain, respectively.

* The data of the analogous compounds containing the substituents in position 4 and 5 inversely [3].

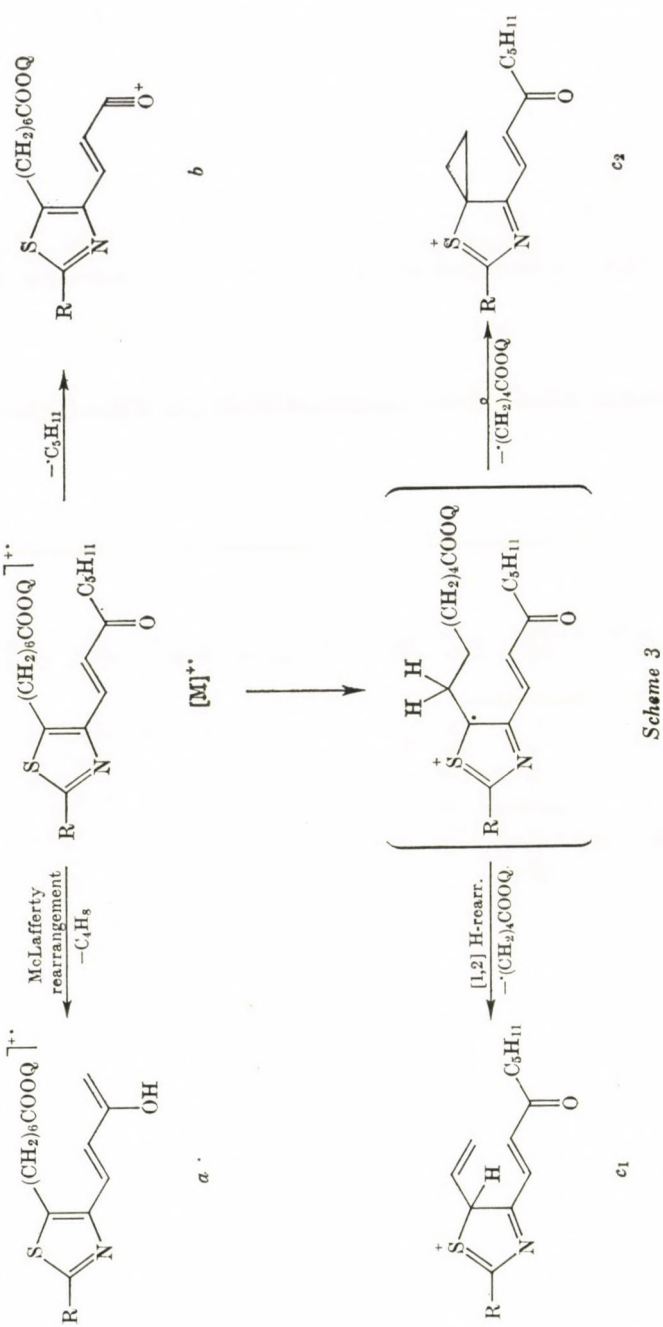
As a similar linear conjugation is not possible in the thiazoles **IXa,b** to **XIa,b** which contain the 1-*trans*-octenyl side chain in position 4, the polarization does not affect the side chain double bond.

Previously we have reported in detail on studies on the mass spectral fragmentation processes which occur in various heterocyclic analogues of prostaglandins, including 4-(6-carboxyhexyl)-5-(3-oxo and 3-hydroxy-1-*trans*-octenyl)thiazoles [3, 10]. It is of considerable interest to check the principles of fragmentation mechanisms outlined there by comparing the mass spectral behaviour of compounds **IXa,b**, **Xa,b**, **XIa,b** and **XII** and the inversely substituted thiazoles mentioned above.

Selected mass spectral data of the compounds discussed are given in Table IV.

The main fragmentation pathways of compounds **IXa,b** and **XII** are depicted in Scheme 3. Comparison of the mass spectral data of these compounds with the corresponding data of the inversely substituted thiazole isomers [3, 10] leads to the following conclusion. In contrast with the analogous process in those thiazoles [3, 10], ion *b* is formed mainly by a direct $\alpha$-cleavage at the carbonyl group, as shown by the large decrease in the abundance of this ion in the 12.5 eV spectrum of **IXa,b** as well as by the low intensity of the metastable peak arising from the transition $[M]^{+\cdot} \rightarrow b$ in the case of **IXa,b** (cf. Table IV).

In accordance with the mechanisms proposed for the formation of the $[M - {}^{\cdot}COC_5H_{11}]^+$ ion in the case of the inversely substituted thiazole isomers, which involved the formation of a four-membered ring with the sulphur atom, the absence of the sulphur atom in the appropriate position results in a low


McLafferty rearrangement
$-C_4H_8$
$[M]^{+\cdot}$
$-\cdot C_5H_{11}$
[1,2] H-rearr.
$-\cdot(CH_2)_4COOQ$
$-\cdot(CH_2)_4COOQ$
a
b
$c_1$
$c_2$

*Scheme 3*

**Table IV**

*Selected mass spectral data of compounds discussed in Schemes 3 and 4*[a]

| Compound | Data[b] | Abundance data | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | Ions | | | | | | | | |
| | | $[M]^{+\cdot}$ | *a* | *b* | *c* | $[M]^{+\cdot}$ — | | | | |
| | | | | | | $\cdot COC_5H_{11}$ | $\cdot(CH_2)_6COOQ$ | $\cdot CH_2COOQ$ | $CH_2=CH\text{-}(CH_2)_3COOQ$ | $\cdot OCH_3$ |
| **IXa** | *m/e* | 351 | 295 | 280 | 236 | 252 | 208 | 278 | 223 | 320 |
| | R.I. (%) A | 34 | 26 | 100 | 23 | 9.6 | 2.8 | 2.6 | 1 | 12 |
| **IXb** | *m/e* | 365 | 309 | 294 | 250 | 266 | 222 | 292 | 237 | 334 |
| | R.I. (%) A | 37 | 20 | 100 | 48 | 12 | 4 | 3.4 | 1 | 12 |
| | B | 100 | 17.3 | 22 | 15.8 | 7.8 | 1.8 | 1.2 | 0.9 | 6 |
| **XII** | *m/e* | 337 | 281 | 266 | 236 | 238 | 208 | 278 | 223 | — |
| | R.I. (%) A | 28 | 48 | 100 | 12 | 3.8 | 2.5 | 1.4 | 1 | |

| | | $[M]^{+\cdot}$ | *d* | *e* | *f* | *e*-QOH | *f*-QOH | $[M]^{+\cdot}$ — | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | $\cdot(CH_2)_4COOQ$[c] | $\cdot CH_2COOQ$ | $CH_2=CH\text{-}(CH_2)_3COOQ$ | $\cdot OCH_3$ |
| **Xa** | *m/e* | 353 | 324 | 282 | 254 | 250 | 222 | 238 | 280 | 225 | 322 |
| | R.I. (%) A | 15 | 2.7 | 12 | 100 | 3.8 | 4.7 | 2.8 | 1.6 | 3.7 | 9 |
| **Xb** | *m/e* | 367 | 338 | 296 | 268 | 264 | 236 | 252 | 294 | 239 | 336 |
| | R.I. (%) A | 10 | 2.1 | 11 | 100 | 3.1 | 2.3 | 2.6 | 1.5 | 2.9 | 6.9 |
| **XIa** | *m/e* | 339 | 310 | 268 | 240 | 250 | 222 | 238 | 280 | 225 | — |
| | R.I. (%) A | 7.5 | 1.7 | 7.5 | 100 | 3.4 | 2.9 | 1.9 | 0.8 | 3.5 | |
| | B | 24.4 | 1.3 | 6 | 100 | 0.4 | 0.3 | 1.5 | 0.6 | 6.2 | |
| **XIb** | *m/e* | 353 | 324 | 282 | 254 | 264 | 236 | 252 | 294 | 239 | — |
| | R.I. (%) A | 9 | 1.8 | 11 | 100 | 2.8 | 1.5 | 2.4 | 0.8 | 2.3 | |

[a] For the experimental conditions, see Experimental
[b] A: 70 eV; B: 12.5 eV
[c] This ion corresponds to ion *c* of oxo compounds

**Table IV** (cont.)

*High resolution mass measurements*

| Compound | Ion symbol | m/e | Mass decimals | | Elemental composition | \| Δ \| (ppm) |
|---|---|---|---|---|---|---|
| | | | measured | calculated | | |
| | *a* | 309 | .13784 | .13986 | $C_{16}H_{23}NO_3S$ | 6.5 |
| **IXb** | *b* | 294 | .11333 | .11639 | $C_{15}H_{20}NO_3S$ | 10.4 |
| | *c* | 250 | .12535 | .12656 | $C_{14}H_{20}NOS$ | 4.8 |
| **XIa** | *d* | 310 | .18407 | .18347 | $C_{17}H_{28}NO_2S$ | 1.9 |

*Measurements on metastable ion decompositions*

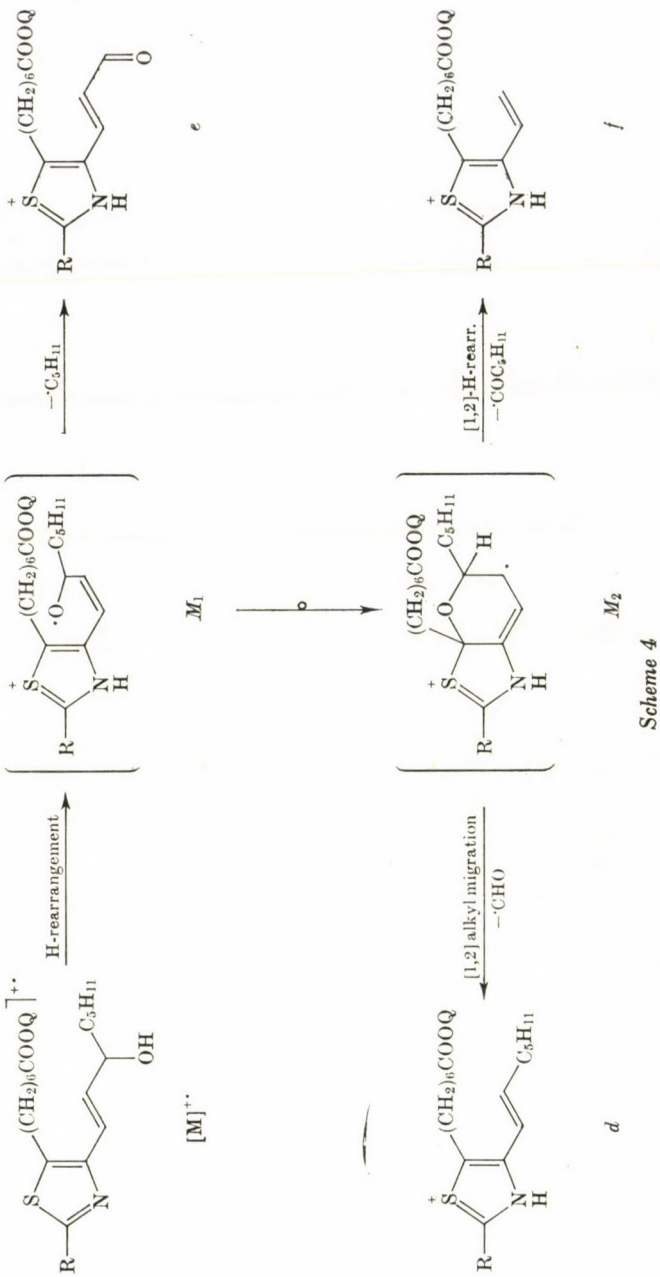
| Compound | Ion symbol | $m_2$ | Voltage ratio | $m_1$ | Intensity |
|---|---|---|---|---|---|
| | *a* | 309 | 1.181 | 365 | medium |
| **IXb** | *b* | 294 | 1.243 | 365 | weak |
| | — | 266 | 1.372 | 365 | very strong |
| | | | 1.162 | 309 | strong |
| | *c* | 250 | 1.460 | 365 | very strong |
| | *e* | 268 | 1.265 | 339 | very weak |
| **XIa** | *f* | 240 | 1.413 | 339 | weak |
| | — | 250 | 1.284 | 321 | weak |
| | | | 1.072 | 268 | very strong |
| | — | 222 | 1.528 | 339 | weak |
| | | | 1.448 | 321 | medium |
| | | | 1.081 | 240 | very strong |

abundance of ion $[M - {}^{\cdot}COC_5H_{11}]^+$ in the spectra of compounds **IXa,b** and **XII** (cf. Table IV). Nevertheless, the loss of this radical from the molecular ion of these compounds should also be preceded by a rearrangement process as indicated by the very intense metastable peak observed in the case of **IXa,b** (cf. Table IV). Similarly to the inversely substituted isomers [10] a part of these ions is formed from ion *a* by loss of $C_2H_3O$ as shown by the corresponding metastable peak (cf. Table IV). Because of the absence of the nitrogen atom in the appropriate position, ions which might have been formed by the interaction of the carboxyhexyl side chain with the thiazole ring are also of low abundance in the spectra of **IXa,b** and **XII**. An exception seems to be the ion formed by the loss of ${}^{\cdot}(CH_2)_4COOQ$ from this side chain. The higher abundance of this ion in the case of compounds **IXa,b** and **XII** could not be satisfactorily explained by the tendency of the sulphur atom to form a four-membered ring,

since the corresponding ion in the spectra of the enols **Xa,b** and **XIa,b** is not abundant *(vide infra)*. Two probable mechanisms are shown in Scheme 3, which may explain the relatively high abundance of the $[M - {}^{\cdot}(CH_2)_4COOQ]^+$ ion in the spectra of compounds **IXa,b** and **XII**. The afore-mentioned difference between the behaviour of the enones **IXa,b** and **XII** and of the enols **Xa,b** and **XIa,b** is assumed to be due to the preferred formation of the intermediate ion $M_1$ (cf. Scheme 4) in the latter compounds, while the intermediate state depicted in Scheme 3 can exist in the enones. In this intermediate state either a [1, 2] hydrogen rearrangement with subsequent loss of the ${}^{\cdot}(CH_2)_4COOQ$ radical, yielding ion $c_1$, or the loss of the same radical in a synchronous cyclization yielding ion $c_2$ can occur. The fact that a very intense metastable peak occurs for transition $[M]^{+\cdot} \rightarrow c$ in the case of **IXa,b** (cf Table IV) indicates that the formation of a new bond is involved in this process.

