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B. LÉNGYEL, et GY. DEÁK

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INDEX

AGÓCS, P. M.: Dealkylation Side Reaction in the Synthesis of Cholesteryl Carbonates and Carbamates	263
AHMAD, M. S. s. HUSAIN, S. R.	
ALI, H. s. SHAFIULLAH	
ALI, H. s. SHAFIULLAH	
BAJUSZ, S. s. TURÁN, A.	
BHARGAWA, P. P. s. MALIK, W. U.	
BITTER, I., SZŐCS, L., TŐKE, L.: Heterocyclization with Iminium Chlorides, II. Synthesis of 4 <i>H</i> -[3, 1]-Benzoxazine-4-ones and Quinazolinones	57
BITTER, I., SZŐCS, L., TŐKE, L.: Heterocyclization with Iminium Chlorides, III. Synthesis of 3,4-Dihydro-(1 <i>H</i>)-1,3,4-benzotriazepine-2,5-diones	171
BOGNÁR, R. s. TŐKÉS, A. L.	
BOSQUEZ, A. s. KISS, L.	
BUDAI, Zs., SZEJTLI, J.: Cyclodextrin Inclusion Complexes of 2-Chloroethyl Phosphonic Acid	231
CHAPMAN, A. V. s. KATRITZKY, A. R.	
DÁVID, E. R., EVERS, R.: Structure and Reactivity of Activated C=N Double Bond, VI. Basicity Measurements on Cyanoguanyl-imido-dithiocarbonic Acid Diesters (in German)	369
DEÁK, Gy. s. GÁLL-ISTÓK, K.	
DOBROVOLSZKY, M., TÉTÉNYI, P., PAÁL, Z.: Metal Catalyzed Dehydrogenation of Cyclohexanol	343
DOWLATSHAHI, H. M. s. KATRITZKY, A. R.	
EVERS, R. s. DÁVID, E. R.	
FARKAS, J. s. KISS, L.	
GÁLL-ISTÓK, K., ZÁRA-KACZIÁN, E., KISFALUDY, L., DEÁK, Gy.: Synthesis of Peptides Containing D-Glucosaminic Acid, II. Synthesis of some Tri- and Hexapeptides	221
GARAI, T., MÉSZÁROS, L.: The Effect of Cell Resistance in A. C. Polarography	35
GYÓRYOVÁ, K., MOHAI, B.: Thermolysis of Complex Cyanides, XVI. Thermal Decomposition of Diphenyl Iodonium Cyanometallates with Linear, Planar and Tetrahedral Anions (in German)	67
GYÓRYOVÁ, K., MOHAI, B.: Thermolysis of Complex Cyanides, XVII. Thermal Decomposition of Diphenyl Iodonium Cyanometallates with Octahedral Anions (in German)	77
HARANCI, J. s. SZURMAI, Z.	
HORKAY, F., NAGY, M.: Mechanical-Rheological Studies on Polymer Networks, I. Effect of the Conditions of Cross-Linking on the Mechanical Properties	321
HUSAIN, M. s. HUSAIN, S. R.	
HUSAIN, S. R., HUSAIN, M., AHMAD, M. S.: Reaction of Steroidal Dienones with Perbenzoic Acid	1
INCZÉDY, J. s. MARTON, A.	
INZELT, G., SZETÉY, É.: Oxidation of Oxalic Acid on a Platinum Electrode	269
KATRITZKY, A. R., CHAPMAN, A. V., DOWLATSHAHI, H. M.: The Preparation of Arylglyoxals and Heteroaromatic Aldehydes Using Pyridona	315
KAUSHIK, N. K. s. KUMAR, S.	
KISFALUDY, L. s. GÁLL-ISTÓK, K.	
KISS, L., BOSQUEZ, A., VARSÁNYI, L. M.: Study of the Anodic Dissolution of Copper in Non-Aqueous Acetic Acid Solutions, IV	11
KISS, L., FARKAS, J.: Anodic Dissolution of Metals, I. Kinetics of the Dissolution Process Involving Two, and Three Consecutive Charge Transfer Steps	181
KOWALAK, S.: Preparation and Properties of Al ₂ O ₃ -AlF ₃ Catalysts, I	19
KOWALAK, S.: Catalytic Properties of the Al ₂ O ₃ -AlF ₃ System	27
KRIPAL, R. s. MISRA, B. N.	
KRISHNAIAH, A. s. RAO, D. N.	

KUMAR, S., KAUSHIK, N. K.: Platinum Metal Complexes of Cycloalkyl Dithiocarbamates	161
LEMPERT, K. s. SIMIG, Gy.	
LÉVAI, A.: Oxazepines and Thiazepines, XI. Conversion of 1-Thioflavanone Derivatives into Benzothiazepinones (Short Communication)	361
LIPTÁK, A. s. SZURMAI, Z.	
MAKLEIT, S. s. TÓTH, Gy.	
MAKLEIT, S. s. TÓTH, Gy.	
MALIK, W. U., BHARGAWA, P. P., SIDDIQUI, M. M.: Mixed Ligand Complexes of Metal Thiocyanates with 2,2'-Dipyridyl and 1,10-Phenanthroline	155
MARTON, A., PAP, T., INCZÉDY, J.: Thermochemical Aspects of Anion-Exchange Reactions, III. Calorimetric and Equilibrium Studies of Anion Exchange Reactions Involving Organic Ions	203
MATHERNY, M., ONDÁŠOVÁ, M.: On Spectrographic Characteristics of Capillary Electrodes, III. Use of Medium Voltage Spark Discharge (in German)	119
MEDZIHRADESKÝ, K.: GYŐZŐ (VIKTOR) BRUCKNER (1900—1980)	287
MÉSZÁROS, L. s. GARAI, T.	
MISRA, B. N., KRIPAL, R.: Bonding Parameters and ESR Hyperfine Linewidth of the Cu(II)-DL-Alanine Complex	101
MOHAI, B. s. GYÓRYOVÁ, K.	
MOHAI, B. s. GYÓRYOVÁ, K.	
NAGY, M. s. HORKAY, F.	
NAIDU, P. R. s. RAO, D. N.	
NÁNÁSI, P. s. SZURMAI, Z.	
ONDÁŠOVÁ, M. s. MATHERNY, M.	
PAÁL, Z. s. DOBROVOLSZKY, M.	
PAP, T. s. MARTON, A.	
RAO, D. N., KRISHNAIAH, A., NAIDU, P. R.: Isentropic Compressibility Ethylenediamine + <i>n</i> -Alcohol at 303.15 and 313.15 K	49
SHAFIULLAH, ALI, H., SHAMSUZZAMAN: Reaction of Lead (IV)acetate with Steroidal 6-Oximino Compounds	97
SHAFIULLAH, ALI, H., SHAMSUZZAMAN: Aromatization of 3 β -Chloro-5,7 β -dibromo-5 α -cholestan-6-one (Short Communication)	115
SHAMSUZZAMAN s. SHAFIULLAH	
SHAMSUZZAMAN s. SHAFIULLAH	
SIDDIQUI, M. M. s. MALIK, W. U.	
SIMIG, Gy., LEMPERT, K.: The Mechanism of the Reaction of 2-Bromo- <i>N,N</i> -dimethyl-2,2-diphenylacetamide and Sodium Methoxide in 2,2-Dimethoxypropane. A Method for Establishing the Radical-Anion Radical Chain Mechanism	375
SUBA, M. s. VÉRTES, A.	
SZABÓ, K., TAKÁCS, M.: The Effect of Thiourea and its Derivatives on Hydrogen Overvoltage at the Dropping Gallium Electrode	131
SZEJTLI, J. s. BUDAI, Zs.	
SZEJTLI, J. s. SZENTE, L.	
SZENTE, L., SZEJTLI, J.: Cyclodextrin Complex of a Volatile Insecticide (DDVP)	195
SZETÉY, É. s. INZELT, G.	
SZŐCS, L. s. BITTER, I.	
SZŐCS, L. s. BITTER, I.	
SZURMAI, Z., LIPTÁK, A., HARANGI, J., NÁNÁSI, P.: Carbohydrate Methyl Ethers, X. Hydrogenolysis of Benzylidene Acetals. Synthesis of mono- and di- <i>O</i> -Methyl Ethers of L-Arabinose	213
TAKÁCS, M. s. SZABÓ, K.	
TÉTÉNYI, P. s. DOBROVOLSZKY, M.	
TÉTÉNYI, P. The Role of Catalyst Surface and Structure of Molecules in Metal Catalysis	237
TÓTH, Gy., MAKLEIT, S.: Azidobarbiturates, I. Synthesis of Barbituric Acid Derivatives Containing Azido Group in Position 5 (in German)	139
TÓTH, Gy., MAKLEIT, S.: Azidobarbiturates, II. Synthesis of Barbituric Acid Derivatives Containing Azido Group in the Substituent (in German)	147
TŐKE, L. s. BITTER, I.	
TŐKE, L. s. BITTER, I.	
TÓKÉS, A. L., BOGNÁR, R.: Synthesis of Chlorflavonin	65
TURÁN, A., BAJUSZ, S.: Optical Rotation of <i>t</i> -Butyloxycarbonyl-L-tyrosine	7
VARSÁNYI, L. M. s. KISS, L.	
VÉRTES, A., VÉRTES, Gy., SUBA, M.: A Study of the Chemical State of Tin Layers Deposited on Various Aluminium Alloys and Electroplated with Copper	335
VÉRTES, Gy. s. VÉRTES, A.	
ZÁRA-KACZIÁN, E. s. GÁLL-ISTÓK, K.	

REACTION OF STEROIDAL DIENONES WITH PERBENZOIC ACID

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The reaction of cholesta-2,4-dien-6-one (**1**) with perbenzoic acid (1 mole equivalent) in the presence of *p*-toluenesulfonic acid monohydrate as catalyst, afforded 4 β ,5 β -oxidocholest-2-en-6-one (**4**), 4 α ,5 α -oxidocholest-2-en-6-one (**5**) and 2 α ,3 α -oxido-5-hydroxy-4 β -methoxy-5 α -cholestan-6-one (**6**). 6-Acetoxycholesta-4,6-dien-3-one (**2**) on similar treatment produced 6 α ,7 α -oxid-6 β -acetoxycholest-4-en-3-one (**9**) and 7 α -hydroxycholest-4-ene-3,6-dione (**10**). 6-Ethoxycholesta-4,6-dien-3-one (**3**) provided 4-hydroxy-6-ethoxycholesta-4,6-dien-3-one (**11**) and 7 α -hydroxy-6 β -methoxy-6 α -ethoxycholest-4-en-3-one (**13**). Characterization of the products has been made on the basis of elemental analysis, spectral properties and by comparison with authentic samples, where available.

In continuation of our studies on the peracid oxidation of steroidal ketones [1—5], dienones **1—3** were treated with perbenzoic acid (1 mole equivalent) using catalytic amounts of *p*-toluenesulfonic acid monohydrate. With 1 mole equivalent of perbenzoic acid, **1** gave **4** (m.p. 115 °C), **5** (m.p. 128 °C) and **6** (m.p. 116 °C). Upon similar treatment, **2** afforded **9** (m.p. 113 °C) and **10** (m.p. 165 °C). Similarly, **3** yielded **11** (m.p. 122 °C) and **13** (m.p. 190°).

The compounds with melting points of 115 °C and 128 °C were correctly analyzed as C₂₇H₄₂O₂. This molecular composition (for each product) suggested the addition of an oxygen atom to the parent dienone. The UV spectra of both compounds were found to be featureless in the region of 220—360 nm, which indicated the absence of an α , β -unsaturated chromophore. From this observation, it becomes evident that these compounds are isomeric 4,5-oxidoketones **4** and **5**. The distinction of oxides **4** and **5** became possible from their NMR spectra, wherein different chemical shifts were observed for the C4-proton. In the NMR spectrum of the compound melting at 128 °C, the C4-proton appeared as a distorted doublet at δ 4.6, whereas, the NMR spectrum of the compound with m.p. 115 °C showed a C4-proton signal (distorted doublet) at δ 3.65. This distortion of the doublet in both cases might be due to the long range coupling of the C4-proton with C2-protons. It has been reported [6] that the C4-proton in 4 α ,5 α -oxidocholestan-6-one (**7**) absorbs at a relatively lower field than in its isomeric 4 β ,5 β -oxidocholestan-6-one (**8**). On the basis

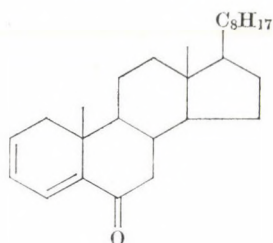
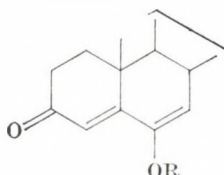
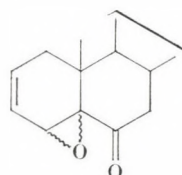
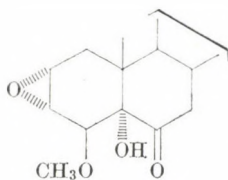
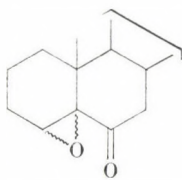
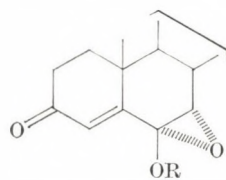
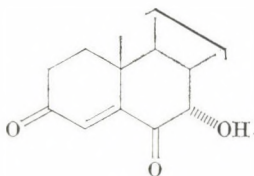
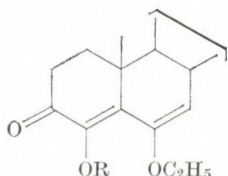
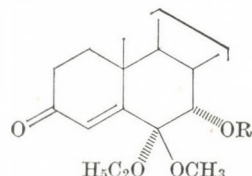
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of this analogy, the compounds with melting points of 115 °C and 128 °C are identified as **4** and **5** respectively.

Compound **6** had a correct analysis as $C_{28}H_{46}O_4$. The UV absorption maximum was found to be featureless in the region of 220-360 nm. Its IR spectrum exhibited bands corresponding to hydroxy and keto functions. The NMR spectrum supported structure **6**, displaying a distorted doublet for one proton at δ 3.75 ascribable to the C4- α H proton. A multiplet for C2- β H and C3- β H at δ 3.25 and a sharp singlet due to methoxy protons ($-OCH_3$) at δ 3.6 also favoured compound **6**.

The elemental analysis of **9** ($_{29}H_{44}O_4$) indicated the addition of an oxygen atom to dienone **2**. Its UV absorption maximum at 238 nm (ϵ 6800) suggested the presence of an α, β -unsaturated carbonyl chromophore. This was also

**1****2** R = Ac**3** R = C₂H₅**4** 4 β , 5 β **5** 4 α , 4 α **6****7** 4 α , 5 α **8** 4 β , 5 β **9** R = Ac**15** R = C₂H₅**10****11** R = H**12** R = Ac**13** R = H**14** R = Ac

supported by a band in the IR spectrum at 1675 cm^{-1} compatible with an α, β -unsaturated chromophore. The composition, UV and IR data lead to structure **9**. To this structure, the NMR spectrum lends further support. A sharp singlet at δ 6.2 and an unresolved broadened singlet at δ 3.3 were ascribable to C4-*H* and C7- β *H*, respectively. The Dreiding model of **9** showed the dihedral angle between C7- β *H* and C8- β *H* to be almost 90° , which accounted for the non-splitting of C7- β *H* [3]. The identity of the compound with m.p. 165°C was established by direct comparison with authentic **10** [7]. Moreover, compound **10**, is a hydrolytic product of **9**; this was proved by the fact that when **9** was subjected to acid hydrolysis, it yielded **10**.

The compound with m.p. 122°C ($\text{C}_{29}\text{H}_{46}\text{O}_3$) showed in its molecular composition the addition of an oxygen atom to **3**. Its UV absorption maximum at 335 nm (ϵ 22090) suggested the presence of a dienone-like chromophore with a hydroxy function α to the keto group. The presence of the hydroxy group was also revealed by its IR spectrum, which exhibited the corresponding band at 3400 cm^{-1} . The assignment of this structure, **11**, was substantiated by the NMR spectrum which displayed an unresolved broadened singlet at δ 5.65 (C7-*H*) (dihedral angle between C7-*H* and C8- β *H* is almost 90°). Treatment of **11** with pyridine-acetic anhydride provided the ester **12**.

The compound with m.p. 190°C , analyzing for $\text{C}_{30}\text{H}_{50}\text{O}_4$, showed a UV absorption maximum at 238 nm (ϵ 6380). The IR spectrum, which exhibited bands at 1680 and 3400 cm^{-1} , also supported structure **13**. Further support for this structure came from the NMR spectrum showing a sharp singlet at δ 6.45 for 1 proton (C4-*H* proton) and also an unresolved broadened singlet integrating for 1 proton at δ 3.8, which can be assigned to C7- β *H* [3]. Compound **13** is probably a product of the methanolysis (methanol present in PBA) of **15**. On treatment with acetic anhydride and pyridine, **13** transformed into **14**. The notable feature of the NMR spectrum of **14** is the downfield appearance of a C7- β *H* proton signal (δ 5.1) relative to that in **13** (δ 3.8). This could be attributed to the presence of an acetate function at C7, as seen in structure **14**.

Experimental

All m.p.'s are uncorrected. IR spectra were determined in Nujol on a Perkin-Elmer spectrophotometer. UV spectra were recorded in 95% ethanol using a Beckman DK2 spectrophotometer. NMR spectra were run in CDCl_3 on a Varian A60 instrument with TMS as internal standard. The data are given on the δ scale in ppm. Thin-layer chromatographic plates were coated with silica gel G (BDH, Bombay). A 20% aqueous solution of perchloric acid was used as spraying agent. Silica gel (BDH, Bombay) was used for column chromatography.

Reaction of cholesta-2,4-dien-6-one (**1**) with perbenzoic acid

To a solution of **1** [8] (2 g) in chloroform (25 mL), was added a chloroform solution of perbenzoic acid (1 mole equivalent) and a few crystals of *p*-toluenesulfonic acid monohydrate as catalyst, and the reaction mixture was allowed to stand at room temperature for 10 h.

The solvent was then removed by distillation under reduced pressure and the residue extracted with ether. The ethereal solution was washed with water, sodium bicarbonate solution (5%) and water, and dried over anhydrous sodium sulfate. The solvent was removed and the residue subjected to chromatography on silica gel (40 g) (each fraction of about 30 mL was collected). Elution with light petroleum-ether (19 : 1) gave **4**, which was crystallized from light petroleum; 210 mg, m.p. 115° C; ν max. 1710, 1620 and 870 cm^{-1} ; δ 6.9 (m, $\text{C}_2\text{-H}$, $\text{C}_3\text{-H}$), 3.65 (distorted d, $J = 4$ Hz; $\text{C}_4\text{-}\alpha\text{H}$), 2.3 (m, $\text{C}_7\text{-H}_2$), 0.92 ($\text{C}_{10}\text{-CH}_3$), 0.7 ($\text{C}_{13}\text{-CH}_3$).

$\text{C}_{27}\text{H}_{42}\text{O}_2$. Calcd. C 81.41; H 10.55. Found C 81.39; H 10.58%.

Elution with light petroleum-ether (15 : 1) gave 850 mg of **6**, m.p. 116° C (from light petroleum); ν max. 3400, 1720, 1210 and 1080 cm^{-1} ; δ 3.75 (distorted d, $J = 1.5$ Hz; $\text{C}_4\text{-}\alpha\text{H}$), 3.6 (s, OCH_3), 3.25 (m, $\text{C}_2\beta\text{-H}$ and $\text{C}_3\beta\text{-H}$), 2.2 ($\text{C}_7\text{-H}_2$), 1.95 (s-OH; disappeared on shaking with D_2O), 0.9 ($\text{C}_{10}\text{-CH}_3$), 0.65 ($\text{C}_{13}\text{-CH}_3$).

$\text{C}_{28}\text{H}_{46}\text{O}_4$. Calcd. C 75.34; H 10.31. Found C 75.30; H 10.30%.

Further elution with light petroleum ether (10 : 1) afforded **5**, which was crystallized from light petroleum; 200 mg, m.p. 128° C; ν max 1705, 1620 and 890 cm^{-1} ; δ 5.7 (m, $\text{C}_2\text{-H}$ and $\text{C}_3\text{-H}$), 4.1 (distorted d, $J = 2$ Hz; $\text{C}_4\text{-}\beta\text{H}$), 2.3 (m, $\text{C}_7\text{-H}$), 0.91 ($\text{C}_{10}\text{-CH}_3$), 0.69 ($\text{C}_{13}\text{-CH}_3$).

$\text{C}_{27}\text{H}_{42}\text{O}_2$. Calcd. C 81.41; H 10.55. Found C 81.38; H 10.59%.

Reaction of 6-acetoxycholesta-4,6-dien-3-one (2) with perbenzoic acid

The dienone **2** [7] (2 g) was treated with perbenzoic acid (1 mole equivalent) in the usual manner. Evaporation of the solvent gave the residue which was chromatographed over silica gel (40 g). Elution with light petroleum-ether (15 : 1) provided 500 mg of **9**, m.p. 113° C which was crystallized from light petroleum ether. λ max 238 nm (ϵ 6800); ν max 1740, 1675, 1620, 1200 and 1180 cm^{-1} ; δ 6.2 (s, $\text{C}_4\text{-H}$), 3.3 (broadened s, $\text{C}_7\text{-}\beta\text{H}$), 2.5 (m, $\text{C}_2\text{-H}_2$), 2.1 (s, CH_3COO), 1.2 ($\text{C}_{10}\text{-CH}_3$), 0.68 ($\text{C}_{13}\text{-CH}_3$).

$\text{C}_{29}\text{H}_{44}\text{O}_4$. Calcd. C 76.31; H 9.65. Found C 76.30; H 9.65%.

Further elution with light petroleum-ether (3 : 1) gave **10** (250 mg), m.p. and m.m.p. 165° C.

Reaction of 6-ethoxycholesta-4,6-dien-3-one (3) with perbenzoic acid

Similarly **3** [9] (2 g) was treated with perbenzoic acid (1 mole equivalent) and worked up in the usual manner. After the removal of the solvent, the residue obtained was chromatographed over silica gel (40 g). Elution with light petroleum-ether (25 : 1) provided **11** (80 mg), m.p. 122° C (from light petroleum); λ max 335 nm (ϵ 22090); ν max 3400, 1600, 1580 and 1190 cm^{-1} ; δ 6.15 (br, OH; disappeared on shaking with D_2O), 5.65 (broadened s, $\text{C}_7\text{-H}$), 3.9 (q, $-\text{OCH}_2\text{CH}_3$), 1.2 ($\text{C}_{10}\text{-CH}_3$), 0.69 ($\text{C}_{13}\text{-CH}_3$).

$\text{C}_{29}\text{H}_{46}\text{O}_3$. Calcd. C 78.73; H 10.41. Found C 78.70; H 10.43%.

Further elution with light petroleum-ether (22 : 1) afforded **13**, 400 mg, m.p. 190° C; crystallized from light petroleum, λ max. 238 nm (ϵ 6380); ν max 3430, 1690, 1610, 1050 and 1040 cm^{-1} ; δ 6.45 (s, $\text{C}_4\text{-H}$), 3.8 (broad s, $\text{C}_7\text{-}\beta\text{H}$), 3.8 (q- OCH_2CH_3), 3.1 (s, $-\text{OCH}_3$), 1.8 (br, $-\text{OH}$; disappeared on shaking with D_2O), 1.1 ($\text{C}_{10}\text{-CH}_3$), 0.75 ($\text{C}_{13}\text{-CH}_3$).

$\text{C}_{30}\text{H}_{50}\text{O}_4$. Calcd. C 75.95; H 10.55. Found C 76.06; H 10.54%.

4-Acetoxy-5-ethoxycholesta-4,6-dien-3-one (12)

Mixture of **11** (100 mg), pyridine (0.3 mL) and acetic anhydride (0.3 mL) was left at room temperature for 24 h under anhydrous condition. The usual work-up and removal of the solvent afforded an oil (ca. 30 mg); λ max 315 nm (ϵ 21080); ν max 1700, 1665, 1600 and 1200 cm^{-1} .

$\text{C}_{31}\text{H}_{48}\text{O}_4$. Calcd. C 76.86; H 9.92. Found C 76.88; H 9.88%.

7 α -Acetoxy-6 β -methoxy-6 α -ethoxycholest-4-en-3-one (14)

A mixture of **13** (50 mg), pyridine (0.5 mL) and acetic anhydride (0.3 mL) was heated on a steam bath for 18 h. The usual work-up and the removal of the solvent provided **14** as an oil (120 mg); λ max 238 nm (ϵ 6830); ν max 1735, 1675, 1610, 1220, 1180 and 1040 cm^{-1} ;

δ 6.3 (s, C₁-H), 5.1 (broadened, s, C₇- β H), 3.5 (q, -OCH₂-CH₃), 3.1 (s, -OCH₃), 2.0 (s, CH₃COO), 0.9 (C₁₀-CH₃), 0.7 (C₁₃-CH₃).
C₃₂H₅₂O₅. Calcd. C 74.42; H 10.10. Found C 74.42; H 10.11%.

*

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OPTICAL ROTATION OF *t*-BUTYLOXYCARBONYL-L-TYROSINE

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Specific rotations of *t*-butyloxycarbonyl-L-tyrosine have been found to be significantly lower than the values reported previously. Enzymic resolution of methyl *t*-butyloxycarbonyl-DL-tyrosinate is described giving an overall yield of 77% based on DL-tyrosine.

In the first synthesis of Boc-Tyr-OH** described by ANDERSON and MCGREGOR [1] tyrosine was acylated with *t*-butyl-*p*-nitrophenyl carbonate in a mixture of aqueous sodium carbonate–sodium bicarbonate and *t*-butyl alcohol. The crystalline product was obtained in a yield of only 29%. Later SCHNABEL [2] could reach a much higher yield (94%) by using *t*-butyloxycarbonyl azide (Boc-N₃) as acylating agent and running the reaction in an autotitrator. To find a more practical route to Boc-Tyr-OH we prepared this compound by saponification of Boc-Tyr-OMe which could be obtained from methyl L-tyrosinate [3] and Boc-N₃ in an easy way as described by SCHRÖDER [4]. This process (method *A*) afforded Boc-Tyr-OH in a yield of 77% based on L-tyrosine.

According to the data summarized in Table I, our product had a melting point and specific rotation different from those given in the literature for this compound. The higher melting point (137–139 °C) was similar to that reported by ANDERSON and MCGREGOR [1] but the values of the optical rotations $[\alpha]_D = +2.5^\circ$ (AcOH) and $[\alpha]_{578} = -10.9^\circ$ (DMF) were lower than those reported, $[\alpha]_D = +3.9^\circ$ and $[\alpha]_{578} = -32.8^\circ$, respectively. The lower specific rotation could be due to a partial racemization occurring during saponification. For checking this possibility, the acylation of tyrosine was also carried out according to the method of GRZONKA and LAMMEK [5] with the sole modification that the reaction between the amino acid, Boc-N₃ and triethylamine was run in aqueous dimethylformamide instead of aqueous dioxane used in the case of other amino acids [5]. Boc-Tyr-OH obtained by this procedure (method *B*) had specific rotations similar to those of our former sample pre-

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** Abbreviations follow IUPAC-IUB recommendations in most cases: AcOH: acetic acid; Boc: *t*-butyloxycarbonyl; DMF: dimethylformamide; Me methyl

Table I
Properties of Boc-Tyr-OH and Boc-D-Tyr-OH prepared by different methods

Compound	Method ^a	Yield ^b (%)	M. p. (C°)	$[\alpha]_D^{20-25}$ ($c=2.04$, AcOH)	$[\alpha]_{578}^{15-25}$ ($c=1$, DMF)
Boc-Tyr-OH	<i>lit.</i> [1]	29	136–137	+3.9 ± 0.5°	
	<i>lit.</i> [2] ^c	94	96–98		–32.8°
	<i>A</i>	77	138–139	+2.5 ± 0.5°	–10.9 ± 0.5°
	<i>B</i>	55	137–138	+2.4 ± 0.5°	–11.1 ± 0.5°
	<i>C</i>	77	136–138	+2.5 ± 0.5°	–10.9 ± 0.5°
Boc-D-Tyr-OH	<i>C + A</i>	77	136–137	–2.5 ± 0.5°	+10.9 ± 0.5°

^a *A*: Boc-Tyr-OMe + NaOH; *B*: H-Tyr-OH + Boc-N₃/NEt₃; *C*: Boc-DL-Tyr-OMe + Subtilisin Carlsberg/NaOH.

^b Based on tyrosine.

^c A footnote in [2] indicated this compound as dicyclohexylamine salt, which, according to the microanalysis given, must be an error.

pared by method *A*. To obtain further evidence that no racemization occurred during the alkaline hydrolysis of Boc-Tyr-OMe, this compound and Boc-DL-Tyr-OMe were also saponified with Subtilisin Carlsberg at pH 7.3. Boc-DL-Tyr-OMe and H-DL-Tyr-OMe. HCl were prepared according to the procedure given for the L compounds [3, 4]. The enzymic hydrolyses were carried out in an autotitrator using a solvent mixture of benzene-dioxane-water, which formed a fine emulsion on stirring. Consumption of NaOH (1 *N*, one equivalent) ceased in three hours. Boc-Tyr-OH obtained by the enzymic hydrolysis (method *C*) showed rotations of $[\alpha]_D = +2.5^\circ$ (AcOH) and $[\alpha]_{578} = -10.9^\circ$ (DMF), respectively, which again were similar to those of our former preparations. Unhydrolyzed Boc-D-Tyr-OMe isolated from the organic layer of the reaction mixture was saponified to yield Boc-D-Tyr-OH, the specific rotation of which corresponded to that of the L isomer (see Table I).

We have no explanation for the differences between the optical rotations of our preparations and those described in the literature [1, 2].

As an additional outcome of this study a simple way was found for the resolution of Boc-DL-Tyr-OMe giving Boc-Tyr-OH and Boc-D-Tyr-OH in an overall yield of 77% based on DL-tyrosine.

Experimental

Melting points were determined on a micro Boetius not plate apparatus and are uncorrected. Optical rotations were measured using an OPTON LEP A2 (Germany) polarimeter. Thin-layer chromatograms (TLC) were run on Silica gel G in the following systems (composed by volume): (A) ethyl acetate-pyridine-acetic acid-water (60 : 20 : 6 : 11); (B) ethyl acetate-pyridine-acetic acid-water (480 : 20 : 6 : 11); (C) methylene chloride-*n*-hexane-acetic acid (8 : 1 : 1).

Boc-Tyr-OH

Method A: To a solution of Boc-Tyr-OMe [4] (59 g, 0.2 mol) in methanol (160 mL), containing thymolphthalein as indicator, 1 *N* sodium hydroxide (approx. 200 mL) was added with stirring and cooling in an ice bath. When saponification was complete (according to TLC, the acidity was adjusted to pH 5, then, after removing methanol under reduced pressure, to 3 with 0.5 *N* sulfuric acid. The separated oil was allowed to crystallize in a refrigerator. Crystals were filtered off, washed with water and dried. Yield 53.5 g (95%); m.p. 137–139 °C; R_f 0.5–0.6 (B), 0.2–0.3 (C); $[\alpha]_D^{20} = +2.5 \pm 0.5^\circ$ ($c = 2.04$, AcOH); $[\alpha]_{578}^{20} = -10.9 \pm 0.5^\circ$ ($c = 1$, DMF).

$C_{14}H_{19}O_5N$ (281.30). Calcd. C 59.77; H 6.81; N 4.98. Found C 59.7; H 6.9; N 4.95%.

Method B: To a solution of L-tyrosine (18.1 g, 0.1 mol) and triethylamine (42 mL, 0.3 mol) in water (150 mL) DMF (150 mL) and Boc-N₃ (18 mL, 0.12 mol) were added. The mixture was stirred at room temperature until a significant amount of L-tyrosine was present (according to TLC; approx. 24 h), then the solvents were removed under reduced pressure. The residue was dissolved in water, extracted with chloroform to remove Boc-Tyr(Boc)-OH, and the pH was adjusted to 3 with 0.5 *N* sulfuric acid. The end product was isolated as described in method A. Yield 15.5 g (55%); m.p. 137–138 °C; R_f 0.5–0.6 (B), 0.2–0.3 (C); $[\alpha]_D^{20} = +2.4 \pm 0.5^\circ$ ($c = 2.04$, AcOH); $[\alpha]_{578}^{20} = -11.1 \pm 0.5^\circ$ ($c = 1$, DMF).

Method C: enzymic resolution of Boc-DL-Tyr-OMe

1) H-DL-Tyr-OMe.HCl: DL-tyrosine (22.4 g, 123.6 mmol) suspended in methanol (100 mL) was converted into the methyl ester hydrochloride by means of SOCl₂ (10 mL) as described by BOISSONNAS *et al.* [3] for the synthesis of the L compound. Yield 25.9 g (90%); m.p. 178–180 °C; R_f 0.5–0.6 (A).

2) Boc-DL-Tyr-OMe.HCl (25.8 g, 111.4 mmol) was reacted with Boc-N₃ (20.5 mL, 133.7 mmol) in pyridine (150 mL) containing triethylamine (47 mL, 336 mmol) as reported by SCHÖRDER [4] for the preparation of the L compound. Yield 29.55 g (90%); m.p. 143–144 °C; R_f 0.6–0.7 (C).

3) enzymic hydrolysis: Boc-DL-Tyr-OMe (29.54 g, 100 mmol) was dissolved in a mixture of dioxane (200 mL) and benzene (100 mL), then water (400 mL) containing Subtilisin Carlsberg (50 mg) was added. The mixture was stirred and the pH was maintained at 7.3 with 1 *N* sodium hydroxide by using an autotitrator. Consumption of sodium hydroxide ceased in 3 h (approx. 50 mL). The aqueous layer was extracted with benzene (3 × 20 mL) and the combined organic solutions were washed with water (3 × 20 mL). The aqueous solutions were combined and filtered, then acidified with solid citric acid. The separated oil was allowed to crystallize in a refrigerator. Crystals were filtered off, washed with water and dried. Yield 13.5 g (96% of theory or 48% based on Boc-DL-Tyr-OMe); m.p. 136–137 °C; R_f 0.5–0.6 (B) 0.2–0.3 (C); $[\alpha]_D^{20} = +2.5 \pm 0.5^\circ$ ($c = 2.04$, AcOH); $[\alpha]_{578}^{20} = -10.5 \pm 0.5^\circ$ ($c = 1$, DMF)

Boc-D-Tyr-OH

The combined organic layer and benzene washing from the previous experiment (method C, step 3) were evaporated under reduced pressure. The residue was dissolved in methanol (40 mL) and saponified as described in method A. Yield 13.48 g (96% of theory or 48% based on Boc-DL-Tyr-OMe); m.p. 136–137 °C; R_f 0.5–0.6 (B), 0.2–0.3 (C); $[\alpha]_D^{20} = -2.5 \pm 0.5^\circ$ ($c = 2.04$, AcOH); $[\alpha]_{578}^{20} = +10.5 \pm 0.5^\circ$ ($c = 1$, DMF).

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STUDY OF THE ANODIC DISSOLUTION OF COPPER IN NON-AQUEOUS ACETIC ACID SOLUTIONS, IV

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The anodic dissolution of copper in non-aqueous acetic acid solutions of HClO_4 , LiClO_4 , and NaClO_4 proceeds according to diffusion kinetics, or according to mixed diffusion and charge-transfer kinetics depending on the composition of the medium. A change in kinetics is most probably caused by the adsorption and desorption respectively, of acetate ions.

In our previous works [1, 2, 3] we studied the anodic dissolution of copper in non-aqueous acetic acid solutions. It has been found that, in the solutions tested, copper is oxidised to Cu^+ ions. In solutions which contain 0.5 mole dm^{-3} perchloric acid, respectively, 0.5 mole dm^{-3} lithium perchlorate, the diffusion of the Cu^+ ions from the metal surface into the bulk of the solution is the rate-determining step of the anodic process. In solutions which contain lithium chloride a copper chloro complex is formed as a result of the anodic process. In the case of lithium chloride it has been found that a multi-step process should be considered, *viz.* charge transfer, chemical reaction, diffusion, and that addition of lithium perchlorate to the solution affects the rate-determining step.

Anodic dissolution of copper in non-aqueous acetic acid solutions of $0.1 \text{ mole dm}^{-3} \text{ NaClO}_4 + 0.01 \text{ mole dm}^{-3} \text{ HClO}_4$ has been studied also by MOLODOV *et al.* [4]. They supposed that an increase in perchloric acid concentration accelerates the processes occurring at the copper. However, this supposition seems to contradict some experimental data given in one of our earlier communications [1].

In order to elucidate this moot point we studied the anodic dissolution of copper in non-aqueous acetic acid media which contained sodium perchlorate, lithium perchlorate, and perchloric acid, severally in various concentrations. Perhaps these experiences will furnish further data also to interpret the effects which the anions exert upon the kinetics of the electrode processes.

Results and Discussion

The experimental apparatus, preparation and quality of chemicals used were the same as described earlier [5]. A rotating copper disc electrode was used: this was prepared in the same way as described in [1]. Tests were carried out at room temperature. The electrode-potential values refer to a calomel electrode which contains a saturated solution of NaCl and a 0.3 mole dm^{-3} solution of NaClO₄, both in acetic acid. The medium was considered to be non-aqueous when its water content was less than 0.028 mole dm^{-3} .

Tests were carried out in solutions given in Table I. For solution 1–9, the character of the polarization curves determined with a rotating disc electrode, is uniform. In the Table also the *b*-coefficients of the Tafel-lines are given. As an example, Figure 1 shows the polarization curves recorded in the solution of 0.1 mole dm^{-3} LiClO₄ + 0.1 mole dm^{-3} HClO₄. With increased r.p.m. value of the disc electrode the curves are shifted toward more negative voltages, but the Tafel *b*-constant of the linear sections is 57 ± 2 mV independently of the speed of rotation of the electrode. On the basis of data in Fig. 1, current density *j* as a function of the square root of electrode-r.p.m., $f^{1/2}$, is plotted in Figure 2. The experimental points belonging to the same electrode potentials give straight lines in a *j* vs. $f^{1/2}$ diagram.

The polarization curve characteristic for solutions 10–13 is shown in Figure 3, and represent tests in 0.25 mole · dm⁻³ solution of NaClO₄ in acetic

Table I

	Composition of the solutions mole dm ³	Tafel <i>b</i> coefficient* mV
1	0.5 LiClO ₄	58
2	0.4 NaClO ₄	60
3	0.5 NaClO ₄	60
4	0.25 HClO ₄	60
5	0.25 LiClO ₄	68
6	0.25 NaClO ₄ + 0.1 HClO ₄	62
7	0.25 LiClO ₄ + 0.1 HClO ₄	58
8	0.1 LiClO ₄ + 0.1 HClO ₄	57
9	0.1 NaClO ₄ + 0.1 HClO ₄	71
10	0.1 NaClO ₄ + 0.01 HClO ₄	101
11	0.1 LiClO ₄ + 0.01 HClO ₄	112
12	0.3 NaClO ₄	90
13	0.25 NaClO ₄	124

* Maximum error in figures for solutions 1–8 is ± 2 mV, for solutions 9–13, ± 10 mV.

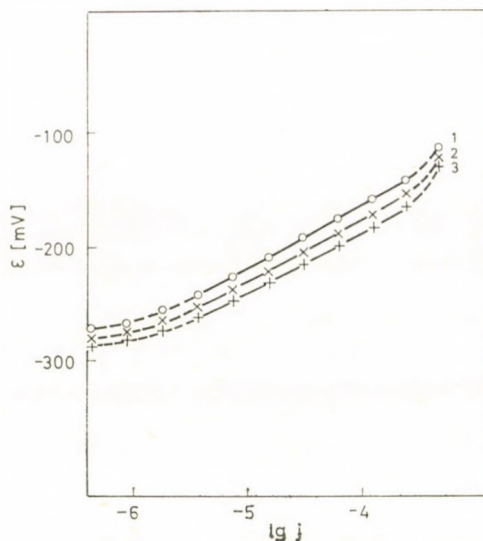


Fig. 1. ε vs. $\log j$ correlation at various r.p.m., in solution of $0.1 \text{ mole dm}^{-3} \text{ LiClO}_4 + 0.1 \text{ mole dm}^{-3} \text{ HClO}_4$ in non-aqueous acetic acid. 1: r.p.m. 160; 2: r.p.m. 610; 3: r.p.m. 3070

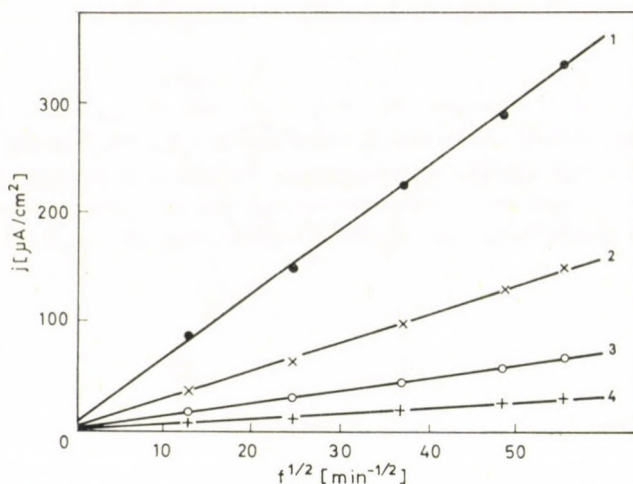


Fig. 2. j vs. $f^{1/2}$ correlation at different constant potentials, in a solution of $0.1 \text{ mole dm}^{-3} \text{ LiClO}_4 + 0.1 \text{ mole} \cdot \text{dm}^{-3} \text{ HClO}_4$ in non-aqueous acetic acid. 1: -180 mV ; 2: -200 mV ; 3: -220 mV ; 4: -240 mV

acid. With increasing speed of rotation of the electrode also here the polarization curve is shifted to the more negative direction. There are two approximately linear sections on these curves. The section at more negative potentials belonging to low current densities indicates copper dissolved in the form of acetato complexes [6]. The increase of current density reaches a limiting current in respect to acetate ion, potentials shift to the positive direction and

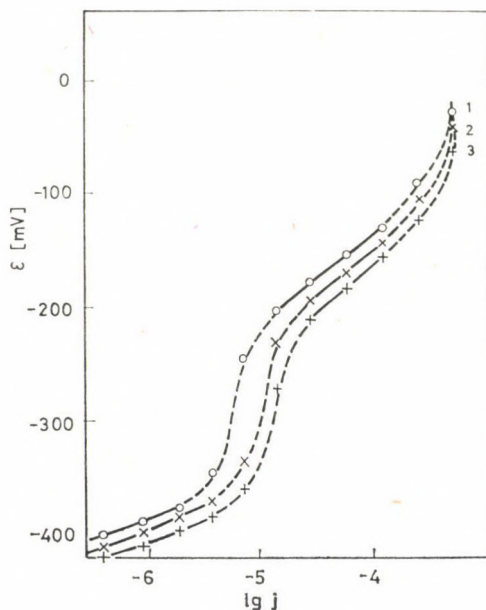


Fig. 3. ε vs. $\log j$ correlation at various r.p.m., found in a solution of $0.25 \text{ mole dm}^{-3} \text{ NaClO}_4$ in non-aqueous acetic acid. 1: r.p.m. 160; 2: r.p.m. 610; 3: r.p.m. 3070

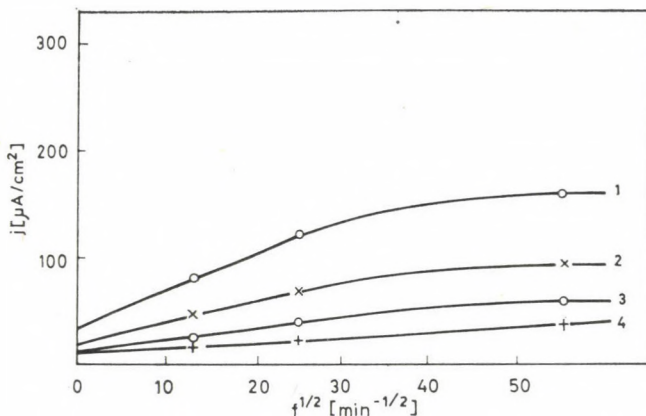


Fig. 4. j vs. $t^{1/2}$ correlation at different constant potentials, in a solution of $0.25 \text{ mole dm}^{-3} \text{ NaClO}_4$ in non-aqueous acetic acid. 1: -140 mV ; 2: -160 mV ; 3: -180 mV ; 4: -220 mV

further on the copper is not dissolved in the form of an acetato complex any more.

The linear section belonging to higher current densities falls into that potential range, where the polarization curves shown in Fig. 1 are to be found. Thus it may be suggested that these sections of the polarization curves for solutions 10–13 should be compared with curves for solutions 1–9. In a diagrammatical presentation as j vs. $t^{1/2}$ functions, as in Fig. 4, no straight

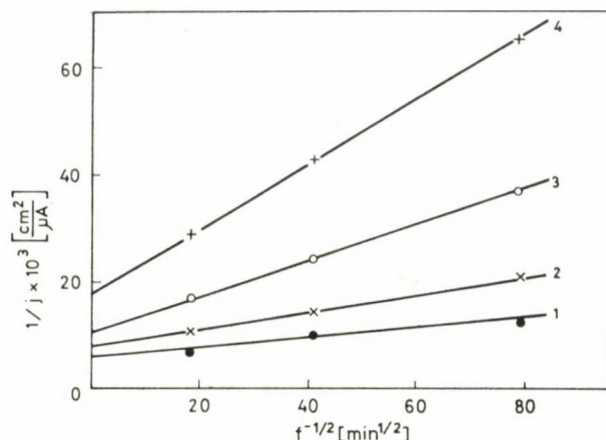


Fig. 5. j^{-1} vs. $f^{-1/2}$ correlation at different constant electrode potential in a solution of $0.25 \text{ mole dm}^{-3} \text{ NaClO}_4$ in acetic acid

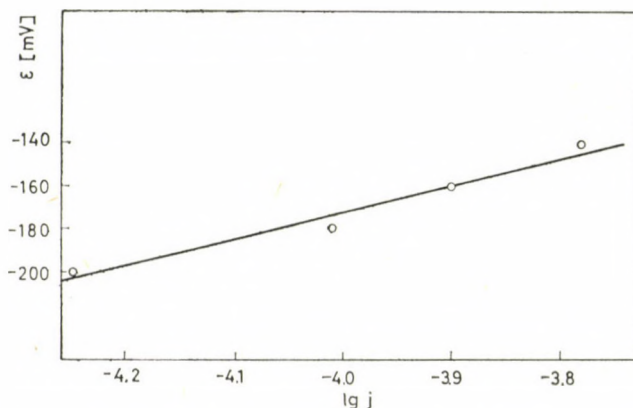


Fig. 6. ε vs. $\lg j$ correlation in a solution of $0.25 \text{ mole dm}^{-3} \text{ NaClO}_4$ in acetic acid; j is the current density when $f^{-1/2} = 0$

lines can be obtained. Therefore, prompted by the idea that the kinetics of the process on the electrode are affected also by transfer- and diffusion-processes, the data in Fig. 3 are plotted also in the coordinate system j^{-1} vs. $f^{-1/2}$: see Fig. 5. It is shown that experimental data give straight lines; the points of intersection of these enable us to calculate the polarization curve not distorted by diffusion effects [7]. This is to be seen in Fig. 6.

The Tafel b coefficient corresponding to transfer polarization, in solution 13 is 124 mV. In Table 1 the b coefficients, found in this way, are given for solutions 10–13. The suggestion is that copper is dissolved anodically as Cu^+ .

Thus, in the cases just discussed the kinetics of the ionization of copper is affected also by charge transfer, and by the diffusion of the metal ions form-

ed into the bulk of the solution. In this case the equation of the polarization curve can be given as follows:

$$j = \frac{k_a}{1 + \frac{k_k}{X}} \quad (1)$$

In Eq. (1)

$$k_a = k'_a \exp \frac{\alpha F \varepsilon}{RT} \quad (2)$$

$$k_k = k'_k \exp - \frac{(1 - \alpha) F \varepsilon}{RT} \quad (3)$$

$$X = 0.62 FD^{2/3} \nu^{-1/6} (2\pi f)^{1/2} \quad (4)$$

k'_a and k'_k stand for rate constants, respectively, of metal ionization and metal ion neutralization (these values depend on reference electrodes), α is the transfer coefficient, F the Faraday constant, R is the gas constant, T the thermodynamical temperature, D the diffusion constant of copper ions, ν is the kinematic viscosity of the solution, f is the r.p.m. value for the rotating electrode.

As Eq. (1) reveals, the process follows a pure diffusion kinetics when

$$k_k \gg X \quad (5)$$

however, when

$$k_k \simeq X \quad (6)$$

both charge transfer and diffusion affect the kinetics of the process.

According to our experimental data condition (5) is realized in solutions 1–9, and condition (6) in solutions 10–13. This can be explained by assuming that in acid solutions of high perchlorate concentration no acetate ion, at best perchlorate ions can be adsorbed on the surface of copper. Therefore cathodic (as well as anodic) processes are very rapid and condition (5) is realized, whereas condition (6) is favoured at lower acid and perchlorate concentrations. For, in these solutions the acetate concentration in given current-density range is not enough for the formation of copper acetate complex during anodic dissolution, but sufficient for adsorption. In turn, the rate constant k_k of the cathode process will decrease as a consequence of the adsorption of acetate ions and the rate of the anode process will remain practically unchanged, and this, indeed, will lead to the realization of condition (6). Thus the suppositions here propounded seem to explain the experimental data.

All these are in accordance with the well-known statement [8] that Li^+ -ions are more "acidic" in an acetic acid medium than Na^+ -ions, and that water added to acetic acid solutions makes it more basic (increases the acetate

ion concentration). Thus, if to a $0.25 \text{ mole dm}^{-3} \text{ LiClO}_4$ solution (solution 5) $0.27 \text{ mole dm}^{-3} \text{ H}_2\text{O}$ is added, polarization curves are similar to those for solutions 10–13 will result.

It can be concluded that the HClO_4 concentration is not responsible for the alteration of the step which determines the kinetics of the dissolution of copper in the solutions studied. Most probably the kinetics is affected by the adsorption and desorption, respectively of acetate ions.

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PREPARATION AND PROPERTIES OF Al_2O_3 — AlF_3 CATALYSTS.

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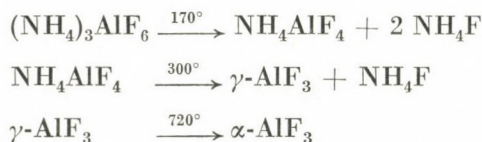
Al_2O_3 — AlF_3 catalysts of various component ratios have been prepared by the reaction of activated alumina with NH_4F followed by the thermal decomposition of the intermediate product obtained at the first stage of the reaction. Structure, thermal stability and surface area of the catalysts have been determined. The thermal decomposition of the intermediate product was investigated as well.

Introduction

Aluminium fluoride differs markedly in its chemical and physical properties from other aluminium halides. It is more ionic in nature and exists in the form of giant molecules. AlF_3 is not as strong Lewis acid as are other aluminium halides, therefore its application to catalyze hydrocarbon reactions is relatively limited. In contrast to other aluminium halides which are catalytically active only if completely anhydrous, AlF_3 is also active in hydrated form. There are suppositions that the presence of water is indispensable to catalyze such reactions of hydrocarbons as: polymerization [1], hydration [2], reforming [3, 4], isomerization, cracking [5–10] and oil refining [11, 12]. Most data concerning catalytic properties of AlF_3 can be found in patent literature.

Two modifications of aluminum fluoride are known. Orthorhombic α -modification has been known for a long time, while the metastable hexagonal β -form has been reported by CHRISTOPH *et al.* only in 1965 [13]. The authors have obtained this new modification by dehydration of $\text{AlF}_3 \cdot 3\text{H}_2\text{O}$. The possibility of obtaining modification other than α - AlF_3 by the thermal decomposition of $(\text{NH}_4)_3\text{AlF}_6$ was reported already in the thirties [14,] but there was no information concerning the structure of the new form. SHINN [15] and THOONEN [16] obtained aluminium fluoride by the decomposition of $(\text{NH}_4)_3\text{AlF}_6$. There was no structural difference between their samples and the one defined by CHRISTOPH as the β - AlF_3 . The preparation of mixtures of Al_2O_3 and β - AlF_3 was investigated by THOONEN [16]. An excess of activated gibbsite was heated with an aqueous, ammoniacal solution of NH_4F at 100 °C. Under such conditions $(\text{NH}_4)_3\text{AlF}_6$ was precipitated in the alumina pores, and then transformed into a mixture of β - AlF_3 and Al_2O_3 by heating at 450 —

-500 °C. According to the authors [16, 19, 20] hexafluoroaluminate decomposes to tetrafluoroaluminate at 225 °C. The latter is transformed to β - AlF_3 . The authors suggest that all HF molecules obtained during the thermal process are linked to the remaining Al_2O_3 . Thus, they recommend to use the excess of alumina in this method of preparation. SHINN [15] has described the thermal decomposition of $(\text{NH}_4)_3\text{AlF}_6$ using the following set of equations:



AlF_3 claimed by the authors [15] as γ -form, has been identified as the β -modification [17] of aluminum fluoride. The $\beta \rightarrow \alpha$ transformation is irreversible. According to Dutch authors [16, 19, 20] this process takes place already at 600 °C.

Experimental

Al_2O_3 - AlF_3 catalysts of various component ratios have been prepared using the method similar to the one described by Dutch authors [16, 19, 20]. Alumina obtained by hydrolyzing of aluminum isopropoxide [21] was used as a starting material. Al_2O_3 was activated at 300 °C for 16 h. Contrary to the above authors [16, 19, 20] the excess of NH_4F (in comparison with the amount of fluorine in the final product) was used in the first reaction step. Our preliminary experiments have shown that fluorine was not completely incorporated into the catalyst during thermal decomposition of $(\text{NH}_4)_3\text{AlF}_6$ obtained in the first stage of preparation. The following wt. ratios were used in the initial mixture:

AlF_3 content in the product	10%	30%	50%	70%	90%	100%
$\text{NH}_4\text{F}/\text{Al}_2\text{O}_3$ wt. ratio in the substrate	0.44	1.33	2.20	3.08	3.96	4.40

Reaction between activated alumina and aqueous solution of NH_4F with the addition of ammonia was carried out in closed polypropylene vessels at 95 °C for 2h. The products of the first preparation step were separated by means of centrifugation and dried at 120 °C without any washing. In the next step, samples were heated for 5 h in platinum crucibles at three different temperatures: 500, 600 and 750 °C. The furnace was flushed with a stream of dry air during the heating. Fluorine content in the samples was determined by WILLARD-WINKLER method [22, 23] using $\text{Th}(\text{NO}_3)_4$. Structure of the samples was characterized by X-ray diffraction using Co-filtred $\text{CuK}\alpha$ radiation (Figs 2 and 4). Thermographic analyses on MOM OD-120 derivatograph were carried out in order to investigate thermal decomposition of semiproducts and thermal stability of final catalyst samples. Results of thermographic analyses are shown in Fig. 1. IR spectra were recorded on Perkin Elmer Model 580 spectrometer (Fig. 3) using KBr water technique. Surface areas of the samples were determined using Sartorius sorptometer "Gravimat" on the ground of low temperature nitrogen adsorption (Fig. 5).

Results and Discussion

The amounts of NH_4F in the reaction mixture applied in our experiments were higher than the content of fluoride in the final products. Basing on the results of thermographic analyses, we have found that fluorine did not react

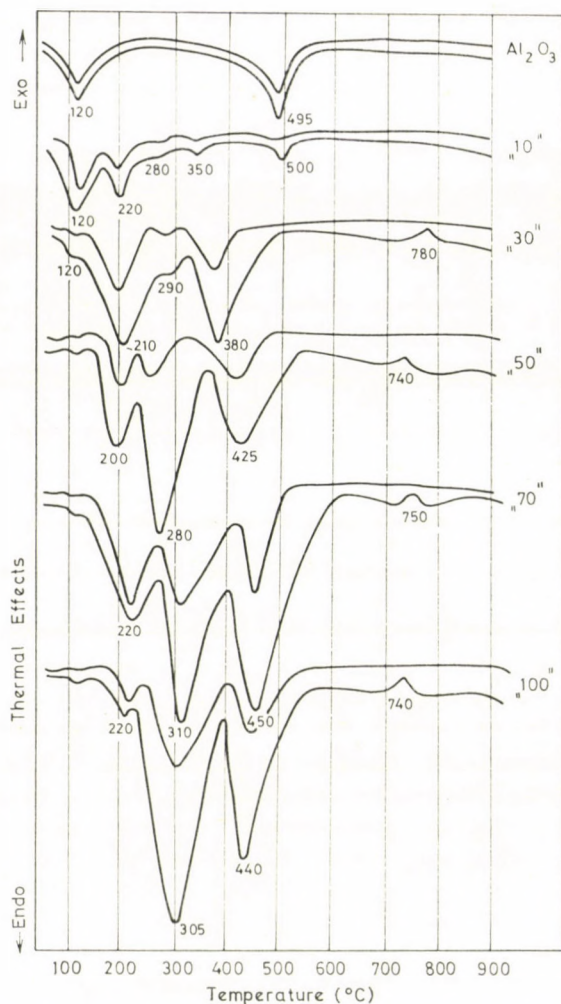


Fig. 1. DTA (upper curves) and DTA (lower curves) of intermediate product obtained at the first stage of preparation of catalyst samples containing different amounts of AlF_3 (concentrations of aluminum fluoride are given on the right hand side of the Figure)

completely with alumina during heating of the samples obtained at the low-temperature stage of preparation. Samples obtained at this stage of synthesis represent $(\text{NH}_4)_3\text{AlF}_6$ or a mixture of $(\text{NH}_4)_3\text{AlF}_6$ and Al_2O_3 . Thermographic data (Fig. 1) show that volatile products of thermal decomposition of $(\text{NH}_4)_3\text{AlF}_6$ (such as HF and NH_3) leave the reaction mixture, thus some part of fluorine cannot combine with alumina. As shown in Fig. 1 the decomposition of $(\text{NH}_4)_3\text{AlF}_6$ occurs in three stages. These three stages are expressed by three endothermic effects on DTA curve and are accompanied by a decrease in mass (DTG curve). An additional endothermic effect at 500°C occurs for the sample

containing the least amount of fluorine. This effect is a result of dehydration of alumina. Proportions between the above three endothermic peaks change depending on the fluorine content in samples. The endothermic effect at about 200 °C is predominant for the samples of low fluorine content. In the case of samples containing more fluorine this effect decreases and effects at about 300 and 450 °C become the main ones. The effect at 450 °C is due to the formation of β - AlF_3 . IR spectra show that N—H bands disappear at this temperature. The X-ray diffraction pattern of the samples obtained at this temperature corresponds to the β - AlF_3 structure (Fig. 2). IR spectra of samples calcinated at 200 and 300 °C are similar to each other (Fig. 3). The spectrum of the one obtained at 300 °C, however, shows more intensive 2920 and 1880 cm^{-1} bands characteristic for NH_4AlF_4 [15]. The X-ray diffraction pattern of 200 °C sample shows lines originating from both $(\text{NH}_4)_3\text{AlF}_6$ and NH_4AlF_4 (Fig. 2). Basing on the above results we can conclude that the intermediate product obtained at 200 °C represents the mixture of $(\text{NH}_4)_3\text{AlF}_6$ and NH_4AlF_4 . Samples prepared at 300 °C contain only tetrafluoroaluminate. There is no indication for the presence of $(\text{NH}_4)_2\text{AlF}_5$ or oxyfluorocompounds. An interesting question is, why the $(\text{NH}_4)_3\text{AlF}_6 \rightarrow \text{NH}_3\text{AlF}_4 + 2 \text{HF} + 2 \text{NH}_3$ reaction proceeds in two steps at two different temperatures. The effect at about 300 °C becomes predominant for samples of high fluorine content. It is not clear what is the

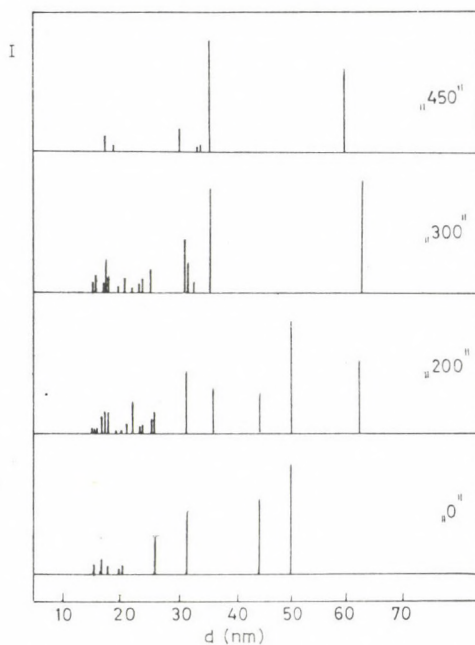


Fig. 2. X-ray pattern of the samples obtained by heating of intermediate product at temperature indicated in the Figure ("0" — sample without heating)

influence of unbound Al_2O_3 on this process, but one can suppose that some volatile products (particularly ammonia) of the thermal decomposition of $(\text{NH}_4)_3\text{AlF}_6$ can adsorb on the alumina surface. The endothermic effect at 200°C could be a result of the desorption of the above mentioned adsorbed species. On DTA curves of all the fluorine-containing samples an exothermic effect appears also at 750°C . There is no mass loss at this temperature. The exothermic effect mentioned above can be assigned to the $\beta\text{-AlF}_3 \rightarrow \alpha\text{-AlF}_3$ transformation. The X-ray diffraction data show that the samples obtained at 750°C have α -structure (Fig. 4). On the other hand, hexagonal β -modification of AlF_3 is present in the samples heated at 500 and 600°C . Irrespectively of the calcination temperature, a decrease in surface area of the samples occurs with an increase in fluorine content. It results from the fact that aluminum fluoride has a considerably smaller area than that of aluminum oxide. The Al_2O_3 - AlF_3 system is a simple resultant of surface areas of components, since slope of the curve shown in Fig. 5 is at first sharp, but it is significantly less pronounced for the samples containing more than 50% AlF_3 . This is in agreement with a recent paper by NEIMARK [25] where differences in porosity and adsorption properties between initial components and resulting mixed adsorbents (such as zeolite-alumina, active carbon-alumina, zeolite-silica gel) are explained by a synergetic mechanism. Another factor showing substantial effect on the surface area is crystal structure. Surface areas of $\beta\text{-AlF}_3$ -containing samples (calcinated at 500 and 600°C) are twice as large as surface areas

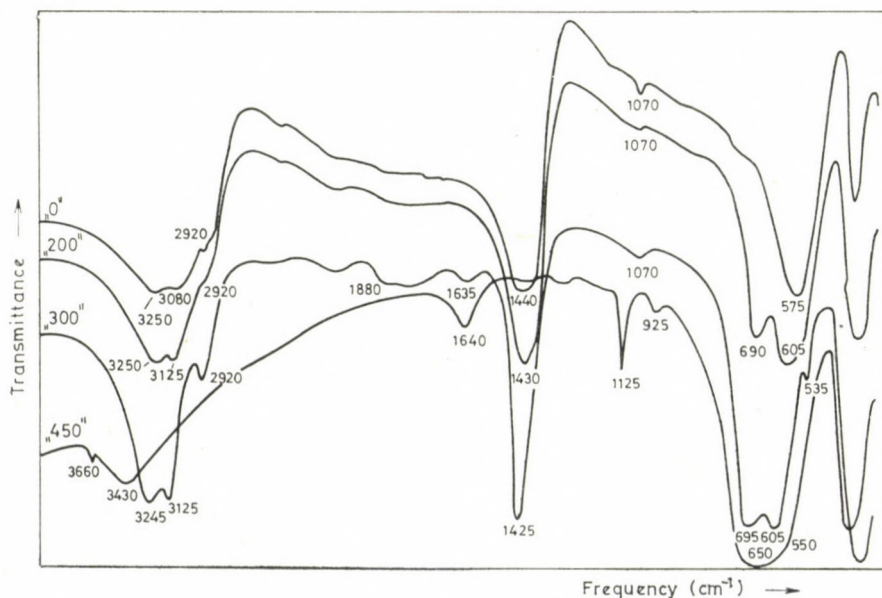


Fig. 3. Infrared spectra of the same samples as shown in Fig. 2

of α - AlF_3 -containing ones, which were obtained by heating at 750°C . The reduction of surface areas observed in the case of the latter samples is partly due the high temperature of calcination (750°C). The observed decrease in

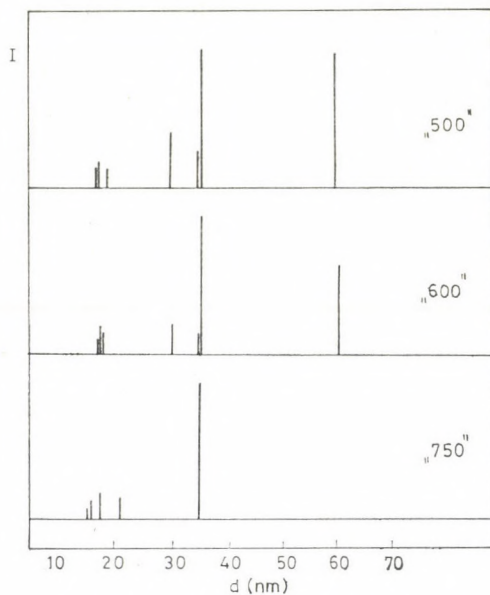


Fig. 4. X-ray pattern of the samples obtained by heating at temperatures indicated in the Figure

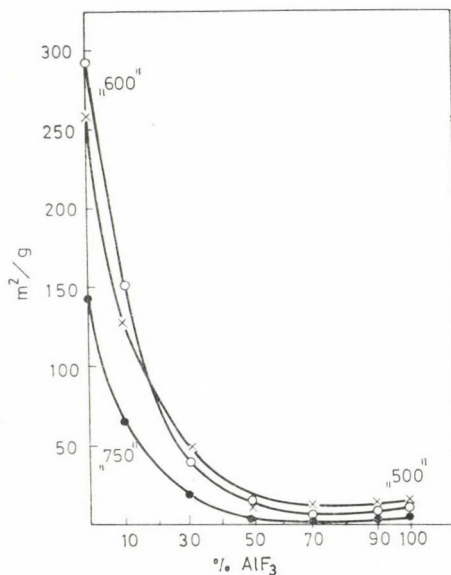


Fig. 5. Correlation between surface area and fluorine content in the catalyst samples. The curves represent samples obtained at 500, 600 and 750°C , respectively

surface area is, however, too high to be a result of pore sintering only. Thus the transformation of crystal structure seems to be a decisive factor for the discussed changes in surface area.

Differences in properties of individual samples are reflected by their catalytic activity. This matter will be a subject of another paper [24].

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CATALYTIC PROPERTIES OF THE Al_2O_3 — AlF_3 SYSTEM

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Catalytic properties of Al_2O_3 — AlF_3 samples have been studied in *n*-butene isomerization and cumene cracking. Results of catalytic measurements are discussed in the light of IR-spectroscopic investigations and structural studies (X-ray diffraction, electron microscopy).

It has been found that the highest catalytic activity for both reactions studied is shown by the samples containing 10 wt.% AlF_3 . IR-spectroscopic data lead to the conclusion that catalysts with the above aluminium fluoride content have the highest concentration of Brønsted acid sites. These sites are formed due to the polarization of OH groups on the alumina surface. Further increases in the fluorine content reduce the catalytic activity. Catalytic activity is influenced also by the size of AlF_3 crystallites. Larger crystallites lead to a decrease in catalytic activity.

Many investigations concerning catalytic properties of fluorinated alumina have been reported [1—7]. Properties of aluminium fluoride were also studied [8—10]. Recently, several papers dealing with the combination of AlF_3 and zeolites were published [11—17]. Aluminium fluoride increases the selectivity of zeolite in toluene disproportionation.