A dramatic change occurs in the spectra of compounds **IXa,b** and **XII** as regards the abundance of ion $[M - {}^{\cdot}(CH_2)_6COOQ]^+$ which has usually been the base peak in the spectra of the inversely substituted isomers [3, 10]. The fact that this ion is almost negligible in the case of **IXa,b** and **XII** (cf. Table IV) is in perfect accordance with the previous assumption [3, 10] that a "mesomeric structure" of the molecular ion, which can only be preferred in those inversely substituted thiazole isomers, should be involved in the process leading to the loss of the whole carboxyhexyl side chain.

The mechanisms proposed for the prominent fragmentation processes of compounds **Xa,b** and **XIa,b** are depicted in Scheme 4. The main difference between the mass spectral fragmentation of **Xa,b** and **XIa,b** and of the inversely substituted isomers [3, 10] lies in the much lower tendency of the former compounds to lose QOH from their prominent ions. As shown in Scheme 4, this difference is assumed to be due to the predominance of an alternative mechanism in which the hydrogen atom of the hydroxyl group migrates to the nitrogen atom of the thiazole ring, leading to the intermediate ion $M_1$. (In the inversely substituted isomers this hydrogen was shown to migrate mainly to the COOQ group [3, 10]). The steric arrangement involved in the formation of ion $M_1$ results in a higher probability of the cyclization step leading to the intermediate ion $M_2$. The high relative abundance of ion *f* in the spectra of **Xa,b** and **XIa,b** — it represents 40–50% of the total ion current — can be explained by this assumption. Accordingly, the relatively weak metastable peak for transition $[M]^{+\cdot} \rightarrow f$ is proposed to be due to the higher rate of formation of the intermediate ion $M_2$ (cf. Ref. [10]). Similarly to the analogous process in the inversely substituted isomers [3], ion *d* is proposed to be formed after a [1, 2] alkyl shift in ion $M_2$. Like that of ion *f*, also the abundance of ion *d* (in $\Sigma$%) is higher in the case of **Xa,b** and **XIa,b** than in the corresponding isomers. The negligible abundance of ions formed by the fragmentation of the carboxyhexyl side chain (cf. Table IV) has been rationalized above.



*Scheme 4*

## Experimental

M. p.'s were measured on a Kofler hot stage apparatus. IR spectra were taken with a Perkin Elmer 475 instrument in liquid films (**IVa, b, VIb, VIIa, VIIIa, b, IXa, b, Xa, b, XIa, b**) and in KBr pellets (**Va, b, VIa, VIIb**).

$^1$H-NMR spectra were recorded on a Jeol C-60 HL spectrometer. The following solvents were used: $CCl_4$ for compounds **IVa, b, VIIa, VIIIb, IXa, Xa, b, XIb**; $CDCl_3$ for compounds of **Va, b, VIa, b, VIIb, VIIIa, IXb, XIa**; $C_6D_6$ for compounds **Xa** and **XIa, b**.

Mass spectra were taken on a Varian MAT SM-1 instrument under the following operating conditions: resolution, 1250; accelerating voltage, 8 kV; electron energy 70 *vs.* 12.5 eV; electron current, 300 $\mu$A; source temperature, 250 °C *vs.* 150 °C (12.5 eV); evaporation temperatures (in °C), **IXa**: 120, **IXb**: 150 *vs.* 110 (12.5 eV), **XII**: 130, **Xa**: 100, **Xb**: 120, **XIa**: 130, **XIb**: 130.

For low-energy electron ionization, the electron accelerating voltage was set to the IP of oxygen (*c.* 12.5 eV).

Measurements on metastable ion decompositions were performed by scanning the accelerating voltage.

High resolution mass measurements were performed at resolution 10,000 using PFK as the reference standard.

In preparative thin layer chromatography a 2 : 1 mixture of Kieselgel G, Typ 60 (Merck) and Kieselgel $HF_{254-366}$, Typ 60 (Merck) was used as the adsorbent.

### Dimethyl 2-oximino-3-oxosebacate (II)

To a stirred solution of dimethyl 3-oxosebacate (**I**) (48.8 g) in acetic acid (110 ml) sodium nitrite (15.2 g) dissolved in water (30 ml) was added dropwise within 1 h, keeping the temperature of the reaction mixture between 25—30 °C. Stirring was continued at ambient temperature for 1.5 h, the reaction mixture was then diluted with water (400 ml) and extracted exhaustively with ethyl acetate. The ethyl acetate extract was washed with 5% sodium hydrogen carbonate and water, dried over anhydrous $Na_2SO_4$ and evaporated *in vacuo* to give a residue containing the crude **II** (46 g). An analytical sample of **II** (oil) was obtained by preparative TLC (solvent: chloroform : ethanol, 96 : 4).

IR (KBr): $\nu$OH 3300, $\nu$C = O 1740 (ester), 1680 (ketone), $\nu$C = N 1620 cm$^{-1}$.

$^1$H-NMR ($CDCl_3$): $\delta$OH 11.0 (1H, s, broad), $\delta OCH_3$ 3.90 (3H, s), 3.70 (3H, s), $\delta COCH_2$ 2.80 (2H, t), 2.35 (2H, t) ppm.

### Dimethyl 2-formamido-3-oxosebacate (IIIa)

Crude product **II** (23 g) obtained in the former reaction was dissolved in 5% methanolic hydrochloric acid (250 ml) and then hydrogenated in the presence of 10% Pd-on-carbon catalyst (6 g). After the absorption of 2 moles of hydrogen the catalyst was removed by filtration and the filtrate evaporated *in vacuo*. The residue (24 g) containing dimethyl 2-amino-3-oxosebacate hydrochloride was dissolved in formic acid (100 ml) and sodium formate (24 g) was added, with stirring. The stirred mixture was heated at 90 °C for 1.5 h. After cooling to ambient temperature the reaction mixture was poured into water (350 ml) and extracted exhaustively with ethyl acetate. The ethyl acetate extract was washed with water, dried over anhydrous $Na_2SO_4$ and evaporated *in vacuo* to give a residue (23 g) containing crude **IIIa**. An analytical sample of **IIIa** (oil) was obtained by preparative TLC (solvent: ethyl acetate : *n*-heptane, 7 : 3).

IR (film): $\nu$NH 3340, $\nu$C = O (ester) 1730, amide I 1680, amide II 1490 cm$^{-1}$.

$^1$H-NMR ($CCl_4$): $\delta$CHO 8.20 (1H, s), $\delta$NH 7.65 (1H, d, $J$ = 7 Hz), $\delta$CH 5.35 (1H, d, $J$ = 7 Hz), $\delta OCH_3$ 3.80 (3H, s), 3.60 (3H, s), $\delta COCH_2$ 2.70 (2H, t), 2.25 (2H, t) ppm.

### Dimethyl 2-acetamido-3-oxosebacate (IIIb)

The crude product **II** (23 g) obtained in the former reaction was dissolved in a mixture of acetic acid (120 ml) and acetic anhydride (40 ml) and then hydrogenated in the presence of 10% Pd-on-carbon catalyst (6 g). After an uptake of 2 moles of hydrogen the catalyst was removed by filtration and the filtrate evaporated *in vacuo* to leave a residue (24 g) containing crude **IIIb**. An analytical sample of **IIIb** (oil) was obtained by preparative TLC (solvent: ethyl acetate : *n*-heptane, 7 : 3).

IR (film): $\nu$NH 3350, $\nu$C = O (ester) 1730, amide I 1670, amide II 1510 $cm^{-1}$.
$^1$H-NMR ($CCl_4$): $\delta$NH 7.70 (1H, d, $J$ = 7 Hz), $\delta$CH 5.55 (1H, d, $J$ = 7 Hz), $\delta OCH_3$ 3.95 (3H, s), 3.70 (3H, s), $\delta COCH_2$ 2.80 (2H, t), 2.30 (2H, t), $\delta COCH_3$ 2.15 (3H, s) ppm.

**Methyl 5-(6-carbomethoxyhexyl)thiazole-4-carboxylate (IVa)**

Crude product **IIIa** (22.5 g) obtained in the former reaction and phosphorus pentasulfide (17.4 g) were taken up in chloroform (100 ml). The reaction mixture was refluxed for 1 h, the chloroform was then evaporated *in vacuo*. The residue was suspended in water (100 ml) and neutralized with dilute NaOH solution and extracted exhaustively with ethyl acetate. The ethyl acetate extract was dried over anhydrous $Na_2SO_4$ and evaporated *in vacuo* to leave a residue (21 g) containing impure **IVa**. An analytical sample of **IVa** (oil) was obtained by preparative TLC (solvent: ethyl acetate : *n*-heptane, 7 : 3).

**Methyl 2-methyl-5-(6-carbomethoxyhexyl)thiazole-4-carboxylate (IVb)**

An impure product **IVb** (22.3 g) was similarly prepared from the crude **IIIb** (23.5 g) and phosphorus pentasulfide (19.1 g) as described for synthesis of **IVa**. An analytical sample of **IVb** (oil) was obtained by preparative TLC using the solvent applied in the purification of **IVa**.

**5-(6-Carboxyhexyl)thiazole-4-carboxylic acid (Va)**

Crude product **IVa** (21 g) obtained in the former reaction was dissolved in ethanol (50 ml) and 10% aqueous NaOH solution (75 ml) was added. The resulting reaction mixture was allowed to stand at ambient temperature for 16 h, it was then acidified with dilute HCl and extracted exhaustively with ethyl acetate. The ethyl acetate extract was dried over anhydrous $Na_2SO_4$ and the solvent was evaporated *in vacuo*. The residue was treated with charcoal in hot acetone. After filtration the solution was evaporated *in vacuo*. The residue (12.5 g) was recrystallized from acetone to give pure **Va**, (m.p. 136–138 °C).

**2-Methyl-5-(6-carboxyhexyl)thiazole-4-carboxylic acid (Vb)**

Crude product **IVb** (22 g) was hydrolyzed by the method described for the preparation of **Va**, to obtain crude **Vb** (15 g). Recrystallization of the crude product from acetone afforded pure **Vb** (m.p. 84–86 °C).

**5-(6-Carbomethoxyhexyl)thiazole-4-carboxylic acid (VIa)**

A solution of the crude product **Va** (12.3 g) obtained in the former reaction and toluene-4-sulfonic acid monohydrate (13.6 g) in methanol (360 ml) was stirred at ambient temperature for 8 h, then diluted with water (1 liter) and extracted with ethyl acetate (three 400 ml portions). The organic extract was washed with water, dried over anhydrous $Na_2SO_4$ and evaporated *in vacuo*. The residue was recrystallized from acetone to give pure **VIa** (6.8 g, m. p. 93–96 °C).

**2-Methyl-5-(6-carbomethoxyhexyl)thiazole-4-carboxylic acid (VIb)**

Crude product **Vb** (14 g) was similarly esterified as described in the preparation of **VIa** to obtain pure **VIb** (8.3 g, m.p. 56–58 °C) after recrystallization from acetone.

**4-Hydroxymethyl-5-(6-carbomethoxyhexyl)thiazole (VIIa)**

A solution of ethyl chloroformate (2.6 g) in tetrahydrofuran (10 ml) was added to a stirred solution of compound **VIa** (6.5 g) and triethylamine (2.4 g) in tetrahydrofuran (50 ml) cooled to −5 °C within 15 min. After stirring for 30 min the reaction mixture was filtered in order to remove the triethylammonium chloride formed. The filtrate containing the mixed anhydride was added dropwise within 30 min to a stirred solution of sodium borohydride (2.7 g) in water (30 ml) cooled to 10 °C. The reaction mixture was stirred for 3 h at ambient

temperature, then neutralized with dilute HCl and extracted with ethyl acetate. The ethyl acetate extract was washed with water, dried over anhydrous $Na_2SO_4$ and evaporated *in vacuo* to give crude **VIIa** (6.1 g).

An analytical sample of **VIIa** was obtained by preparative TLC (solvent: ethyl acetate : *n*-heptane, 8 : 2).

### 2-Methyl-4-hydroxymethyl-5-(6-carbomethoxyhexyl)thiazole (VIIb)

Transformation of **VIb** (8 g) by the method described for the preparation of **VIIa** gave crude **VIIb** (7.4 g). An analytical sample of **VIIb** (m.p. 55–57 °C) was obtained by recrystallization of the crude product from acetone.

### 4-Formyl-5-(6-carbomethoxyhexyl)thiazole (VIIIa)

A solution of crude **VIIa** (5.8 g) in dichloromethane (50 ml) was added dropwise to a stirred solution of chromium trioxide dipyridine complex (34.9 g), prepared according to Collins *et al.* [6] in dichloromethane (600 ml) cooled to 0 °C. The reaction mixture was stirred at ambient temperature for 1 h and then filtered. The filtrate was evaporated *in vacuo*, and the residue was chromatographed on silicic acid (200 g); elution was effected with 500 ml each of 5, 10, 15, 20 and 25% ethyl acetate–*n*-heptane. From the 20% ethyl acetate–*n*-heptane fractions pure **VIIIa** (1.9 g, oil) was obtained.

### 2-Methyl-4-formyl-5-(6-carbomethoxyhexyl)thiazole (VIIIb)

Oxidation of crude **VIIb** (7 g), carried out by the method described in the preparation of **VIIIa**, resulted in impure **VIIIb** which was chromatographed on silicic acid (200 g); elution was accomplished with 500 ml each of 5, 10, 15 and 20% ethyl acetate–*n*-heptane. From the 15% ethyl acetate–*n*-heptane fractions pure **VIIIb** (2.2 g, oil) was obtained.

### 4-(3-Oxo-1-*trans*-octenyl)-5-(6-carbomethoxyhexyl)thiazole (IXa)

A solution of **VIIIa** (1.7 g) and hexanoylmethylene triphenylphosphorane (4.98 g) in carbon tetrachloride (15 ml) was stirred under nitrogen for 16 h and then evaporated *in vacuo*. The residue was chromatographed on silicic acid (100 g), eluting with 300 ml each of 2.5, 5, 7.5, 10, 12.5 and 15% ethyl acetate–*n*-heptane. From the 12.5% ethyl acetate–*n*-heptane fractions pure **IXa** (1.65 g, oil) was obtained.

### 2-Methyl-4-(3-oxo-1-*trans*-octenyl)-5-(6-carbomethoxyhexyl)thiazole (IXb)

Compound **VIIIb** (2 g) was transformed by the method described in the preparation of **IXa** into crude **IXb** which was chromatographed on silicic acid (100 g), eluting with 300 ml each of 2.5, 5, 7.5, 10 and 12.5% ethyl acetate–*n*-heptane. From the 10% ethyl acetate–*n*-heptane fractions pure **IXb** (1.8 g, oil) was obtained.