Combination of Al_2O_3 and AlF_3 was also described in respect to its catalytic activity. HOLM and CLARK [18, 19] have investigated the catalytic activity of the samples containing up to 20% of fluorine for *n*-octane cracking, *o*-xylene isomerization, and propylene polymerization. The most intensive increase in activity was found in the case of samples containing 1.6—3.0% fluorine. Maximal activity was reached for the catalysts containing about 6% F. A further increase in incorporated fluorine did not cause a substantial change in catalytic activity. The authors, basing on ammonia adsorption data, concluded that fluorine reduced the strength of alumina acid sites. Weaker sites allowed higher surface mobility and permitted easier desorption of the products. COVINI *et al.* [20, 21] investigated the activity of Al_2O_3 — AlF_3 catalysts in cumene hydrodealkylation, xylene isomerization and *tert*-butylbenzene hydrodealkylation. The authors have compared the catalytic data and the results of the titration with *n*-butylamine, using H_0 and H_R indicators. They have found a good correlation between the results of catalytic tests and the concentration of the strongest acid sites, as determined by using H_R indicators.

MÖERKERKEN *et al.* [22] have pointed out that the crystal structure of AlF_3 should be taken into consideration when studying mixed Al_2O_3 — AlF_3

catalysts. Samples containing β - AlF_3 were more active in cumene cracking than the ones containing the α -form. The highest activity was reached for the catalysts containing 40–80% of β - AlF_3 . Increase in fluorine content in the α -series catalysts leads to a decrease in the catalytic activity. The authors did not find any correlation between catalytic activity of the samples and their acidity and specific surface area. REITSMA *et al.* [23] maintain that catalytic sites are located on the crystallite boundary between Al_2O_3 and AlF_3 particles. The smaller size of β - AlF_3 crystallites leads to an increase in the number of edges adjacent to alumina crystallites. This may explain the higher catalytic activity of β - AlF_3 containing catalysts. The importance of the size of AlF_3 crystallites for catalytic activity was also emphasized by Japanese authors studying mordenite-supported AlF_3 as a catalyst for toluene disproportionation [13].

Experimental

The samples described previously [24] were examined in cumene cracking and *n*-butene isomerization. The pulse-technique microreactor was used in the catalytic tests. The microreactor was connected directly to a gas chromatograph. Catalyst samples were pretreated at 450 °C for 1 h in a stream of dry helium, whose flow rate was 30 cm³/min both during pretreatment and during catalytic measurements in the above reactions. The tests for cumene cracking were carried out in the temperature range of 300–400 °C and the reaction products were separated using a 2 m column packed with Silicone SE-30. The measurements of catalytic activity for butene isomerization were carried out in the range of 100–250 °C and the reaction products were analyzed in a 10 m long column filled with propylene carbonate. Only butene isomers were found in the reaction products. IR spectra of selected samples were recorded on a Perkin-Elmer Model 580 double-beam grating spectrometer. Catalyst wafers 2.3 cm in diameter, weighing about 0.05 g, were pretreated at 450 °C for 4 h in a vacuum cell at 10⁻⁵ Torr. Pyridine vapour was adsorbed on the wafers at room temperature for 1 h and then desorber during 2 h evacuation at 200 °C.

Electron micrographs were taken for some of the investigated samples using a JEOL JEM-7A electron microscope.

Results and Discussion

The data obtained show that the Al_2O_3 - AlF_3 samples under study are catalytically active in both reactions investigated. Conversions, as measured at the reaction temperature of 400 °C for cracking and 250 °C for isomerization, are given in Figs 1 and 2. The curves representing conversion as a function of AlF_3 percentage at the other temperatures studied were similar to those shown in these Figures.

Catalyst samples calcined at 500 °C are most active for *n*-butene isomerization (Fig. 1). The activity of the samples heated at 600 °C is equally high in the case of low fluorine contents (up to 30 wt.% AlF_3). A further increase in the fluorine content leads to a decrease in catalytic activity. Samples containing 70 and 90% AlF_3 are completely inactive, whereas aluminium fluoride by itself calcined at 600 °C shows some activity. Among the samples heated

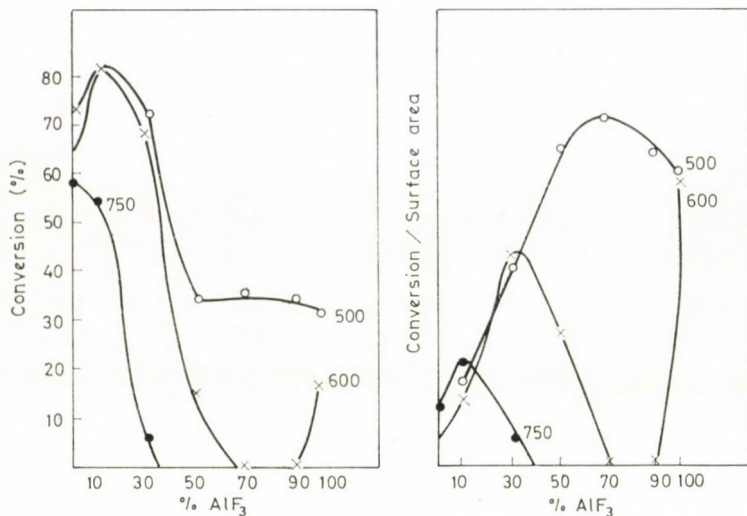


Fig. 1. Catalytic activity of $\text{Al}_2\text{O}_3\text{--AlF}_3$ samples for *n*-butene isomerization at 250 °C as a function of AlF_3 content.

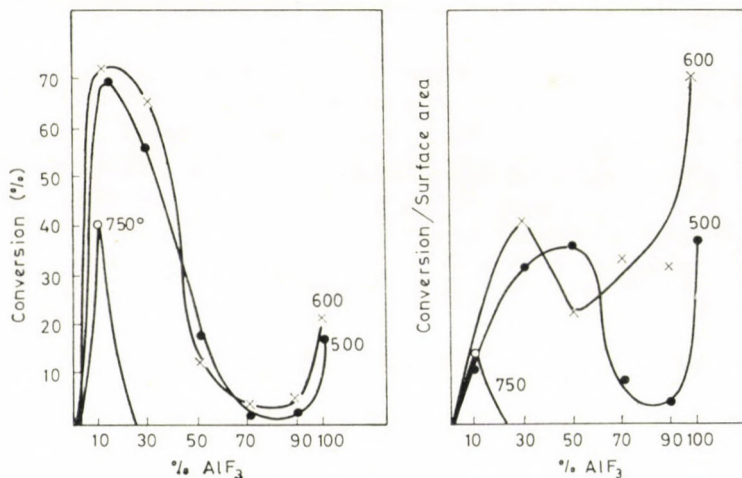


Fig. 2. Catalytic activity of $\text{Al}_2\text{O}_3\text{--AlF}_3$ samples for cumene cracking at 400 °C as a function of AlF_3 content.

at 750 °C only those containing up to 30 wt.% AlF_3 are catalytically active for butene isomerization (Fig. 1). The above reaction can proceed on both basic and acid sites of Lewis and Brønsted type. In the case of alumina, the sites active for butene isomerization are most probably Lewis acid centres. Their presence is indicated by the very intensive band at 1455 cm^{-1} in the IR spectra of adsorbed pyridine (Fig. 3), while there is no band originating from

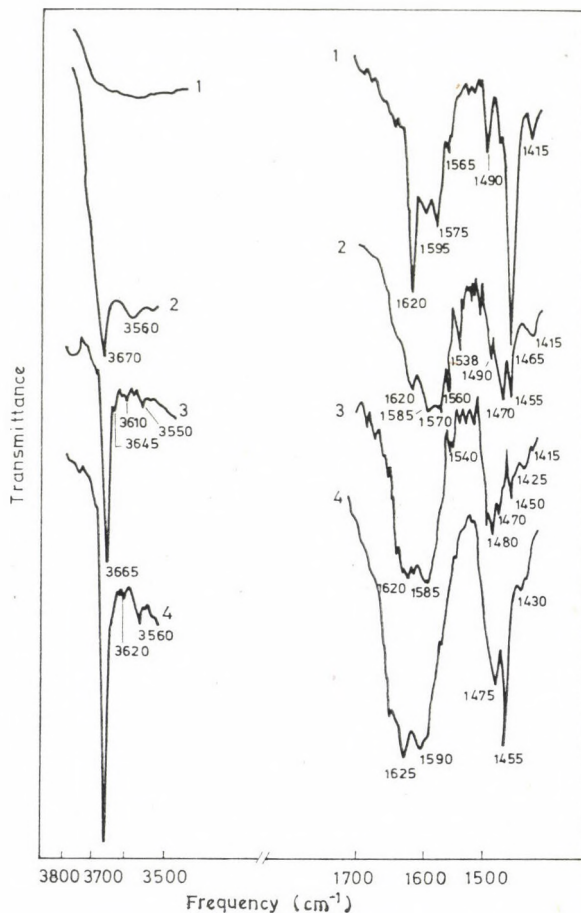


Fig. 3. IR spectra of pyridine adsorbed on the samples obtained at 500 °C: 1 — Al_2O_3 ; 2 — $\text{Al}_2\text{O}_3\text{--AlF}_3$ (10%); 3 — $\text{Al}_2\text{O}_3\text{--AlF}_3$ (50%)

pyridinium ion in the case of alumina exposed to pyridine vapour. The last observation is in agreement with literature data on the nature of alumina acidity [26–29]. The isomerizing activity of AlF_3 should also be ascribed to Lewis acidity since aluminium fluoride is typical Lewis acid. This is clearly visible in the IR spectrum of pyridine adsorbed on AlF_3 (Fig. 3), where the band at 1455 cm^{-1} coming from pyridine, coordinatively bonded to Lewis acid sites, is present, whereas a band at 1540 cm^{-1} ascribed to pyridinium ion is absent. The highest catalytic activity is observed for the samples containing 10 wt.% AlF_3 . In the case of catalysts calcined at 750 °C, the activity of the sample containing 10 wt.% AlF_3 is, however, lower than that of alumina alone. Reactions proceeding on mixed $\text{Al}_2\text{O}_3\text{--AlF}_3$ catalysts most probably occur with the participation of Brønsted acid centers. The presence of the

1540 cm^{-1} band in the IR spectrum of pyridine adsorbed on such catalysts confirms the above opinion. The band at 1540 cm^{-1} originating from the reaction between pyridine and protonic sites of the catalyst are present in the spectra of all the samples of mixed catalysts calcined at 500 and 600 °C and can be seen even in the case of the sample containing 10 wt.% AlF_3 heated at 750 °C. The ratio between Brønsted and Lewis centers (expressed by the ratio of intensities of the 1540 and 1450 cm^{-1} bands) changes depending on the fluorine content. For instance, the intensity of the 1540 cm^{-1} and 1450 cm^{-1} bands for the samples heated at 500 °C is as follows: Al_2O_3 — 0.00; Al_2O_3 - AlF_3 (10%) — 0.75; Al_2O_3 - AlF_3 (50%) — 0.31; AlF_3 — 0.00. The acidic hydroxyl groups giving the 1540 cm^{-1} band on their reaction with pyridine are those responsible for the bands at about 3560 and 3610 cm^{-1} in the OH stretching vibration region. Such a conclusion may be drawn basing on a decrease in intensities of these bands after pyridine adsorption. The intensive band at 3660 cm^{-1} present in the spectra of all the fluorine-containing samples (including AlF_3) does not belong to acidic OH groups because its intensity does not change when pyridine is adsorbed on the samples (Fig. 3). The detection of acidic hydroxyl groups in the Al_2O_3 - AlF_3 sample containing 10 wt.% AlF_3 and calcined at 750 °C may be due either to a partial rehydroxylation of the surface when it exposed to atmospheric moisture, or to their survival even under such drastic thermal conditions.

The composition of isomerization products testifies to the acidic mechanism of this reaction. The ratio of *cis/trans* isomers is close to 1, which means that the reaction proceeds *via* a butyl carbonium ion formed on acid sites [25, 30, 31].

The second model reaction investigated in this study, cumene cracking, is known to occur first of all on strong protonic centers [32]. The absence of such centers from the alumina surface is the reason why none of the alumina samples (irrespective of calcination temperature) is active in the above reaction (Fig. 2). The highest activity in cumene cracking is shown by the catalysts containing 10 wt.% AlF_3 (Fig. 2) likewise in the case of butene isomerization. This observation is in a good agreement with the results of IR-spectroscopic investigations, which show that the contribution of Brønsted acid sites to the total acidity is the highest for the samples with 10 wt.% AlF_3 . Even the mixed catalyst heated at a temperature as high as 750 °C and having the above aluminium fluoride content shows cracking activity as the only of the samples calcined at this temperature (Fig. 2).

In our previous paper [24], we have found that the surface area of the investigated samples decreases with increasing fluorine content. Taking the above fact into consideration, we calculated the conversion degree per 1 m^2 of catalyst surface and the course of activity curves (Figs 1 and 2) appeared to be different from that observed when the conversion degree is plotted against

the AlF_3 content. As the samples with higher fluorine contents have considerably lower surface areas, the maxima of curves representing conversion degree per unit catalyst surface area as a function of aluminium fluoride content are shifted towards higher percentage of AlF_3 . The absence of protonic sites both on Al_2O_3 and AlF_3 surfaces and their appearance on the surfaces of mixed catalysts testify to the formation of a new catalytic system. Though, according to the X-ray data presented in our previous paper, Al_2O_3 — AlF_3 catalysts are mixtures of the above compounds, their catalytic behaviour is not the resultant of the catalytic action of both components. The introduction of such a negative element as fluorine leads to weakening of the O—H bonds in surface hydroxyl groups, making protons more mobile. Thus Brønsted acid centers (which were absent from the surfaces of the components taken alone) are formed on the mixed catalysts. The observation that samples with 10 wt. % AlF_3 are the most active is in agreement with the results obtained by COVINI *et al.* [20, 21] and HOLM and CLARK [19]. Results obtained in this study are at variance with the opinion [5], according to which, hydrated fluoride anions can be the source of acidity. If this concept was right, samples with higher fluorine concentration should be more active and this has not been observed in our measurements. The reduction of catalytic activity after thermal treatment at 750 °C, which is particularly sharp in the case of cumene cracking, is a result of the removal of the acidic hydroxyl groups. In the case of butene isomerization, where the catalytic activity comes from Lewis acid centers as well, the decrease in activity of the samples heated at 750 °C may be caused by the transformation of aluminium fluoride crystal structure. It has been found in our previous paper [24] that catalysts calcined at 750 °C contain α - AlF_3 , whereas those heated at lower temperature contain the β -modification of aluminium fluoride. As is shown by electron micrographs (Fig. 4), α - AlF_3 crystallites are several times larger than those of β - AlF_3 . According to BOELHOUWER *et al.* [22, 23] and SATO and OTANI [13], the size of AlF_3 crystallites is an essential factor influencing the catalytic activity of aluminium fluoride containing catalysts. Our results confirm their opinion. It has been shown in the present study that one can obtain active, mixed Al_2O_3 — AlF_3 catalysts rich in Brønsted acid centers, using the preparation procedure described previously [24]. As was already mentioned, the highest catalytic effect is observed at 10 wt. % AlF_3 . IR-spectroscopic investigations have proved that the concentration of protonic centers is the highest for the above AlF_3 content. The formation of these centers results from the polarizing effect of fluorine on hydroxyl groups present on the alumina surface. Catalytic activity depends also on the size of AlF_3 crystallites. This is particularly clearly seen in the case of butene isomerization, which can occur on Lewis acid sites. The catalytic inactivity of the majority of samples heated at 750 °C results from changes in the AlF_3 structure, because at least a part of Lewis acid

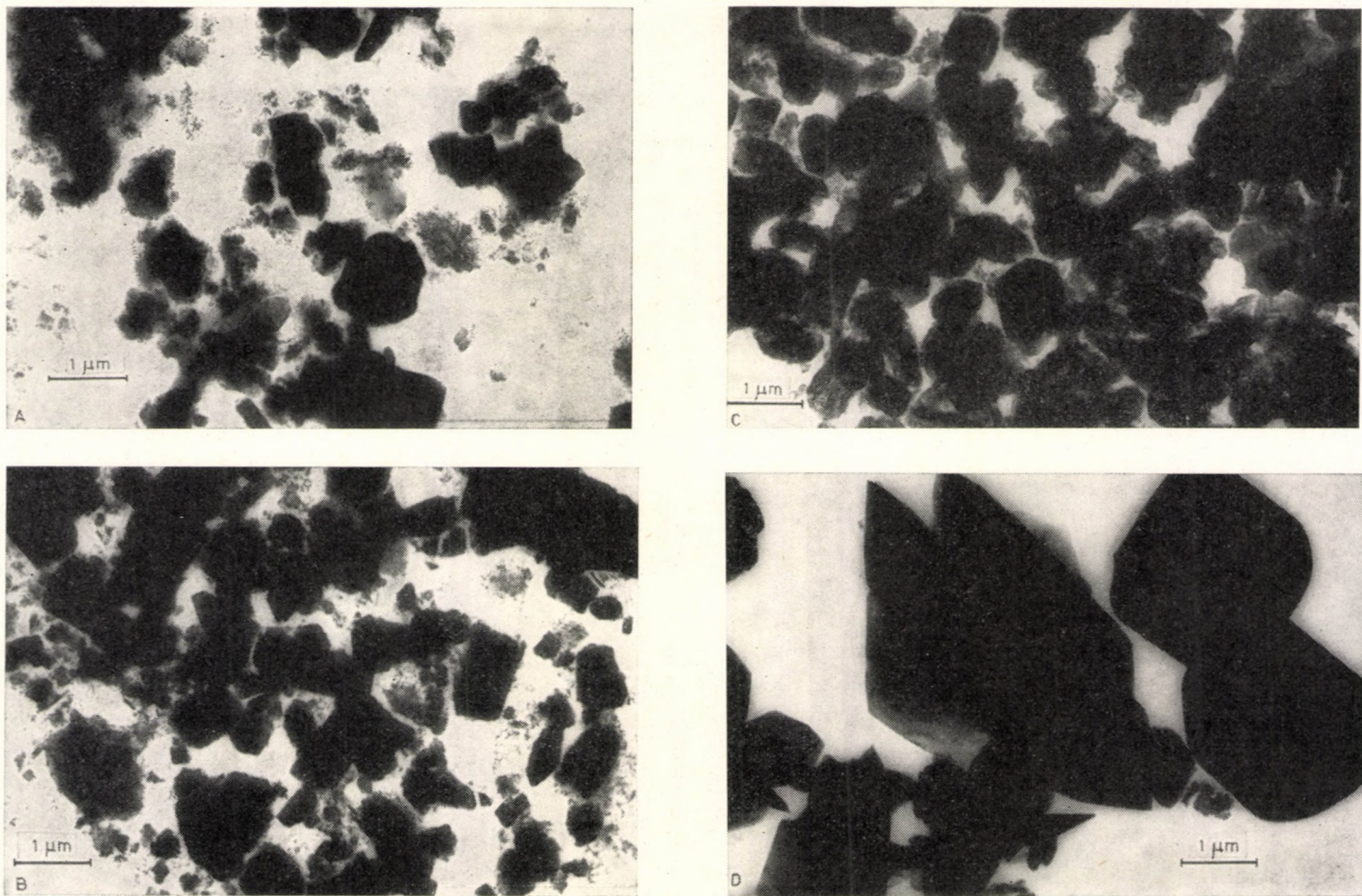


Fig. 4. Electron micrographs of the catalysts studied: A — Al_2O_3 heated at 500 °C, B — Al_2O_3 - AlF_3 (10%) heated at 500 °C, C — β - AlF_3 heated at 500 °C, D — α - AlF_3 heated at 750 °C

centers should survive thermal treatment at the above temperature. Though the results presented in this study have provided explanation for some aspect of the catalytic behaviour of mixed Al_2O_3 - AlF_3 catalysts, many problems are still to be solved. Further studies on the matter in question are underway in this Laboratory.

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THE EFFECT OF CELL RESISTANCE IN A.C. POLAROGRAPHY

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The effect of the ohmic drop on the cell resistance was studied in fundamental harmonic and second harmonic a.c. polarography during the drop growth of the d.m.e. The ohmic drop increases when the cell resistance and the concentration of the solution are increased, when the frequency of the a.c. voltage is higher and when the number of electrons exchanged in the electrode reaction is larger. The relative decrease of the amplitudes of the a.c. harmonic components under the effect of the ohmic drop varies during drop growth. Thus, anomalous $i = f(t)$ curves observed during the drop growth in second harmonic a.c. polarography at higher frequencies *viz.* the appearance of a current maximum at the beginning of the drop life can be attributed to ohmic effects.

The iR drop is a source of error in electrochemical measurements even when potentiostatic method and a three-electrode cell are employed as it is usual in modern electrochemical practice. In the latter case the iR drop exists in the resistance between the measuring electrode (*i.e.* between the cold junction of the potentiostat) and the tip of the Luggin capillary of the reference electrode [1, 2]. In what follows, this resistance will be referred to as the cell resistance.

The ohmic drop in the cell resistance is not significant in most of the cases in d.c. polarography. Nevertheless, several authors turned their attention to this phenomenon [3—10].

In the case of a.c. polarography, the effect of the voltage generated on the cell resistance must also be taken into consideration with respect to the alternating current components. The iR drop caused by the polarographic direct current affects the a.c. components only in that the potential of the dropping mercury electrode will differ from the applied potential. The a.c. iR drop, however significantly alters the harmonic components of the alternating current since the electrode impedance, *i.e.* the faradaic impedance characteristic of the electrode processes connected in parallel to the double-layer capacity, represents a much smaller resistance to a.c. than to d.c. Thus the voltage division on cell resistance and electrode impedance connected in series may reduce the alternating voltage applied to the faradaic impedance. In earlier communications [11, 12, 13] detailed theoretical and experimental studies have been presented concerning the influence of ohmic drop in fundamental harmonic as well as in second, and third harmonic a.c. polarography.

In those studies the change of the surface area of the dropping mercury electrode during drop growth was not taken into account: calculations referred to the constant electrode area observed immediately before the dislocation of the drop.

In the present paper we attempt to consider the effect of cell resistance on the harmonic components of the a.c. during the growth of the mercury drop of the dropping mercury electrode. This subject did not attract much attention as far as higher harmonic and intermodulation a.c. polarography are concerned.

The time-dependence of the cell resistance and that of the harmonic components of the alternating current are discussed first.

According to KOLTHOFF [10], the cell resistance is composed of two parts:

$$R = R_{\text{Hg}} + R_{\text{sol}} \quad (1)$$

where R_{Hg} is the resistance of the mercury thread in the d.m.e. capillary which is constant in a given cell and independent of time; R_{sol} is the resistance of the solution between the electrode surface and the tip of the Luggin-capillary of the reference electrode. This resistance changes in time and, according to ILKOVIC [3], it linearly varies with the reciprocal of the radius of the drop. Resistance R_{sol} is given by the following formula if the reference electrode is considered, as a simplification, to be concentric with the mercury drop and placed on an equipotential surface at distance r_2 from the centre of the growing drop:

$$R_{\text{sol}} = \frac{\rho}{4\pi} \left[\frac{1}{r_1} - \frac{1}{r_2} \right] \quad (2)$$

where r_1 is the radius of the mercury drop, in cm, ρ is the specific resistance of the solution, in ohm · cm. The increase of radius r_1 is proportional to $t^{1/3}$.

$$r = \left(\frac{3}{4\pi d} \right)^{1/3} (mt)^{1/3} \quad (3)$$

where m is the flow rate of mercury in $\text{g} \cdot \text{s}^{-1}$, t , the time elapsed since the beginning of the formation of the drop in seconds, d , the density of mercury in $\text{g} \cdot \text{cm}^{-3}$ at 25 °C. Thus the decrease in cell resistance is inversely proportional to $t^{1/3}$.

The variation of the harmonic components of the a.c. during the life of the mercury drop differs from the relationship valid for d.c. polarography. In the latter case the current intensity increases with the $\frac{1}{6}$ th power of time, however, in a.c. polarography the amplitudes of the harmonic components

of the current are proportional to the surface area of the mercury drop which increases as a function of $t^{2/3}$:

$$A = \left(\frac{36\pi}{d^2}\right)^{1/3} (mt)^{2/3} = 0.851m^{2/3} t^{2/3} \quad (4)$$

where A is the surface area of the mercury drop in cm^2 and the other symbols are identical to those given in the preceding equations.

Consequently, the experimental error caused by ohmic drop continuously changes during the life of the mercury drop as the current intensity increases proportionally to $t^{2/3}$ while the cell resistance decreases proportionally to $t^{1/3}$ during drop growth. In other words, the ohmic drop at the beginning of drop growth is smaller than that observed at the end of the drop life. According to BOND [14], this fact is one of the advantages of the introduction into a.c. polarography of a mercury electrode with short drop time.

It is noteworthy that the phase angle of the a.c. harmonic components also changes during drop growth. This phenomenon was studied by JEE [15] from the point of view of phase-sensitive fundamental harmonic a.c. polarography.

In order to evaluate the effect of ohmic drop in a.c. polarography, numerical calculations were performed using the pertinent relationships derived in our former communications [11, 12, 13], taking into account the time dependence of the quantities in question.

From the point of view of a.c. polarography, the dropping mercury electrode can be represented by the equivalent circuit shown in Figure 1a, where R is the cell resistance, varying in time as a function of mercury drop radius according to Eq. (2); $C = A(t) \cdot C_d$ is the double-layer capacity proportional

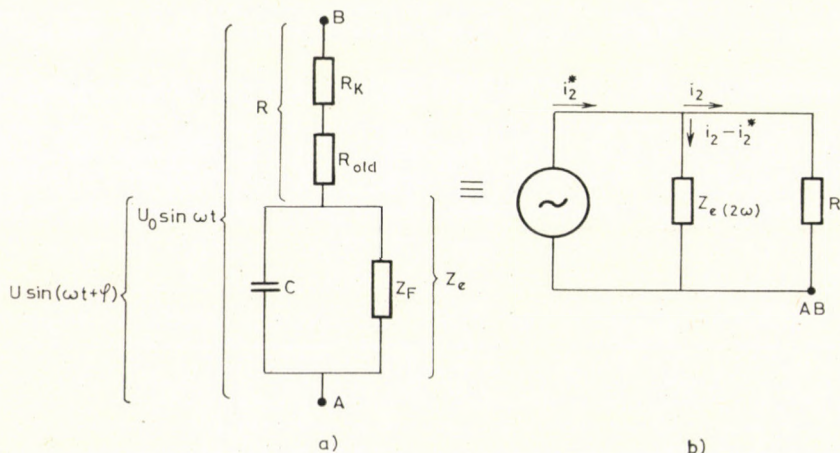


Fig. 1. a: Equivalent circuit of the electrode in the case of solution resistance R . b: Equivalent circuit of the electrode in respect of the second harmonic a.c.

to the drop surface area $A(t)$ and C_d is the double layer capacity referred to unit surface area of the electrode; Z_F is the faradaic impedance inversely proportional to the drop surface area: $Z_F = Z_F^0/A(t)$, where Z_F^0 is the faradaic impedance referred to unit surface area. $U_0 \sin \omega t$ is the alternating voltage superimposed on the cell, $U \sin(\omega t + \varphi)$ is the alternating voltage across the electrode impedance. U_0 and U are amplitudes of the alternating voltages, ω is their angular frequency and φ is the phase angle.

Amplitude U can be derived from the following formula relating to the voltage division on components R , C and Z_F :

$$\left| \frac{U}{U_0} \right| = \frac{\left| \frac{Z_F \frac{1}{j\omega C}}{Z_F + \frac{1}{j\omega C}} \right|}{\left| R + \frac{Z_F \frac{1}{j\omega C}}{Z_F + \frac{1}{j\omega C}} \right|} = \frac{1}{\left| 1 + R \left(\frac{1}{Z_F} + j\omega C \right) \right|} \quad (5)$$

In the case of a polarographically reversible, diffusion controlled electrode process, faradaic impedance is equal to the Warburg impedance which is the resultant of parallelly coupled diffusion resistance (R_p) and diffusion capacity (C_p) [1, 11, 12, 13], *i.e.*

$$\frac{1}{Z_F} = \frac{1}{R_p} + j\omega C_p \quad (6)$$

$$\frac{1}{R_p} = \omega C_p = \frac{(zF)^2}{\sqrt{2RT}} \sqrt{\omega} (C_{10} \sqrt{D_1} + C_{20} \sqrt{D_2}) \frac{e^{[zF/RT] \cdot [E-E_{1/2}]}}{(1 + e^{[zF/RT] \cdot [E-E_{1/2}]})^2} \quad (7)$$

where D_1 and D_2 are diffusion constants, while C_{10} and C_{20} are bulk concentrations of the reduced and the oxidized forms of the components taking part in the electrode reaction, respectively; z is the number of electrons exchanged in the electrode reaction, ω is the angular frequency of the alternating voltage E and $E_{1/2}$ are the d.c. potential and the polarographic half-wave potential of the electrode reaction, respectively, referred to any reference electrode; T is the temperature, R the universal gas constant, and F the Faraday constant.

Amplitude U of the alternating voltage appearing on the electrode impedance is obtained by substituting Eqs (6) and (7) into Eq. (5):

$$U = \frac{U_0}{\sqrt{\left(1 + \frac{R}{R_p}\right)^2 + \left(\frac{R}{R_p} + \omega RC\right)^2}} \quad (8)$$

The fundamental harmonic component of the current in the case of diffusion polarization is given by the following formula [11–13, 16]:

$$i_1 = \left\{ \left(\frac{(zF)^2}{\sqrt{2} RT} \sqrt{\omega} (C_{10} \sqrt{D_1} + C_{20} \sqrt{D_2}), \frac{e^{[zF/RT] \cdot [E-E_{1/2}]}}{(1 + e^{[zF/RT] \cdot [E-E_{1/2}]})^2} \right)^2 + \left(\frac{(zF)^2}{\sqrt{2} RT} \sqrt{\omega} (C_{10} \sqrt{D_1} + C_{20} \sqrt{D_2}) \frac{e^{[zF/RT] \cdot [E-E_{1/2}]}}{(1 + e^{[zF/RT] \cdot [E-E_{1/2}]})^2} + \omega C \right)^2 \right\}^{1/2} U \quad (9)$$

The fundamental harmonic component observed in the case of cell resistance R can be expressed by substituting Eq. (8) into Eq. (9) and noting Eq. (7)

$$i_1 = U_0 \frac{\sqrt{\left(\frac{1}{R_p}\right)^2 + \left(\frac{1}{R_p} + \omega C\right)^2}}{\sqrt{\left(1 + \frac{R}{R_p}\right)^2 + \left(\frac{R}{R_p} + \omega RC\right)^2}} \quad (10)$$

The effect of cell resistance on the second harmonic a.c. can be calculated as follows. Voltage $U_0 \sin \omega t$ imposed on the cell does not contain higher harmonic components since the latter are generated in the current as a consequence of the non-linearity of the faradaic impedance. Consequently the electrode impedance can be substituted by a current generator having internal resistance $Z_{e(2\omega)}$ and current i_2^* with respect to the second harmonic frequency (2ω). Further, points A and B in Fig. 1a have the same potential as regards the second harmonic and thus can be represented as short-circuited in the equivalent circuit in Figure 1b.

The electrode impedance at frequency 2ω is given by the following expression

$$Z_{e(2\omega)} = \frac{1}{Z_{F(2\omega)}} + j2\omega C \quad (11)$$

while current i_2^* of the generator can be calculated using the formula referring to the second harmonic component of the current [11, 12, 13, 16]:

$$|i_2| = \frac{(zF)^3}{2\sqrt{2} (RT)^2} \sqrt{2\omega} (C_{10} \sqrt{D_1} + C_{20} \sqrt{D_2}) \frac{e^{[zF/RT] \cdot [E-E_{1/2}]} |1 - e^{[zF/RT] \cdot [E-E_{1/2}]}|}{(1 + e^{[zF/RT] \cdot [E-E_{1/2}]})^3} U^2 \quad (12)$$

and noting that voltage U across the electrode impedance is given by Eq. (8). The second harmonic component of the current $|i_2|$ in the cell including ohmic

resistance R is obtained by applying Kirchoff's law to the equivalent circuit in Figure 1b. Hence

$$i_2 = \frac{i_2^*}{1 + \frac{R}{Z_{e(2\omega)}}} = \frac{i_2^*}{\left(1 + \frac{R}{R_{p(2\omega)}}\right) + j \left(\frac{R}{R_{p(2\omega)}} + 2\omega RC\right)} \quad (13)$$

by combining Eqs (8), (10), (11), (12) and (13), the expression of the amplitude of the second harmonic can be written in the following form:

$$|i_2| = \frac{(zF)^3}{2\sqrt{2}(RT)^2} \sqrt{2\omega} (C_{10} \sqrt{D_1} + C_{20} \sqrt{D_2}) \frac{e^{[zF/RT] \cdot [E-E_{1/2}]} |1 - e^{[zF/RT] \cdot [E-E_{1/2}]}|}{(1 + e^{[zF/RT] \cdot [E-E_{1/2}]})^3} \times \\ \times \frac{U_0^2}{\left[\left(1 + \frac{R}{R_{p(\omega)}}\right)^2 + \left(\frac{R}{R_{p(\omega)}} + \omega RC\right)^2\right] \sqrt{\left(1 + \frac{R}{R_{p(2\omega)}}\right)^2 + \left(\frac{R}{R_{p(2\omega)}} + 2\omega RC\right)^2}} \quad (14)$$

It is obvious from Eqs (10) and (14) that the amplitude of the harmonic components of the a.c. is decreased by ohmic drop. This effect is increased when the cell resistance is large as compared to the electrode impedance [11, 13].

It is noteworthy that, in the usual cell arrangement, the resistance of the mercury thread in the capillary of the dropping mercury electrode is larger than that of the solution at the end of the drop life if the supporting electrolyte is relatively concentrated, *viz.* about 1 molar, as it is usually employed in a.c. polarography. A few characteristic data of cell resistance are collected in Table I.

Table I

Components of cell resistance, with various supporting electrolytes and dropping mercury electrodes

Solution		R_{sol}^* ohm	Capillary length, cm	\varnothing cm	R_{Hg} ohm
Concentration mol/dm ³	ρ ohm. cm				
HCl 0.1	25.57	34.2	10	$5 \cdot 10^{-3}$	48.8
HCl 1.0	3.01	4.0	10	$1 \cdot 10^{-2}$	12.2
KCl 1.0	8.95	13.0			

* Calculated according to Eq. (2), if $r_2 = 1$ cm, $m = 2.5$ mg \cdot s⁻¹ and $t = 4$ s

The components of electrode impedance — the impedance of the double layer capacity and the faradaic impedance — decrease at higher frequencies (*cf.* Eqs (6) and (7)). The faradaic impedance decreases when the concentration of the electroactive component is increased and when the number of electrons exchanged in the electrode reaction is larger.

Figures 3 to 11 show the results of numerical calculations carried out for the quantitative evaluation of Eqs (10) and (14). The diagrams were constructed on the basis of the following data: flow rates of the dropping mercury electrode $m = 5 \times 10^{-4} \text{ g} \cdot \text{s}^{-1}$ and $2.5 \times 10^{-3} \text{ g} \cdot \text{s}^{-1}$, resistances of the d.m.e. capillary thread: 10, 25, or 50 ohms, supporting electrolyte: 1 mol/dm^{-3} KCl (cf. Table I); electroactive component: $D = 1 \times 10^{-5} \text{ cm}^2 \cdot \text{s}^{-1}$, $C^\circ = 1 \cdot 10^{-3} \text{ mol/dm}^{-3}$, $z = 1$ and 2. Calculations were carried out at the d.c. potential corresponding to the maximum of the a.c. harmonics i.e. $E = E_{1/2}V$, in the case of the fundamental harmonic while in the case of the second harmonic

$$E = E_{1/2} + \frac{0.034}{z} \quad (\text{Volts}) \quad (15)$$

The amplitude of alternating voltage was assumed to be $U_0 = 1 \times 10^{-2} \text{ V}$, its frequency was varied between 400 and $40,000 \text{ s}^{-1}$. The constants of the equations are the following: capacity of the double layer $C_d = 25 \mu\text{F} \cdot \text{cm}^{-2}$; $F = 96,500 \text{ C}$; $T = 298 \text{ K}$; $R = 8.3144 \text{ J}$; $d_{\text{Hg}} = 13.456 \text{ g} \cdot \text{cm}^{-3}$ [1].

Figure 3 shows the variation of the amplitude of the a.c. fundamental harmonic during drop life. It is apparent that, in agreement with literature data [14, 15], the error caused by ohmic resistance increases during the growth of the mercury drop. Figures 2, 3, and 4 illustrate the decrease of the amplitude of the fundamental harmonic due to ohmic resistance. This effect increases when cell resistance R , and the number of electrons involved in the electrode reaction are larger and the frequency of the alternating voltage is higher.

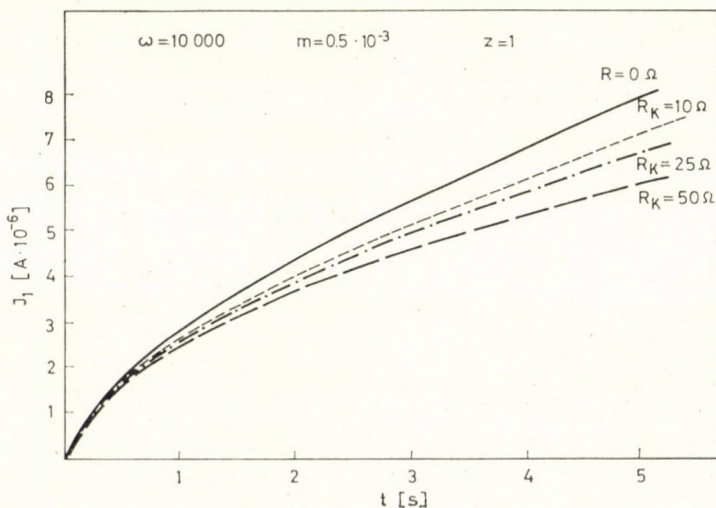


Fig. 2. Variation of the fundamental harmonic a.c. during the growth of the mercury drop $m = 5 \times 10^{-4} \text{ g} \cdot \text{s}^{-1}$; $R = 0$; $R_{\text{Hg}} = 10$; 25 and 50 ohm; $\rho = 10 \text{ ohm} \cdot \text{cm}$; $z = 1$; $\omega = 1 \times 10^4 \text{ s}^{-1}$

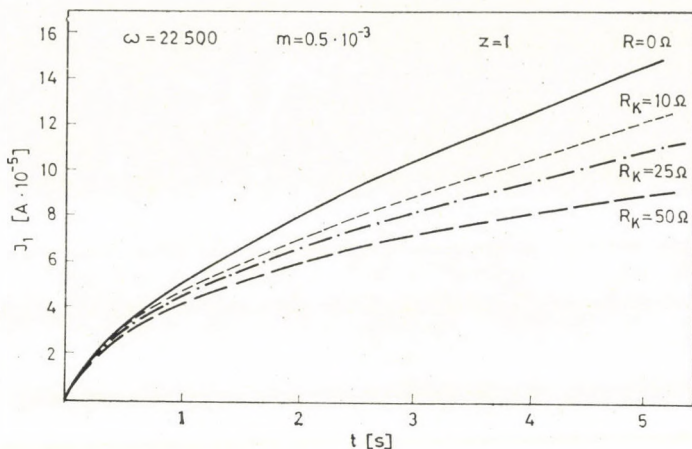


Fig. 3. Variation of the fundamental harmonic a.c. during the growth of the mercury drop $m = 5 \times 10^{-4} \text{ g} \cdot \text{s}^{-1}$; $R = 0$; $R_{\text{Hg}} = 10, 25$ and 50 ohm ; $\varrho = 10 \text{ ohm} \cdot \text{cm}$; $z = 1$; $\omega = 2.25 \times 10^4 \text{ s}^{-1}$

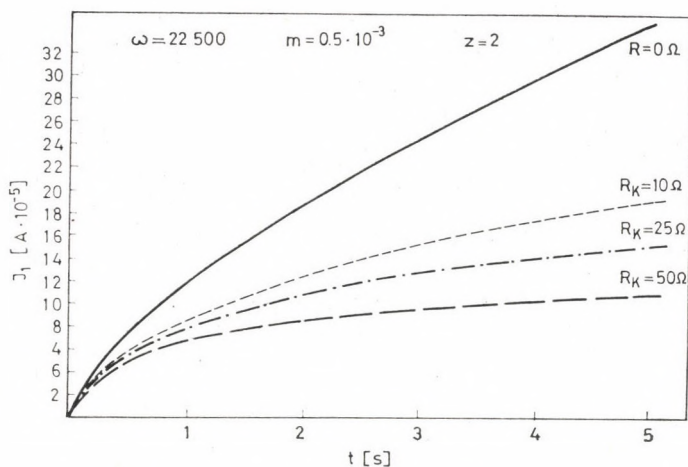


Fig. 4. Variation of the fundamental harmonic a.c. during growth of the mercury drop $m = 5 \times 10^{-4} \text{ g} \cdot \text{s}^{-1}$; $R = 0$; $R_{\text{Hg}} = 10, 25$ and 50 ohm ; $\varrho = 10 \text{ ohm} \cdot \text{cm}$; $z = 2$; $\omega = 2.25 \times 10^4 \text{ s}^{-1}$

The amplitude of the second harmonic is more strongly affected by ohmic drop than that of the fundamental harmonic. A comparison of Figures 5 and 6 shows that the ohmic drop increases with the frequency of a.c. since $1/R_F$ increases proportionally to $\omega^{1/2}$, cf. Eq. (7), while it is apparent by comparing Figures 5 and 7 that the decrease of the amplitude due to ohmic effect is considerably larger when the number of electrons exchanged in the electrode reaction is 2. The increase of ohmic drop during the growth of a mercury drop may

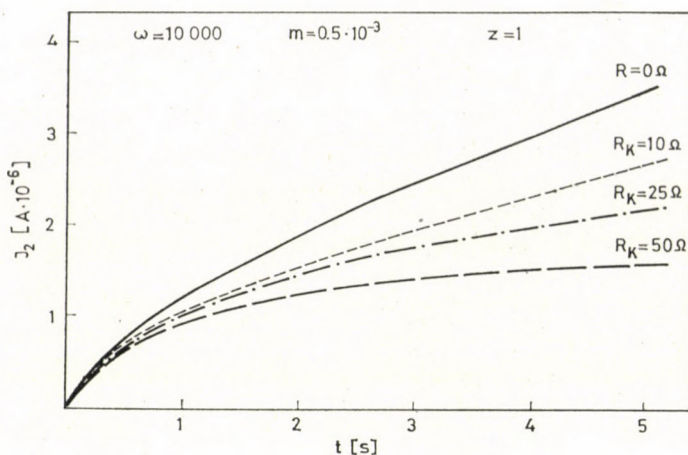


Fig. 5. Variation of the second harmonic a.c. during the growth of the mercury drop $m = 5 \times 10^{-4} \text{ g} \cdot \text{s}^{-1}$; $R = 0$; $R_{\text{Hg}} = 10, 25$ and 50 ohm ; $\rho = 10 \text{ ohm} \cdot \text{cm}$; $z = 1$; $\omega = 1 \times 10^4 \text{ s}^{-1}$

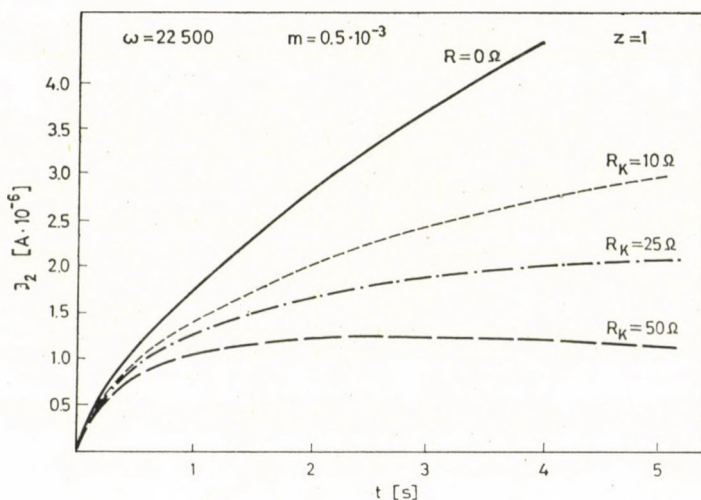


Fig. 6. Variation of the second harmonic a.c. during the growth of the mercury drop $m = 5 \times 10^{-4} \text{ g} \cdot \text{s}^{-1}$; $R = 0$; $R_{\text{Hg}} = 10, 25$ and 50 ohm ; $\rho = 10 \text{ ohm} \cdot \text{cm}$; $z = 1$; $\omega = 2.25 \times 10^4 \text{ s}^{-1}$

cause the second harmonic to exhibit a maximum in the first period of the life of the mercury drop when the frequency and the resistance of the solution are sufficiently large as shown in Figure 8.

SCHMID and REILLEY [17] recorded current *vs.* time curves having similar forms in their studies of some surfactants. This phenomenon was interpreted as follows: the diffusion of the surfactant from the bulk of the solution and the adsorption of the surfactant on the electrode surface were supposed

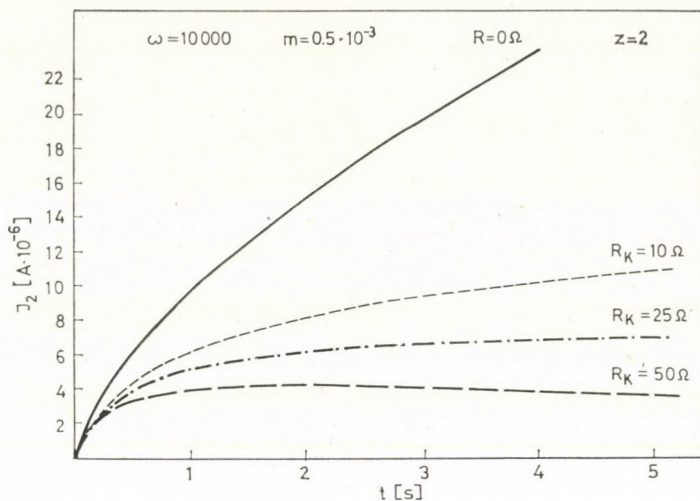


Fig. 7. Variation of the second harmonic a.c. during the growth of the mercury drop $m = 5 \times 10^{-4} \text{ g} \cdot \text{s}^{-1}$; $R = 0$; $R_{\text{Hg}} = 10, 25$ and 50 ohm ; $\rho = 10 \text{ ohm} \cdot \text{cm}$; $z = 2$; $\omega = 1 \times 10^4 \text{ s}^{-1}$

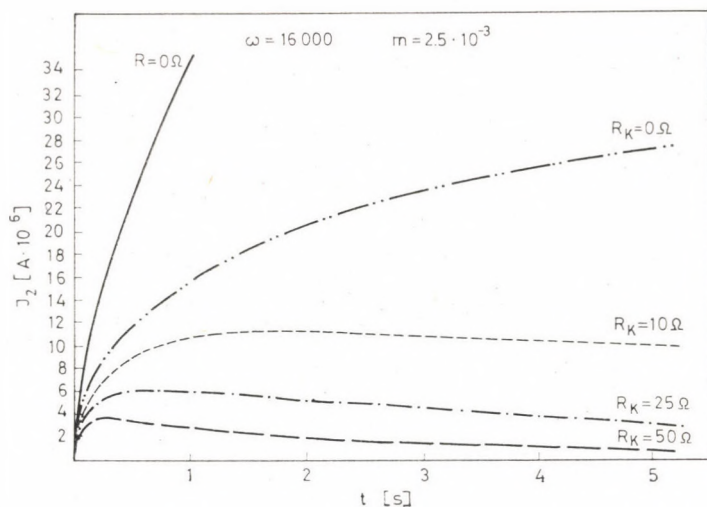


Fig. 8. Variation of the second harmonic a.c. during the growth of the mercury drop $m = 2.5 \times 10^{-3} \text{ g} \cdot \text{s}^{-1}$; $R = 0$; $R_{\text{Hg}} = 10, 25$ and 50 ohm ; $\rho = 10 \text{ ohm} \cdot \text{cm}$; $z = 2$; $\omega = 1.6 \times 10^4 \text{ s}^{-1}$

to be relatively slow processes. Thus the inhibition of the electrode process could only be observed a few seconds after the emergence of the mercury drop. The above mentioned distortion of the current vs. time curves, however, can also be observed in a.c. polarography as an effect of cell resistance and in this case adsorption phenomena on the mercury surface need not be involved.

Experimental

The above considerations were also supported by experiments. The block diagram of the experimental apparatus is shown in Figure 9. Potentiostat (1) (Tacussel, type PRT 20-2x) was controlled by means of helipot (2) used for the adjustment of direct voltage, and by means of generator (3) (type EMG) supplying a distortion-free sinusoidal alternating voltage. Three-electrode cell (4) consisted of dropping mercury electrode (6), 1 normal calomel reference electrode (5), and counter-electrode (7) made of a platinum ring with a large surface. The voltage proportional to the cell current appearing on resistor R_M (8) was measured at the appropriate frequency by means of a selective voltmeter (9) (Rhode-Schwarz, type FNA) and recorded by a X-Y recorder (10) (Hewlett-Packard, type 7000 AM) as a function of time. The X-axis of the recorder was controlled by the built-in time base circuit.

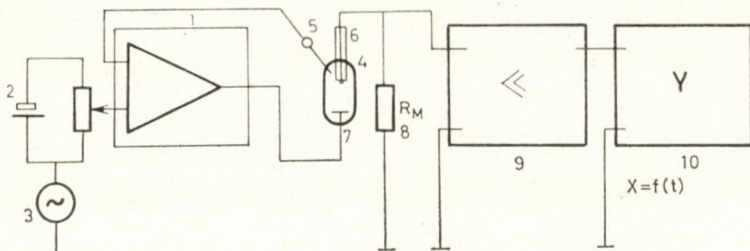


Fig. 9. Block-diagram of the experimental apparatus

trode (5), and counter-electrode (7) made of a platinum ring with a large surface. The voltage proportional to the cell current appearing on resistor R_M (8) was measured at the appropriate frequency by means of a selective voltmeter (9) (Rhode-Schwarz, type FNA) and recorded by a X-Y recorder (10) (Hewlett-Packard, type 7000 AM) as a function of time. The X-axis of the recorder was controlled by the built-in time base circuit.

The data of the dropping mercury electrode were as follows: $m = 2.4 \times 10^{-3} \text{ g} \cdot \text{s}^{-1}$, $t_{\text{max}} = 3.9 \text{ s}$, length of capillary about 100 mm. The experimentally found resistance R_{Hg} of the mercury thread in the capillary was 52 ohm.

The experiments were carried out in a thermostated cell at 25 °C, using $1 \times 10^{-4} \text{ mol} \cdot \text{dm}^{-3} \text{ Cd}^{2+}$ solution in $1 \text{ mol} \cdot \text{dm}^{-3} \text{ HCl}$ as the supporting electrolyte. The potential was adjusted to 660 mV referred to 1 normal calomel electrode corresponding to the maximum current of the second harmonic. $E_{1/2}$ was found to be 680 mV as referred to 1 normal calomel electrode. The amplitude of the alternating voltage was 10 mV at each measuring frequency. The measuring resistance was 50 ohm.

Some experimental records of the second harmonic as a function of time are shown in Figures 10, 11 and 12. The $i = f(t)$ curves calculated on the basis of the theoretical relationships are also shown. The parameters needed for this calculation, namely the specific resistance of the solution and the differential capacity of the mercury electrode were experimentally determined.

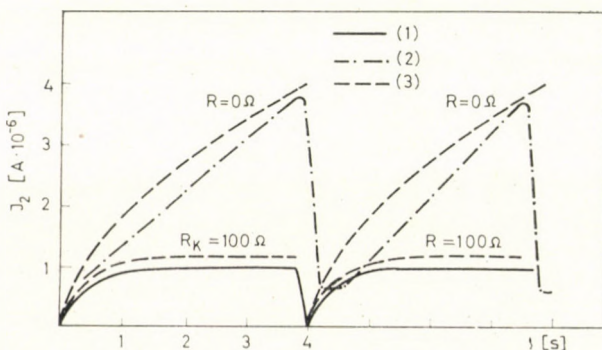


Fig. 10. Second harmonic a.c. as a function of time during the growth of the mercury drop $1 \times 10^{-4} \text{ mol} \cdot \text{dm}^{-3} \text{ Cd}^{2+}$ in $1 \text{ mol} \cdot \text{dm}^{-3} \text{ HCl}$. A.c. frequency: $\omega = 5 \times 10^3 \text{ s}^{-1}$, amplitude: 10 mV. Experimental data (1); data with iR -compensation (2); calculated curve (3)

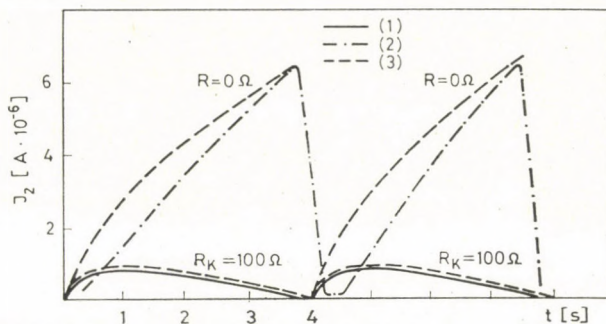


Fig. 11. Second harmonic a.c. as a function of time during the growth of the mercury drop $1 \times 10^{-4} \text{ mol} \cdot \text{dm}^{-3} \text{ Cd}^{2+}$ in $1 \text{ mol} \cdot \text{dm}^{-3} \text{ HCl}$. A.c. frequency $\omega = 1 \times 10^4 \text{ s}^{-1}$, amplitude: 10 mV . Experimental data (1); data with iR -compensation (2); calculated curve (3)

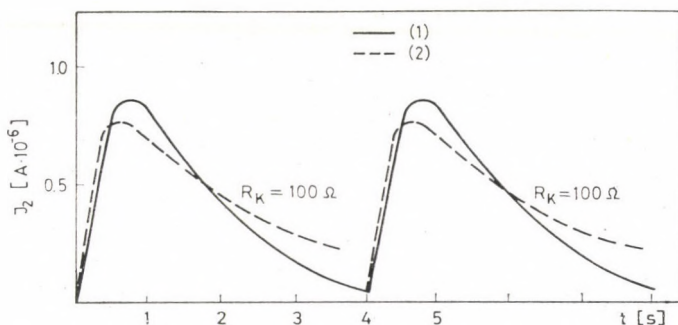


Fig. 12. Second harmonic a.c. as a function of time during the growth of the mercury drop $1 \times 10^{-4} \text{ mol} \cdot \text{dm}^{-3} \text{ Cd}^{2+}$ in $1 \text{ mol} \cdot \text{dm}^{-3} \text{ HCl}$. A.c. frequency $\omega = 1.5 \times 10^4 \text{ s}^{-1}$, amplitude: 10 mV . Experimental data (1); calculated curve (2)

Specific resistance of $1 \text{ mol} \cdot \text{dm}^{-3} \text{ HCl}$ was found to be $3.0 \text{ ohm} \cdot \text{cm}$.

The differential capacity of the dropping mercury electrode was also measured in the supporting electrolyte. An alternating voltage having an amplitude of 10 mV and a frequency of 64 Hz was superimposed on the dropping mercury electrode and the fundamental harmonic component of the a.c. was measured at the potential used in the experiments. Since faradaic reaction cannot occur at this potential in the absence of electroactive component, the cell impedance is the resultant of resistance R and double-layer capacity C in series (cf. Fig. 1). The amplitude of the a.c. across the cell is inversely proportional to the cell impedance, thus, double-layer capacity C can be calculated as follows:

$$C = \frac{1}{\omega} \left[\left(\frac{U}{i_1} \right)^2 - R^2 \right]^{-1/2} \quad (16)$$

The diffusion constant of cadmium ion is $D = 0.82 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ according to literature data. The agreement between calculated and observed data was found to be satisfactory. The deviations can be explained by two facts. Namely, the screening effect of the capillary was not taken into account in the calculations, and the effect of charge transfer polarization was also disregarded which causes deviation at higher frequencies from Eqs (12) and (14) referring to diffusion polarization.

The foregoing results indicate that the ohmic drop causes an error in the measurement of the harmonic components of the alternating current. That error increases when the cell resistance and the concentration of the electroactive component are increased, when the number of electrons involved in the electrode reaction is larger and finally when the frequency of the

alternating voltage is higher. That is the reason why relatively low frequency alternating voltage *viz.* $\omega < 1000$ is generally used in polarographic experiments.

Measurements were also carried out with *iR*-compensation, using *iR*-compensator Tacussel type CDCO (not shown in Fig. 9) which permitted the elimination of the ohmic drop in the case of constant cell resistance [2]. Thus the instrument was adjusted in such a manner as to compensate the cell resistance at the end of the mercury drop life. The data of these measurements are represented by dashed lines in Figures 10 and 11. The data calculated for cell resistance $R = 0$ are also shown in the Figures.

The curves obtained with ohmic compensation differ from curves calculated for $R = 0$ because the cell resistance during drop growth is larger than the resistance compensated at the end of the life of the mercury drop.

It is apparent that the compensation of the cell resistance at the end of the life of the mercury drop permits the use of higher frequencies than the usual ones in a.c. polarographic measurements and thus the sensitivity of analytical determination can be enhanced, since the harmonic components of the alternating current increase proportionally to $\omega^{1/2}$.

The increase in frequency is advantageous as long as the electrode reaction is diffusion controlled *i.e.* the diffusion impedance is much larger than the charge transfer resistance [16].

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ISENTROPIC COMPRESSIBILITY OF ETHYLENEDIAMINE + *n*-ALCOHOL AT 303.15 AND 313.15 K

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Isentropic compressibility of binary mixtures of ethylenediamine with 1-propanol, 1-butanol, 1-pentanol and 1-hexanol were determined at 303.15 and 313.15 K. The four mixtures exhibit negative deviations in compressibility. This is ascribed to dominant character of structure-making effect of the components. The results also show that there is regular trend between the deviation in compressibility and temperature.

Introduction

A survey of the literature has shown that few attempts have been made to study isentropic compressibilities of binary mixtures made up of a diamine and a homologous series of *n*-alcohols. Isentropic compressibility study of these mixture throws light on self-association of the components in the mixture and also on the extent of interaction between unlike molecules. Hence new isentropic compressibility data for mixtures of ethylenediamine with 1-propanol, 1-butanol, 1-pentanol and 1-hexanol, which are self-associated through hydrogen bonding [1—5], have been determined at 303.15 and 313.15 K. The data have been analysed in terms of structure breaking and structure making effects of components and the influence of alcohol chain length.

Experimental

Isentropic compressibility was calculated from precise density and sound speed, determined at 303.15 and 313.15 K. Density was computed from the measured excess volume reported elsewhere [6], and using the relation

$$\rho = \frac{\alpha_1 M_1 + \alpha_2 M_2}{V + VE} \quad (1)$$

α_1 and α_2 denote mole fractions of two components and M_1 and M_2 stand for molecular weights. V represents molar volume of the mixture. Ultrasonic sound speed was measured with a single-crystal interferometer at a frequency of 2 MHz, and was accurate to $\pm 0.15\%$ [7]. The isentropic compressibility was calculated from the relation

$$K_s = u^{-2} \rho^{-1} \quad (2)$$

where u and ρ denote sound speed and density. The values of K_s are accurate to $\pm 2 \text{ TPa}^{-1}$. A quantity was calculated employing the relation [8]

$$K_s = K_s - \Phi_1 K_{s,1} - \Phi_2 K_{s,2} \quad (3)$$

where K_s , $K_{s,1}$ and $K_{s,2}$ are the isentropic compressibilities of the mixtures and the pure components and Φ_1 and Φ_2 are volume fractions. K_s represents the deviation from ideal behaviour.

Ethylenediamine was purified by the method described by RIDDICK and BUNGER [9]. The anhydrous grade ethylenediamine was kept over potassium hydroxide pellets for several hours and then fractionated over metallic sodium using a column containing 30 theoretical plates. Alcohols were purified by the method described by RAO and NAIDU [10]. 1-Propanol and 1-butanol were refluxed over lime for five hours and then distilled using a fractionating column containing 30 theoretical plates. 1-Pentanol and 1-hexanol were dried over Drierite and fractionally distilled. The purity of the samples was checked by comparing the measured densities with those reported in the literature [11]. The data are given in Table I.

Table I
Density of the pure components at 303.15 K

Component	Present work	Literature
Ethylenediamine	0.88600	0.88595
1-Propanol	0.79596	0.79600
1-Butanol	0.80195	0.80206
1-Pentanol	0.80760	0.80764
1-Hexanol	0.81195	0.81201

Results and Discussion

Experimental data for density, sound, speed isentropic compressibility, and K_s defined in Eq. (2) are included in Table II, for the four binary mixtures at both temperatures. Values of K_s are also graphically represented in Figs 1–4. The dependence of K_s on volume fraction is expressed by an empirical equation of the form

$$K_s = \Phi_1 \Phi_2 [b_0 + b_1(\Phi_1 - \Phi_2) + b_2(\Phi_1 - \Phi_2)^2] \quad (4)$$

The values of b_0 , b_1 and b_2 determined by the method of least-squares are given in Table III along with standard deviation $\sigma(K_s)$.

The data included in Table II indicate that K_s values are negative over the entire composition range in the four systems at both temperatures. The values of K_s may be interpreted in terms of two opposing effects: (i) Mutual breakup of O—H—...O and N—H—...N bonds present in aggregates of alcohol and amine. (ii) Hydrogen bond interaction, leading to the formation of O—H—N bonds, between unlike molecules. The former effect contributes to

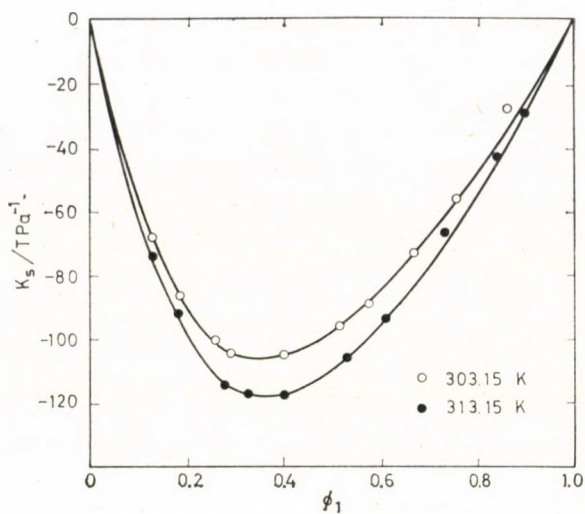


Fig. 1. K_s vs ϕ_1 plots for ethylenediamine and 1-propanol mixtures

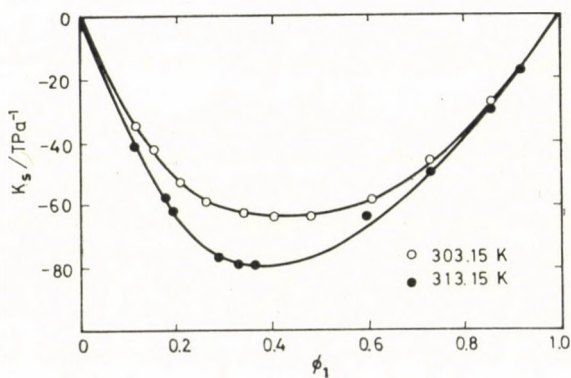


Fig. 2. K_s vs ϕ_1 plots for ethylenediamine and 1-butanol mixtures

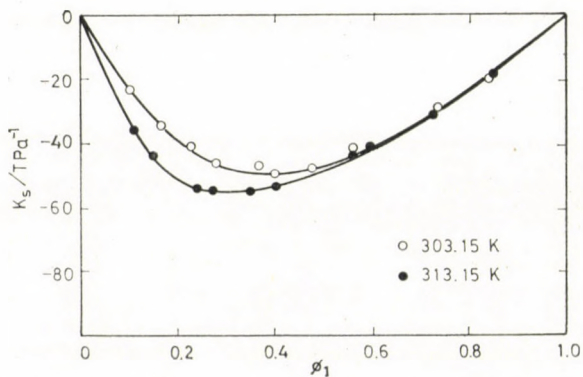


Fig. 3. K_s vs ϕ_1 plots for ethylenediamine and 1-pentanol mixtures

Table II

Volume fraction Φ_1 of ethylenediamine, density ρ , sound velocity u , isentropic compressibility κ_s [from equation (1) and K_s from equation (2)] for ethylenediamine + *n*-alcohol mixtures

Results at 303.15 K					Results at 313.15 K				
	$\frac{\rho}{\text{g cm}^{-3}}$	$\frac{u}{\text{ms}^{-1}}$	$\frac{\kappa_s}{\text{TPa}^{-1}}$	$\frac{K_s}{\text{TPa}^{-1}}$		$\frac{\rho}{\text{g cm}^{-3}}$	$\frac{u}{\text{ms}^{-1}}$	$\frac{\kappa_s}{\text{TPa}^{-1}}$	$\frac{K_s}{\text{TPa}^{-1}}$
Ethylenediamine + 1-propanol									
0	0.79596	1191	886	0	0	0.78762	1151	958	0
0.1318	0.81442	1275	755	- 69	0.1363	0.80695	1234	815	- 72
0.1805	0.82042	1306	715	- 86	0.1869	0.81357	1264	769	- 91
0.2514	0.82875	1344	668	-100	0.2757	0.82309	1316	701	-114
0.2977	0.83345	1367	642	-104	0.3288	0.82823	1345	671	-117
0.4046	0.84346	1416	591	-105	0.4027	0.83487	1374	632	-117
0.5133	0.85249	1471	542	- 97	0.5329	0.84534	1434	576	-106
0.5693	0.85933	1495	520	- 89	0.6060	0.85060	1462	550	- 94
0.6655	0.86353	1522	500	- 73	0.7384	0.85969	1514	508	- 61
0.7587	0.86991	1562	471	- 55	0.8490	0.86691	1558	475	- 43
0.8684	0.87732	1578	458	- 20	0.9043	0.87060	1580	461	- 29
1.0000	0.88600	1650	416	0	1.0000	0.87650	1608	441	0

Ethylenediamine + 1-butanol

0	0.80195	1224	832	0	0	0.79451	1188	892	0
0.1108	0.81653	1277	759	- 35	0.1118	0.80939	1242	801	- 41
0.1500	0.81923	1294	729	- 43	0.1716	0.81595	1271	758	- 57
0.2042	0.82684	1319	695	- 52	0.1993	0.81865	1284	740	- 62
0.2677	0.83299	1347	662	- 58	0.2819	0.82614	1324	689	- 76
0.3425	0.84016	1377	628	- 62	0.3219	0.82934	1342	669	- 78
0.4078	0.84471	1417	590	- 63	0.3703	0.83306	1362	647	- 78
0.4785	0.85003	1437	570	- 63	0.5944	0.84900	1450	561	- 62
0.6060	0.85918	1492	523	- 58	0.7258	0.85798	1502	516	- 48
0.7275	0.86765	1545	483	- 46	0.8547	0.86683	1552	478	- 28
0.8495	0.87579	1593	450	- 28	0.9109	0.87055	1572	462	- 18
1.0000	0.88600	1650	416	0	1.0000	0.87650	1608	441	0

Table II (cont.)