### *dl*-4-(3-Hydroxy-1-*trans*-octenyl)-5-(6-carbomethoxyhexyl)thiazole (Xa)

To a solution of **IXa** (1.5 g) in isopropanol (20 ml) was added a solution of sodium borohydride (120 mg) in water (20 ml). After stirring at ambient temperature for 2 h, the solution was diluted with water, acidified with dilute HCl and extracted exhaustively with ethyl acetate. The ethyl acetate extract was washed with water, dried over anhydrous $Na_2SO_4$ and evaporated *in vacuo*. The residue was purified by preparative TLC (solvent: ethyl acetate : *n*-heptane, 1 : 1) to give homogeneous **Xa** (1.26 g, oil).

### *dl*-2-Methyl-4-(3-hydroxy-1-*trans*-octenyl)-5-(6-carbomethoxyhexyl)thiazole (Xb)

Compound **IXb** (1.65 g) was reduced by the method described in the preparation of **Xa**. The crude product was purified with preparative TLC (solvent: ethyl acetate : *n*-heptane, 4 : 6) to give homogeneous **Xb** (1.38 g, oil).

### *dl*-4-(3-Hydroxy-1-*trans*-octenyl)-5-(6-carboxyhexyl)thiazole (XIa)

To a solution of **Xa** (1.1 g) in methanol (130 ml) was added 10% aqueous potassium carbonate (21.5 ml). The reaction mixture was stirred under nitrogen at ambient temperature for 48 h, then diluted with cold water, acidified with dilute $H_2SO_4$ and extracted exhaustively with ethyl acetate. The ethyl acetate extract was washed with water, dried over anhydrous $Na_2SO_4$ and evaporated *in vacuo*. The residue was purified by preparative TLC (solvent: ethyl acetate : *n*-heptane : acetic acid, 60 : 37 : 3) to give homogeneous **XIa** (0.85 g, oil).

### *dl*-2-Methyl-4-(3-hydroxy-1-*trans*-octenyl)-5-(6-carboxyhexyl)thiazole (XIb)

**Xb** (1.2 g) was hydrolyzed as described in the preparation of **XIa**. The crude product was purified by preparative TLC under the conditions given for **XIa**, affording homogeneous **XIb** (1.05 g, oil).

### 4-(3-Oxo-1-*trans*-octenyl)-5-(6-carboxyhexyl)thiazole (XII)

To a solution of **IXa** (50 mg) in methanol (6 ml) was added 10% aqueous potassium carbonate (1 ml). After stirring under nitrogen at ambient temperature for 48 h the reaction mixture was worked up and the resulting residue was purified by preparative TLC similarly to the case of **XIa**, to obtain pure **XII** (31 mg).

## REFERENCES

[1] Ambrus, G., Barta, I., Méhesfalvi, Zs., Horváth, Gy.: Hung. Pat. 169072 (May 14, 1974)
[2] Ambrus, G., Barta, I.: Prostaglandins **10**, 661 (1975)
[3] Ambrus, G., Barta, I., Horváth, Gy., Méhesfalvi, Zs., Sohár, P.: Acta Chim. Acad. Sci. Hung. **97**, 413 (1978)
[4] Gabriel, S.: Chem. Ber. **43**, 134, 1283 (1910)
[5] Ishizumi, K., Koga, K., Yamada, S.: Chem. Pharm. Bull. **16**, 492 (1968)
[6] Collins, J. C., Hess, W. W., Frank, F. J.: Tetrahedron Letters 3363 (1968)
[7] Caton, M. P. L., Coffee, E. C. J., Watkins, G. L.: Tetrahedron Letters 773 (1972)
[8] Corey, E. J., Becker, K. B., Varna, R. K.: J. Am. Chem. Soc. **94**, 8616 (1972)
[9] Sohár, P.: Nuclear Magnetic Resonance Spectroscopy (In Hungarian) Vol. **1**, p. 215. Akadémiai Kiadó, Budapest, 1976
[10] Horváth, Gy., Ambrus, G.: in Advances in Mass Spectrometry in Biochemistry and Medicine, Vol. II, pp. 281—294. A. Frigerio (ed.), Spectrum Publications, New York, 1976

István Barta
Gábor Ambrus
Gyula Horváth
Márta Sóti
Pál Sohár

H-1045 Budapest, Szabadságharcosok útja 47/49.

*Acta Chimica Academiae Scientiarum Hungaricae, Tomus 98 (4), pp. 479—489 (1978)*

# FURTHER DATA RELEVANT TO THE PHYSICAL AND CHEMICAL PROPERTIES OF DIAZOSULFIDES

A. B. SAKLA, B. Y. RIAD, S. ABDOU and B. N. BARSOUM

*(Chemistry Department, Faculty of Science, Cairo University, Giza, A. R. Egypt)*

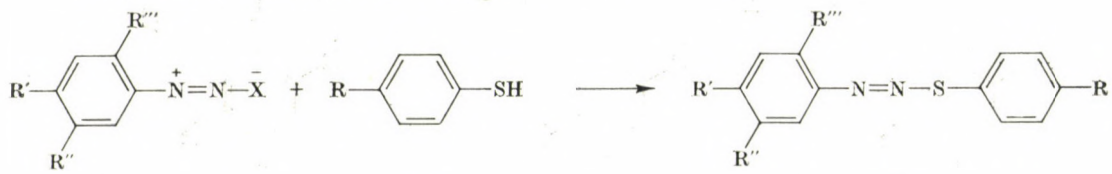
Received June 22, 1976; in revised form February 17, 1978

Diaryl diazosulfides were prepared from diazotized arylamines and solutions of different thiols at carefully controlled pH values. A single isomer of the diaryl diazosulfide was only isolated, the *Z* isomer formed first undergoing thermal rearrangement in solution of the more stable *E* isomer. The reverse isomerization (*E*—*Z*) was achieved by diffuse daylight; the *Z* isomer formed couples readily in the presence of β-naphthol, or decomposed in the absence of the coupling reagent. The rate of coupling is accelerated by exposure to diffuse daylight.

Diaryl diazosulfides have been known since 1884, when STADLER [1] described the reaction between ethanedithiol and aryldiazonium solutions to produce unstable yellow substances. HANTZSCH and FREESE [2] reported the isolation of a single isomer — presumably the *trans* compound — when preparing a number of diaryl diazosulfides (**IIi**, $R' = NO_2$, Cl, Br and $SO_3Na$; $R'' = R''' = H$). These authors stated that their compounds did not combine with naphthols either in alkaline, alcoholic or in dilute acid media, and concentrated acid split them into their components.

SAKLA *et al.* [3] have shown that diazophenyl sulfides (**II**) prepared from diazotized arylamines (**I**) and thiophenol (**IIIi**) at controlled pH coupled with β-naphthol yielding the corresponding azo dyes.

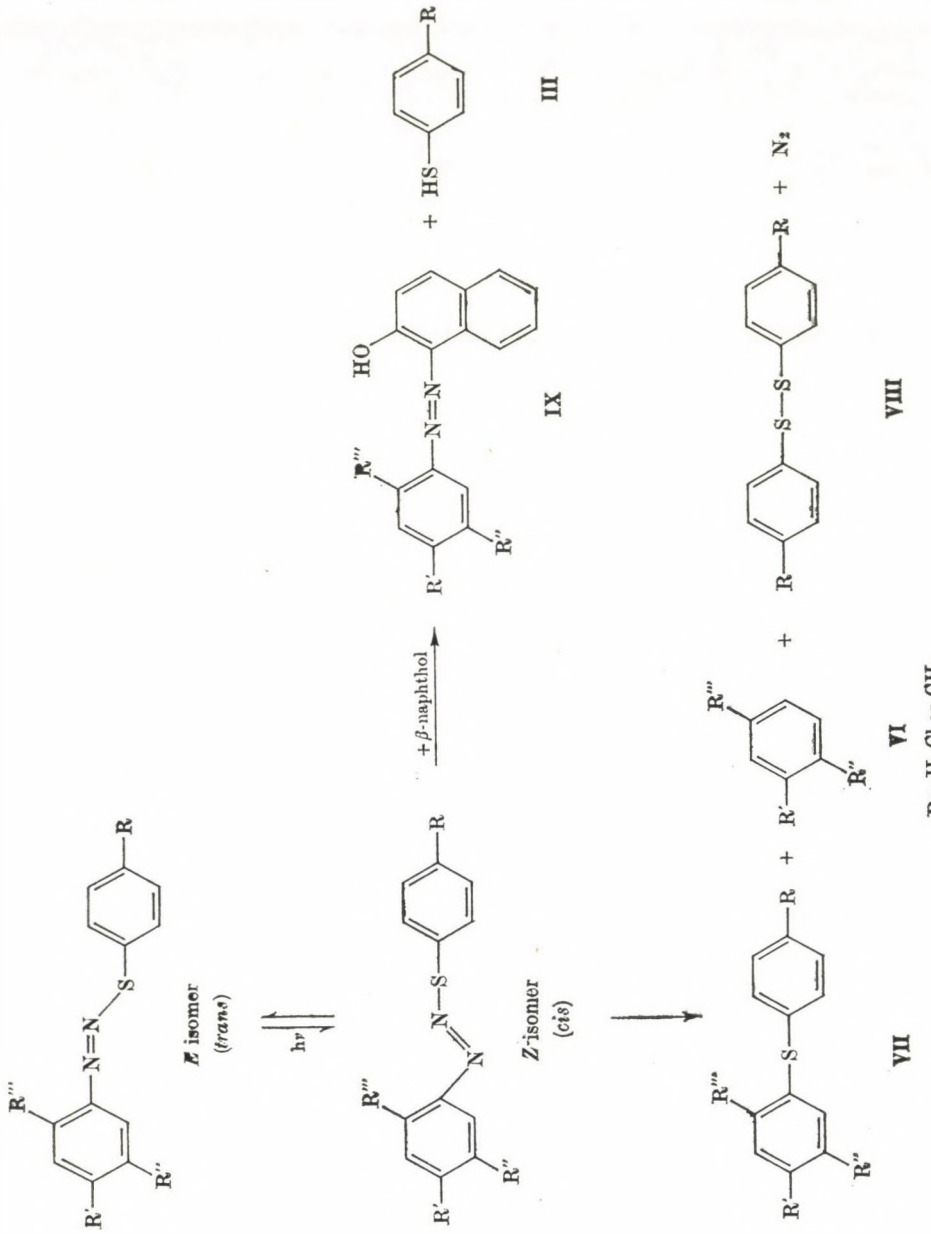
It has been found that the presence of a methyl group (with $+I$ effect) and a chlorine atom (with $-I$ and $+M$ effect) in the *para* position of the benzene nucleus of the thiol, also led to the formation of the corresponding diaryl diazosulfides (**IIii** and **IIiii**):



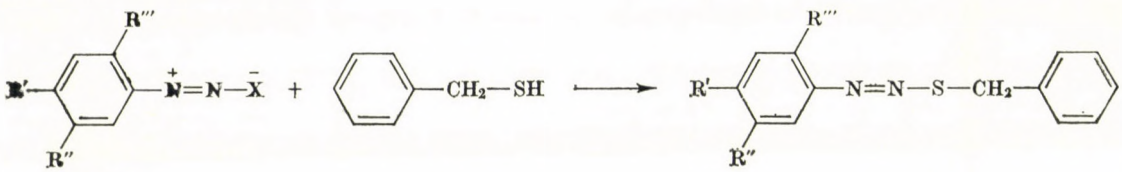
**I** **III** **II**

**III**, **i**, R = H
**ii**, R = $CH_3$
**iii**, R = Cl

**II**, **i**, with thiophenol, R = H
**a**, $R' = NO_2$ ; $R'' = R''' = H$
**b**, $R' = NO_2$ ; $R'' = R''' = CH_3$
**c**, $R' = Cl$ ; $R'' = R''' = H$
**d**, $R' = CH_3$ ; $R'' = R''' = H$
**e**, $R' = OCH_3$ ; $R'' = R''' = H$
**ii**, with *p*-toluenethiol, R = $CH_3$
**a**, $R' = NO_2$ ; $R'' = R''' = H$
**b**, $R' = R'' = H$ ; $R''' = NO_2$
**c**, $R' = NO_2$ ; $R'' = H$ ; $R''' = CH_3$
**d**, $R' = Cl$ ; $R' = R''' = H$
**e**, $R' = CH_3 \cdot C_6H_4\text{-}S\text{-}N = N \cdot C_6H_4\text{-}$; $R'' = R''' = H$
**iii**, with *p*-chlorothiophenol, R = Cl
**a** $R' = NO_2$ ; $R'' = R''' = H$
**b** $R' = Cl$ ; $R'' = R''' = H$


E isomer
(trans)
hν
Z isomer
(cis)
+β-naphthol
III
IX
VII
VIII
VI
R = H, Cl or CH3

The fact whether the —SH group is present in the benzene nucleus or in the side chain also has an influence on the reaction of the thiol with the aryldiazonium salts. Whereas thiophenol, *p*-toluenethiol and *p*-chlorothiophenol give the corresponding aryldiazophenyl sulfides in high yields, with benzyl mercaptan (**IV**) the corresponding aryldiazobenzyl sulfides (**V**) are obtained in low yields.



**I** **IV** **V**

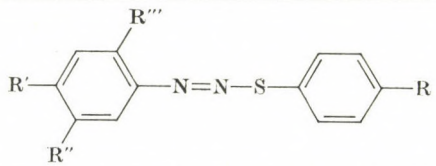
**Va**, $R' = NO_2$ ; $R'' = R''' = H$
**b**, $R' = R'' = NO_2$ ; $R''' = H$
**c**, $R' = NO_2$ ; $R'' = H$ ; $R''' = CH_3$
**d**, $R' = COOH$ ; $R'' = R''' = H$

Ultraviolet spectral studies of the prepared diaryl diazosulfides have shown that substituents affect the $\pi$—$\pi^*$ absorption maximum (Table I). It has been found that the introduction of a *p*-nitro group in the N-aryl part of the diaryl diazosulfides (**IIi a**, **IIii a**, **IIiii a**, **Va** and **Vb**) results in a bathochromic shift, whereas the $OCH_3$ group (**IIi e** and **IIii c**), *o*-$NO_2$ group (**IIii b**) and *p*-COOH (**Vd**) result in a hypsochromic shift of the absorption band. Substituents in the S-aryl part of the diaryl diazosulfides also influence the position of the absorption maximum. Introduction of *p*-$CH_3$ (**IIii a** or **IIii c**) or *p*-Cl (**IIiii a**) results in a bathochromic shift. In the case of diazobenzyl sulfides the presence of the sulfur atom in the side chain causes a hypsochromic shift. Thus, when solutions of diaryl diazosulfides (**IIi a**; **IIi b**; **IIii a**; **IIii b**; **IIii d**; **IIii e**; **IIiii a**; **Va**; **Vb** or **Vd**) in benzene or acetic acid are exposed to diffuse daylight for 20 minutes, the absorption maxima characteristic of the *E* isomer show lower intensity with the appearance of new peaks at lower wave lengths. After 60 minutes exposure to diffuse daylight, the peaks for the *E* isomers completely disappear, and the new peaks at lower wave lengths increase in intensity (Figs 1, 2). From these solutions the corresponding sulfides, disulfides, substituted benzenes, together with a trace of the diaryl diazosulfide were isolated. Thus, diaryl diazosulfides decompose immediately as soon as the *E*—*Z* isomerization takes place in the absence of a coupling reagent.