Results at 303.15 K					Results at 313.15 K				
	$\frac{\rho}{\text{g cm}^{-3}}$	$\frac{u}{\text{ms}^{-1}}$	$\frac{\kappa_s}{\text{TPa}^{-1}}$	$\frac{K_s}{\text{TPa}^{-1}}$		$\frac{\rho}{\text{g cm}^{-3}}$	$\frac{u}{\text{ms}^{-1}}$	$\frac{\kappa_s}{\text{TPa}^{-1}}$	$\frac{K_s}{\text{TPa}^{-1}}$
Ethylenediamine + 1-pentanol									
0	0.80760	1256	785	0	0	0.79992	1224	840	0
0.1025	0.81972	1295	724	-23	0.1055	0.81185	1271	762	-36
0.1658	0.82590	1325	690	-34	0.1483	0.81593	1290	737	-44
0.2209	0.83063	1346	663	-41	0.2370	0.82343	1325	691	-54
0.2842	0.83358	1376	634	-46	0.2777	0.82664	1340	674	-55
0.3622	0.84152	1404	603	-48	0.3459	0.83159	1363	647	-55
0.4032	0.84453	1420	587	-49	0.4024	0.83556	1382	626	-53
0.4723	0.84940	1446	563	-47	0.5611	0.84668	1435	573	-43
0.6034	0.85859	1497	520	-42	0.5956	0.84907	1450	561	-41
0.7301	0.86739	1543	484	-32	0.7298	0.85822	1520	518	-30
0.8415	0.87524	1585	455	-20	0.8572	0.86686	1552	479	-18
1.0000	0.88600	1650	416	0	1.0000	0.87650	1608	441	0

Ethylenediamine + 1-hexanol

0	0.81195	1288	742	0	0	0.80448	1251	792	0
0.0735	0.81881	1312	710	-12	0.0625	0.81179	1264	736	-12
0.1276	0.82414	1335	681	-21	0.1169	0.81732	1296	728	-22
0.1478	0.82792	1357	662	-26	0.1600	0.81888	1307	715	-28
0.2173	0.83148	1368	643	-32	0.2064	0.82422	1331	685	-32
0.2752	0.83697	1394	615	-37	0.2754	0.82829	1353	660	-37
0.4067	0.84546	1438	572	-37	0.4020	0.83674	1396	613	-39
0.4625	0.85258	1478	537	-36	0.5120	0.84028	1416	594	-38
0.5438	0.85796	1506	514	-32	0.5976	0.84518	1440	570	-33
0.7272	0.87233	1580	459	-23	0.8135	0.85706	1506	514	-18
0.8598	0.87877	1611	438	-12	0.9031	0.86597	1556	478	-9
1.0000	0.88600	1650	416	0	1.0000	0.87650	1608	441	0

increase in free lengths described by JACOBSON [12]. This leads to negative deviation in sound speed and positive deviation in isentropic compressibility. The latter effect, on the other hand, contributes to positive deviation in sound speed and negative deviation in isentropic compressibility. The sign and mag-

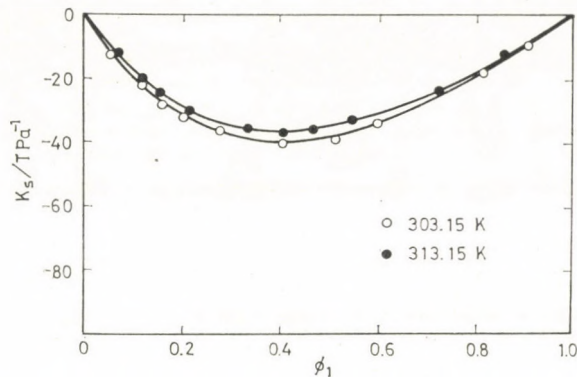


Fig. 4. K_s vs Φ_1 plots for ethylenediamine and 1-hexanol mixtures

Table III

Values of the parameters of equation (4) and the standard deviation, $\sigma(K_s)$

System	T(K)	$\frac{b_0}{\text{TPa}^{-1}}$	$\frac{b_1}{\text{TPa}^{-1}}$	$\frac{b_2}{\text{TPa}^{-1}}$	$\frac{\sigma(K_s)}{\text{TPa}^{-1}}$
Ethylenediamine + 1-propanol	303.15	-401	266	- 1	2
Ethylenediamine + 1-butanol	303.15	-248	78	- 69	1
Ethylenediamine + 1-pentanol	303.15	-189	69	- 20	1
Ethylenediamine + 1-hexanol	303.15	-152	67	- 13	1
Ethylenediamine + 1-propanol	313.15	-438	209	- 76	3
Ethylenediamine + 1-butanol	313.15	-290	134	- 56	2
Ethylenediamine + 1-pentanol	313.15	-189	143	-122	1
Ethylenediamine + 1-hexanol	313.15	-148	54	5	2

nitude of the actual deviation depends on the relative strengths of the two effects. The experimental values of K_s , which are negative, point out that the latter effect dominates in the four mixtures.

The negative values of K_s fall in the order: 1-propanol > 1-butanol > 1-pentanol > 1-hexanol. This order suggests that the extent of interaction between unlike molecules decrease with an increase in chain length of alcohols.

The curves in Figs 1—4 show that there is a regular trend between K_s and temperature. The temperature coefficient of K_s is negative for mixtures of ethylenediamine with 1-propanol, 1-butanol, 1-pentanol and 1-hexanol.

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HETEROCYCLIZATION WITH IMINIUM CHLORIDES, II* SYNTHESIS OF 4H-[3,1]-BENZOXAZINE-4-ONES AND QUINAZOLINONES

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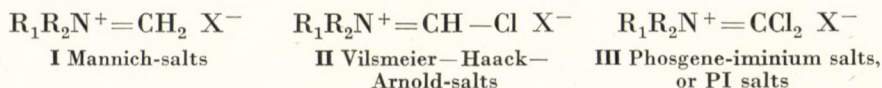
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Reactions between methyl anthranilate and a variety of PI salts afforded 2-ammonio-4H-[3,1]-benzoxazine-4-one chlorides which were subjected to nucleophilic reactions. With primary amines, 2-ureidoanthraniloyl amides were obtained, which were smoothly cyclized in boiling acetic anhydride or dimethylformamide to give 1H,3H-quinazoline-2,4-diones.

Among reactive iminium chlorides, there are a number of useful reagents which are frequently employed in heterocyclizations. Three fundamental representatives of these "iminium synthons" (the name coined by VIEHE [2]) are as follows:



An excellent review has recently been published on the above iminium salts [3]. Each of them is a strong electrophile, especially II and III.

Both II and III are gaining in use, not only in laboratory work, but also in industrial practice. Their widespread application is due to their superior reactivity, easy preparation (cheap materials, simple methods) and versatility. Many ring closure reactions have been recorded in the literature in which I and II are directly used as one-carbon components, but many more cyclizations have been accomplished with the 1,3-dielectrophiles generated from the reaction of I or II with simple ketones, amides, lactams etc.

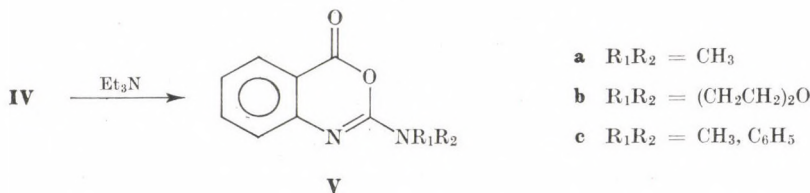
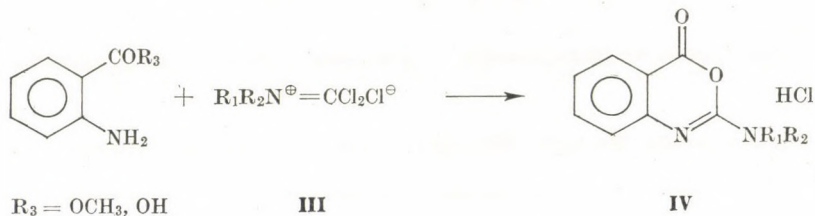
In our earlier papers we reported both kinds of cyclizations.

Nucleophilic splitting of trisubstituted amidines, prepared from derivatives of anthranilic acid and II, with different amines and hydrazines resulted in the formation of a great number of [3H]-quinazolin-4-ones and 4-aminoquinazolines [4]. Cyclizing aromatic amines and 2-aminopyridine with 1,3-dichlorocyanines and azacyanines, prepared from tertiary amides, cyanamides and PI salt or phosgene, resulted in the preparation of different quinazolines, pyrido-[1,2a]pyrimidines and triazines [5].

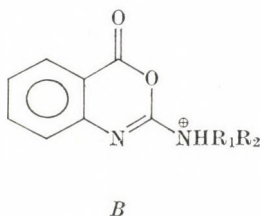
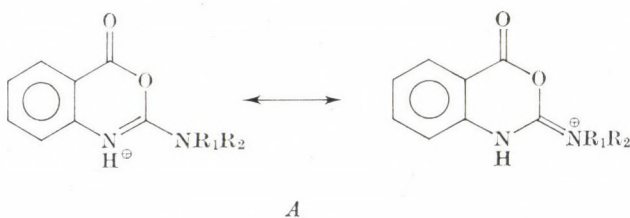
* For the previous communication, see Ref. [1].

Realizing the remarkable reactivity of PI salts, we have studied their conversions with anthranilates and now we wish to report the reaction of methyl anthranilate and anthranilic acid with different PI salts and a few nucleophilic reactions of the [4*H*]-3,1-benzoxazin-4-ones so obtained.

Methyl anthranilate smoothly reacted with PI salts in dichloromethane at 40 °C to give 2-ammonio-4*H*-[3,1]-benzoxazin-4-one chlorides (IV) in high yields. Anthranilic acid afforded the same products, but the yields were lower.



The IR spectra of the salts IV are very characteristic: νCO bands near 1815 cm^{-1} and $\nu\text{C}=\text{N}^+$ around 1670 cm^{-1} are present, while the νNH^+ band occurs as a wide absorption between 2800 and 2400 cm^{-1} . In the spectra of the base (V) the same bands are shifted to the vicinity of 1765 cm^{-1} and 1620 cm^{-1} , and the NH band is absent.

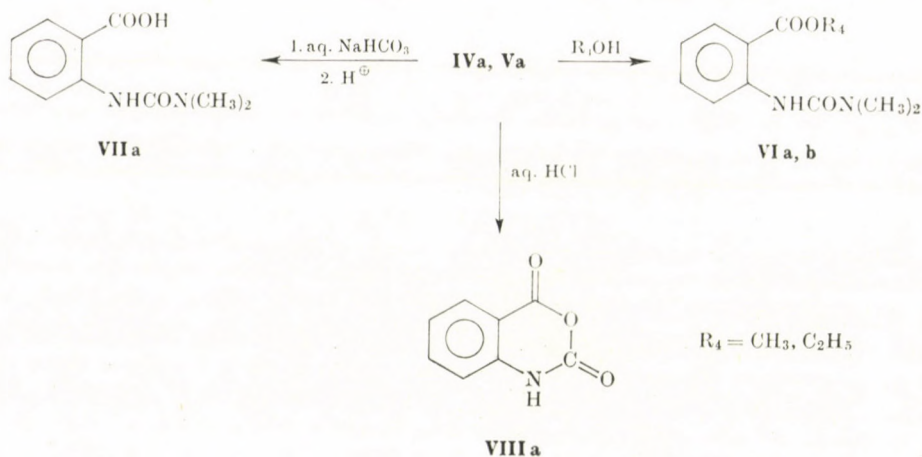


The structures of compounds **IV** can be depicted in two different forms.

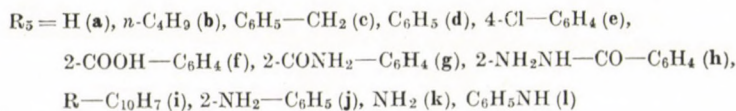
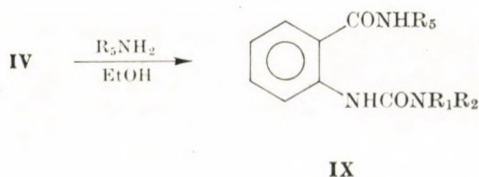
It is worth noting that compounds of type **V** are fairly stable in spite of their *O*-acylisourea feature.

To our best knowledge only one similar example has been reported in the literature [6]: LEMPERT and DOLESCHALL described the reaction of anthranilic acid and cyanogen bromide which furnished **V** ($R^1 = R^2 = H$). According to the IR spectroscopic data, the *B* tautomer may exist in the solid state, similarly to DOLESCHALL's observation in the case of $R^1 = R^2 = H$.

It is not surprising that compounds **IV** and **V** are very reactive towards nucleophiles. Their base-catalyzed alcoholysis and hydrolysis gave ring-cleaved products **VI**, **VII**, while acid hydrolysis did not cleave the ring, but resulted in the formation of isatoic anhydride (**VIIIa**).



Compound **IV** readily reacted with different amines and hydrazines in anhydrous ethanol at ambient temperature to give 2-ureidobenzoic acid amides and hydrazides **IX** in good yields. The reaction was accomplished in the presence of an acid acceptor, sodium acetate or excess of base.

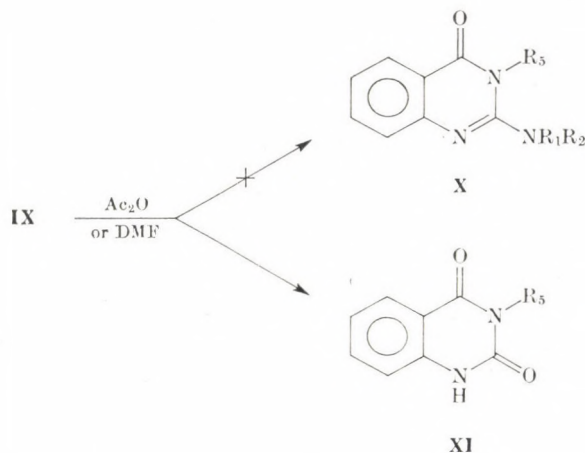


In the IR spectra of compounds of type **IX**, two strong νCO bands appear at $1640\text{--}1690\text{ cm}^{-1}$, and broad νNH bands between 2500 cm^{-1} and 3400 cm^{-1} are present because of association.

Recently a new aspect of the aminolysis of different 2-alkyl-4*H*-[3,1]-benzoxazine derivatives has been reported [7]. Influenced by the substituents at the 2-position, by the amine and by the solvent, two types of ring opening have been observed depending on the site of the nucleophilic attack. Beside a rare appearance of type **IX** anthraniloyl amides, mostly *N*-2-carboxyphenylamidine intermediates could be isolated indicating the possibility of nucleophilic attack at the C_2 -atom. This carboxyamidine exists in a zwitterionic form, and on the addition of base it is instantly transformed into a quinazoline.

In our experience no other compounds such as **IX** could be detected.

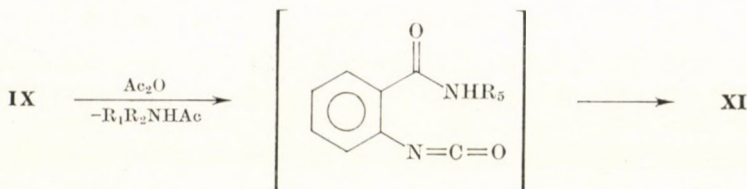
The cyclization of 2-ureidobenzamides (**IX**, $\text{R}_1, \text{R}_2 = \text{H}$) into 3*H*-quinazoline-2,4-diones is described in the literature [9]. We hoped that compounds **IX** might be suitable for the preparation of 3*H*-quinazolin-4-ones containing tertiary amino groups at the 2-position, which have not been prepared so far by direct cyclization. Our expectation failed, however, because when the reaction was run in boiling acetic anhydride or dimethyl formamide 1*H*,3*H*-quinazoline-2,4-diones **XI** were obtained in good yields.



In the IR spectra of the cyclized products **XI** the νCO bands are shifted to $1670\text{--}1730\text{ cm}^{-1}$; the R_1, R_2 signals are missing in the NMR spectra.

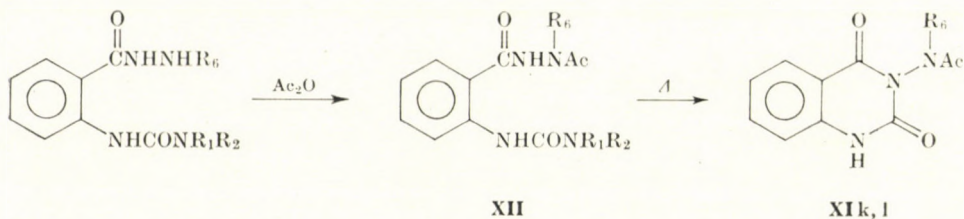
Ring closure takes place much more rapidly in boiling Ac_2O than in DMF, requiring only 5 minutes even if $\text{R}_1 = \text{phenyl}$ and $\text{R}_2 = \text{CH}_3$. This reaction is a rather rare example of acylation by a reverse mechanism, *i.e.* not addition-elimination but elimination-addition. Compounds **IX**, like trisubstituted ureas, readily dissociate into isocyanates and secondary amines in proton-catalyzed

reactions. The amine is trapped by Ac_2O , and the amide nitrogen is attacked by the isocyanate in a rapid intramolecular reaction:



Our conclusion is supported by the fact that in the cases where R_1 , R_2 are methyl and phenyl or diethyleneoxy groups, which are poor leaving groups, ring closure is as rapid as when $\text{R}_1=\text{R}_2=\text{methyl}$. In boiling DMF or pyridine, a few hours are necessary to attain the same result, since proton catalysis or amine trapping is absent.

If hydrazines are used instead of amines, in Ac_2O the end-products are acetylated, so that three νCO bands (at 1680 cm^{-1} , 1710 cm^{-1} and 1745 cm^{-1}) are observed in the IR spectra of **XI**, **I**.



$\text{R}_6 = \text{H, C}_6\text{H}_5$

Experimental

Preparation of 2-ammonio-4H-[3,1]-benzoxazin-4-one chlorides (IV)

The PI salt* (**III**) (0.1 mole) was suspended in 80 mL dry dichloromethane and 15.1 g (0.1 mole) of methyl anthranilate in 20 mL dichloromethane was added at ambient temperature. An exothermic reaction and strong gas evolution ensued, while a white solid material precipitated from the solution. After short boiling the evolution of gas ceased; the product was then filtered off with suction, washed with dry ether and dried in a vacuum desiccator.

IVa: $\text{R}_1=\text{R}_2=\text{CH}_3$. Yield: 18.4 g (81%), m.p. 211–213 °C (d).

$\text{C}_{10}\text{H}_{11}\text{N}_2\text{O}_2\text{Cl}$ (226.47). Calcd. C 52.90; H 4.86; N 12.36; Cl- 15.68. Found C 53.12; H 4.87; N 12.38; Cl- 15.75%.

IR (KBr): νCO 1815 cm^{-1} ; $\nu\text{C}=\text{N}^+$ 1680 cm^{-1} .

$^1\text{H-NMR}$ (TFA): NMe_2 3.39 s (3H), 4.43 s (3H); ArH 7.5–7.75 m (2H); 7.98 t (1H), 8.22 d (1H), $J_0 = 8\text{ Hz}$.

IVb: $\text{R}_1\text{R}_2 = (\text{CH}_2\text{CH}_2)_2\text{O}$. Yield: 16.0 g (60%), m.p. 200–201 °C (d.).

$\text{C}_{12}\text{H}_{13}\text{N}_2\text{O}_3\text{Cl}$ (268.50). Calcd. C 53.65; H 4.84; N 10.44; Cl- 13.23. Found C 53.63; H 4.99; N 10.82; Cl- 13.31%.

*The PI salts were prepared by chlorination of the respective thiuram disulfides or methyl dithiocarbamates in dichloromethane at 40 °C.

Table I
Physical properties of compounds IX

IX	R ₁	R ₂	R ₆	M.p., °C	Yield, %	Analysis					
						Calcd.			Found		
a	CH ₃	CH ₃	H	176—8 (d)	72.0	C 57.9	H 628 .	N 20.3	C 57.15	H 6.21	N 20.45
b	CH ₃	CH ₃	<i>n</i> -C ₄ H ₉	93—5	76.2	C 63.9	H 7.99	N 15.95	C 63.43	H 7.78	N 15.51
c	CH ₃	CH ₃	C ₇ H ₅ CH ₂	124—6	87.5	C 68.8	H 6.4	N 14.15	C 68.87	H 6.34	N 13.80
d	CH ₃	CH ₃	C ₆ H ₅	160—2 (d)	78.0	C 67.8	H 6.0	N 14.83	C 67.85	H 6.10	N 14.75
e	CH ₂ CH ₂ O	CH ₂ CH ₂	C ₆ H ₅	275—7	71.5	C 66.4	H 5.83	N 12.92	C 66.52	H 5.69	N 12.97
f	CH ₃	C ₆ N ₅	C ₆ H ₅	189—91	90.0	C 74.95	H 5.51	N 12.18	C 72.57	H 5.57	N 12.06
g	CH ₃	CH ₃	4-ClC ₆ H ₄	176—7 (d) 290—2	91.5	C 60.05	H 5.04	N 13.25	C 60.15	H 5.09	N 13.14
h	CH ₃	CH ₃	2-COOH—C ₆ H ₄	180—1 (d)	81.0	C 62.4	H 5.20	N 12.84	C 62.29	H 5.26	N 12.71
i	CH ₃	CH ₃	2-COOCH ₃ —C ₆ H ₄	173—4 (d)	85.0	C 53.2	H 5.57	N 12.32	C 62.93	H 5.67	N 12.43
j	CH ₂ CH ₂ O	CH ₂ CH ₂	2-COOCH ₃ —C ₆ H ₄	155—9 (d)	35.0	C 62.6	H 5.48	N 10.96	C 62.28	H 5.40	N 10.89
k	CH ₃	CH ₃	2-CONH ₂ —C ₆ H ₄	195—6 (d)	89.0	C 61.55	H 5.52	N 17.18	C 62.15	H 5.58	N 17.57
l	CH ₃	CH ₃	2-CONHNH ₂ —C ₆ H ₄	115—7 (d)	87.0	C 59.75	H 5.58	N 20.53	C 59.3	H 5.61	N 20.45
m	CH ₃	CH ₃	2-C ₁₀ H ₉	171—3 (d) 294—5	84.0	C 72.10	H 5.71	N 12.61	C 71.94	H 5.90	N 11.91
n	CH ₂ CH ₂ O	CH ₂ CH ₂	2-C ₁₀ H ₉	185—8	59.0	C 70.04	H 5.61	N 11.20	C 70.51	H 5.56	N 11.47
o	CH ₃	C ₆ H ₅	2-C ₁₀ H ₉	176—8	74.0	C 75.93	H 5.31	N 10.62	C 75.78	H 5.32	N 10.56
p	CH ₃	CH ₃	2-NH ₂ —C ₆ H ₄	168—70 (d) 310—2	71.0	C 64.40	H 6.03	N 18.78	C 64.49	H 6.11	N 18.68

IR (KBr): ν_{CO} 1810 cm^{-1} ; $\nu_{\text{C}=\text{N}^+}$ 1670 cm^{-1} .

IVc: $\text{R}_1=\text{CH}_3$, $\text{R}_2=\text{C}_6\text{H}_5$. Yield: 18.0 g (62%). m.p. 181–184 °C (d.)

$\text{C}_{15}\text{H}_{13}\text{N}_2\text{O}_2\text{Cl}$ (288.47). Calcd. C 62.40; H 4.51; N 9.72; Cl 12.32. Found C 62.08; H 4.53; N 9.68; Cl 12.45%.

IR (KBr): ν_{CO} 1815 cm^{-1} ; $\nu_{\text{C}=\text{N}^+}$ 1670 cm^{-1} .

Preparation of 2-dialkylamino-4H-[3,1]-benzoxazin-4-ones

A mixture consisting of 0.002 mole of IV, 10 mL of water, and 0.35 mL (0.0026 mole) of triethylamine, was stirred for 30 min at room temperature. The white solid was filtered off, washed with water and dried in air.

Va: 2-Dimethylamino-4H-[3,1]-benzoxazin-4-one

Yield: 0.35 g (87%), m.p. 127–128 °C (EtOH).

Table II

Spectral data of compounds IX

IX	IR(KBr), cm^{-1}	$^1\text{H-NMR}$ (TMS = 0), δ ppm (CDCl_3)
a	1690, 1660, 3340, 3170	3.15 s (6H); 7.02 t (1H); 7.45 td (1H); 7.70 dd (1H); 8.28 d (1H); $J_0 = 8$ Hz, $J_m = 2$ Hz, 10.8 s (1H)
b	3330, 3250, 1670, 1640	3.10 s 3.12 s (6H); 4.34 q (2H); 6.79 t, 6.92 t (1H); 7.2–7.5 m (2H); 8.21 d, 8.49 d (1H); 7.55 _s (1H); 10.4, 38 s (1H)
c	3240, 3060, 1660, 1640	2.95 s (6H); 4.51 d (2H) ($J = 5$ Hz); 7.20 s (5H); 6.67 t (1H); 7.08 t (1H); 7.41 d (1H); 8.12 d (1H); 8.05 s (1H); 10.52 s (1H)
d	3250, 3210, 1660, 1635	3.09 s (6H); 6.70 t (1H); 7.00–7.2 m (2H); 7.2–7.4 m (2H); 7.27 d (2H); 7.97 d (1H); 9.51 s (1H); 9.81 s (1H)
e	3260, 3210, 1660, 1640	
f	3280, 3200, 1665, 1640	
g	3260, 3220, 1665, 1650	3.15 s (6H); 6.75 t (1H); 7.0–7.4 m (4H); 7.70 d (2H); 7.95 d (1H) ($J_0 = 8$ Hz), 9.50 s (1H); 9.84 s (1H)
h	3280–2700, 1695, 1675, 1650	
i	3250, 3210, 1690, 1680, 1655	3.12 s (6H); 3.91 s, 4.01 s (3H); 7.0 m (2H); 7.5 m (2H); 7.78 dd (1H); 7.96 td (1H); 8.52 dd (1H); 8.73 d (1H); ($J_0 = 8$ Hz, $J_m = 2$ Hz) 10.76 s (1H); 11.85 s (1H)
j	3265, 3210, 1695, 1680, 1655	
k	3360, 3200, 3105, 1680, 1660, 1640	
l	3460, 3360, 3250, 1665, 1650, 1635	
m	3280–2850, 1660, 1640	3.19 s (6H); 6.47 t (1H); 7.08 t (1H); 7.4 m (3H); 7.8 m (4H); 8.02 d (1H) ($J_0 = 8$ Hz), 8.33 s (1H), 9.70 s (1H); 9.93 s (1H)
n	3360–2820, 1665, 1640	
o	3250–2800, 1665, 1650	
p	3420, 3340, 3240, 1660, 1640	3.10 s (6H); 6.7–7.25 m (5H); 7.45 t (1H); 7.70 d (1H); 8.20 d (1H) ($J_0 = 8$ Hz)

$C_{10}H_{10}N_2O_2$ (190.01). Calcd. C 63.15; H 5.26; N 14.71. Found C 63.07; H 5.22; N 14.76%.

IR (KBr): ν_{CO} 1765 cm^{-1} ; $\nu_{C=N}$ 1630 cm^{-1} .

1H -NMR ($CDCl_3$): NMe_2 3.25 s (6H); ArH 7.09 t (1H), 7.20 d (1H), 7.93 dd (1H), 7.55 d (1H), $J_m = 2$ Hz, $J_0 = 8$ Hz.

Vb: 2-Diethyleneoxyamino-4H-[3,1]-benzoxazin-4-one

Yield: 0.4 g (86%), m.p. 150–151 °C (benzene).

$C_{12}H_{12}N_2O_3$ (232.01). Calcd. C 61.95; H 5.17; N 12.06. Found C 62.09; H 5.07; N 12.18%.

IR (KBr): ν_{CO} 1760 cm^{-1} ; $\nu_{C=N}$ 1615 cm^{-1} .

Vc: 2-Methyl-phenyl-amino-4H-[3,1]-benzoxazin-4-one

Yield: 0.45 g (89%), m.p. 130–132 °C (EtOH)

$C_{15}H_{12}N_2O_2$ (252.28). Calcd. C 71.35; H 4.76; N 11.11. Found C 70.98; H 4.70; N 10.95%.

IR (KBr): ν_{CO} 1770 cm^{-1} ; $\nu_{C=N}$ 1620 cm^{-1} .

Preparation of 2-(N, N-dimethylureido)-benzoic acid (VIIa)

Compound IVa (2.3 g; 0.01 mole) was mixed with 20 mL of 5% $NaHCO_3$ solution. The mixture was boiled for 15 min. The resulting solution was acidified with HCl to obtain 1.55 g (77%) of VIIa, m.p. 160–161 °C (EtOH).

Table III

Physical properties of compounds XI

IX	R ₃	M.p., °C	Yield, %	Analysis					
				Calcd.			Found		
a	H	350–2	81.0	C 59.26	H 3.73	N 17.28	C 59.09	H 3.70	N 17.34
		[8] <i>lit.</i> 351–2							
b	<i>n</i> -C ₄ H ₉	154–6	82.5	C 66.05	H 6.42	N 12.83	C 65.85	H 6.52	N 13.06
c	C ₆ H ₅ CH ₂	225–7	96.5	C 71.41	H 4.76	N 11.11	C 71.25	H 4.78	N 11.25
		[8] <i>lit.</i> 227–8							
d	C ₆ H ₅	277–9	98.0	C 70.58	H 4.23	N 11.75	C 70.47	H 4.31	N 11.47
		[8] <i>lit.</i> 278–80							
e	4-Cl–C ₆ H ₄	293–5							
f	2-COOH–C ₆ H ₄	297–	93.0	C 63.83	H 3.57	N 9.93	C 63.67	H 3.61	N 10.17
		300 [6a] <i>lit.</i> 298–300							
g	2-COOCH ₃ – C ₆ H ₄	249–50	90.5	C 64.80	H 4.06	N 9.46	C 64.73	H 4.10	N 9.19
h	2-H ₂ NCO– C ₆ H ₄	265–6	18.0	C 64.05	H 3.92	N 14.95	C 63.85	H 3.90	N 14.72
i	2-H ₂ NHCO– C ₆ H ₄	229–31	77.0	C 60.80	H 4.05	N 18.91	C 60.47	H 4.0	N 18.47
j	2-C ₁₀ H ₉	289–92	96.0	C 74.90	H 4.17	N 9.72	C 74.51	H 4.09	N 9.60
k	2-CH ₃ CONH– C ₆ H ₄	322–5	89.0	C 65.05	H 4.41	N 14.25	C 64.81	H 4.48	N 14.36

$C_{10}H_{12}N_2O_3$ (208.22). Calcd. C 57.80; H 5.78; N 13.45. Found C 57.67; H 5.75; N 13.52%. IR (KBr): ν_{CO} 1695, 1650 cm^{-1} ; ν_{OH} , NH 3300–2400 cm^{-1} . 1H -NMR ($CDCl_3$): NMe_2 3.15 s (6H); ArH 7.0 t (1H), 7.50 td (1H), 8.03 dd (1H), 8.50 d (1H), $J_0 = 8$ Hz, $J_m = 2$ Hz, NH 4.36 s (1H).

Preparation of 2-(*N,N*-dimethylureido)benzoates (VI)

IVa (2.3 g; 0.01 mole) was boiled in 10 mL of alcohol for 30 min. After evaporation of the solvent, the residue was suspended in water to obtain a white solid.

VIa: Methyl 2-(*N,N*-dimethylureido)-benzoate

Yield: 1.95 g (88%), m.p. 88–90 °C (MeOH).

$C_{11}H_{14}N_2O_3$ (222.25). Calcd. C 59.40; H 6.31; N 12.61. Found: C 59.58; H 6.25; N 12.57%.

IR (KBr): ν_{CO} 1695, 1660 cm^{-1} ; ν_{NH} 3290, 3260 cm^{-1} .

1H -NMR ($CDCl_3$): NMe_2 3.13 s (6H); OMe 3.92 s (3H); ArH 6.6 t (1H) 7.87 td (1H); 7.86 dd (1H); 8.44 d (1H); NH 10.4 s (1H).

VIb: Ethyl 2-(*N,N*-dimethylureido)-benzoate

Yield: 1.90 g (80%), m.p. 100–102 °C (EtOH).

$C_{12}H_{16}N_2O_3$ (236.27). Calcd. C 61.05; H 6.77; N 11.86. Found C 60.97; H 6.90; N 11.71%.

IR (KBr): ν_{CO} 1690, 1670 cm^{-1} ; ν_{NH} 3280, 3250 cm^{-1} .

Preparation of 2-ureidobenzamides (IX)

A solution of **IV** (0.01 mole) and of the appropriate primary amine (0.02 mole) in 15 mL of EtOH (in some cases 0.01 mole of the amine and 0.01 mole of sodium acetate were used) was stirred at ambient temperature for 2 h. To the reaction mixture there was added some water to obtain a white solid, which was recrystallized from EtOH. The physical properties of the products are summarized in Table I; the spectroscopic data are shown in Table II.

Table IV

Spectral data of compounds XI

IX	IR (KBr), cm^{-1}	1H -NMR (TMS = 0), δ ppm ($CDCl_4$)
a	3250–2850, 1720, 1685	7.25 m (2H); 7.63 d (1H); 8.03 d (1H); $J_0 = 8$ Hz
b	3190–3000, 1720, 1665	1.05 t (3H); 1.3–1.9 m (4H); 4.17 t (2H); 7.2 m (2H); 7.57 td (1H); 8.06 d (1H); $J_0 = 8$ Hz, 10.93 s (1H)
c	3180–2800, 1720, 1670	
d	3200–2750, 1730, 1670	7.0–7.7 m (8H); 7.98 d (1H) $J_0 = 8$ Hz
e	3190–2890, 1730, 1675	7.22 m (3H); 7.45 m (3H); 7.65 td (1H); 8.04 d (1H)
f	3180–2890, 1730, 1685	
g	3260, 1730, 1680, 1655	
h	3460, 3350, 3200, 1750, 1680, 1650	
i	3450, 3340–2850, 1735, 1680, 1660	
j	3200–2800, 1730, 1670	7.25 t (1H); 7.4–7.65 m (5H); 7.75–8.0 m (4H); 8.08 d (1H) $J_0 = 8$ Hz
k	3360–3250, 1730, 1710, 1670	2.12 s (3H); 7.1–7.75 m (6H); 7.92 d (1H); 8.20 d (1H) $J_0 = 8$ Hz

Preparation of 1*H*,3*H*-quinazoline-2,4-diones (XI)

Compounds IX (0.01 mole) were refluxed in 10 mL of acetic anhydride for 10 min (or in DMF for 1–2 h). On cooling, white crystals precipitated (in the case of DMF some water was added). The products were washed, and recrystallized from ethanol. The physical properties of compounds XI are summarized in Table III; the spectroscopic data are listed in Table IV.