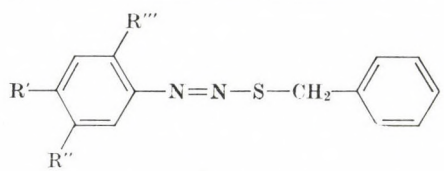
The rate of coupling of diaryl diazosulfides with $\beta$-naphthol in acetic acid, measured colorimetrically, was accelerated by exposure to diffuse daylight (Table II; Fig. 3). The formation of coupling products with $\beta$-naphthol is due to the possible fact that the *cis*-isomers in polar solvents are in equilibrium

**Table I**

*UV absorption maxima of diaryl diazosulfides*



| R | R′ | R″ | R‴ | max., nm |
|---|---|---|---|---|
| H | $NO_2$ | H | H | 345 |
| H | $NO_2$ | H | $CH_3$ | 320 |
| $CH_3$ | $NO_2$ | H | H | 360 |
| $CH_3$ | $NO_2$ | H | $CH_3$ | 335 |
| $CH_3$ | Cl | H | H | 340 |
| $CH_3$ | $p$-$CH_3$-$C_6H_4$-S-N = N-$C_6H_4$ | H | H | 360 |
| $CH_3$ | H | H | $NO_2$ | 320 |
| Cl | $NO_2$ | H | H | 360 |



| R′ | R″ | R‴ | max., nm |
|---|---|---|---|
| $NO_2$ | H | H | 340 |
| $NO_2$ | H | $NO_2$ | 350 |
| COOH | H | H | 330 |

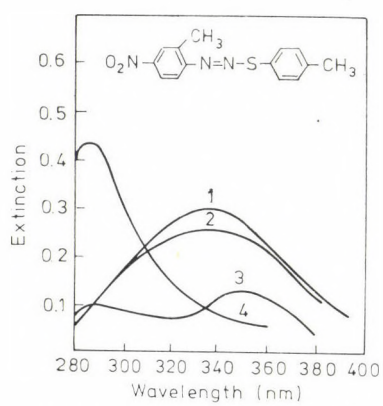



*Fig. 1.* (1) UV Spectrum of the *trans* compound in benzene solution; (2) Absorption spectrum of the same solution after 5 minutes exposure to diffuse daylight (3) Absorption spectrum after 20 minutes exposure to diffuse daylight; (4) Absorption spectrum after 60 minutes exposure to diffuse daylight

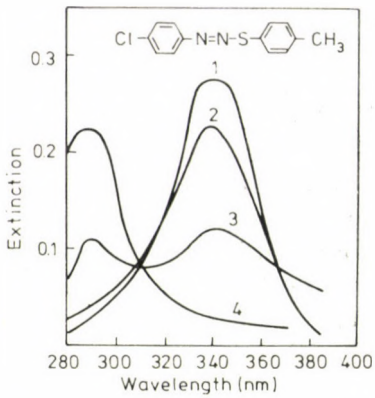



*Fig. 2.* (1) Uv Spectrum of the *trans* compound in benzene solution; (2) Absorption spectrum of the same solution after 5 minutes exposure to diffuse daylight; (3) Absorption spectrum after 60 minutes exposure to diffuse daylight. (4) Absorption spectrum after 60 minutes exposure to diffuse daylight

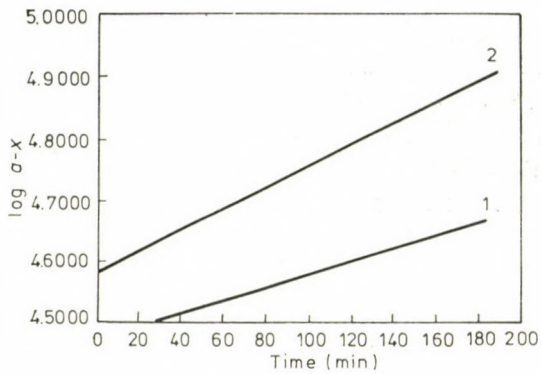



*Fig. 3.* The rate of coupling of *p*-Nitrophenyldiazophenyl sulfide with β-naphthol in acetic acid–acetone mixture in the dark (1) and after exposure to diffuse daylight (2)

**Table II**

*Comparison of the rates of coupling of p-nitrophenyldiazophenyl sulfide with β-naphthol in acetic acid–acetone mixture in the dark and on exposure to diffuse daylight*

| Time (min) | Dark | | | Diffuse daylight | | |
|---|---|---|---|---|---|---|
| | O.D. | $(a-x)$ | $-\log(a-x)$ | O.D. | $(a-x)$ | $-\log(a-x)$ |
| 0 | 10.0 | $3.2 \cdot 10^{-5}$ | 4.4949 | 16.5 | $2.6 \cdot 10^{-5}$ | 4.5850 |
| 30 | 10.5 | $3.14 \cdot 10^{-5}$ | 4.5031 | 28.2 | $2.52 \cdot 10^{-5}$ | 4.5986 |
| 60 | 18.0 | $2.92 \cdot 10^{-5}$ | 4.5346 | 40.5 | $2.08 \cdot 10^{-5}$ | 4.6819 |
| 90 | 20.0 | $2.84 \cdot 10^{-5}$ | 4.5467 | 54.0 | $1.56 \cdot 10^{-5}$ | 4.8069 |
| 120 | 28.2 | $2.52 \cdot 10^{-5}$ | 4.5986 | 47.2 | $1.62 \cdot 10^{-5}$ | 4.7905 |
| 180 | 36.3 | $2.24 \cdot 10^{-5}$ | 4.6498 | 64.3 | $1.3 \cdot 10^{-5}$ | 4.8861 |

$K = 0.24 \cdot 10^{-3}$ $K = 3.49 \cdot 10^{-3}$

O.D. = optical density

with the corresponding diazonium ion and negative ion, whereas ionization does not occur with the *trans* isomer [4].

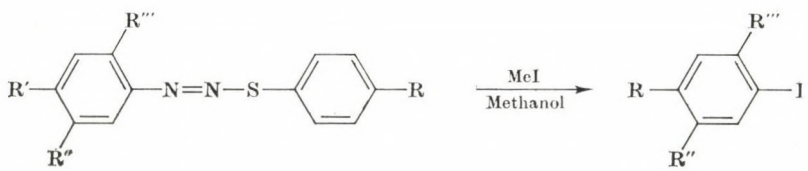
$$Ar—N_2^+ + X^- \rightleftharpoons \textit{cis}\text{-}Ar—N = NX \longrightarrow \textit{trans}\text{-}Ar—N = N \cdot X$$

It can be concluded that $E - Z$ isomerization can be achieved by diffuse daylight; the $Z$ isomer formed then couples readily in the presence of $\beta$-naphthol or decomposes in the absence of the coupling reagent according to Scheme 1. Aryl diazobenzylsulfides (**V**) decompose in the same manner to aryl benzylsulfides, sulfides and substituted benzenes.

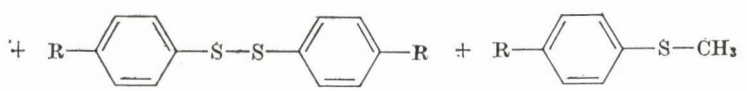
The same decomposition products are obtained on boiling the diaryl diazosulfides in acetic acid or methanol.

Partial decomposition occurs in non-polar solvents such as dioxan, benzene and cyclohexane. This indicates that the decomposition of diaryl diazosulfides is greatly influenced by the polarity of the solvent used. The nature of the reaction products does not depend on the solvent used, but the ratio of the products does, and when increasing the polarity of the solvent used, the reaction rate increases drastically [5].

However, when methanolic solutions of the diaryl diazosulfides (**IIi a**; **IIii a** and **IIiii a**) and methyl iodide are heated to boiling, the corresponding aryl iodide is mainly isolated together with small quantities of the disulfide (**VIII**) and the S-methyl thiol (**X**):




**II**




**VIII** **X**

The IR spectra of the diaryl diazosulfides (**II** and **V**) had the two characteristic bands at 1406 $\pm$ 14 $cm^{-1}$ and at 1577 $\pm$ 8 $cm^{-1}$ which were assigned by Le Fèvre *et al.* to the —N=N linkage [6].

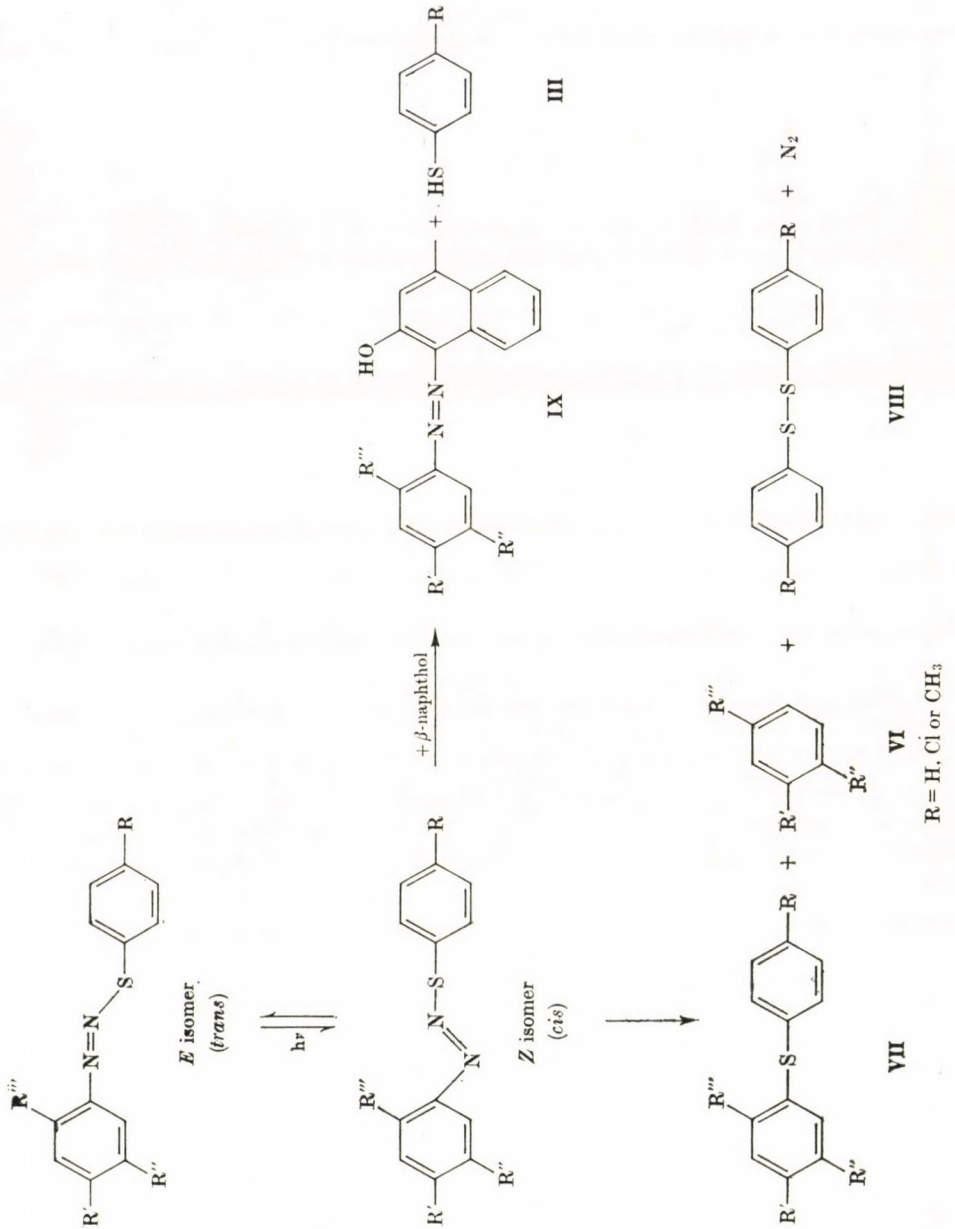

E isomer
(trans)
hν
Z isomer
(cis)
+β-naphthol
IX
III
VII
VI
VIII
R = H, Cl or CH3