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THERMOLYSE VON CYANOKOMPLEXEN, XVI*

THERMISCHE ZERSETZUNG VON LINEARE, PLANARE UND
TETRAEDRISCHE ANIONEN ENTHALTENDEN
[DIPHENYL-JODONIUM]-[CYANOMETALLATEN]

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Die Zersetzung der [Diphenyl-jodonium]-[Cyanometallate] beginnt zumeist mit einer heftigen exothermen Reaktion, die damit erklärt wird, daß die bei der Abspaltung von PhI verbleibende Phenylgruppe des Jodoniumkations über eine CN-Brücke vorübergehend an das Zentralatom gebunden wird (M-CN-Ph) und der exotherme Effekt auf eine Isocyanidbildung zurückzuführen ist. Die Art und Reihenfolge der Abspaltung der flüchtigen Zersetzungsprodukte (PhI, *n*-PhCN, *i*-PhNC) wurden IR-spektrophotometrisch ermittelt. Endprodukte der Zersetzungs Vorgänge waren metallisches Ag, Au, Ni, Pd, Pt und Cu(C); beim Hg-, Cd- und Zn-Komplex blieb kein fester Rückstand zurück.

Einleitung

Von den Elementen der V-ten Hauptgruppe bildet der Phosphor und in geringerem Maße auch das Arsen den *quartären* Ammoniumsalzen ähnliche »Onium«-Komplexe. Die analogen Verbindungen der Elemente der VI-ten Hauptgruppe sind die *tertiäre* Oxonium-, Sulfonium- und Selenonium-, bzw. in der VII-ten Hauptgruppe die *sekundäre* Chloronium-, Bromonium- und Jodoniumkationen enthaltenden Komplexe.

Die Thermolyse der einfachen [1] und der verschiedenen quartären Ammonium-Cyanometallate [2, 3] wurde schon früher untersucht. In dieser und einigen weiteren Arbeiten sollen die Zersetzungs Vorgänge der Cyanokomplexe mit tertiären Sulfonium- und sekundären Jodoniumkationen mitgeteilt und zunächst miteinander, im weiteren aber auch mit den Zersetzungsreaktionen der quartären Ammonium-Cyanometallate verglichen werden.

Von den *sekundäre Jodoniumkationen* enthaltenden Verbindungen wurde in erster Linie die Thermolyse der stabilen [Diphenyl-jodonium]-[Cyanometallate] untersucht. Zur Gewinnung dieser Verbindungen wurden wässrige Lösungen der entsprechenden Alkali-Cyanometallate mit äquivalenten Mengen [Diphenyl-jodonium]-chlorid, [Ph₂I]Cl versetzt, wobei die erwünschten

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Doppelkomplexe als kristalline Niederschläge erhalten wurden [4, 5]. Mit Rücksicht auf die große Zahl der komplexen Cyanide wird der thermische Abbau der Doppelkomplexe im folgenden nach der Form des Cyanometallat-Anions (linear, planar, tetraedrisch usw.) gruppenweise behandelt.

I. Meßergebnisse: Auswertung der thermischen Kurven

Wie schon in unseren früheren Mitteilungen [6], so wurden auch diesmal in den Tabellen I—III nicht die unmittelbaren Meßergebnisse, sondern die auf 1 mol des Ausgangskomplexes umgerechneten Werte angegeben. Dementsprechend sind die an den TG-Stufen auftretenden Gewichtsverluste in den Abb. 1—3 in der Einheit g/mol aufgetragen. Dadurch werden die Stufenhöhen mit den Molekulargewichten der Zersetzungsprodukte gleich, was ihre *qualitative* Identifizierung erleichtert. Bei stöchiometrischen Stufen wurde die Molzahl und (in Klammern) auch das Molekulargewicht der entweichenden flüchtigen Produkte angegeben. Ein Vergleich der in der dritten und vierten Spalte der Tabellen angeführten Werte ermöglicht eine direkte Beurteilung des *quantitativen* Verlaufs der Teilprozesse.

a) Grundverbindung und lineare Cyanometallate

Das weiße kristalline $[\text{Ph}_2\text{I}]\text{Cl}$ dissoziiert bei 190 °C in einer einzelnen endothermen Stufe unter Bildung von PhI und PhCl (Abb. 1a). Die Stufenhöhe ist etwas kleiner als das Molekulargewicht (Tabelle I), da die Substanz

Tabelle I
Zersetzungs Vorgänge von [Diphenyl-jodonium]-[Cyanometallaten]
(Grundverbindung und lineare Cyanometallat-Anionen)

Verbindung (Farbe)	Zersetz- temp. (°C)	Gewichts- abnahme (g/mol)	Flüchtige Zersetzungsprodukte (mol/mol)	Bemerkungen zum DTA-Peak
$\text{Ph}_2\text{I} \cdot \text{Cl}$ (weiß)	190	313	1 PhI + 1 PhCl (316,6)	schwach, flach: endo.
	~330	1—2	{ NH_4Cl (Verunrei- gung: sublimiert bei 335 °C)	} endotherm
$[\text{Ph}_2\text{I}][\text{Ag}(\text{CN})_2]$ (weiß)	100	—	Ladungstransfer- effekt	schwach, scharf: endo.
	135	—	Schmelzpunkt	schwach, scharf: endo.
	155 } 175 }	306	{(n-PhCN) 1 PhI + 1 i-PhNC (307,1)	schwach, flach: endo. schwach, scharf: exo.
	~400	25,7	0,5 (CN) ₂ (26,0)	schwach, scharf: endo.
$[\text{Ph}_2\text{I}][\text{Au}(\text{CN})_2]$ (weiß)	140	—	Schmelzpunkt	schwach, scharf: endo.
	180 } 190 }	308	{(n-PhCN) 1 PhI + 1 i-PhNC (307,1)	schwach, flach: endo. schwach, scharf: exo.
	~450	27	0,5 (CN) ₂ (26,0)	schwach, scharf: endo.

während der Herstellung [5] mit wenig NH_4Cl verunreinigt wird. Der kleine endotherme Effekt bei etwa 330°C ist auf die Sublimation des NH_4Cl (335°C) zurückzuführen.

Die DTA-Kurve des $[\text{Ph}_2\text{I}][\text{Ag}(\text{CN})_2]$ zeigt — noch vor dem Beginn der Zersetzung — zwei endotherme Peaks (Abb. 1b). Der kleinere (100°C) wurde von uns als Ladungstransfereffekt gedeutet, der größere (135°C) ist dem Schmelzen des Komplexes zuzuschreiben. Die Zersetzung der Schmelze beginnt bei 155°C unter *endothermer* Abgabe von wenig *n*-PhCN, und schreitet bei 175°C in einer *exothermen* Reaktion fort. Die Höhe der Doppelstufe entspricht in guter Annäherung der gleichzeitigen Entfernung von 1 mol PhI und 1 mol *i*-PhNC (Tabelle I). Da in der letzten Stufe bei 400°C 0,5 mol Dicyan freigesetzt wird, ist das feste Endprodukt metallisches Silber. (Auf die Deutung des Ladungstransfereffektes kommen wir im Zusammenhang mit ähnlichen Erscheinungen bei anderen Komplexen noch zurück).

Die Zersetzungsreaktionen von $[\text{Ph}_2\text{I}][\text{Au}(\text{CN})_2]$ entsprechen denen der Silberverbindung, nur verlaufen sie bei etwas höheren Temperaturen (Abb. 1c). Von den zwei linearen Cyanometallaten ist also der Goldkomplex die thermisch stabilere Verbindung.

b) Planare Cyanometallate

Die Thermolyse der planare quadratische Anionen enthaltenden Verbindungen wurde am Beispiel der Tetracyanokomplexe des Nickels, Palladiums und Platins untersucht. Die thermische Stabilität dieser Komplexe nimmt — laut der Verschiebung sowohl der ersten exothermen, als auch der zweiten endothermen Stufe zu höheren Temperaturen hin — mit zunehmender Ord-

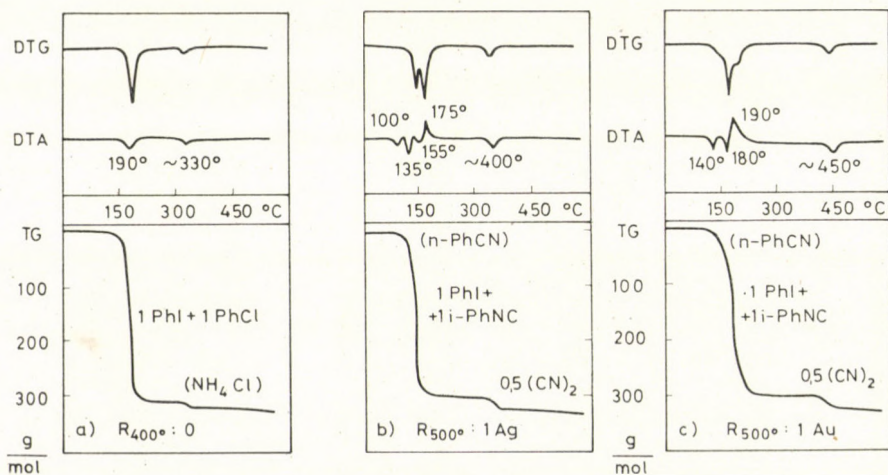


Abb. 1. TG-, DTG- und DTA-Kurven von a) $[\text{Ph}_2\text{I}]\text{Cl}$ (Grundverbindung), b) $[\text{Ph}_2\text{I}][\text{Ag}(\text{CN})_2]$, c) $[\text{Ph}_2\text{I}][\text{Au}(\text{CN})_2]$ (lineare Anionen)

nungszahl des Zentralatoms zu (Tabelle II, Abb. 2). Die erste Zersetzungsstufe des blaßgelben $[\text{Ph}_2\text{I}]_2[\text{Ni}(\text{CN})_4]$ geht mit dem größten Gewichtsverlust ($2 \text{ PhI} + 2 \text{ PhCN}$), jedoch mit der geringsten Reaktionswärme voran. Der exotherme Effekt ist beim Palladiumkomplex am ausgeprägtesten, bei dem aber neben 2 mol PhI nur 1 mol PhCN abgespaltet wird. Die Platinverbindung nimmt hinsichtlich der Größe des Wärmeeffektes und der Menge der Zersetzungsprodukte ($2 \text{ PhI} + 1,5 \text{ PhCN}$) gleichermaßen eine Zwischenstellung ein.

Aus Abb. 2 ist zu ersehen, daß bei jenen Verbindungen, bei denen die Abspaltung des PhCN gegenüber der des PhI »verzögert« verläuft, in den nachfolgenden Zersetzungsphasen *i*-PhNC gebildet wird. Man kann beobachten, daß der exotherme Effekt umso größer ist, je weniger *n*-PhCN mit dem PhI zusammen absplattet. Zur Klärung dieser Tatsache nahmen wir an, daß bei der Freisetzung von PhI die andere Phenylgruppe des Jodoniumkations durch eine sich ausbildende M—CN—Ph-Bindung vorübergehend an das Zentralatom des Komplexes gebunden wird. Demnach hängt die Verzögerung der PhCN-Abspaltung mit der Ausbildung von *Isocyanid-Intermediären* zusammen, deren Bildungswärme den *exothermen Effekt* verursacht.

c) Tetraedrische Cyanometallate

Die thermische Stabilität der tetraedrische Anionen enthaltenden [Diphenyl-jodonium]-[Cyanometallate] nimmt — ähnlich wie bei den linearen und planaren Verbindungen — mit zunehmender Ordnungszahl des Zentral-

Tabelle II
Zersetzungsvergänge von [Diphenyl-jodonium]-[Cyanometallaten]
(planare Cyanometallat-Anionen)

Verbindung (Farbe)	Zersetz- temp. (°C)	Gewichts- abnahme (g/mol)	Flüchtige Zersetzungsprodukte (mol/mol)	Bemerkungen zum DTA-Peak
$[\text{Ph}_2\text{I}]_2[\text{Ni}(\text{CN})_4]$ (blaßgelb)	175	616	$2 \text{ PhI} + 2 \text{ PhCN}$ (614,2)	schwach, scharf: exo.
	400	25,5	$0,5 (\text{CN})_2$ (26,0)	schwach, flach: endo.
	500	25,5	$0,5 (\text{CN})_2$ (26,0)	schwach, flach: endo.
$[\text{Ph}_2\text{I}]_2[\text{Pd}(\text{CN})_4]$ (weiß)	200	513	$2 \text{ PhI} + 1 \text{ PhCN}$ (511,1)	stark, scharf: exo.
	250—450	53,7	$0,5 \text{ PhNC}$ (51,5)	endotherm
	460	26,5	$0,5 (\text{CN})_2$ (26,0)	schwach, scharf: endo.
$[\text{Ph}_2\text{I}]_2[\text{Pt}(\text{CN})_4]$ (weiß)	200	—	Schmelzpunkt	schwach, scharf: endo.
	220	566	$2 \text{ PhI} + 1,5 \text{ PhCN}$ (562,6)	mittelm., scharf: exo.
	250—550	50	$0,5 \text{ PhNC}$ (51,5)	endotherm
	575	27	$0,5 (\text{CN})_2$ (26,0)	schwach, scharf: endo.

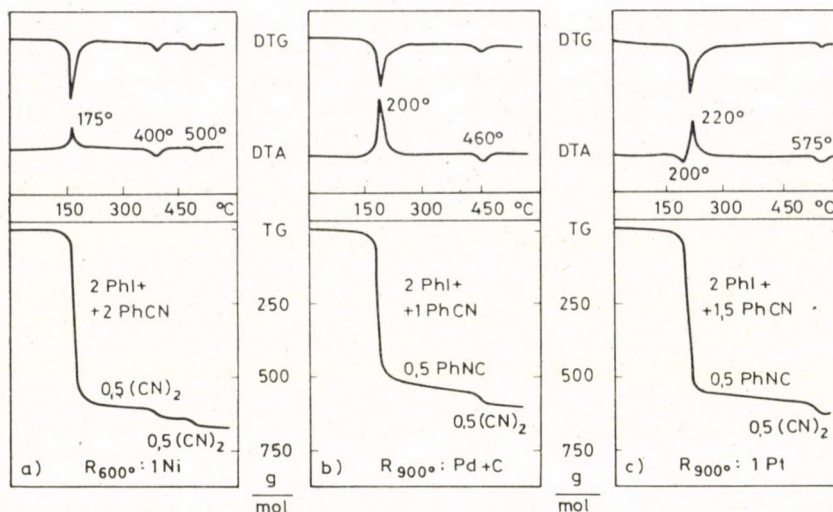


Abb. 2. TG-, DTG- und DTA-Kurven von a) $[\text{Ph}_2\text{I}]_2[\text{Ni}(\text{CN})_4]$, b) $[\text{Ph}_2\text{I}]_2[\text{Pd}(\text{CN})_4]$, c) $[\text{Ph}_2\text{I}]_2[\text{Pt}(\text{CN})_4]$ (planare Anionen)

atoms zu. Die Annahme der Bildung von Isocyanid-Zwischenverbindungen wird auch durch die Thermolyse der tetraedrischen Cyanometallate gestützt.

Die $\text{PhI}-\text{PhCN}$ -Zersetzungsphasen konnten im Falle des $[\text{Ph}_2\text{I}]_2\text{Hg}[(\text{CN})_4]$ am besten getrennt werden (Abb. 3a). Die Isocyanidbildung ist folglich bei diesem Komplex am meisten bevorzugt, d.h. der größte exotherme Effekt zu beobachten. Die Stufenhöhe entspricht genau der Abgabe von 2 mol PhI (Tabelle III). Die weitere Zersetzung des Komplexes zeigt beim Siedepunkt des Quecksilbers wieder eine maximale Geschwindigkeit. In dieser Etappe bilden sich — im Einklang mit den obigen — 2 mol $i\text{-PhNC}$ und je 1 mol Quecksilber und Dicyan. ($\text{Hg}(\text{CN})_2$ zersetzt sich bei 450, $\text{K}_2[\text{Hg}(\text{CN})_4]$ bei 435 °C [7].)

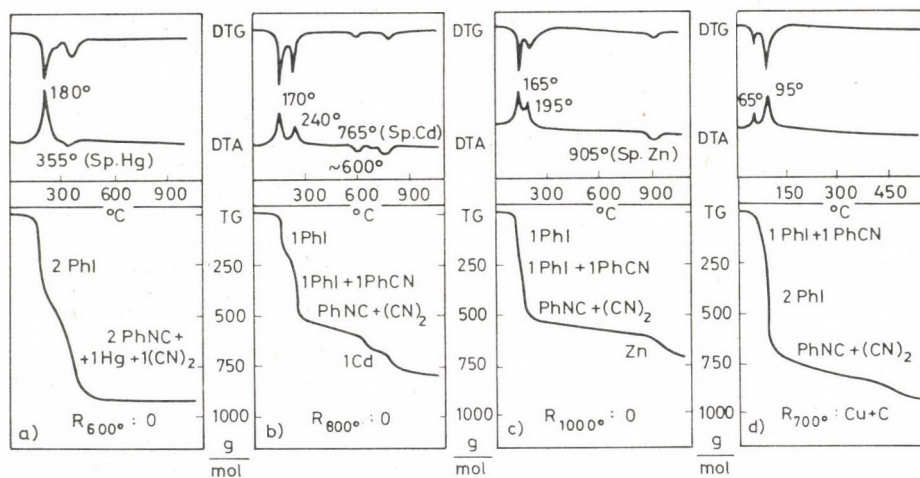
Bei der Zersetzung von $[\text{Ph}_2\text{I}]_2[\text{Cd}(\text{CN})_4]$ überlappt sich schon die Abspaltung des PhI und die des PhCN (Abb. 3b). Da in der ersten Etappe nur 1 mol PhI freigesetzt wird (Isocyanidbildung), ist der erste exotherme Peak (170 °C) wesentlich größer als der zweite (240 °C), der neben der Abspaltung von 1 mol PhI auch mit der von 1 mol PhCN einhergeht. Dementsprechend sind die weiteren Zersetzungsprodukte $i\text{-PhNC}$ und $(\text{CN})_2$. Die letzte Stufe wird durch die Verdampfung des metallischen Kadmiums bei seinem Siedepunkt (765 °C) hervorgerufen.

Die Zersetzung des Zinkkomplexes unterscheidet sich von der der Kadmiumverbindung nur darin, daß die Teilvorgänge bei etwas niedrigeren Temperaturen (165, 195 °C) und mit größerer Überlappung verlaufen (Abb. 3c). Demzufolge entsprechen die einzelnen Stufen weniger der Stöchiometrie. Da

Tabelle III

Zersetzungsvorgänge von [Diphenyl-jodonium]-[Cyanometallaten]
(tetraedrische Cyanometallat-Anionen)

Verbindung (Farbe)	Zersetz- temp. (°C)	Gewichts- abnahme (g/mol)	Flüchtige Zersetzungsprodukte (mol/mol)	Bemerkungen zum DTA-Peak
[Ph ₂ I] ₂ [Hg(CN) ₄] (weiß)	180	409	2 PhI (408,0)	stark, scharf: exo. schwach, breit: endo.
	355	455	2 PhNC + 1 Hg + + 1 (CN) ₂ (458,8)	
[Ph ₂ I] ₂ [Cd(CN) ₄] (weiß)	170	207	1 PhI (204,0)	mittelm., scharf: exo.
	240	300	1 PhI + 1 PhCN (307,1)	schwach, scharf: exo.
	300–750	~160	1 PhNC + 1 (CN) ₂ (155,1)	endotherm
	765	110	1 Cd (112,4)	endotherm
[Ph ₂ I] ₂ [Zn(CN) ₄] (weiß)	165	190	1 PhI (204,0)	mittelm., scharf: exo.
	195	300	1 PhI + 1 PhCN (307,1)	schwach, scharf: exo.
	250–900	~150	PhNC + (CN) ₂	endotherm
	900–	(kontin.)	Zn	endotherm
[Ph ₂ I] ₃ [Cu(CN) ₄] (weiß)	65	305	1 PhI + 1 PhCN (307,1)	schwach, scharf: exo.
	95	410	2 PhI (408,0)	mittelm., scharf: exo.
	150–650	~200	PhNC + (CN) ₂	endotherm

Abb. 3. TG-, DTG- und DTA-Kurven von a) [Ph₂I]₂[Hg(CN)₄], b) [Ph₂I]₂[Cd(CN)₄],
c) [Ph₂I]₂[Zn(CN)₄], d) [Ph₂I]₃[Cu(CN)₄] (tetraedrische Anionen)

das im Verlaufe der Zersetzung gebildete Zink bei seinem Siedepunkt (905 °C) verdampft, bleibt auch hier kein fester Rückstand zurück.

[Ph₂I]₃[Cu(CN)₄] ist am wenigsten stabil (65, 95 °C) und zeigt auch einen abweichenden Zersetzungsverlauf. Beim Kupfer(I)-Komplex tritt die

gemeinsame Abspaltung von PhI und PhCN schon in der ersten Stufe ein, der größte Teil des PhI entweicht aber in der zweiten Etappe. Dementsprechend ist von den zwei exothermen Effekten — im Gegensatz zum Kadmium- und Zinkkomplex — der zweite der ausgeprägtere (Abb. 3d). Der thermische Abbau nimmt auch bei dieser Verbindung mit der Bildung von $i\text{-PhNC}$ und $(\text{CN})_2$ seinen Fortgang. Der feste Rückstand besteht aus elementarem Kupfer (Schmp. 1083°C) und aus einer mehr oder weniger großen Menge von Kohlenstoff.

2. Identifizierung der Zersetzungsprodukte

(IR-spektrophotometrische Untersuchungen)

Obwohl nach den bisher gesagten die den Stufenhöhen der TG-Kurven zuzuordnenden Zersetzungsprodukte (PhI oder PhCN) und die endothermen und exothermen Effekte der DTA-Kurven (Abspaltung von $n\text{-PhCN}$ bzw. Bildung von $i\text{-PhNC}$) im Einklang stehen und einander gegenseitig unterstützen, ist die quantitative Auswertung der TG-Stufen doch durch zwei Umständen bis zu einem gewissen Grade erschwert. Da erstens die Siedepunkte des PhI und PhCN sehr nahe beieinander liegen ($65\text{--}70^\circ\text{C}$), kann die Reihenfolge der Abgabe auf Grund ihrer Flüchtigkeiten nicht angegeben werden. Die zweite Schwierigkeit ergibt sich aus dem Zufall, daß das Molekulargewicht des PhI (204,0) beinahe zweimal so groß ist, als das des PhCN (103,1). Deswegen konnten wir uns bei der Identifizierung der Zersetzungsprodukte nicht nur auf die Gewichtsabnahmen stützen, sondern mußten dazu auch die IR-Spektren heranziehen.

Da die Zersetzungstemperaturen der Komplexe aus den Derivatogrammen schon bekannt waren, wurden die zu untersuchenden Proben auf diese Temperaturen erhitzt. Das Kondensat der im Laufe der exothermen Reaktion herausdestillierenden flüchtigen Komponenten wurde in CH_2Cl_2 gelöst. Der feste Rückstand wurde mit CH_2Cl_2 behandelt und das Extrakt abgetrennt. Anschließend wurden die IR-Spektren des Destillats und Extraktes aufgenommen und mit den Spektren von ebenfalls in CH_2Cl_2 gelöstem PhI bzw. PhCN verglichen.

Das PhI kann vom PhCN anhand der vertikalen Deformationsschwingungen der Phenylgruppe unterschieden werden [8]. Die sehr starke und scharfe Absorptionsbande tritt im Falle des PhI bei 450 , beim PhCN bei 550 cm^{-1} auf. Zur Unterscheidung der *Normal-* bzw. *Isocyanide* sind die CN -Valenzfrequenzen geeignet: im Falle des $n\text{-PhCN}$ liegen diese bei 2230 , beim $i\text{-PhNC}$ bei 2130 cm^{-1} , sind also ebenfalls gut unterscheidbar.

In Abb. 4 sind die IR-Spektren der Zersetzprodukte von $[\text{Ph}_2\text{I}][\text{Ag}(\text{CN})_2]$ angegeben. Wie ersichtlich, ist im Destillat (a) neben viel PhI hauptsächlich $n\text{-PhCN}$ zu finden. Dagegen enthält der Extrakt (b) nur ganz wenig PhI und besteht überwiegend aus $i\text{-PhNC}$. Diese Verteilung der flüchtigen Zersetzungsprodukte bestätigte die Annahme, daß im Laufe der Zersetzung (s. Abb. 1b) erst wenig $n\text{-PhCN}$ (endotherm) abgespalten wird, danach in quantitativer Reaktion PhI (exotherm) und schließlich $i\text{-PhNC}$ entsteht.

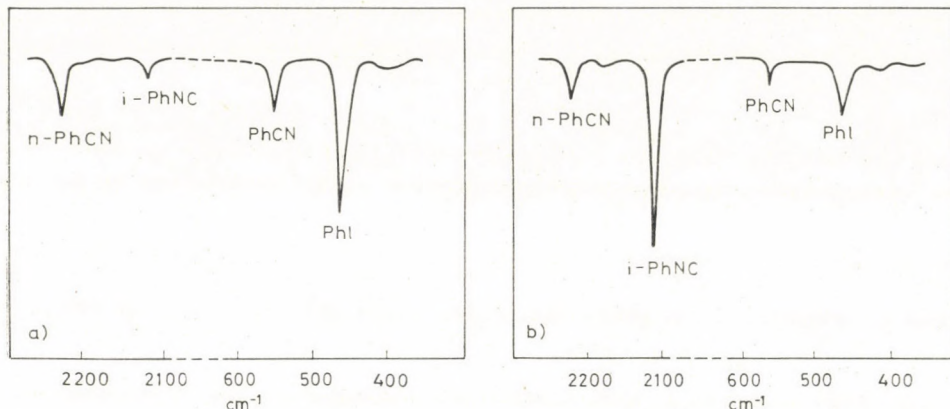


Abb. 4. IR-Spektren der flüchtigen Zersetzungsprodukte von $[\text{Ph}_2\text{I}][\text{Ag}(\text{CN})_2]$ bei 180 °C: a) im Destillat, b) im Extrakt

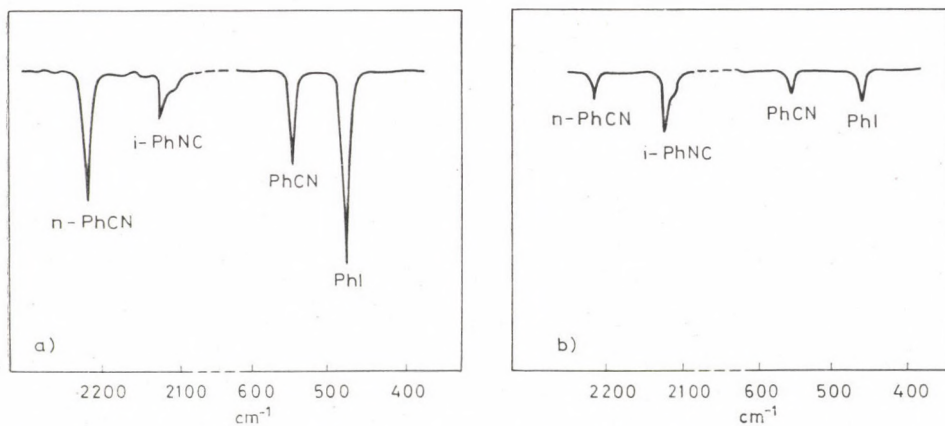


Abb. 5. IR-Spektren der flüchtigen Zersetzungsprodukte von $[\text{Ph}_2\text{I}]_2[\text{Cd}(\text{CN})_4]$ im Destillat: a) bei 195 °C, b) bei 240 °C

Der größere und der darauf folgende kleinere exotherme Peak in der DTA-Kurve des $[\text{Ph}_2\text{I}]_2[\text{Cd}(\text{CN})_4]$ konnte dadurch erklärt werden (s. Abb. 3b), daß im ersten Abschnitt der Zersetzung PhI, im zweiten gleichzeitig PhI und *n*-PhCN und im dritten *i*-PhNC freigesetzt werden. Dementsprechend enthält das Destillat der bis 195 °C erhitzten Probe neben viel PhI vorwiegend *n*-PhCN. Erhitzt man dieselbe Probe jedoch weiter auf 240 °C, so weist das IR-Spektrum auf das Vorliegen von verhältnismäßig wenig PhI und besonders auf die Anwesenheit von *i*-PhNC hin (Abb. 5).

Auf ähnliche Weise wurde auch die abweichende Stöchiometrie der Zersetzung des Nickel- und Palladiumkomplexes bewiesen. Im Einklang mit

den thermischen Kurven (s. Abb. 2) ist die Reihenfolge der Bandenintensitäten im ersten Fall $n\text{-PhCN} - \text{PhI} - i\text{-PhNC}$, im zweiten aber gerade umgekehrt.

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THERMOLYSE VON CYANOKOMPLEXEN, XVII*

THERMISCHER ABBAU VON OKTAEDRISCHE ANIONEN ENTHALTENDEN [DIPHENYL-JODONIUM]-[CYANOMETALLATEN]

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Die Thermolyse der [Diphenyl-jodonium]-Hexacyanometallate sowie die der Gemischtligand-Penta- und -Tetracyanometallate wird von einer heftigen exothermen Reaktion eingeleitet. Bei der Abspaltung von PhI bildet nämlich die andere Phenylgruppe des Jodoniumkations nur später entweichendes *i*-PhNC. Die Temperatur, bei der die exothermen Reaktion verläuft, ist umso niedriger, je kleiner die CN-Valenzfrequenzen in den Doppelkomplexen sind. Diese Tendenz kann durch eine zunehmende Wechselwirkung zwischen den Phenylgruppen der Kationen und den Cyanidliganden der Anionen — die die alleinige Abspaltung von PhI ohne *n*-PhCN begünstigt — erklärt werden.

1. Ergebnisse der thermischen Untersuchungen

Die Meßergebnisse sind in den Tabellen I und II auf die gleiche Weise wie in der voranstehenden Mitteilung zusammengefaßt. Wie ersichtlich enthält ein Teil der Komplexe 2—3 mol Kristallwasser, die Wasserstufen wurden aber der besseren Übersichtlichkeit wegen in den Abbildungen 1 und 3 weggelassen.

a) [Diphenyl-jodonium]-[Hexacyanometallate]

Die thermischen Zersetzungsvorgänge dieser Verbindungsgruppe werden am Beispiel des Mn(III)-, Cr(III)-, Co(III)-, Fe(III)- und Fe(II)-Komplexes dargelegt (Tabelle I). Von diesen ist das Cyanokobaltat die stabilste, das Cyanomanganat die instabilste Verbindung. Auf diese Tatsache weist außer den Zersetzungstemperaturen (140 bzw. 215 °C) auch die Menge der in der exothermen Reaktion gebildeten Zersetzungsprodukte hin. Im Falle des Mangankomplexes (Abb. 1a) werden in einer einzigen Stufe je 3 mol PhI und PhCN abgespalten. Die Zersetzung des bekanntlich sehr stabilen Cyanokobaltats(III) verläuft mehrstufig [1, 2]. In der ersten Etappe wird neben 3 mol PhI nur 1 mol PhCN freigesetzt (Abb. 1c). Nach unserer Annahme

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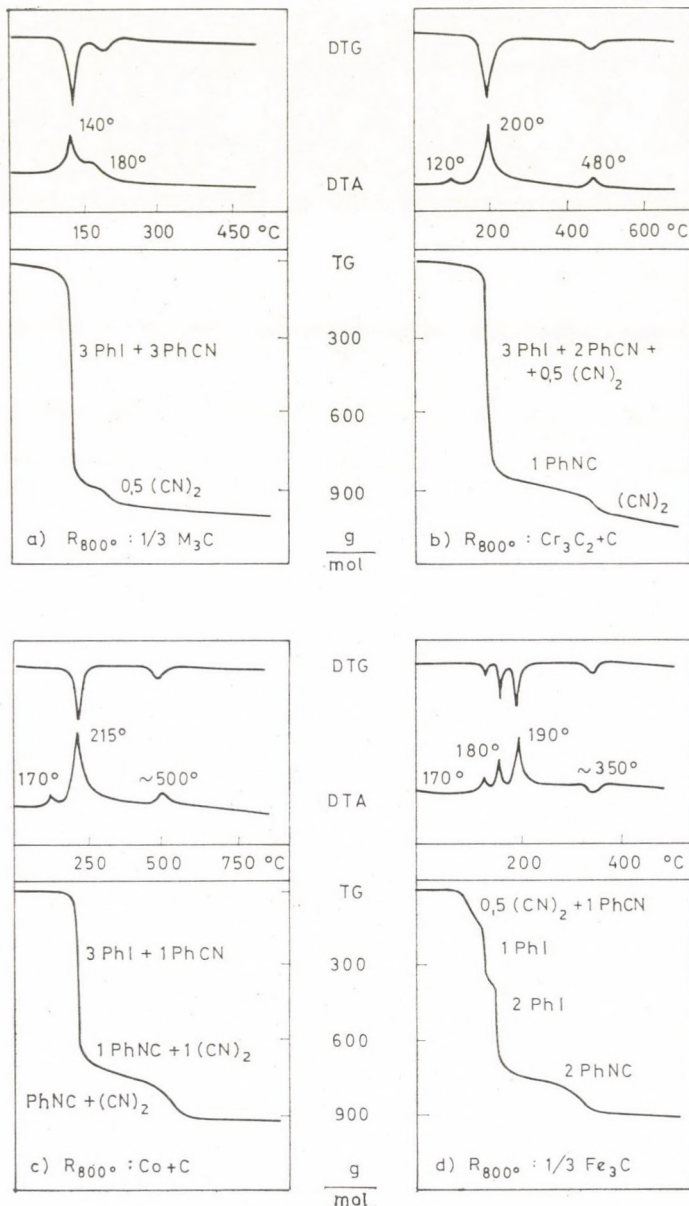


Abb. 1. TG-, DTG- und DTA-Kurven von a) $[\text{Ph}_2\text{I}]_3[\text{Mn}(\text{CN})_6]$, b) $[\text{Ph}_2\text{I}]_3[\text{Cr}(\text{CN})_6]$, c) $[\text{Ph}_2\text{I}]_3[\text{Co}(\text{CN})_6]$, d) $[\text{Ph}_2\text{I}]_3[\text{Fe}(\text{CN})_6]$

bildet ein Teil der Phenylgruppen durch Ausbildung von Co—CN—Ph-Bindungen Isocyanid-Zwischenprodukte, die nur bei höheren Temperaturen zersetzt werden. Die resultierende exotherme Zersetzungswärme ist also der Isocyanidbildung zuzuschreiben. Da diese im Falle des Kobaltkomplexes

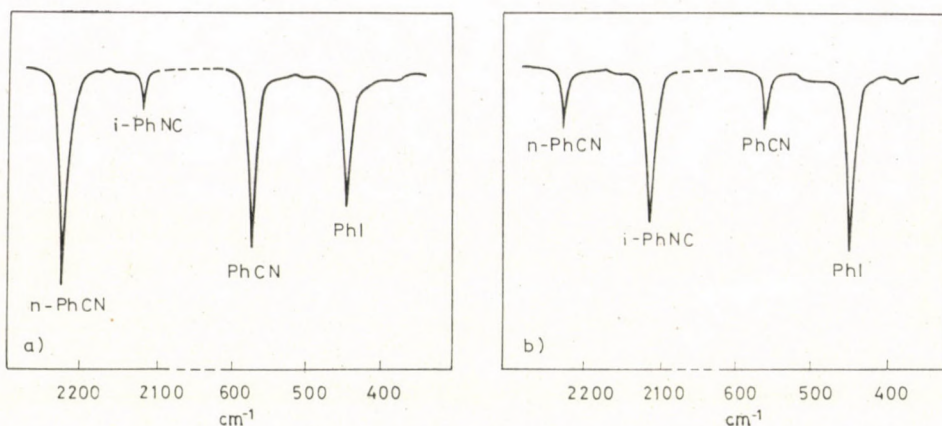


Abb. 2. IR-Spektren der flüchtigen Zersetzungsprodukte von a) $[\text{Ph}_2\text{I}]_3[\text{Mn}(\text{CN})_6]$ bei 155°C , b) $[\text{Ph}_2\text{I}]_3[\text{Co}(\text{CN})_6]$ bei 220°C

begünstigt ist, ist auch der exotherme Effekt hier viel größer als bei der Manganverbindung.