**Table III**

*Diaryl diazosulfides prepared from diazonium chlorides and thiols*

| Name | Formula | M.p., °C | Analytical results, % |
|---|---|---|---|
| I. *Aryldiazophenyl sulfides* | | | |
| *p*-Chlorophenyldiazophenyl sulfide | $C_{12}H_9ClN_2S$ | 60 | Calcd.: C 57.9; H 3.6; N 11.3 S 12.9.<br>Found: C 58.2; H 3.6; N 11.0; S 13.1 |
| *p*-Tolyldiazophenyl sulfide | $C_{13}H_{12}N_2S$ | Yellow oil | Calcd.: C 68.4; H 5.3; S 14.0<br>Found: C 68.0; H 5.1; S 14.3 |
| *p*-Methoxyphenyldiazophenyl sulfide | $C_{13}H_{12}N_2OS$ | Red oil | Calcd.: C 63.9; H 4.9; N 11.4; S 13.1<br>Found: C 63.3; H 4.5; N 11.7; S 13.3 |
| *p*-Nitrophenyldiazophenyl sulfide | $C_{12}H_9N_3O_2S$ | 96 | Calcd.: C 55.6; H 3.4; N 16.2; S 12.4<br>Found: C 55.6; H 3.5; N 16.0; S 12.5 |
| *p*-Nitro-*o*-tolyldiazophenyl sulfide | $C_{13}H_{11}N_3O_2S$ | 72 | Calcd.: C 57.1; H 4.0; N 15.4; S 11.7<br>Found: C 57.5; H 4.1; N 15.2; S 11.7 |
| II. *Aryldiazo-p-tolyl sulfides* | | | |
| (a) *p*-Nitrophenyldiazo-*p*-tolyl sulfide | $C_{13}H_{11}N_2O_2S$ | 97 | Calcd.: C 57.1; H 4.0; N 15.4; S 11.7<br>Found: C 56.9; H 4.4; N 15.0; S 11.6 |
| (b) *o*-Nitrophenyldiazo-*p*-tolyl sulfide | $C_{13}H_{11}N_3O_2S$ | 66 | Calcd.: C 57.1; H 4.0; N 15.4; S 11.7<br>Found: C 57.5; H 4.5; N 15.2; S 11.9 |
| (c) *p*-Nitro-*o*-tolyldiazo-*p*-tolyl sulfide | $C_{14}H_{13}N_3O_2S$ | 85 | Calcd.: C 58.5; H 4.5; N 14.6; S 11.2<br>Found: C 58.5; H 4.5; N 14.2; S 11.3 |
| (d) *p*-Chlorophenyldiazo-*p*-tolyl sulfide | $C_{13}H_{11}N_2SCl$ | 78 | Calcd.: C 55.6; H 4.4; N 10.6; S 12.1<br>Found: C 56.0; H 4.3; N 10.6; S 11.9 |
| (e) Diphenyl-4.4-bisdiazo-*p*-tolyl sulfide | $C_{26}H_{22}N_4S_2$ | 110 | Calcd.: C 68.7; H 4.8; N 12.3; S 14.0<br>Found: C 68.5; H 5.0; N 12.2; S 13.8 |
| III. *Aryldiazo-p-chlorophenyl sulfides* | | | |
| (a) *p*-Nitrophenyldiazo-*p*-chlorophenyl sulfide | $C_2H_8N_3O_2SCl$ | 111 | Calcd.: C 49.1; H 2.7; N 14.2<br>Found: C 49.1; H 2.9; N 14.4 |
| (b) *p*-Chlorophenyldiazo-*p*-chlorophenyl sulfide | $C_{12}H_8N_2SCl_2$ | 97 | Calcd.: C 50.9; H 2.9; N 9.9; S 11.3<br>Found: C 50.6; H 3.0; N 10.0; S 11.1 |
| IV. *Aryldiazobenzyl sulfides* | | | |
| (a) *p*-Nitrophenyldiazobenzyl sulfide | $C_{13}H_{11}N_3O_2S$ | 85 | Calcd.: C 57.1; H 4.6; N 15.4; S 11.7<br>Found: C 57.4; H 4.3; N 15.3; S 11.9 |
| (b) 2,4-Dinitrophenyldiazobenzyl sulfide | $C_{13}H_{10}N_4O_4S$ | 87 | Calcd.: C 49.1; H 3.1; N 17.6; S 10.1<br>Found: C 49.5; H 3.3; N 17.2; S 9.9 |
| (c) *p*-Nitro-*o*-tolyldiazobenzyl sulfide | $C_{14}H_{13}N_3O_2S$ | 89 | Calcd.: C 58.5; H 4.5; N 14.6; S 11.2<br>Found: C 58.7; H 4.6; N 14.5; S 11.4 |
| (d) *p*-Carboxyphenyldiazobenzyl sulfide | $C_{14}H_{12}N_2O_2S$ | 120 | Calcd.: C 61.7; H 4.4; N 10.2; S 11.7<br>Found: C 62.0; H 4.8; N 10.0; S 11.6 |

## Experimental

### Reagents

The arylamines used in this investigation, namely *p*-nitroaniline, *o*-nitroaniline, 2,4-dinitroaniline, *p*-chloroaniline, *p*-nitro-*o*-toluidine, *p*-methoxyaniline, *p*-aminobenzoic acid, sulfanilic acid and benzidine, were purified by standard techniques [7]. The other reagents were β-naphthol (pure, Eastman Kodak Co.), acetic acid for analysis (Fein Chemic K. H. Kallies), thiophenol (provided by Prolabo Co.), *p*-chlorothiophenol, *p*-toluenethiol and benzyl mercaptan (provided by Aldrich).

### Preparation of aryldiazophenyl sulfides

The example given here is the preparation of *p*-nitro-*o*-tolyldiazophenyl sulfide. It was prepared by coupling equimolecular quantities of diazotized *p*-nitro-*p*-toluidine (7.69 g; 0.05 mole) and thiophenol (5.59 g; 0.05 mole) at pH 5.6. The product separated as yellow plates from 95% ethanol, m.p. 72 °C (yield 85%).

The following phenyl sulfides listed in Table III were similarly prepared and gave correct analytical results.

### Coupling of aryldiazophenyl sulfides

This reaction is exemplified by the coupling of *p*-nitro-*o*-tolyldiazophenyl sulfide with β-naphthol in 95% ethanolic solution which yielded 1-(*p*-nitro-*o*-tolylazo)-2-naphthol. The product crystallized from 95% ethanol as yellow orange crystals, m.p. and mixed m.p. 258 °C [8]. The compounds listed in Table IV were similarly prepared.

**Table IV**

*Coupling of diaryl diazo sulfides with β-naphthol in 95% ethanolic solution*

| Name | M.p., °C |
|---|---|
| 1-(*p*-Nitrophenylazo)-2-naphthol (Para Red) [9] | 251.2 |
| 1-(*p*-Chlorophenylazo)-2-naphthol [8] | 160 |
| 1-(*p*-Tolylazo)-naphthol [10] | 134 |
| 1-(*p*-Methoxyphenylazo)-2-naphthol [11] | 141 |
| 1-(*o*-Nitrophenylazo)-2-naphthol [12] | 209 |
| 1-(*p*-Nitro-*o*-tolylazo)-2-naphthol [8] | 258 |
| 1-(Diphenyl-4,4-bis-azo)-2-naphthol [13] | 275 |
| 1-(2,4-Dinitrophenylazo)-2-naphthol [14] | 302 |
| 1-(*p*-Carboxyphenyldiazo)-2-naphthol [15] | 301 |

### Action of acetic acid on diaryl diazosulfides

This reaction is exemplified by the following.

*p*-Nitrophenyldiazophenyl sulfide (2.69 g; 0.01 mole) was refluxed in acetic acid for 7 h. The hot solution was allowed to cool, whereupon an orange solid separated. This was crystallized from ethanol to obtain orange needles of *p*-nitrophenyl-phenyl sulfide, m.p. and mixed m.p. with an authentic sample 55 °C [16] (1.6 g; 60%). The filtrate was diluted with water to give white hairy crystals of diphenyl disulfide, m.p. and mixed with an authentic sample 61 °C [7] (0.6 g; 27%).

The mother liquor was steam-distilled, the distillate was extracted with ether and the solution dried over, anhydrous $Na_2SO_4$. Evaporation of the ether left a yellow oil which was identified by TLC as nitrobenzene. The diazo compounds shown in Table V were similarly treated to give the decomposition products indicated.

**Table V**

| Name | Yield, % | M.p., °C |
|---|---|---|
| (I) *Aryldiazophenyl sulfides* | | |
| *p*-Nitro-*o*-tolyl diazosulfide | | |
| *p*-Nitro-*o*-tolyl-phenyl sulfide | 44 | 82 |
| Diphenyl disulfide | 50 | 61 |
| *m*-Nitrotoluene | Yellow oil | |
| (II) *Aryldiazo-p-tolyl sulfides* | | |
| (a) *p*-Nitrophenyldiazo-*p*-tolyl sulfide | | |
| *p*-Nitrophenyl-*p*-tolyl sulfide | 53 | 81 |
| Di-*p*-tolyl disulfide | 46 | 48 |
| Nitrobenzene | Yellow oil | |
| (b) *p*-Nitro-*o*-tolyldiazo-*p*-tolyl sulfide | | |
| *p*-Nitro-*o*-tolyl sulfide | 55 | 95 |
| Di-*p*-tolyl disulfide | 42 | 48 |
| *m*-Nitrotoluene | Yellow oil | |
| (III) *Aryldiazo-p-chlorophenyl sulfides* | | |
| *p*-Nitrophenyldiazo-*p*-chlorophenyl sulfide | | |
| *p*-Nitrophenyl-*p*-chlorophenyl sulfide | 40 | 95 |
| Di-*p*-chlorophenyl disulfide | 58 | 72 |
| Nitrobenzene | | |
| (IV) *Aryldiazobenzyl sulfides* | | |
| *p*-Nitrophenyldiazobenzyl sulfide | 78 | 123 |
| Dibenzyl disulfide | 72 | 22 |
| Nitrobenzene | | |

## REFERENCES

[1] STADLER, O.: Ber. **17,** 2075 (1884)
[2] HANTZSCH, A. R., FREESE, H.: Ber. **28,** 3237 (1895)
[3] SAKLA, A. B., MASOUD, N. K., SAWIRIS, Z., EBAID, W. S.: Helv. Chim. Acta **57,** 481 (1974)
[4] ZOLLINGER, H.: "Azo and Diazo Chemistry", Interscience Publishers, New York, 1961
[5] BROKKEN-ZIJPP, J., VAN DE BOGAERT, H.: Tetrahedron **29,** 4169 (1973)
[6] LE FÈVRE, R. J. W., O'DWYER, M. F., WERNER, R. L.: Austr. J. Chem. **6,** 341 (1953)
[7] VOGEL, A. I.: "A Text Book of Practical Chemistry", 3rd Ed., Longman, Green and Co. Ltd., London, 1966
[8] ORTON, K. J. P., EVERETT, R. W.: J. Chem. Soc., 1020 (1908)
[9] HODGSON, H. H., MARSDEN, E. M.: J. Chem. Soc., 470 (1943)
[10] VAN BEEK, L. K. H., VAN BEEK, J. R. G. C. M., BOVEN, J., SCHOOT, C. T.: J. Org. Chem., **36,** 2194 (1971)

[11] HANTZSCH, A.: Wechsler, Ann. **325,** 226 (1902)
[12] MELDOLA, R., HUGHES, F.: J. Chem. Soc., **59,** 374 (1891)
[13] CHARRERI, G., FERRERI, G.: Gazz. Chim. Ital. II, 242 (1943)
[14] ROWE, F. M., LEVIN, E.: J. Soc. Dyers and Colourists **41,** 355 (1925)
[15] VON NIEMENTOWSKI, S.: Bull. Acad. Sci. Cracow 413 (1902)
[16] GILMAN, H., BROADHENT, H. S.: J. Chem. Soc., 2053 (1947)

A. B. SAKLA
B. Y. RIAD
S. ABDOU
B. N. BARSOUM
Cairo Univ. Giza, A. R. Egypt.

*Acta Chimica Academiae Scientiarum Hungaricae, Tomus 98 (4), pp. 491—493 (1978)*

# SYNTHESIS OF ALKALOIDS USING REISSERT COMPOUNDS, II*

## A NEW SYNTHESIS OF (±)-RETICULINE

*(PRELIMINARY COMMUNICATION)*

P. KEREKES, S. MAKLEIT and R. BOGNÁR

*(Institute of Organic Chemistry, Kossuth Lajos University, Debrecen)*

Received June 9, 1978

A new multi-step synthesis of (±)-reticuline starting from 1-cyano-2-benzoyl-6-methoxy-7-benzyloxy-1,2-dihydroisoquinoline and 3-benzyloxy-4-methoxybenzyl chloride is described.

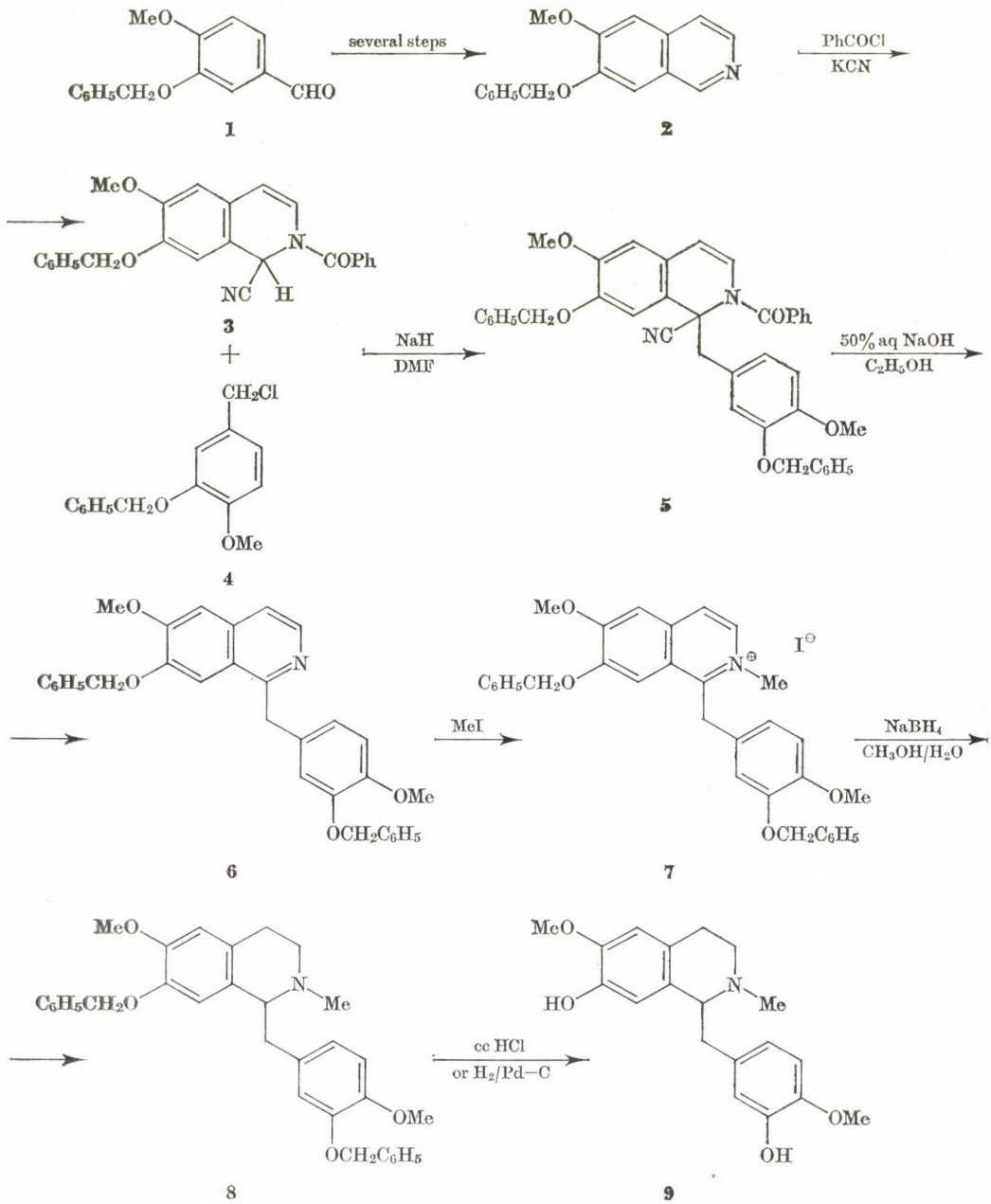
Reticuline is an intermediate of fundamental importance in the biosynthesis of isoquinoline alkaloids. The synthesis of this compound has been achieved by different methods [2—7].

Application of Reissert compounds for the synthesis of isoquinoline alkaloids is a generally used method [8]. In the course of our investigations on Reissert compounds several alkaloids have been prepared [1]. In the present paper we describe our recent investigation on the synthesis of (±)-reticuline using Reissert compounds.

6-Methoxy-7-benzyloxyisoquinoline (**2**) was prepared from O-benzyl-isovanilline (**1**) applying the modified method of POMERANZ und FRITSCH [9]. Compound **2** was made to react with benzoyl chloride and potassium cyanide in the usual manner to obtain the Reissert compound **3** (1-cyano-2-benzoyl-6-methoxy-7-benzyloxy-1,2-dihydroisoquinoline; yield: 77%, m.p. 163—165 °C, IR: $\nu$C≡N 2240 cm$^{-1}$, very weak).

The anion formed from the Reissert compound on treatment with sodium hydride in dry N,N-dimethylformamide at —20 °C was allowed to react with 3-benzyloxy-4-methoxybenzyl chloride (**4**) [10] and the corresponding crystalline 1-substituted Reissert compound (**5**) was obtained in 71% yield (m.p. 164—166 °C, IR: $\nu$C≡N 2240 cm$^{-1}$, very weak). Alkaline hydrolysis of **5** led to 1-(3-benzyloxy-4-methoxybenzyl)-6-methoxy-7-benzyloxyisoquinoline (**6**) in a good yield (88%; m.p. 169—171 °C). Quaternization of the latter compound with methyl iodide resulted in the corresponding N-methylammonium iodide (**7**) in almost quantitative yield (98%; m.p. 189—190 °C). Reduction of the quaternary salt with sodium borohydride gave 74% of (±)-dibenzyl-reticuline (**8**) (m.p. 88—91 °C, lit. [5] m.p. 89 °C). Debenzylation of **8** was

* Part I, See Ref. [1]


MeO
C6H5CH2O
CHO
1
several steps
N
2
PhCOCl
KCN
COPh
NC
H
3
+
CH2Cl
4
NaH
DMF
OMe
OCH2C6H5
5
50% aq NaOH
C2H5OH
6
MeI
I⊖
Me
7
NaBH4
CH3OH/H2O
8
cc HCl
or H2/Pd–C
HO
OH
9

effected either with Pd/C in glacial acetic acid, or with concentrated hydrochloric acid in the presence of benzene [6] to yield (±)-reticuline (**9**). The free base could not be isolated in crystalline form, although there are several authors [5—7] reporting on the crystallization of the compound. The structure of (±)-reticuline was proved by $^1$H-NMR investigation and it was transformed into its crystalline perchlorate (m.p. 106—108 °C lit. [5] m.p. 108 °C).

$^1$H-NMR: $\delta(CDCl_3)$: 2.39 (3H, s, $NCH_3$), 2.6—3.2 (6H, m. $3CH_2$), 3.74 and 3.76 (6H, 2s, $2OCH_3$), 6.27, 6.49 and 6.55—6.70 (5 Ar*H*, 2s, m).

## REFERENCES

[1] KEREKES, P., HORVÁTH, G., GAÁL, GY., BOGNÁR, R.: Acta Chim. Acad. Sci. Hung., **97,** 353 (1978)
[2] GOPINATH, K. W., GOVINDACHARI, T. R , VISWANATHAN, N.: Chem. Ber., **92,** 1657 (1959)
[3] JAIN, M. K.: J. Chem. Soc., **1962,** 2203
[4] KUNITOMO, J., J. Pharm. Soc. Japan, **81,** 1253 (1961); C. A. **56,** 11640 f (1962)
[5] BAXTER, I., ALLAN, L. T., SWAN, G. A.: J. Chem. Soc. (C), **1965,** 3645
[6] WAN-CHIN-CHEU, W., MAITLAND, P.: J. Chem. Soc. (C), **1966,** 753
[7] BORKOWSKI, P. R., HORN, J. S., RAPOPORT, H.: J. Am. Chem. Soc., **100,** 276 (1978)
[8] POPP, F. D.: Heterocycles **1,** 165 (1973)
[9] JACKSON, A. H., STAWART, G. W., CHARNOCK, G. A., MARTIN, J. A.: J. C. S. Perkin I, **1974,** 1911
[10] BATTERSBY, A. R., BINKS, R., FRANCIS, R. J., MCCALDIN, D. J., RAMUZ, M.: J. Chem. Soc., **1964,** 3600

Péter KEREKES
Sándor MAKLEIT
Rezső BOGNÁR

H-4010 Debrecen P.O.B. 20

# RECENSIONES

## A. GRAOVAC, I. GUTMAN, N. TRINAJSTIC: *Topological Approach to the Chemistry of Conjugated Molecules*

Lecture Notes in Chemistry

Springer-Verlag, Berlin—Heidelberg—New York, 1977. pp. 123

Despite the considerable success of numerical quantum chemistry, simple, qualitative rules remain important in the study of molecular phenomena. These rules are especially useful when organic reactions are designed. Some of them, depending on the topology of conjugated molecules, are summarized in this booklet. The discussion is based on graph theory. Thus a chapter is devoted to graphs in chemistry: definitions and theorems. After this introduction the total pi-electron energy, resonance energy and reactivity of conjugated molecules are treated in detail.

Graph theory is used in this book to reproduce rules which are inherent in simple Hückel theory. Some of these rules have been obtained earlier using other mathematical tools. However, several interesting theorems are derived exclusively on the basis of graph theory. An example is the topological rule for predicting substituent orientation. It is apparent that application of graph theoretical methods permits a general and rigorous treatment of all these problems.

Though graph theory does not require computers, its users have to possess certain skill in the mathematical way of thinking. Those who are willing to make an exercise find here a didactic and clear introduction to the field. Others are advised to read the text without formulas and proofs, believing in their validity. This book is an interesting contribution from the Zagreb group to the chemistry of conjugated molecules. It can be recommended mostly to specialists having experience in the subject.

G. NÁRAY-SZABÓ

## Martin J. BUERGER: *Kristallographie. Eine Einführung in die geometrische und röntgenographische Kristallkunde*

Deutsche Übersetzung: Kurt Weber und Margret Weber

Walter de Gruyter Verlag, Berlin—New York 1977. 386 Seiten, 194 Abbildungen.

Die deutsche kristallographische Literatur wurde durch die Ausgabe der deutschen Übersetzung von BUERGERS Buch mit einem bedeutenden Werk bereichert. "Contemporary Crystallography" wurde vom lehrbeauftragten Professor der Mineralkunde und Kristallkunde der Westberliner Technischen Universität übersetzt und umgearbeitet, so daß diese Übersetzung außer den Unterrichtserfahrungen von BUERGER auch die Resultate der deutschen

Unterrichtsform beinhaltet. Im Vorwort wird sowohl vom Übersetzer als auch vom Verfasser betont, daß dieses Werk keine wörtliche Übersetzung des ursprünglichen Werkes, sondern aufgrund der Erfahrungen etwas umgestaltet wurde. K. WEBER weist auch in separaten Fußnoten auf die wichtigeren Unterschiede hin.

Das Buch ist ausdrücklich als ein Lehrbuch für solche gedacht, die sich mit der Kristallkunde nur als ergänzende Wissenschaft befassen, und behandelt dementsprechend vor allem die Resultate und die Methoden der röntgenographischen Kristallkunde. Die 14 Abschnitte. sind durch ein englisch-deutsches Fachwörterbuch und durch ein Autorenverzeichnis sowie ein ausführliches Sachverzeichnis ergänzt.

Bereits im ersten Abschnitt nimmt der Verfasser von dem üblichen, die Morphologie behandelnden und einer hundertjährige Tradition folgenden Aufbau der Kristallographiebücher Abstand und da ja auch die Geometrie des kristallinen Zustands auf den inneren strukturellen Aufbau beruht, wird der periodische Aufbau als Basis des kristallinen Zustands betrachtet.

In Abschnitt 2 werden die 32 Kristallklassen aufgrund der Symmetrieelemente und deren Kombinationen abgeleitet, und zwar abweichend von der Tschermakschen Ableitung Die Erörterung der Elementarzellen, sodann die der inneren Symmetrieelemente führt zur Darlegung der Raumgruppen. Der Abschnitt endet mit einem historischen Überblick, dem sich das Literaturverzeichnis der wichtigeren Werke anschließt. Abschnitt 3 behandelt die Röntgenstrahlbeugung an Kristallen. Die Beugung an einem einzigen Atom leitet den Abschnitt ein. Dem folgt die Beschreibung der Beugung an einer Punktreihe, sodann an einem Raumgitter. Auch der Ableitung der Laueschen Gleichung, die heutzutage eher von historischem Interesse ist, wird Platz eingeräumt, die Braggsche Gleichung wird jedoch in einem separaten Unterabschnitt behandelt, um auch damit ihre Nutzbarkeit zu betonen. Ähnlich wie bei den vorangehenden Abschnitten, schließt sich auch hier eine historische Übersicht und ein Literaturverzeichnis an.

Die Grundkenntnisse werden im vierten Abschnitt mit der Behandlung des reziproken Gitters abgeschlossen. Statt der üblichen, ziemlich schwerfälligen Ableitungen ist in diesem Buch auch dieser Teil leicht verständlich und erlernbar formuliert. Den Grundkenntnissen sind 93 Seiten des Buches, ein Drittel des Inhaltes gewidmet, die weiteren zwei Drittel beschäftigen sich bereits mit verschiedenen röntgenographischen Verfahren.

Routinartige Symmetriebestimmung mittels Röntgenstrahlbeugung ist Gegenstand von Abschnitt 5. Nach einer kurzen Einleitung, in der der Begriff der reziproken Struktur eingeführt und behandelt wird, diskutiert der Verfasser die Laue-Symmetrien und deren Zusammenhang mit den Raumgruppen. Die Beziehungen zwischen verschiedenen Elementarzellen und Gittern werden geometrisch abgeleitet. Aufgrund der Auslöschungsgesetze werden die einzelnen möglichen Symmetrien untersucht.

Vom sechsten Abschnitt an behandelt das Buch bereits die praktischen Untersuchungsmethoden. Zuerst werden Zustandekommen und Eigenschaften der Röntgenstrahlen behandelt, sodann in Abschnitt 7 die Pulver- und Drehkristallaufnahmeverfahren sowie das Schwenkverfahren kurz beschrieben. Abschnitt 8 beschäftigt sich sehr eingehend mit dem Weissenbergschen Verfahren, so daß die Methode auch für jene leicht verständlich erscheint, die sich noch nicht mit ihr befaßt haben.

Der wertvollste Abschnitt des Buches ist die Beschreibung des Präzisionsverfahrens, das unter dem Namen BUERGER-Verfahren allgemein bekannt ist. Dies ist die erste deutsche Beschreibung der Methode, aus der eigenen Feder des Verfassers, so daß sie von besonderem Interesse ist. Nach einigen grundlegenden theoretischen Erwägungen wird die Präzisionskammer, danach die praktische Ausführung der Aufnahme beschrieben. Besondere Richtlinien werden für die Ausmessung und Auswertung der Aufnahmen gegeben. In diesem Abschnitt sind die ausgezeichnet reproduzierten Abbildungen des Buches besonders hervorragend und nützlich.

Der zehnte Abschnitt befaßt sich mit der Strukturbestimmung, wobei die Kristalldichte und der Zusammenhang zwischen Elementarzelle und chemischer Zusammensetzung besprochen werden. Abschnitt 11 enthält die zur Bestimmung der genaueren Lage der Elementarteilchen dienenden Methoden. Die zur Kontrolle der supponierten Kristallstruktur dienenden Testmethoden werden ebenfalls in diesem Abschnitt diskutiert.

Abschnitt 12 behandelt Verfahren zur Bestimmung der Elektronenverteilung in Kristallen und zur Verfeinerung der Strukturbestimmung: die Fourier-Synthese, die Schweratom-Methode und die Direktmethode. Abschnitt 13 befaßt sich mit der Patterson-Funktion und Abschnitt 14 mit den weiteren Verfeinerungsverfahren. Beim Überblicken des Inhaltes kann wiederholt festgestellt werden, daß das Buch ein Meilenstein der modernen kristallographischen Literatur ist. Von der herkömmlichen Kristallkunde wurde beibehalten, was für die Strukturuntersuchungen wichtig und unerläßlich ist, während die vom Verfasser als überflüssig erachteten morphologischen Teile weggelassen wurden. An den die einzelnen Untersuchungsverfahren

beschreibenden Teilen ist zu erkennen, daß diese von einem Autor verfaßt sind der mit diesen Verfahren auch eigenhändig arbeitet und diese nicht nur aus der Literatur ausgewählt hat. Leider werden sich aus der Struktur ergebende Folgerungen, wie Polymorphie, Wachstumsunregelmäßigkeiten usw. im Buch nicht diskutiert. Das im Vorwort versprochene, in Vorbereitung befindliche Buch von BUERGER über diesen Themenkreis wird sehr erwartet.

Die sehr schöne Ausführung des Buches muß besonders hervorgehoben werden. Die klaren, gut lesbaren Liniendiagramme und die ausgezeichneten Photoreproduktionen tragen viel zum Verständnis und zur Verwendbarkeit des Buches bei.

G. BIDLÓ

## LANDOLT-BÖRNSTEIN *Numerical Data and Functional Relationships in Science and Technology*

New Series, Editor in Chief: K.-H. HELLWEGE
Group II: Atomic and Molecular Physics
Volume 9
Magnetic Properties of Free Radicals
Editors: H. Fischer and K.-H. Hellwege

Part a: Atoms, Inorganic Radicals, and Radicals in Metal Complexes
C. DAUL, H. FISCHER, J. R. MORTON, K. F. PRESTON, A. v. ZELEWSKY
Springer-Verlag, Berlin—Heidelberg—New York 1977, 341 pp.
Part b: Organic C-Centered Radicals
A. BERNDT, H. FISCHER, H. PAUL
Springer-Verlag, Berlin—Heidelberg—New York 1977, pp. 782

It was a decade ago that the LANDOLT-BÖRNSTEIN New Series volume II/1 appeared under the title "Magnetic Properties of Free Radicals". Papers up to March 1964 were considered in that volume. Four books will be needed to cover the literature in the same field up to 1977 in order to supplement volume II/1. Two of these have already appeared and are reviewed here. All four are expected to appear before the end of 1978. Parts c and d will cover Organic N-, O-, P-, S-, Si-, Ge-, Sn-, Pb-, As-, Se-Centered Radicals, and Organic Radical Ions and Polyradicals, Spin Labelled Biomolecules, respectively.