Die Richtigkeit dieser Annahme wurde durch den Vergleich der IR-Spektren der flüchtigen Zersetzungsprodukte von $[\text{Ph}_2\text{I}]_3[\text{Mn}(\text{CN})_6]$ und $[\text{Ph}_2\text{I}]_3[\text{Co}(\text{CN})_6]$ nachgewiesen (Abb. 2). Beim Mangankomplex wurden neben ganz wenig $i\text{-PhNC}$ ungefähr gleiche Mengen von PhI und $n\text{-PhCN}$ gefunden, im Falle der Kobaltverbindung enthielt dagegen das Zersetzungsprodukt neben viel PhI hauptsächlich $i\text{-PhNC}$ (siehe auch voranstehende Mitteilung).

Das $[\text{Ph}_2\text{I}]_3[\text{Cr}(\text{CN})_6]$ nimmt sowohl bezüglich seiner Zersetzungstemperatur (200°C), als auch hinsichtlich des Molverhältnisses der fraglichen Zersetzungsprodukte ($3 \text{ PhI} + 2 \text{ PhCN}$) eine Zwischenstellung ein; der mittelgroße exotherme Effekt steht damit in völligem Einklang (Abb. 1b).

Der Abgabe der »organischen« Bestandteile schließt sich immer eine Dicyanbildung an. Die in diesem Redoxvorgang gebildeten zweiwertigen Übergangsmetall-cyanide setzen sich zum entsprechenden Metallkarbid (Mn_3C , Cr_3C_2) bzw. zu elementarem Metall um [3, 4].

In der DTA-Kurve des $[\text{Ph}_2\text{I}]_3[\text{Fe}(\text{CN})_6]$ treten nacheinander — sozusagen alleinstehend — drei ständig zunehmende exotherme Effekte auf. Die gute Auftrennung der Peaks wurde durch kleine Aufheizgeschwindigkeit ($3^\circ/\text{min}$) erreicht (Abb. 1d). Die Zersetzung des paramagnetischen Eisen(III)-Komplexes beginnt — ähnlich den mit anderen Kationen gebildeten Verbindungen — mit einer exothermen Dicyanabgabe [5, 6]. Da zusammen mit dem Dicyan auch PhCN entweicht (endotherm), ist der exotherme Peak bei 170°C verhältnismäßig klein. In der zweiten und dritten Etappe (180 und 190°C) werden 1 bzw. 2 mol PhI freigesetzt. Die Isocyanidbildung findet also in

Tabelle I

Zersetzungs Vorgänge von [Diphenyl-jodonium]-[Cyanometallaten]
(oktaedrische Hexacyano-Anionen)

Verbindung (Farbe)	Zersetz.- temp. (°C)	Gewichts- abnahme (g/mol)	Flüchtige Zersetzungsprodukte (mol/mol)	Bemerkungen zum DTA-Peak
[Ph ₂ I] ₃ [Mn(CN) ₆] · 3,5 H ₂ O (ocker gelb)	80–100	65	3,5 H ₂ O (63,1)	schwach, flach: endo. mittelm., scharf: exo. schwach, flach: exo.
	140	947	3 PhI + 3 PhCN + { + 0,5 (CN) ₂ (947,3)	
	180			
[Ph ₂ I] ₃ [Cr(CN) ₆] · 2 H ₂ O (blaß gelb)	80–110	37	2 H ₂ O (36,0)	schwach, flach: endo. schwach, scharf: exo. } mittelm., scharf: exo. endotherm schwach, scharf: exo.
	120	—	Ladungstransfereffekt	
	200	842	{ 3 PhI + 2 PhCN + { + 0,5 (CN) ₂ (844,2)	
	250–450	~100	1 PhNC (103,2)	
480	~30	(CN) ₂		
[Ph ₂ I] ₃ [Co(CN) ₆] · 2 H ₂ O (weiß)	90–110	38,5	2 H ₂ O (36,0)	schwach, flach: endo. schwach, scharf: exo. stark, scharf: exo. endotherm schwach, flach: exo.
	170	—	Ladungstransfereffekt	
	215	717	3 PhI + 1 PhCN (715,1)	
	250–450	~150	1 PhNC + 1 (CN) ₂ (155,1)	
~500	~75	PhNC + (CN) ₂		
[Ph ₂ I] ₃ [Fe(CN) ₆] · 3 H ₂ O (zitronengelb)	90–110	53,5	3 H ₂ O (54,0)	schwach, flach: endo. schwach, scharf: exo. } mittelm., scharf: exo. { stark, scharf: exo. schwach, breit: endo.
	170	127	0,5 (CN) ₂ + 1 PhCN (129,1)	
	180	607	(1 + 2) PhI (612,0)	
	190			
	~350	208	2 PhNC (206,2)	
[Ph ₂ I] ₄ [Fe(CN) ₆] grüngelb	155	815	4 PhI (816,0)	stark, scharf: exo. stark, breit: endo. endotherm
	200–400	205	2 PhNC (206,2)	
	400–800	~250	PhNC + (CN) ₂ + N ₂	

dieser Zersetzungsphase statt, deswegen nehmen Reaktionswärme und Zersetzungsgeschwindigkeit gleichermaßen zu. Im vierten Abschnitt werden 2 mol *i*-PhNC abgespalten und $\text{Fe}(\text{CN})_2$ bleibt zurück.

Der stärkste exotherme Effekt konnte beim $[\text{Ph}_2\text{I}]_4[\text{Fe}(\text{CN})_6]$ beobachtet werden. Der Grund dafür ist, daß am Anfang der Zersetzung (155 °C) 4 mol PhI in einer einzigen wohldefinierten Stufe abgegeben werden (s. Tabelle I). Im weiteren bilden sich *i*-PhNC, Dicyan und Stickstoff, das feste Endprodukt ist Zementit, Fe_3C [7, 8].

b) Gemischtligand-Penta- und -Tetracyanometallate

Von den [Diphenyl-jodonium]-Kationen enthaltenden Gemischtligand-Cyanometallaten wurden die in Tabelle II angeführten Doppelkomplexe untersucht.

Die Zersetzung des $[\text{Ph}_2\text{I}]_2[\text{Fe}(\text{CN})_5\text{NO}]$ beginnt bei 150 °C mit einer kleinen endothermen Stufe (Abb. 3a). Ob diese der Bildung von 0,5 mol $(\text{CN})_2$ oder 1 mol NO zuzuschreiben ist, konnte weder auf Grund der Stufenhöhe, noch der Reaktionswärme entschieden werden: die Abspaltung der fast gleiche Molekulargewichte aufweisenden Produkte vom *diamagnetischen* Prussiatkomplex ist nämlich in beiden Fällen ein *endothermer* Vorgang. Da aber die den NO-Valenzfrequenzen (1890 cm^{-1}) entsprechenden Banden im IR-Spektrum einer bis 185 °C erhitzten Probe noch unverändert auftreten, muß als Anfangsschritt eine Dicyanbildung angenommen werden.

Bei den Komplexen $[\text{Ph}_2\text{I}]_3[\text{Mn}(\text{CN})_5\text{NO}]$ und $[\text{Ph}_2\text{I}]_3[\text{Cr}(\text{CN})_5\text{NO}]$ bleibt die mit Dicyanentwicklung verlaufende Redoxreaktion infolge ihrer niederwertigen Zentralatome aus (Abb. 3b und 3c). Die Zersetzung beginnt mit der gleichzeitigen Abgabe von PhI und *n*-PhCN (105 bzw. 190 °C). Die NO-Gruppe wird, zusammen mit mehr oder weniger *i*-PhNC, nur in der zweiten Zersetzungsstufe abgespalten. Die Abgabe des NO-Liganden in einer verhältnismäßig »späten« Zersetzungsphase steht übrigens mit der früheren Erfahrung [3] im Einklang, nach der die Abspaltungstemperatur der NO-Gruppe bei den Alkali-[Pentacyanonitrosyl-metallaten] — im Einklang mit den ν_{NO} -Werten [9] — in der Reihenfolge Fe—Mn—Cr beträchtlich zunimmt.

Das $[\text{Ph}_2\text{I}]_3[\text{Fe}(\text{CN})_5\text{PBu}_3]$ gibt bei 100 bzw. 150 °C in zwei Stufen von gleicher Höhe unter beinahe gleichen Zersetzungswärmen insgesamt 3 mol PhI und 1 mol PhCN ab (Abb. 3d). Im weiteren bilden sich noch 2 mol *i*-PhNC und 1 mol Bu_3P . Von kleineren Abweichungen abgesehen verläuft auch die Zersetzung des Triphenylphosphino-Komplexes im wesentlichen auf gleiche Weise (s. Tabelle II).

Von den Bipyridyl enthaltenden Tetracyanoferraten ist wieder die Eisen(III)-Verbindung stabiler, aber der Unterschied ist viel größer als bei den Hexacyanoferraten (vgl. mit Tabelle I). Die Zersetzung des diamagnetischen Eisen(II)-Komplexes (Abb. 3e) beginnt schon bei 80 °C unter exothermen

Tabelle II

Zersetzungsvorgänge von [Diphenyl-jodonium]-[Cyanometallaten]
(Gemischtligand-Penta- und -Tetracyano-Anionen)

Verbindung (Farbe)	Zersetz- temp. (°C)	Gewichts- abnahme (g/mol)	Flüchtige Zersetzungsprodukte (mol/mol)	Bemerkungen zum DTA-Peak	
[Ph ₂ I] ₂ [Fe(CN) ₅ NO] (drappfarbig)	150}	570	{0,5 (CN) ₂ + 1 PhCN + + 2 PhI + 1 NO	schwach, scharf: endo. mittelm., breit: exo.	
	190}				(567,1)
	~350	100	1 PhNC	(103,1)	
[Ph ₂ I] ₃ [Mn(CN) ₅ NO] (olivbraun)	85}	765	3 PhI + 1,5 PhCN	schwach, scharf: endo. mittelm., scharf: exo.	
	105}				(766,6)
	150 – 400	136	1 NO + 1 PhNC	(133,1)	
[Ph ₂ I] ₃ [Cr(CN) ₅ NO] (gelbgrün)	65, 110	—	Landungstransfereffekte	beide: schwach, exo. mittelm., scharf: exo. endotherm	
	190	~800	3 PhI + 2 PhCN		(818,2)
	200 – 450	82,6	1 NO + 0,5 PhNC		(81,5)
[Ph ₂ I] ₃ [Fe(CN) ₅ PBu ₃] (bläßgelb)	100, 150	710	3 PhI + 1 PhCN	Doppelstufe: scharf, exo. endotherm	
	150 – 400	410	2 PhNC + 1 PBu ₃		(408,5)
[Ph ₂ I] ₃ [Fe(CN) ₅ PPh ₃] (bläßgelb)	90, 120	612	2 PhI + 2 PhCN	Doppelstufe: scharf, exo. endotherm	
	150 – 400	520	{1 PhI + 0,5 PhNC + + 1 PPh ₃		(517,8)
[Ph ₂ I] ₂ [Fe ^{II} (CN) ₄ Bipy] (violettbraun)	80	412	2 PhI	mittelm., scharf: exo. schwach, breit: endo. schwach, breit: endo.	
	220	100	1 PhNC		(408,0)
	280	260	PhNC + Bipy		(103,1)
[Ph ₂ I][Fe ^{III} (CN) ₄ Bipy] (goldgelb)	200	265	1 PhI + 0,5 (CN) ₂ + (PhCN)	mittelm., scharf: exo. endotherm	
200 – 500	250	PhNC + Bipy	(230,1)		

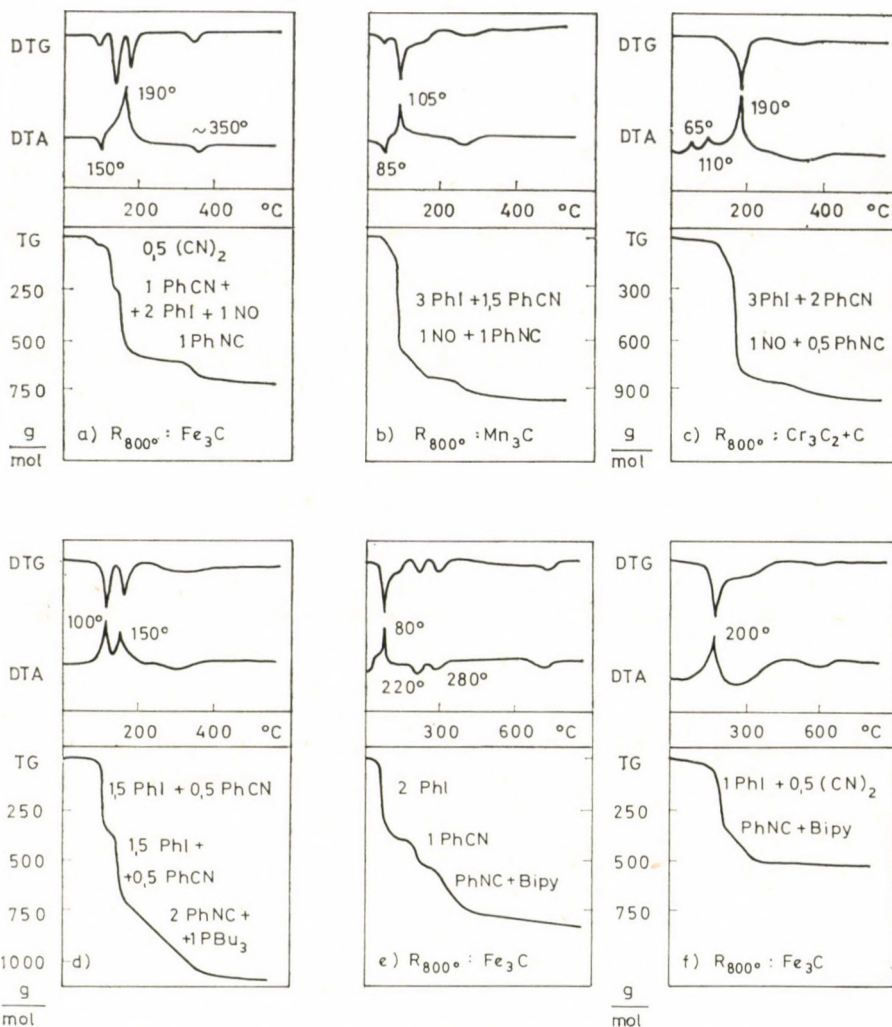


Abb. 3. TG-, DTG- und DTA-Kurven von a) $[Ph_2I]_2[Fe(CN)_5NO]$, b) $[Ph_2I]_3[Mn(CN)_5NO]$, c) $[Ph_2I]_3[Cr(CN)_5NO]$, d) $[Ph_2I]_3[Fe(CN)_5PBU_3]$, e) $[Ph_2I]_2[Fe^{II}(CN)_4Bipy]$, f) $[Ph_2I][Fe^{III}(CN)_4Bipy]$

Abgabe von 2 mol PhI. In derselben Zersetzungsphase bildet sich im Falle der paramagnetischen Eisen(III)-Verbindung bei 200 °C auch Dicyan zusammen mit PhI (Abb. 3f). Ein weiteres Zersetzungsprodukt ist *i*-PhNC, das zum Teil allein in einer Stufe bei 220 °C, zum Teil zusammen mit Bipyridyl in einer Stufe bei 280 °C entweicht.

Die festen Rückstände der Gemischtligand-Penta- und -Tetracyanokomplexe sind mit denen der entsprechenden Hexacyanoverbindungen identisch (Fe_3C , Mn_3C , Cr_3C_2).

2. Zusammenhang zwischen Zersetzungstemperatur und CN-Valenzfrequenzen

Die charakteristischste Kennzahl für die thermische Stabilität irgendeiner Verbindung ist die *Temperatur* der beginnenden Zersetzung. Eine ähnliche Bedeutung haben die Wellenzahlen der *CN-Valenzschwingungen* für die strukturelle Charakterisierung der Cyanokomplexe. Diese zwei Kennzahlen der [Diphenyl-jodonium]-[Cyanometallate] sind in Tabelle III und IV einander gegenübergestellt.

Es muß erwähnt werden (da dies aus den Tabellen nicht hervorgeht), daß die CN-Frequenzen in den [Diphenyl-jodonium]-[Cyanometallaten] im Vergleich zu denen der entsprechenden Alkali-Cyanometallaten um 10–20 Wellenzahlen kleiner sind. Die Tatsache berücksichtigend, daß bei der Thermolyse der [Diphenyl-jodonium]-[Cyanometallate] in jedem Fall auch mehr oder weniger Isophenylcyanid gebildet wird, kann die Verminderung der ν_{CN} -Werte — wie im weiteren dargelegt — erklärt werden.

Die Kationen und Anionen der Doppelkomplexe treten miteinander in Wechselwirkung, d.h. die π -Elektronen der $[\text{Ph}_2\text{I}]$ -Gruppen überlagern sich

Tabelle III

*CN-Valenzfrequenzen und Zersetzungstemperaturen
von [Diphenyl-jodonium]-[Cyanometallaten]
(oktaedrische Anionen)*

Verbindung	ν_{CN} (cm^{-1})	T ($^{\circ}\text{C}$)
$[\text{Ph}_2\text{I}]_2[\text{Fe}^{\text{II}}(\text{CN})_4\text{Bipy}]$	2000, 2020, 2060	80
$[\text{Ph}_2\text{I}]_3[\text{Fe}^{\text{II}}(\text{CN})_5\text{PPh}_3]$	2050	90
$[\text{Ph}_2\text{I}]_3[\text{Fe}^{\text{II}}(\text{CN})_5\text{PBu}_3]$	2065	100, 150
$[\text{Ph}_2\text{I}]_3[\text{Mn}(\text{CN})_5\text{NO}]$	2080, (2090), (2105), 2135	105
$[\text{Ph}_2\text{I}]_3[\text{Mn}(\text{CN})_6]$	2085, (2105), 2115, (2120)	140
$[\text{Ph}_2\text{I}]_4[\text{Fe}^{\text{II}}(\text{CN})_6]$	2090, 2105, 2115	155
$[\text{Ph}_2\text{I}]_3[\text{Fe}^{\text{III}}(\text{CN})_6]$	2095, 2100, 2110, (2120)	180, 190
$[\text{Ph}_2\text{I}]_3[\text{Cr}(\text{CN})_5\text{NO}]$	2095, (2100), 2115, 2130	190
$[\text{Ph}_2\text{I}]_2[\text{Fe}(\text{CN})_5\text{NO}]$	2125, (2135), 2140	190
$[\text{Ph}_2\text{I}]_3[\text{Cr}(\text{CN})_6]$	2110, (2115), 2120, 2135	200
$[\text{Ph}_2\text{I}][\text{Fe}^{\text{III}}(\text{CN})_4\text{Bipy}]$	2110	200
$[\text{Ph}_2\text{I}]_3[\text{Co}(\text{CN})_6]$	2110, 2125, 2140	215

partiell mit den *lockernden* π -Orbitalen der Cyanidliganden. Als Folge dessen nehmen die CN-Valenzfrequenzen ab und zugleich bildet sich eine »polymerartige« Struktur aus. (Dafür spricht z. B. auch die geringe Löslichkeit der Doppelkomplexe.) Die CN...Ph-Wechselwirkung wird aber beim Beginn der Zersetzung nicht aufgehoben, sondern im Gegenteil stabilisiert, da die Abgabe von PhI das Zustandekommen einer CN—Ph Sigmabindung ermöglicht. Der die Abspaltung des PhI begleitende exotherme Effekt wird demnach durch die Isocyanidbildung verursacht. Dadurch wird verständlich, daß einerseits der exotherme Effekt umso ausgeprägter ist, je weniger *n*-PhCN gleichzeitig mit PhI abgespalten wird, weiterhin auch, daß in den nachfolgenden Zersetzungsphasen bereits *i*-PhNC als Zersetzungsprodukt freigesetzt wird.

Diese Voraussetzungen werden auch von den Daten der Tabelle III bestätigt. Wie ersichtlich, tritt die exotherme Reaktion (PhI-Bildung) bei umso niedrigerer Temperatur ein, je kleiner die Wellenzahlen der CN-Valenzschwingungen sind. Da dieser Effekt mit der Stärke der CN...Ph Wechselwirkung zusammenhängt, wird mit Verringerung der ν_{CN} -Werte die getrennte Abspaltung von PhI (ohne *n*-PhCN) immer mehr begünstigt. Im Einklang damit wird die Zersetzungstemperatur der oktaedrische Anionen enthaltenden [Diphenyl-jodonium]-[Cyanometallate] mit zunehmenden ν_{CN} -Werten erhöht.

Was diese Feststellung betrifft, so bildet allein das $[\text{Ph}_2\text{I}]_2[\text{Fe}(\text{CN})_5\text{NO}]$ insofern eine Ausnahme, daß im Verhältnis zur Zersetzungstemperatur die CN-Frequenzen zu hoch sind. Der Grund dafür ist, daß der NO-Ligand als

Tabelle IV

CN-Valenzfrequenzen und Zersetzungstemperaturen von
[Diphenyl-jodonium]-[Cyanometallaten]
(nicht-oktaedrische Anionen)

Verbindung	ν_{CN} (cm ⁻¹)	T (°C)
$[\text{Ph}_2\text{I}][\text{Ag}(\text{CN})_2]$	2095, 2115, 2125	175
$[\text{Ph}_2\text{I}][\text{Au}(\text{CN})_2]$	(2100), 2145	190
$[\text{Ph}_2\text{I}]_2[\text{Ni}(\text{CN})_4]$	(2075), 2115	175
$[\text{Ph}_2\text{I}]_2[\text{Pd}(\text{CN})_4]$	(2087), 2127	200
$[\text{Ph}_2\text{I}]_2[\text{Pt}(\text{CN})_4]$	(2085), 2125	220
$[\text{Ph}_2\text{I}]_3[\text{Cu}(\text{CN})_4]$	(2075), 2080, 2090, 2115	65, 95
$[\text{Ph}_2\text{I}]_2[\text{Zn}(\text{CN})_4]$	2150	165, 195
$[\text{Ph}_2\text{I}]_2[\text{Cd}(\text{CN})_4]$	(2125), 2140, 2170	170, 240
$[\text{Ph}_2\text{I}]_2[\text{Hg}(\text{CN})_4]$	2150	180
$[\text{Ph}_2\text{I}]_4[\text{Mo}(\text{CN})_8]$	2090, 2110, 2125	125

sehr guter π -Akzeptor vom Elektronenüberschuß der Phenylringe einen viel größeren Anteil als der CN-Ligand übernimmt. Dies bestätigt auch die Tatsache, daß die Frequenz der NO-Valenzschwingung beim Doppelkomplex (1890 cm^{-1}) beträchtlich kleiner als beim Nitroprussidnatrium (1945 cm^{-1}) ist.

Ein ähnlicher Zusammenhang ist auch im Falle der nicht-oktaedrische Anionen enthaltenden [Diphenyl-jodonium]-[Cyanometallate] zwischen den Wellenzahlen der CN-Valenzschwingungen und den Temperaturen, bei denen die exothermen Reaktionen verlaufen, zu konstatieren (s. Tabelle IV). Es ist natürlich in Betracht zuziehen, daß die thermische Stabilität der Doppelkomplexe auch von der Form des Cyanometallat-Anions abhängig ist. Deshalb kommt die Tendenz, daß zu höheren CN-Frequenzen zugleich höhere Zersetzungstemperaturen gehören, nur bei Verbindungen desselben Anionentyps (linear, planar usw.) zur Geltung.

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RECENSIONES

Flow-induced crystallization in polymer systems

Edited by Robert L. MILLER

Gordon and Breach Science Publishers. New York, London, Paris, 1979. pp. 370

This volume with the title above collects the proceedings of a symposium organized by the Midland Macromolecular Institute which latter gained already a high reputation in the fields of macromolecular chemistry and physics. It offers a survey about the crystallization principles of polymers (A. PETERLIN), and gives an analysis of the kinetical investigation of such crystallizations (R. L. MILLER).

Crystallization phenomena from different media are discussed further on. It is regrettable that the manuscript of A. J. PENNINGS, entitled Crystallization from Solution, was not submitted for publication hence, somewhat reduced the completeness of the book. The review lecture about crystallization processes from melt (J. N. HAY) is supplemented by a series of utmost interesting contributed papers. Among these, the Solidification of Quasi-Binary Systems of Polyethylene Fractions (P. SMITH, R. St. JOHN MANLEY) has to be mentioned because of its novel viewpoint and many-sided experimental methods. Fiber-formation from solid phase is the third main tendency, which is covered by the paper of W. T. MEAD and R. S. PORTER (The Influence of Initial Morphology on the Physical and Mechanical Properties of Extruded High Density Polyethylene Fibers). The following chapters deal with the effects of the technological parameters, e.g. with the influence of the extreme temperature and pressure gradients on the crystallization process (H. D. NOETHER).

In the chapter entitled Stiff-Chain Aromatic Polymer Solutions, Melts and Fibers (W. BRUCE BLACK) again a valuable and entirely new area is presented, the factors affecting the processing conditions of liquid crystalline fibers with superior mechanical strength. The subject of Polymer Crystallizations Induced by Biaxial Stretching During Film Manufacture (T. ALFREY) has a technological importance, when it enlightens the relationships among the manufacturing parameters and the obtained properties.

L. JARECKI and A. ZIABICKI present a high level thermodynamical theory on the role of crystal orientation in non-crosslinked and crosslinked polymer systems in the chapter Thermodynamically Controlled Crystal Orientation in Stressed Polymers. Finally, in chapter Optical Studies of Stress-Induced Crystallization of Polymer Melts, R.S. STEIN, M. HASHIYAMA and M. K. PARPART expound their most recent results in the development of optical evaluation methods that permit the characterization of even the shapes and Size of crystalline superstructures.

As a conclusion it can be established that this book is an excellent summary of an area that is very rapidly developing, and has a primary importance in fields of both the polymer physics and the technology, by covering the most recent leading achievements of science.

Gy. HARDY

Yale L. MELTZER: *Water-soluble polymers*

Recent Developments

Chemical Technology Review No. 126.
Noyes Data Corporation, New Jersey, USA, 1979. pp. 496

The book comprehends the detailed description of 240 U. S. patents. Among these patents the earliest one was issued in March 1977. Due to many reasons, the markets and application fields of the water-soluble polymers are developing rapidly. Water as solvent is

harmless for the environment and has no fire or explosion hazard. Hence, their application in the areas of motor-car paints, binders and adhesives grows very dynamically. There is a similar situation in the branches of pharmaceutical, food and cosmetic industry where they are consumed as auxiliary materials that increase the value of the products significantly. The survey of the 240 U.S. patents is divided into groups in accordance with the chemical structure of the polymers. Beginning with acrylamide polymer, — cellulose derivatives, epoxy resins, natural gums, polyurethanes until starch and related products, — the whole subject is covered by this book. The descriptions are well arranged and are rich in information.

By studying this book one may obtain a view that enables the discovery of other, novel fields of application. From the last part of the book the reader may get acquainted with those up to date technologies in which water soluble polymers are used. Most of these deal with the modern methods of sewage purification and with such special applications as the crosslinking of hydrophilic colloids chelate forming aqueous resin compositions, water-based magnetic inks and alike. This book is worth to be used by the specialists who care for the production and application of unique water-soluble polymers.

Gy. HARDY

M. William RANNEY: *Antioxidants*
Recent Developments

Chemical Technology Review No. 127.

Noyes Data Corporation, Park Ridge, New Jersey, USA, 1979. pp. 372

This book presents brief and essential information about U.S. patents issued since October 1974. The patents are divided into groups according to the fields of application. Hence more than 4/5th of the content covers antioxidants for plastics and elastomers and 1/5th concerns antioxidants used in food products.

In case of plastics, substances applied mostly in polyolefin resins are described namely, phenolic compounds and their derivatives, piperidine and other nitrogen-containing compositions, metal-organic compounds and others.

For polyvinyl chloride resins organotin compounds and metalcontaining compositions are listed. Polyesters, polycarbonates and polyurethanes are the last among the plastics.

In the chapter on elastomers antiozonants, phenolic antioxidants and copolymerizable antioxidants are surveyed. The chapter about antioxidants, of petroleum products and synthetic lubricants involves oxidation hindering additives of mineral oil lubricants, gasoline compositions, polyester lubricants and phosphate ester fluids. As protective ingredients of food products patents about nonabsorbable and general antioxidants, ascorbic acid compositions and other systems are described. The last chapter makes one acquainted with some antioxidants applied in other fields, e.g. additives against oxidations of herbicides, light-sensitive photo papers, dental products, hair treatment preparations and sun tan lotions.

As a conclusion it can be stated that this book gives a valuable review about the U.S. patents relating to antioxidants and it can be an effective aid for specialists who deal with the application of ingredients or elaboration and development of technological prescriptions in the plastic, elastomer, food and cosmetic industries.

Gy. HARDY

Recent Results in Chemistry, Vol. 45

Editor B. CSÁKVÁRI, Akadémiai Kiadó, Budapest, 1979. 384 pages (In Hungarian)

The number of books dealing with mass spectroscopy in Hungarian is low; hence the publication of the most recent volume of the series giving a picture of some new fields of application of mass spectroscopy, is particularly welcome. The following papers are included in the book.

István CORNIDES: *Mass Spectroscopy Today and Tomorrow*

The paper gives a systematic survey of the past, present and future of mass spectroscopy and outlines the directions of the future development expected. It is very instructive to follow, by the help of the author, the explosion-like appearance of mass spectroscopy in the field of chemical and physical research; this description is useful not only for researchers just

wishing to obtain a picture of mass spectroscopy, but also for experts working in some special field of chemical science.

The survey clearly shows that the field of mass spectroscopy is alarmingly widespread, in which orientation is possible only by means of a system developed on the basis of carefully selected points of view. The author presents a system based on the character of the mass spectrometric information, from methodical points of view and according to the fields of application of mass spectroscopy; this system is illustrated in clearly constructed tables.

The final short chapter deals with the future of mass spectroscopy, in the knowledge of present trends of requirements and of the expected possibilities of technical development
Olivér KAPOSÍ: *High-temperature Mass Spectrometry*

In high-temperature chemical research, mass spectrometry is one of the most important methods. The paper surveys the theory, experimental technique and the most recent research results of high-temperature mass spectrometry.

The first chapter deals with the theory of evaporation processes. It clearly draws up the problems that must be elucidated unambiguously to describe an evaporation process, then the methods widely employed in high-temperature mass spectrometry for measuring tension are discussed in detail: the Langmuir free evaporation and the Knudsen effusion method.

In the second chapter the experimental basis of the method is described. This deals with the fundamental principles of mass spectrometry only to the extent necessary for the topics discussed. Then the types of vaporization cells and the task of coupling to the ion source are treated in detail. The clearly constructed figures can greatly help experts who intend to work in this field of science.

In the next chapter the evaluation of mass spectrometric data, the identification of ions and vaporized neutral molecules, as well as the correlation between the ion current and the partial pressure are discussed.

In the fourth chapter thermochemical and thermodynamical calculations are shown which allow the establishment of thermodynamic data of vapour phase and condensed phase in equilibrium, once the vaporized components have been identified and their partial pressures determined. Then the parameters affecting the equilibrium conditions in the Knudsen cell furthermore the stability of high-temperature molecules are discussed.

The last chapter is a survey of the field of application of the method discussed. The problems considered include the determination of the activity of the individual components in salt melts and alloys, and the isothermal vaporization of binary systems. Finally, the author summarizes the research fields of high-temperature mass spectrometry and the most important results achieved.

The clear and logical construction, the high-level treatment of the subject, as well as the ample amount of references included up to 1978 make the paper a source of comprehensive and thorough knowledge concerning this field of high-temperature chemistry.

Lajos MATUS, István ÓPAUSZKY: *Investigations on Gas Phase Reactions by means of a Mass Spectrometer*

In the paper the research aiming at the examination of gas phase reactions taking place in the ion source of the mass spectrometer as in a reaction space is reviewed.

In the first chapter a historical survey of the ion-molecule reactions and the reactions of excited states is given. The authors follow the research of secondary ions formed in the ion source, from the time of the birth of mass spectrometry, when it was a "by-process to be eliminated", up to today, the appearance of theories interpreting these processes.

The next chapter deals with the measurement principles and the experimental apparatuses. It discusses in detail the types of ion sources having a fundamental importance in research. The Nier inner ionization source, as well as the impulse, the two-chamber and photon impact ion sources, their fields of application, advantages and disadvantages are then reviewed. In the next two sub-chapters such types of mass spectrometers are described (ion-cyclotron resonance and tandem mass spectrometers), which can be employed very advantageously in the investigation of certain types of reactions (processes of small effective cross section and processes between reaction partners with exact critical energies).