All substances considered are paramagnetic deriving their paramagnetism from a single unpaired *s*- or *p*-electron. Most though not all of them have a short lifetime under ordinary laboratory conditions.

The magnetic properties of free radicals are represented by the parameters describing their interaction with external magnetic fields and the parameters of intramolecular hyperfine interactions. The parameters are given by the elements of the $g$ and $a_\lambda$ tensors of the spin Hamiltonian. The physical techniques applied for the determination of the various parameters of the spin Hamiltonian are electron paramagnetic or spin resonance (EPR, ESR), electron nuclear double resonance (ENDOR), electron electron double resonance (ELDOR), nuclear magnetic resonance (NMR), and others.

The arrangement of the Tables is the following: 1. gross formula, name, structural formula; 2. description of the generation of the radical and of the matrix or solvent in which the measurement was performed; 3. physical technique used; 4. $g$-factor; 5. $a$-value; 6. references. Thus the numerical data are given in the fourth and fifth columns of the Tables.

Inorganic radicals and radicals in metal complexes are considered in Part a. A radical is called inorganic here if it contains not more than one carbon atom except that ligands like $CO_2$- or CN were regarded as inorganic *per se*. The latter are not even included in the carbon enumeration.

The organic C-centered radicals (Part b) are divided into two parts: nonconjugated carbon radicals and carbon radicals with conjugated $\pi$-systems. A nonconjugated radical is defined as a species described by essentially only one resonance structure locating the unpaired electron on one particular carbon atom. The two main groups here are the radicals with three ligands of the radical carbon atom (alkyls), and the radicals with two ligands of the radical carbon atom (vinyls, aryls, acyls). A radical with a conjugated $\pi$-system is defined as a species

described by at least two resonance structures locating the unpaired electron on two or more carbon atoms. The species are ordered according to the number of conjugated $\pi$-electrons of unsubstituted basic radicals. Within each group the open chain radicals are followed by the cyclic systems.

The succint and very instructive general introduction and introductions to the main Tables are worth special mention. The clarity of the Tables, the organization of the references and the structural formulae all facilitate the use of these important sources.

I. HARGITTAI

## *Synergetics. A Workshop*

Edited by H. HAKEN. (274 pp.). Springer-Verlag, Berlin—Heidelberg—New York, 1977.

Synergetics is not a new science, but a new and interesting field of interdisciplinary research, investigating the common principles of structure-forming processes. In many disciplines, ranging from astrophysics over biology to sociology, we observe that very often the cooperation of many individual elements of a system leads to macroscopic structures or functioning. Synergetics investigates how the elements produce these changes in an entirely self-organized manner.

This volume contains most of the invited papers presented at the International Workshop on Synergetics, Schloss Elmau, Bavaria, May 2 to 7, 1977. The volume is subdivided into the following chapters: General Concepts, Bifurcation Theory, Instabilities in Fluid Dynamics, Instabilities in Astrophysics, Solitons, Nonequilibrium Phase Transitions in Chemical Reactions, Chemical Waves and Turbulence, Morphogenesis, Biological Systems, General Systems. The great diversity of the disciplines covered by the chapters shows the generality of the problem of structure formation. In fact, among the papers we find pure mathematical problems, such as solitons (R. K. BULLOUGH and R. K. DODD), purelly physical problems, e.g. the Benard convection or Taylor vortices (E. L. KOSCHMIEDER; P. R. FENSTERMACHER and J. P. GOLLUB), stellar evolution problems (R. KIPPENHAHN), spatial and temporal chemical structures (e.g., A. PACAULT, Y. KURAMOTO or O. E. RÖSSLER), some problems of the biogenesis (H. KUHN), neurosynergetics (J. D. COWAN) or sociocultural systems (W. BUCKLEY). The control of the morphogenesis of biological organisms by autocatalysis is also a really interesting paper (H. MEINHARDT).

Most of the papers investigate periodic phenomena. These papers are mathematically well-founded and have their common phenomenologic bases. It seems that at present this is the real field of synergetics, although this represents only the smaller part of structure formation. Most of the systems have not periodic, but individual organisation, e.g. molecules, cells, organisms, engines, etc., the discussion of which needs deterministic description. The deterministic discussion of the genesis of structures is almost absent in this volume, as well as in synergetics itself. The systems investigated by H. KUHN or M. WELGE are, for instance, typically such systems, but these papers could not give a mathematical description of the phenomena discussed.

T. GÁNTI

## W. P. WEBER, G. W. GOKEL: *Phase Transfer Catalysis in Organic Chemistry* Volume 4 of the series, Reactivity and Structure

Springer-Verlag, Berlin—Heidelberg—New York 1977, pp. 280

This work differs from the preceding volumes of the series, because it presents a synthesic method, to help everyday's laboratory practice. The past of scarcely a decade of phase transfer catalysis (PTC) is a veritable triumphal march: it proved suitable for chemically distant syntheses, it raised certain reactions of theoretical interest to the level of utilizability by improving the yield and by simplifying reaction conditions. Results of this period are collected in the book of WEBER and GOKEL.

Chapter 1 gives a brief description of the pioneer work on the method, to discuss then general problems of phase transfer catalysis. They class catalysts into the groups of catalysts with charge (more correctly, ionic catalysts) and without charge. Ionic catalysts are the quaternary ammonium and phosphonium salts. Uncharged catalysts are the amines, crown ethers and cryptands, though the amines presumably become active after previous quaternization. This chapter truly shows that even today there are many unclarities among the theoretical problems of PTC (*e.g.* comparison of the efficiency of the catalysts and the role of water in the reaction). On the other hand, possibilities of preparative application are more widely elucidated.

The second, third and fourth chapters describe applications in carbenechemistry, one of the synthetic fields most closely connected with PTC, its renaissance being due to the fact that dichlorocarbene, earlier generated in strictly nonaqueous media, is prepared with the aid of PTC from chloroform with aqueous alkali. Syntheses realized with dihalocarbenes are summarized in a table.

The fifth chapter describes the synthesis of ethers, the sixth that of esters and the seventh that of nitriles. Chapter 8 deals with synthesic possibilities presented for peroxides. Owing to reasons of solubility, it is rather difficult to use alkali peroxides without PTC.

In Chapter 9 the authors list under the title "other nucleophiles" reagents, such as, *e.g.* halide, azide, nitrite ions, to discuss then alkylations in the most extensively documented chapter. The weight of this chapter is indicated by the fact that the table reporting alkylating results obtained so far amounts to more than 20% of the full extent of the book.

Chapter 11 deals with oxidations, Chapter 12 with hydridic reductions, Chapter 13 with the preparation of sulfur-containing compounds, and Chapter 14 with the use of ylides. Ylides can be prepared in aqueous alkaline medium.

Chapter 15 discusses the mode in which the direction, product and stereochemistry of reactions can be influenced by PTC effect. It seems that in this field the phenomena have only just been recognized.

At the end of the book there is a supplement to certain chapters. It contains literature published between the closing of the subject (1976) and the printing of the book (mid-1977).

The book can be profitably used for general orientation in the PTC theme, as an auxiliary book facilitating orientation in the literature, and can be recommended to chemists engaged in preparative and industrial work.

L. TŐKE

# INDEX

## ANALYTICAL CHEMISTRY

Photometric Determination of Oxalic Acid as Iron(III)-Oxalate Complex in the Presence of Ethylene Glycol, Glyoxalic Acid, Glycolic Acid and Glyoxal, E. SZETEY, G. INZELT, G. HORÁNYI ..... 367

## PHYSICAL AND INORGANIC CHEMISTRY

Mechanism of the Pyrolysis of Propane and *n*-Butane at Low (about 800 K) and High (about 1100 K) Temperatures, N. S. NAMETKIN, R. A. KALINENKO, L. V. SHEVELKOVA, L. ZALOTAI, D. HALÁSZ, T. BÉRCES, F. MÁRTA ..... 375
Static Dielectric Properties of Polar Liquids, J. LISZI ..... 395
Electrochemical Behaviour of Ethylene Glycol and its Oxidation Products on a Platinum Electrode, III. Effect of Chemisorption on the Kinetics of Oxidation of Glyoxal and Glyoxalic Acid, G. INZELT, G. HORÁNYI ..... 403
Ionic Potential of Moderately Highly Concentrated Aqueous Solution of Strong Electrolytes, E. DATTA, B. K. SENGUPTA ..... 421
Investigation on the Distribution of 4-(2-pyridilazo)-resorcinol (PAR) in Aqueous Solution–Chloroform and Aqueous Solution–Chloroform Solution of Quaternary Ammonium Chloride Two-Phase Systems, E. PAPP, J. INCZÉDY ..... 429
Investigations on Mercury(II)-PAN Complexes. Indirect Photometric Determination of Chloride Ion, Z. PUCHONY, J. INCZÉDY ..... 439

## ORGANIC CHEMISTRY

Kinetics of the Perkow Reaction, I. PETNEHÁZY, GY. SZAKÁL, K. RUSZ, L. TŐKE ..... 447
Cleavage of the Heterocyclic Ring of Isoflavonoids by Nucleophilic Reagents, VII. Reactions of Isoflavone and its 4-thione Derivative with Hydrazine and its Derivatives, V. SZABÓ, J. BORDA, V. VÉGH ..... 457
Heterocyclic Analogues of Prostaglandins. Thiazoles, II, I. BARTA, G. AMBRUS, GY. HORVÁTH, M. SÓTI, P. SOHÁR ..... 463
Further Data Relevant to the Physical and Chemical Properties of Diazosulfides, A. B. SAKLA, B. Y. RIAD, S. ABDOU, B. N. BARSOUM ..... 479
Synthesis of Alkaloids Using Reissert Compounds, II. A new Synthesis of (+)-reticuline (Preliminary Communication), P. KEREKES, S. MAKLEIT, R. BOGNÁR ..... 491

RECENSIONES ..... 495

*Printed in Hungary*

A kiadásért felel az Akadémiai Kiadó igazgatója — Műszaki szerkesztő: Zacsik Annamária

A kézirat nyomdába érkezett: 1978. VI. 27. — Terjedelem: 11,90 (A/5) ív, 57 ábra

78.6030 Akadémiai Nyomda, Budapest — Felelős vezető: Bernát György

ACTA CHIMICA

ТОМ 98—ВЫП. 4

РЕЗЮМЕ

## Фотометрическое определение щавелевой кислоты в форме комплекса оксалата железа(III), в присутствии этиленгликоля, глиоксаловой кислоты, гликольной кислоты и глиоксаля

З-НЕ СЕТЕИ, ДЬ. ИНЗЕЛЬТ, и ДЬ. ХОРАНИ

Было показано, что в сильно кислых средах ($[H^+] > 0{,}1$ моль/дм$^3$) в основном электролите надхлорной и серной кислот имеется возможность фотометрического определения щавелевой кислоты в форме комплекса с жетезом(III), на основе светопоглощения последнего. Определению не мешают этиленгликоль, глиоксаль, глиоксаловая кислота и гликольная кислота, находящиеся даже в большом избытке, что позволяет применение метода в определении щавелевой кислоты, в ходе электрохимического окисления этих соединений.

## Механизм пиролиза пропана и н-бутана при низких (оксало 800°К) и высоких (около 1100°К) температурах

А. В. НАМЕТКИН, Р. А. КАЛИНЕНКО, Л. В. ШЕВЕЛЬФОВА, Л. ЗАЛОТАИ, Д. ХАЛАС, Т. БЕРЦЕШ и Ф. МАРТА

На основе изменений в распределении продуктов с конверсией, процесс пиролиза парафинов может быть разделен на три участка: область низких, средних и глубоких превращений.

При низких (807—833°К) и повышенных (973—1113°К) температурах были исследованы процессы самоингибирования для пропана и бутана, а также эффект олефинов на распределение продуктов. Было установлено, что в области средних конверсий при низких и высоких температурах изменения в распределении продутов термического распада пропана и бутана с конверсией связаны с реакциями между атомом водорода и олефинами. При термическом разложении н-бутана, в особенности при низких температурах, наиболее доминирующими вторичными процессами являются реакции, протекающие с участием алкильных радикалов и олефинов и приводящие к образованию аллильных радикалов.

Были выяснены те элементарные реакции, протекающие с участием олефинов при разложении пропана и бутана в области низких и высоких температур, которые играют существенную роль в процессе ингибирования.

## Статические диэлектрические свойства полярных жидкостей

Я. ЛИСИ

Получено уравнение, описывающее статические диэлектрические свойства полярных жидкостей, основанное на приближении непрерывности в окружении молекул. Применяемая модель представляет собой в основном расширение модели Онсагера и заключает в себе концентрическую диэлектрическую непрерывность. Уравнение, основанное на этой модели, принимает во внимание тот факт, что взаимодействие молекул с их ближайшими соседями отличается от их взаимодействий с массой жидкости.

## Электрохимическое поведение этиленгликоля и его окисленных производных, III

### Влияние хемосорбции глиоксаля и глиоксиловой кислотю на кинетику окисления

ДЬ. ИНЗЕЛЬТ и ДЬ. ХОРАНИ

Были сделаны попытки объяснить первую ступень на начальном участке поляризационных кривых, снятых при электрохимическом окислении глиоксаля и глиоксиловой кислоты.

Опираясь на результаты более ранних исследований, полагали протекание двух различных реакций. Одна из них протекает через сильно хемосорбированные молекулы и приводит к образованию $CO_4$. Было показано, что другая реакция, протекающая также через хемосорбированные молекулы, но приводящая к образованию глиоксиловой и щавелевой кислот, является основным процессом в исследованной области потенциалов. На основе упрощенных кинетических зависимостей, выведенных для этих двух реакций, уравнения зависимости скорости реакции от концентрации и потенциала хорошо совпадают с экспериментальными данными. На основе этого было сделано заключение, что первая ступень, наблюдаемая на поляризационной кривой, связана с уменьшением ингибирующего эффекта, являющегося результатом ускорения окисления хемосорбированных молекул с возрастанием потенциала.

## Ионные потенциалы умеренно концентрированных водных растворов сильных электролитов

Р. ДАТТА и Б. К. СЕНГУПТА

Были рассмотрены термодинамические свойства, а в частности коэффициенты активности водных растворов сильных электролитов. Здесь, также как и в предыдущей статье авторов, исходной является формула распределения, выведенная М. Дутта в 1952 г. Результирующее уравнение Пуассона решено как методом Дутта и Сенгупта (1954), так и методом Онсагера и Фуосса (1961). Вывод не ограничен условиями высоких разбавлений.

## Исследование распределения 4-(2-пиридилазо)-резорцинола в водном растворе — хлороформе и в двуфазных системах с раствором четвертичного хлористого аммония в воде — хлороформе

Э. ПАПП и Й. ИНЦЕДИ

Распределение 4-(2-пиридилазо)-резорцинола (ПАР) было исследовано в водном растворе — хлороформе и в системах водный раствор — хлороформ — TOMACl. Константа распределения нейтральных $H_2L$ в системе водный растворхлороформ равна $\lg d_{H_2L} = 1{,}25 \pm 0{,}01$ ($I = 0{,}1$). В системе водный раствор — хлороформ — TOMACl $H_2L$ ассоциирует с TOMACl при pH ниже 4. Константа ассоциации в интервале концентраций TOMACl $4 \cdot 10^{-3} \div 10^{-3}$ равна $\lg K_A = 3{,}84 \pm 0{,}07$. Наблюдалась ионообменная реакция, протекающая между частицами $HL^-$ ПАР-а и TOMACl при pH выше 7. Величина константы ионообменной реакции равна $\lg K^X = 2.99 \pm 0{,}94$.

## Исследование комплексов ртуть(II)-ПАН Косвенное фотометрическое определение хлористях иоиов

З. ПУХОНИ и Й. ИНЦЕДИ

Образование комплекса Hg(II)-ПАН было исследовано экстракционным и прямым фотометрическим методами в гомогенной фазе. Комплеск, экстрагированный $CCl_4$, представляет собой $HgL_2$ с экстракционной константий равновесия $\lg K^e = 1{,}58$.

В смесях этанол — вода (1 : 1) состав комплекса равен 1 : 1 и 1 : 2 при pH = 4 и pH = 6, соответственно. Были определены также константы устойчивости этих комплексов.

Образование комплекса $HgL^+$ ингибируется присутствием галогенидных ионов. Это явление может быть использовано для косвенного спектрофотометрического определения хлористых ионов в интервале концентраций $10^{-5} \div 6 \cdot 10^{-5}$ $MCl^-$/л.

## Кинетика реакции Перкова

И. ПЕТНЕХАЗИ, ДЬ. САҚАЛ, Қ. РУС и Л. ТЁКЕ

На основе проведенных опытов был предложен новый, до сих пор еще не использованный, быстрый и точный кинетический метод с высокой чувствительностью для реакции Перкова. Было исследовано влияние растворителя и температурная зависимость, а также рассчитаны энтальпии и энтропии активации.

Исследуя роль ароматических заместителей, полученные постоянные уравнения Гаммета подтверждают нуклеофильный характер реакции замещения на трехвалентном фосфоре.

## Расщепление гетероциклического кольца изофлаваноидов с помощью нуклеофильных реагентов, VII

### Реакции изофлавона и его 4-тиона с гидразином и его производными

В. САБО, Й. БОРДА и В. ВЕГ

Гидразин, его метильные и фенильные производные атакуют изофлавон (*I*) — подобно уже ранее изученным нуклеофильным реагентам [1, 2, 10] — в положении $C_2$ с образованием пиразольных производных.

В противоположность 4-тионфлавону, 4-тионизофлавон с этими реагентами не дает нормальных карбонильных производных.

Соединение I в обычных условиях не реагирует с семикарбазидом, тиосемикарбазидом и 2,4-динитрофенилгидразином, обладающими меньшей нуклеофильной силой.

## Гетероциклические аналоги простагландиновых тиазолей, II

И. БАРТА, Г. АМБРУШ, ДЬ. ХОРВАТ, М. ШОТИ и П. ШОХАР

Онисывается синтез dl-4-(3-тидрокси-1-транс-окленил)-5-(6-карбоксигексил)-тиазола и его 2-метилового аналога. Приводится и обсуждается ИК, ПМР и МС поведение этих новых тиазоловых производных.

## Дальнейшие данные, относящиеся к физическим и химическим свойствам диазосульфидов

А. Б. САҚЛА, Б. Й. РИАД, С. АБДОУ и Б. Н. БАРСОУМ

Диарилдиазосульфиды были получены из диазотированных ариламинов и растворов различных тиолов при строго контролируемых величинах pH. Был изолирован единственный изомер диарилдиазосульфида; изомер *Z*, образующийся вначале, претерпевает термическую перегруппировку в растворе, превращаясь в более стабильный изомер *E*. Обратная изомеризация (*E*–*Z*) была достигнута руссеянным солнечным светом; в присутствии *β*-нафтола образующийся изомер *Z* легко димеризуется, а в отсутствии димеризующего реагента разлагается. Скорость димеризации увеличивается под влиянием рессеянного солнечного света.

Les Acta Chimica paraissent en français, allemand, anglais et russe et publient des mémoires du domaine des sciences chimiques.

Les Acta Chimica sont publiés sous forme de fascicules. Quatre fascicules seront réunis en un volume (4 volumes par an).

On est prié d'envoyer les manuscrits destinés à la rédaction à l'adresse suivante:

*Acta Chimica*
*H-1521 Budapest, Hongrie*

Toute correspondance doit être envoyée à cette même adresse.

La rédaction ne rend pas de manuscript.

Le prix de l'abonnement: $ 36,00 par volume.

Abonnement en Hongrie à l'Akadémiai Kiadó (1363 Budapest, P. O. B. 24, C. C. B. 215 11488), à l'étranger à l'Entreprise du Commerce Extérieur « Kultura » (H-1389 Budapest 62, P. O. B. 149 Compte-courant No. 218 10990) ou chez représentants à l'étranger.

---

Die Acta Chimica veröffentlichen Abhandlungen aus dem Bereich der chemischen Wissenschaften in deutscher, englischer, französischer und russischer Sprache.

Die Acta Chimica erscheinen in Heften wechselnden Umfanges. Vier Hefte bilden einen Band. Jährlich erscheinen 4 Bände.

Die zur Veröffentlichung bestimmten Manuskripte sind an folgende Adresse zu senden:

*Acta Chimica*
*H-1521 Budapest, Ungarn*

An die gleiche Anschrift ist jede für die Redaktion bestimmte Korrespondenz zu richten.

Manuskripte werden nicht zurückerstattet.

Abonnementspreis pro Band: $ 36,00.

Bestellbar für das Inland bei Akadémiai Kiadó (1363 Budapest, Postfach 24, Bankkonto Nr. 215 11488), für das Ausland bei »Kultura« Außenhandelsunternehmen (H-1389 Budapest 62, P. O. B. 149. Bankkonto Nr. 218 10990) oder seinen Auslandsvertretungen.

---

«Acta Chimica» издают статьи по химии на русском, английском, французском и немецком языках.

«Acta Chimica» выходит отдельными выпусками разного обектъка, 4 выпус составляют один том и за год выходят 4 тома.

Предназначенные для публикации рукописи следует направлять по адресу:

*Acta Chimica*
*H-1521 Budapest, BHP*

Всякую корреспонденцию в редакцию направляйте по этому же адресу.

Редакция рукописей не возвращает.

Подписная цена — $ 36,00 за том.

Отечественные подписчики направляйте свои заявки по адресу Издательства Академии Наук (1363 Budapest, P. O. B. 24, Текущий счет 215 11488), а иностранные подписчики через организацию по внешней торговле «Kultura» (H-1389 Budapest 62, P. O. B. 149. Текущий счет 218 10990) или через ее заграничные представительства и уполномеченных.

## Reviews of the Hungarian Academy of Sciences are obtainable at the following addresses:

**AUSTRALIA**
C.B.D. LIBRARY AND SUBSCRIPTION SERVICE, Box 4886, G.P.O., *Sydney N.S.W. 2001*
COSMOS BOOKSHOP, 145 Ackland Street, *St. Kilda (Melbourne), Victoria 3182*

**AUSTRIA**
GLOBUS, Höchstädtplatz 3, *1200 Wien XX*

**BELGIUM**
OFFICE INTERNATIONAL DE LIBRAIRIE, 30 Avenue Marnix, *1050 Bruxelles*
LIBRAIRE DU MONDE ENTIER, 162 Rue du Midi, *1000 Bruxelles*

**BULGARIA**
HEMUS, Bulvar Ruszki 6, *Sofia*

**CANADA**
PANNONIA BOOKS, P.O. Box 1017, Postal Station "B", *Toronto, Ontario M5T 2T8*

**CHINA**
CNPICOR, Periodical Department, P.O. Box 50, *Peking*

**CZECHOSLOVAKIA**
MAD'ARSKÁ KULTURA, Národní třida 22, *115 66 Praha*
PNS DOVOZ TISKU, Vinohradská 36, *Praha 2*
PNS DOVOZ TLAČE, *Bratislava 2*

**DENMARK**
EJNAR MUNKSGAARD, Norregade 6, *1165 Copenhagen*

**FINLAND**
AKATEEMINEN KIRJAKAUPPA, P.O. Box 128, *SF-00101 Helsinki 10*

**FRANCE**
EUROPERIODIQUES S. A., 31 Avenue de Versailles, *78170 La Celle St.-Cloud*
LIBRAIRIE LAVOISIER, 11 rue Lavoisier, *75008 Paris*
OFFICE INTERNATIONAL DE DOCUMENTATION ET LIBRAIRIE, 48 rue Gay-Lussac, *75240 Paris Cedex 05*

**GERMAN DEMOCRATIC REPUBLIC**
HAUS DER UNGARISCHEN KULTUR, Karl-Liebknecht-Strasse 9, *DDR-102 Berlin*
DEUTSCHE POST ZEITUNGSVERTRIEBSAMT, Strasse der Pariser Kommüne 3—4, *DDR-104 Berlin*

**GERMAN FEDERAL REPUBLIC**
KUNST UND WISSEN ERICH BIEBER, Postfach 46, *7000 Stuttgart 1*

**GREAT BRITAIN**
BLACKWELL'S PERIODICALS DIVISION, Hythe Bridge Street, *Oxford OX1 2ET*
BUMPUS, HALDANE AND MAXWELL LTD., Cowper Works, *Olney, Bucks MK43 4BN*
COLLET'S HOLDINGS LTD., Denington Estate, *Wellingborough, Northants NN8 2QT*
WM. DAWSON AND SONS LTD., Cannon House, *Folkes-one, Kent CT19 5EE*
H. K. LEWIS AND CO., 136 Gower Street, *London WC1E 6BS*

**GREECE**
KOSTARAKIS BROTHERS, International Booksellers, 2 Hippokratous Street, *Athens-143*

**HOLLAND**
MEULENHOFF-BRUNA B.V., Beulingstraat 2, *Amsterdam*
MARTINUS NIJHOFF B.V., Lange Voorhout 9—11, *Den Haag*
SWETS SUBSCRIPTION SERVICE, 347b Heereweg, *Lisse*

**INDIA**
ALLIED PUBLISHING PRIVATE LTD., 13,14 Asaf Ali Road, *New Delhi 110001*
150 B-6 Mount Road, *Madras 600002*
INTERNATIONAL BOOK HOUSE PVT. LTD., Madame Cama Road, *Bombay 400069*
THE STATE TRADING CORPORATION OF INDIA LTD., Books Import Division, Chandralok, 36 Janpath, *New Delhi 110001*

**ITALY**
EUGENIO CARLUCCI, P.O. Box 252, *70100 Bari*
INTERSCIENTIA, Via Mazzé 28, *10149 Torino*
LIBRERIA COMMISSIONARIA SANSONI, Via Lamarmora 45, *50121 Firenze*
SANTO VANASIA, Via M. Macchi 58, *20124 Milano*
D. E. A., Via Lima 28, *00198 Roma*

**JAPAN**
KINOKUNIYA BOOK-STORE CO. LTD., 17-7 Shinjuku-ku 3 chome, Shinjuku-ku, *Tokyo 160-91*
MARUZEN COMPANY LTD., Book Department, P.O. Box 5050 Tokyo International, *Tokyo 100-61*
NAUKA LTD., IMPORT DEPARTMENT, 2-30-19 Minami Ikebukuro, Toshima-ku, *Tokyo 171*

**KOREA**
CHULPANMUL, *Phenjan*

**NORWAY**
TANUM-CAMMERMEYER, Karl Johansgatan 41—43, *1000 Oslo*

**POLAND**
WĘGIERSKI INSTYTUT KULTURY, Marszałkowska 80, *Warszawa*
CKP I W ul. Towarowa 28 *00-958 Warsaw*

**ROUMANIA**
D. E. P., *Bucureşti*
ROMLIBRI, Str. Biserica Amzei 7, *Bucureşti*

**SOVIET UNION**
SOJUZPETCHATJ — IMPORT, *Moscow*
and the post offices in each town
MEZHDUNARODNAYA KNIGA, *Moscow G-200*

**SPAIN**
DIAZ DE SANTOS, Lagasca 95, *Madrid 6*

**SWEDEN**
ALMQVIST AND WIKSELL, Gamla Brogatan 26, *101 20 Stockholm*
GUMPERTS UNIVERSITETSBOKHANDEL AB, Box 346, *401 25 Göteborg 1*

**SWITZERLAND**
KARGER LIBRI AG, Petersgraben 31, *4011 Basel*

**USA**
EBSCO SUBSCRIPTION SERVICES, P.O. Box 1943, *Birmingham, Alabama 65201*
F. W. FAXON COMPANY, INC., 15 Southwest Park, *Westwood, Mass, 02090*
THE MOORE-COTTRELL SUBSCRIPTION AGENCIES, *North Cohocton, N. Y. 14868*
READ-MORE PUBLICATIONS, INC., 140 Cedar Street, *New York, N. Y. 10006*
STECHERT-MACMILLAN, INC., 7250 Westfield Avenue, *Pennsauken* N.J. 08110

**VIETNAM**
XUNHASABA, 32, Hai Ba Trung, *Hanoi*

**YUGOSLAVIA**
JUGOSLAVENSKA KNJIGA, Terazije 27, *Beograd*
FORUM, Vojvode Mišiča 1, *21000 Novi Sad*

*16. II. 1979* HU ISSN 0001—5407 **Index: 26.007**