The third chapter gives a survey of the chemical systems examined, in an arrangement based on the type of the interaction. Atom- or ion transfer reactions accompanied by charge transfer, furthermore, the processes where neutral reaction partners produce ionic products during collisions are described and illustrated by examples. Finally, the correlation between the research field discussed and other physical-chemical investigations (plasma state, electric discharge, flames) is mentioned in a short sub-chapter.

The very readable paper is useful not only for researchers working in mass spectroscopy, but also for those engaged in reaction kinetics; the carefully compiled reference list is of great assistance.

Miklós RIEDEL: *Secondary Ionization Mass Spectrometry*

The methods suitable for examining surfaces have developed greatly in the last decade, their number is about 70. Among them can be found the secondary ionization mass spectrometry (SIMS), which is an analytical method for solids gaining increasing importance today.

The paper is divided into five chapters; the first presents the fundamental units of the experimental apparatus and the grouping of the types of instruments.

The second chapter deals with the fundamental phenomena of secondary ion emission, including the dependence of the secondary ion current on energy, the energy- and angle-distribution of secondary ions, and the effects of the nature, surface and temperature of the sample.

Further on, the author gives a short summary of the theories regarding ion distribution and the various models developed to describe the ion formation.

The following chapters survey the applications of the SIMS. Chapter 3 is devoted to the problems of qualitative and quantitative analysis. Like in all analytical methods, quantitative determination requires great care in the case of the SIMS, too; the limits and the methods suitable for practical application are outlined by the author. The chapter also contains a description of ion microscope mass spectrometry.

In the fourth chapter the problems of secondary ion emission surface analysis, furthermore, two practical realizations, the dynamic and static SIMS techniques, are discussed. The author also deals with investigations on solid-gas interface reactions, on the composition of monomolecular layers developed previously in chemical reactions, and a short literature survey is given regarding adsorption studies.

In the last chapter the determination of concentration distribution in depth by the SIMS technique, and the factors affecting the accuracy of the measurement of depth are treated. Examples of application are also included.

The paper which contains 422 references, can be regarded as a fundamental work in the literature of secondary ionization mass spectrometry published in Hungarian.

The only flaw of the book is that the authors neglected the recommendations regarding the use of SI units.

L. SZEPES

Topics in Current Chemistry, Vol. 86
Spectroscopy

Ed. F. L. BOSCHKE, Springer-Verlag, Berlin—Heidelberg—New York, 1979
294 pages, 136 figures, 22 tables

The 86th volume of the popular series contains four chapters written by different authors.

The title of the first chapter is: *Photochemistry and spectroscopy of simple polyatomic molecules in the vacuum ultraviolet*, written by M. N. R. ASHFOLD, M. T. MACPHERSON and J. P. SIMONS.

In the vacuum ultraviolet range of the ultraviolet spectrum also the atmospheric gases absorb, thus here the substances can be examined only in vacuum. However, a more characteristic notation for vacuum ultraviolet is the "high-energy optical spectrum". The absorption of higher energies may result partly in the excitation of more stable bonding electrons ("intravalence spectrum"), partly in excitations with more than one principal quantum numbers (Rydberg spectrum). Interpretation of the high-energy spectra can help the solution of several photochemical problems, the direct determination of dissociation energies, the dynamics of photodissociation, the kinetic properties of molecule species with excited electrons, astromic problems, the further development of chemical lasers. In the chapter, the spectroscopic and photochemical problems are discussed parallel for the types of molecules. The following molecules are discussed systematically: H₂O and D₂O, H₂S, H₂Se, H₂Te, NH₃, ND₃, PH₃, PD₃, HCN and DCN, CO, OCS, OCS₂, CS₂, CS₂, N₂O, ICN, BrCN, ClCN, (CN)₂ and cyanoacetylenes, CH₃CN, CH₃NC, CF₃CN.

The second chapter was written by C. SÁNDORFY under the title: *Far ultraviolet absorption spectra of organic molecules: valence-shell and Rydberg transitions*.

The author particularly stressed the connection between the electronic spectra and photochemistry. In order to elucidate the reaction mechanisms, all excited electronic states should be known, in principle. However, the number of problems that can be solved by the ultraviolet spectroscopy is limited, due to the selection rules. Therefore, the electron impact spectroscopy can be an important supplementary technique, as well as the circular dichroism and the several-photon spectroscopy provided by the laser technique. The author separately

treated the σ -, non-shared electron pair and π -spectra, and the C=C and C=O bonds in high-energy excitation are compared.

The title of the third chapter in: *Some of aspects of the photoelectron spectroscopy of organic sulfur compounds*. The authors are Rolf GLEITER and Jens SPANGET-LARSEN. Sulfur compounds have important X-ray and ultraviolet photoelectron spectra. In the X-ray spectrum, the closed 2p electron of the sulfur atom can be excited, but the structure of ions with various electron structures can be understood more deeply in the ultraviolet photoelectron spectra. The ionisation energies indicate the site of the electron removed, the adiabatic or vertical structure of the bands refer to the extent of loosening of bonds (adiabatic: hardly changing, vertical: more strongly changing atomic distances), while the fine structure of the vertical bands reflect the change in vibration frequencies in ionic state. The compound families discussed are: saturated, unsaturated sulfides, thiocarbonyls and multivalent sulfur compounds. At the end of the chapter the authors give the ionisation energies of about hundred organic sulfur compounds determined from spectra, in tabular form.

The title of the fourth chapter is: *Photoelectron spectra and bonding in small ring hydrocarbons*, written by Rolf GLEITER. In the absence of heavier atoms, evidently only ultraviolet photoelectron spectra are discussed. The author treated first cyclopropane and its derivatives including the bicyclopropyl compounds, then cyclobutane derivatives, as well as the derivatives of bicyclohexane and tricyclooctane containing condensed cyclobutane rings. Then again the bicyclobutane and its derivatives containing condensed cyclopropane rings are discussed, and the treatment of the bond system and photoelectron spectra of hydrocarbons with strained rings are finished with two interesting skeletons, hexacyclooctane and tetracyclobutane. Ionisation energies of about two hundred compounds are given in tables.

The number of literature references is 800. The book represents a great step towards the knowledge of the electron structure of small and medium size molecules. It gives an important experimental matter for the understanding of the mechanism of photochemical reactions and for quantum chemists.

Gy. VARSÁNYI

M. T. GILLIES: *Nonwoven Materials*

Chemical Technology Review No. 141

Noyes Data Corporation, Park Ridge, N. J., USA, 1979. 372 p.

The book is a comprehensive and detailed review of U.S. patents granted after January 1976 on nonwoven materials. The previous volume by the same publisher, entitled *Nonwoven Textiles*, appeared in 1975.

Nonwoven materials are fibres formed into webs and bonded by chemical, thermal or mechanical means. Their industrial and commercial importance has been rising steadily during the past 25 years. Since nonwovens can be manufactured at much less cost and with much higher productivity, they can — in certain applications — successfully compete with woven fabrics, knitted goods and felts.

In the first part of the book, general methods of web formation and fibre bonding are dealt with. In web formation particular interest is attached to the more recent techniques, as compared to the traditional mechanical process based on carding and the wet-laying of fibres similar to the papermaking process; such new methods are

- spunbonding, a technique in which synthetic filaments are utilized directly as they leave the spinneret by laying them on a conveyor belt, and
- air-laying, that is, dispersing the compressed fibres by means of a high-velocity air stream and laying them on perforated rollers, screens or conveyor belts.

The subsequent chapters review the patents for processes serving to link the fibres together and give the web cohesion.

In the second part of the book, patents for the manufacture of nonwoven materials for specific applications are covered.

CONTENTS (the figures in brackets after each subject group indicate the number of patents reviewed):

Part One: Processes

Web formation

Air-laying techniques (5)

Spunbonding techniques (6)

- Postdrawing melt-blown webs (1)
- Radial extrusion and fibrillation (1)
- Using special fibres (polyvinyl alcohol, polyacrylonitrile, regenerated cellulose, polyarylene-1,3,4,-oxydiazoles) (4)
- Miscellaneous processes (11)
- Chemical bonding of webs
 - Web chemical binding systems (10)
 - Dry adhesives (5)
- Thermal and mechanical bonding
 - Thermal bonding (10)
 - Ultrasonic bonding (3)
 - Fibre entanglement by hydraulic means (4)
 - Other processes (mechanical entanglement, fusion by high frequency electric field, affixing by vibration, needle tracking) (4)

Part Two: Products

- Disposables
 - Diapers (15)
 - Diaper liners (3)
 - Sanitary napkins (2)
 - Flushable products (5)
- Leather substitutes
 - Improvement of shape retention and strength (6)
 - Improving appearance of synthetic leather (2)
 - Improvement of breathability (2)
 - Base sheets (2)
- Products from inorganic fibres
 - Glass fibres (11)
 - Refractory metal oxide fibres (2)
 - Asbestos fibres (1)
 - Carbon fibres (2)
 - Lead fibres (1)
- Carpeting
 - Carpet backings (11)
 - Carpets (3)
 - Resilient carpet padding (1)
- Industrial applications
 - Filtration (9)
 - Insulation (7)
 - Battery separators (2)
 - Laminates for circuit boards (2)
 - Papermakers' felt (2)
 - Other industrial uses (gaskets for luminaires, conveyor belts, artificial leather, flexible laminates, etc.) (6)
- Materials for use in home building
 - Roofing (4)
 - Decorative coverings (3)
 - Floor coverings (2)
 - Wall coverings (3)
 - Other products (2)
- Materials for medical use and packaging
 - Medical and hospital products (8)
 - Packaging materials (5)
- Products with miscellaneous uses (19).

All in all, the review covers a total of 230 patents. Its handling is facilitated by indexes according to the names of the inventors and the patent holders and according to U.S. patent numbers.

The work will be of particularly great value not only to manufacturers of nonwoven materials, but also to manufacturers of synthetic fibres and to adhesive manufacturers, and above all to the rapidly expanding circle of all those who apply nonwoven materials, both for industrial purposes and for consumers' goods.

I. RUSZNÁK

L. H. YAVERBAUM: Nitrogen Oxides Control and Removal

Noyes Data Corporation, Park Ridge, N.J., 1979

This book presents methods suitable for preventing the contamination of our environment by nitrogen oxides. The 387 pages contain the specifications of relevant patents issued in the U.S.A. since April 1975. In fact, this volume continues the information the Noyes Data Corporation has already published under the title "Nitrogen Oxide Removal".

The task this book performs is twofold. On the one hand it makes detailed technological information available, on the other it greatly facilitates a survey of the many patents in this field granted by the U.S.A., these patents being sources of knowledge not published in literature.

For easier reading the specifications are abridged in this book and, on the supposition that the readers will be technologically schooled persons, the rather particular juristic language is done without. What one reads in this book offers good help in research and development work, may spark off novel ideas towards studies in new directions.

The book is divided into two main parts. The first deals with the ways and means how to minimize the emission of nitrogen oxide fumes by power-stations, boilers, nitric acid works, i.e. by stationary industrial facilities. A short introduction summarizes the mechanisms that produce nitrogen oxides in flue gas when some fossile fuel is being burnt. The various techniques conducive to a diminished generation of nitrogen oxides are reviewed, further, those suitable for the removal of these gases (together with that of sulphur dioxide present in flue gas).

According to what we find in this book, catalytic reduction of nitrogen oxides, in view of the de-contamination of industrial flue gases which contain these, is the method most extensively studied. This is evidenced also by the conspicuously great number of patents issued in the U.S.A., in the last five years, for the preparation and application of catalysts. The chapter that deals with these is mostly about metal- and oxide-catalysts, and also about types of reactors recently developed.

A separate chapter is about sorption methods, of which the majority is characterized by being suitable for the removal also of sulphur dioxide present in flue gases.

Exposing effluent gases which carry nitrogen oxides to very high temperatures, and the conversion of the badly absorbable nitrogen monoxide into well absorbable dioxide, are the topics in the next chapter.

The first part of this book is made complete by patents which concern the purification of air, and relevant analytical methods.

The second main part concerns mobile apparatus, equipment, and machinery: internal combustion engines first of all. Patents relevant to the diminution of nitrogen oxide contents in exhaust gas are discussed here. First and foremost are the patents for the preparation of various catalysts, arranged under sub-heads severally pertinent to copper/nickel, nickel/noble metal, iron, platinum/palladium, rhodium and ruthenium catalysts. The next chapter describes carrier substances for catalysts and particular catalytic methods; the following one is about catalytic converters and reactors.

In the last chapter we find the "other" methods, for instance reduction of nitrogen oxides with carbon monoxide at high temperatures, or filtration apparatus with calcium carbonate packing.

A list of the names of patent holders, inventors, and of the patents arranged in sequence of increasing registration numbers completes this book.

In sum: this is a very useful book, full of fresh information, for research as well as for production engineering personnel that has to wrestle with the labours of reducing or preventing the contamination of natural environment.

P. KÁLDI

J. C. JOHNSON: *Industrial starch technology* *Recent Developments*

Chemical technology review, No.: 142.

Noyes Data Corporation, Park Ridge, New-Jersey, USA 1979. p. 372

During the last two decades a definite separation of informations published in periodical papers and in patents can be observed. Those, who rely exclusively on the periodical journals overlook essential details of commercially useful informations. Therefore the importance of patent literature is continuously growing.

However, in contrast to well organized scientific papers the patent literature has two disadvantages: the considerable lag between the application and the granting of patent, as well as the lack of easily accessible comprehensive surveys on the patents. This title, together with the previous one (published in 1974) is a substantial aid for those who are interested in US patents issued since July 1976 on the technology and utilization of starches, their derivatives and analogous hydrocolloids.

This book contains detailed descriptive informations, eliminating legal jargon and juristic phraseology. Being an advanced, commercially oriented review, is recommended to everyone who is interested in technological transfer or want to establish a sound background before starting research and development activity in this field.

The content is as follows:

- Modified (oxidized, enzymatically degraded, irradiated) starches
- Starch derivatives (esters, ethers, cationic derivatives)
- Starch polymers and copolymers (high water absorbent polymers, biodegradable copolymers, graft polymers, block copolymers, crosslinked starches, etc.).
- Starch-plastic compositions
- Starch in papermaking
- Binders and adhesives
- Coatings and inks
- Utilization in pharmaceuticals (cyclodextrin complexes and derivatives, tableting materials, medical-dental products, chromatographic matrices, etc.).
- Consumer products (detergents, laundry aids, pesticides)
- Other products (well-drilling aids, fibres and films, etc.).

J. SZEJTLI

F. A. RIDDEL: *The Conformational Analysis of Heterocyclic Compounds*

Academic Press, London, 1980, 152 pages

RIDDEL's book makes enjoyable reading. It contains a remarkable wealth of information but it is still small enough to be read from cover to cover within reasonable time. This is mainly owing rather to an intelligent selection of what should be covered and what should be omitted, and not to a compression of the material in a Chemical Abstracts fashion.

In the first two chapters the reader is introduced to the essentials of conformational analysis and its methodology with special emphasis on the problems of heterocyclic compounds. The rest of the book is devoted to the presentation of our current knowledge about the conformations and conformational changes of specific heterocyclic compounds. Though the author does not claim to be comprehensive, it seems that as far as saturated monocyclic compounds with up to eight-membered rings are concerned, not much of relevant information was left out. In this light it seems that the fundamental conformational problems in this class of compounds have been adequately solved, and the knowledge gathered provides a sound basis for extrapolations to more complex systems. It is therefore only natural that little is said about unsaturated and condensed heterocyclic systems.

Facts are always accompanied by interpretations, sometimes at variance with that given by the original authors, and it is clearly pointed out when, in the authors opinion, there is no adequate explanation for a given phenomenon.

Two minor criticism concerning terminology may be raised: species related by nitrogen inversion should not be termed different conformations (p. 54) and chair conformations of 1,3-oxathian are not dissymmetric but asymmetric (p. 113).

M. NÓGRÁDI

Peter LUGER: *Modern X-Ray Analysis on Single Crystals*

Walter de Gruyter, Berlin—New York 1980 pp XIII + 312

The determination of molecular and crystal structure by the X-ray diffraction analysis on single crystals has become a routine technique performed even in commercial laboratories by order. It has also become a routine technique in chemical research laboratories where it is often performed by workers who may have only a very superficial knowledge of the basics in this ever increasingly automated technique. For chemists who would like to be better prepared,

who are not crystallographers themselves but who are to perform X-ray diffraction analysis on single crystals, Professor LUGER's book is just the right introduction and guide.

A theoretical basis is presented in the first part with mathematical introduction and a brief summary of fundamental results of diffraction theory. All subsequent chapters consist of general descriptions of experiment, analysis procedure or symmetry concepts and the practical considerations and applications for three selected examples. The following compounds were chosen for detailed presentation of their analysis:

- (1) Potassium hydrogen tartarate ($C_4H_5O_6K$)
- (2) Ammonium tetrasulfurpentanitride oxide ($NH_4[S_4N_5O]$)
- (3) Sucrose ($C_{12}H_{22}O_{11}$)

Of course, these examples are not randomly picked but their choice has well-defined purpose.

Considerable attention (and space) is given to the description of the preliminary experiments. Naturally they are the least automated part of the single crystal structure analysis where the scientist's experience and intuition may still play an important role. The introduction to crystal symmetry is illustrated by some pleasant figures of the symmetry operations using a "baby-head" motif. The last three chapters prepare the reader for collecting the data and analysing them. They are on the diffractometer measurements, the solution of the phase problem, and the refinement.

The book is up-to-date, well-balanced and nicely produced. It fulfills its stated aim "to serve as guide and enable the reader to solve his structural problems almost without further preparation." Of course, the meaning of *almost* here may well widely differ for different readers and different tasks.

I. HARGITTAI

M. EIGEN, P. SCHUSTER: *The Hypercycle. A Principle of Natural Self-organization*

Springer Verlag, Berlin, Heidelberg, New York. pp. 92. With 64 Figures

In 1971, Manfred EIGEN, the Nobel-prize winner German physicochemist published a conceptionally new theory on the spontaneous dynamical self-assembling of macromolecules into self-reproducing systems. These systems, the so-called hypercycles were considered as internal stages of abiogenesis (Naturwiss., 58 465, 1971). After an essentially six year silence EIGEN and his coworker, Peter SCHUSTER published three new papers on the hypercycles investigating in this case mostly the evolutionary properties of these systems (Naturwiss., issues 11/1977, 1/1978 and 7/1978). These short series of papers is available now as a book, published by the Springer Verlag.

The book is divided into three parts. In part A, the behaviour of the Darwinian systems are discussed under the title "Emergence of the Hypercycle". The results show that the macromolecules having self-reproducing capacities or the "non-cooperative" systems of them are not able to undergo such evolution processes the result of which would be the presently living world of the Earth. The authors declare the necessity the appearance of the systems having hypercyclic organization during the evolutionary processes.

The title of part B is "The Abstract Hypercycle". Topologic methods are used in this part to investigate the stability properties of some self-reproducing networks. The accumulating systems are divided into three groups here by the authors according to the type of the growth of the systems: into the linear ($\dot{x} = k$), the exponential ($\dot{x} = kx$) and the hyperbolic ($\dot{x} = kx^2$) ones. The hypercycles are considered as hyperbolically growing systems, however the detailed proof of this declaration is missing. Although the hypercyclic growth plays an important role in this part of the theory, the given abstract example of the hypercycles (hypercycle with translation) seems to have either linear or exponential growth depending on the fact whether the E_i enzymes or the I_i nucleic acids are in excess. Among the network's studied, the hypercyclic organization is proved to be a necessary prerequisite for maintaining the stability of information and for promoting its further evolution.

In part C, entitled "The Realistic Hypercycle" the primordial coding problems are discussed on the basis of the hypercycle theory, giving some interesting new aspects for the solution of this problem.

The theories outlined in this book are quite new and interesting. Their real values depend on the veracity of the declared properties of hypercycles. This book may be an extremely important step towards the founding of theoretical biology.

T. GÁNTI

INDEX

PHYSICAL AND INORGANIC CHEMISTRY

Study of the Anodic Dissolution of Copper in Non-Aqueous Acetic Acid Solutions, IV., L. KISS, A. BOSQUEZ, L. M. VARSÁNYI.....	11
Preparation and Properties of $Al_2O_3-AlF_3$ Catalysts, I, S. KOWALAK	19
Catalytic Properties of the $Al_2O_3-AlF_3$ System, S. KOWALAK.....	27
The Effect of Cell Resistance in A. C. Polarography, T. GARAI, L. MÉSZÁROS	35
Isentropic Compressibility of Ethylenediamine + <i>n</i> -Alcohol at 303.15 and 313.15 K, D. N. RAO, A. KRISHNAIAH, P. R. NAIDU	49
Thermolysis of Complex Cyanides, XVI. Thermal Decomposition of Diphenyl Iodonium Cyanometallates with Linear, Planar and Tetrahedral Anions, K. GYŐRYOVÁ, B. MOHAI (in German)	67
Thermolysis of Complex Cyanides, XVII. Thermal Decomposition of Diphenyl Iodonium Cyanometallates with Octahedral Anions, K. GYŐRYOVÁ, B. MOHAI (in German)	77

ORGANIC CHEMISTRY

Reaction of Steroidal Dienones with Perbenzoic Acid, S. R. HUSAIN, M. HUSAIN, M. S. AHMAD	1
Optical Rotation of <i>t</i> -Butyloxycarbonyl-L-tyrosine, A. TURÁN, S. BAJUSZ.....	7
Heterocyclization with Iminium Chlorides, II. Synthesis of 4 <i>H</i> -[3,1]-Benzoxazine-4-ones and Quinazolinones, I. BITTER, L. SZŐCS, L. TŐKE.....	57
RECENSIONES	87

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REACTION OF LEAD(IV) ACETATE WITH STEROIDAL 6-OXIMINO COMPOUNDS

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The reaction of 6-oximino-5 α -cholestane (1) with lead(IV) acetate in AcOH–benzene mixture gives 6 α -nitroso-6 β -acetoxy-5 α -cholestane (3) and 6 β -nitro-5-acetoxy-5 α -cholestane (4). Under similar reaction conditions, 3 β -hydroxy-6-oximino-5 α -cholestane (2) yielded 3 β -hydroxy-6 α -nitroso-6 β -acetoxy-5 α -cholestane (5) and 3 β -hydroxy-6 β -nitro-5-acetoxy-5 α -cholestane (6). The reaction of 3 α -5-cyclo-6-oximino-5 α -cholestane (10) afforded 3 α -5-cyclo-5 α -cholestan-6-one (11), 3 β -5-diacetoxy-5 α -cholestan-6-one (12), 3 β ,7 α -diacetoxy-5 α -cholestan-6-one (13) and 3 β -acetoxy-5-methyleneacetoxy-*A*-nor-5 α -cholestan-6-one (14). The structures of these compounds were established on the basis of their spectral properties and comparison with authentic samples, where available.

A previous paper [1] has dealt with the synthesis of steroidal nitroso- and nitro acetate derivatives by the oxidation of oximes with Pb(OAc)₄. The present work has been undertaken in order to extend the scope of the reaction and to check the product distribution when a cyclopropane ring is present.

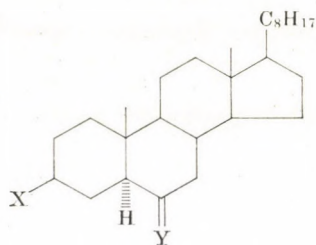
Treatment of 1 with Pb(OAc)₄ in a mixture of AcOH and benzene furnished two compounds, one of them blue (3), m.p. 88 °C and the other (4) white, m.p. 130 °C. The blue colour of the solid 3 suggested that it was a geminal nitroso acyloxy compound, since IFFLAND and CRINER [2] and YUKAWA *et al.* [3] reported that such compounds are characterized by blue colouration. The elemental analysis of 3 showed the composition C₂₉H₄₉NO₃. Its IR spectrum had bands at 1755 (CH₃COO–), 1555 (–N=O), 1240 and 1220 cm⁻¹ (C–O; axial acetate) [4]. In the NMR spectrum, the broad multiplet for 3H, centered at δ 2.96 can be assigned to methine and methylene protons (C5-H; C7-H₂) [5]. Additional evidence for the geminal nitroso acyloxy structure was obtained by treatment of 3 with 10–20% aqueous hydrochloric acid, which generated the parent ketone 9, m.p. and mixed m.p. 96 °C (*lit.* [6] m.p. 97–98 °C).

Compound 4 had correct analysis for C₂₉H₅₀NO₄. The IR spectrum exhibited bands at 1758 (CH₃COO–), 1555, 1325 (–NO₂), 1230, 1220 cm⁻¹ (C–O, axially-oriented acyloxy group). In the NMR spectrum a double of doublets for one proton at δ 3.13 (ABX system, *J* = 7 Hz and 3 Hz) can be assigned to the C-6 equatorial α -proton.

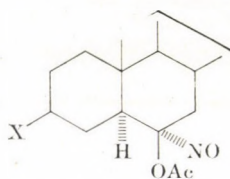
* In final form accepted October 14, 1980.

Similarly, the treatment of **2** afforded **5**, m.p. 108 °C and **6**, m.p. 170 °C. The acetylation (Ac₂O/Py) of compound **5** furnished **7**, m.p. and mixed m.p. 89 °C (*lit.* m.p. 89 °C), while **6** gave **8**, m.p. and mixed m.p. 115 °C (*lit.* [1] m.p. 115 °C).

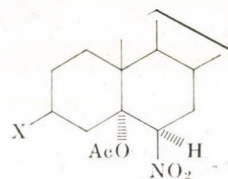
The oxime **10**, when subjected to similar reaction conditions, gave compounds **11**, m.p. and mixed m.p. 96 °C (*lit.* [7] m.p. 97 °C), **12**, m.p. and mixed m.p. 170 °C (*lit.* [8] m.p. 170 °C), **13** and **14**. The elemental analysis of com-



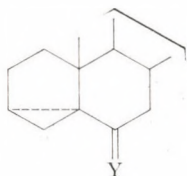
	X	Y
1	H	NOH
2	OH	NOH
9	H	O



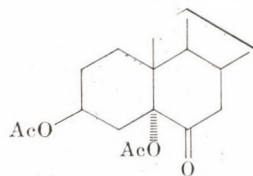
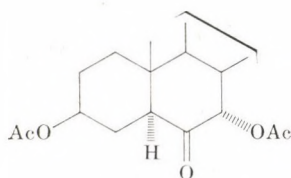
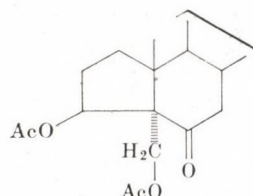
3	X = H
5	X = OH
7	X = OAc



4	X = H
6	X = OH
8	X = OAc



10	Y, NOH
11	Y, O

**12****13****14**

pound **13** showed the composition C₃₁H₅₀O₅ and its IR spectrum had bands at 1745, 1755 (2 CH₃COO-), 1710 (C=O), 1235 and 1220 cm⁻¹ (C-O; *axial*). The NMR spectrum had a signal at δ 5.2 (, 1 H, C3-*α*-H; *W*_{1/2} = 16 Hz; ring junction *trans*), 4.5 (broad, s, 1 H, C7-*β*-H).

An examination of the Dreiding model of **13** revealed that the dihedral angle between the planes of C8- β -H (*axial*) and C7- β -H was almost 90°; this may account for the C7- β -H appearing as a broad singlet.

Compound **14** had correct analysis for C₃₁H₅₀O₅. Its IR spectrum had bands at 1755, 1740 (CH₃COO—), 1710 (C=O) and 1240 cm⁻¹ (C—O). The NMR spectrum showed a singlet at δ 4.98 for the methylene protons in CH₂-OAc and also indicated attachment at a tertiary position; there was a multiplet at δ 5.12 (C3- α -H; $W_{\frac{1}{2}} = 4$ Hz; *equatorial*; ring junction *trans*).

In conclusion, the lead(IV) acetate cleavage of the cyclopropane ring of bicyclic compounds occurs mainly at the external C—C bond to give *trans*-2-acetoxycycloalkyl acetates; internal C—C bond cleavage occurs to a lesser extent, the product being 1,3-diacetate [9].

Experimental

M.p.'s are uncorrected. IR spectra were obtained in Nujol with a Perkin—Elmer 237 spectrophotometer. NMR spectra were run in CDCl₃ on a Varian A60 instrument with Me₄Si as the internal standard. TLC plates were coated with silica gel. A 20% aqueous solution of perchloric acid was used as the spraying agent. Light petroleum refers to a fraction of b.p. 60—80 °C. NMR values are given in ppm (s = singlet, d = doublet, br = broad, m = multiplet).

Reaction of **1** with lead(IV) acetate

Lead(IV) acetate (1.0 g) was added in portions to a stirred solution of the oxime **1** [10] (1.0 g) in a mixture of benzene (20 mL) and acetic acid (10 mL). The reaction mixture was stirred at room temperature for 3 h. The solvent was then removed under reduced pressure and the residue was taken up in ether (100 mL). The ethereal solution was washed successively with water, NaHCO₃ (5%), and water and dried (Na₂SO₄). Evaporation of the ether left an oil (1.10 g) which was chromatographed on silica gel (20 g). Elution with light petroleum gave an oil, which was crystallized from methanol to obtain **3** (400 mg), m.p. 88 °C.

NMR: δ 2.96 (m, C5-H and C7-H₂); 1.91 (CH₃COO—); methyl signals appeared at δ 1.1, 0.9 and 0.8 (for 5 methyl protons).

C₂₉H₄₆NO₃. Calcd. C 75.81; H 10.6; N 3.05. Found C 75.71; H 10.51; N 3.03%.

Further elution with light petroleum-ether (20 : 1) furnished a solid (**4**) which was recrystallized from light petroleum, m.p. 130 °C (30 mg).

NMR: δ 3.13 (dd, C6- α -H); 2.1 (s, CH₃COO—); methyl signals were present at δ 0.92, 0.84, 0.75 and 0.68 (for 5 methyl protons).

C₂₉H₄₆NO₄. Calcd. C 73.2; H 10.3; N 2.94. Found C 73.0; H 10.28; N 2.89%.

Reaction of **2** with lead(IV) acetate

The oxime **2** (1.0 g) was treated as above and the reaction product was chromatographed. Elution with light petroleum-ether (5 : 1) gave a blue solid **5**, which was recrystallized from light petroleum (300 mg), m.p. 108 °C.

ν_{\max} 3530 (—OH), 1755 (CH₃—COO—), 1555 (—N=O), 1235 and 1220 cm⁻¹ (C—O). C₂₉H₄₉NO₄. Calcd. C 73.26; H 10.30; N 2.90. Found C 73.24; H 10.28; N 2.87%.

Further elution with light petroleum-ether (4 : 1) afforded **6** which was recrystallized from ethanol (450 mg), m.p. 170 °C.

ν_{\max} 3535 (—OH), 1750 (CH₃COO—), 1550, 1330 (—NO₂), 1230 and 1210 cm⁻¹ (C—O). C₂₉H₄₉NO₅. Calcd. C 70.81; H 9.9; N 2.83. Found C 70.87; H 9.9; N 2.85%.

Reaction of 10 with lead(IV) acetate

Lead(IV) acetate (2.0 g) was added in portions to a stirred solution of the oxime **10** [11] (2.0 g) in benzene (40 mL) and acetic acid (15 mL). The mixture was refluxed on a water bath for 3 h and, after the usual-work up, was chromatographed on silica gel (40 g). Elution with light petroleum-ether (20 : 1) yielded **11**; recrystallized from methanol (150 mg), m.p. and mixed m.p. 96 °C [7].

Elution with light petroleum-ether (18 : 1) yielded **12**; recrystallized from methanol (200 mg), m.p. and mixed m.p. 170 °C.

ν_{\max} : 1735, 1720 (2 $\text{CH}_3\text{COO}-$), 1240 and 1235 cm^{-1} (C—O).

NMR: δ 4.75 (br, 3C- α -H, $J = 16$ Hz), 2.1, 1.95 (s, 2 $\text{CH}_3\text{COO}-$); methyl signals were seen at δ 0.84, 0.80, 0.78 and 0.59 (for 5 methyl protons).

$\text{C}_{31}\text{H}_{50}\text{O}_5$. Calcd. C 74.10; H 9.96. Found C 73.98; H 9.94%.

Elution with light petroleum-ether (15 : 1) afforded **13** as a non crystallizable oil (350 mg).

NMR: δ 5.2 (m, C3- α -H, $W_{\frac{1}{2}} = 16$ Hz), 4.5 (br, s, C7- β -H), 2.12 and 1.95 (2 $\text{CH}_3\text{COO}-$); methyl signals were seen at δ 0.88, 0.82, 0.79 and 0.50 (for 5 methyl protons).

$\text{C}_{31}\text{H}_{50}\text{O}_5$. Calcd. C 74.10; H 9.96. Found C 73.98; H 9.93%.

Further elution with light petroleum-ether (5 : 1) afforded **14** as an oil (300 mg).

NMR: δ 5.2 (m, C3-H); 4.98 (s, CH_2-OAc), 2.07s, 2.0s, (2 $\text{CH}_3\text{COO}-$), 0.95, 0.90, 0.85 and 0.8 (for 5 methyl protons).

$\text{C}_{31}\text{H}_{50}\text{O}_5$. Calcd. C 74.10; H 9.96. Found C 73.95; H 9.95%.

*

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BONDING PARAMETERS AND ESR HYPERFINE LINEWIDTH OF THE Cu(II)-DL-ALANINE COMPLEX

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An electron spin resonance study of the Cu(II) complex with DL-alanine has been carried out in three different phases, namely polycrystalline, glassy and solution states. Optical absorption and magnetic susceptibility measurements have also been performed. Various magnetic and non-magnetic parameters have been determined. These parameters have further been used to compute the different bonding parameters. The linewidth of each hyperfine line has been measured. The data obtained in this way have been interpreted using KIVELSON's theory of linewidth in solution. The magnetic susceptibility of the complex has also been calculated theoretically. The data obtained from all the three measurements are complementary to each other.

Introduction

YOKOI [1] and JEZOWSKA-TRZEBIATOWSKA *et al.* [2] obtained an immense amount of information from ESR, optical absorption and magnetic susceptibility studies of copper amino acid complexes. Keeping this in view, the above three studies have been carried out to obtain interesting information regarding the magnetic as well as non-magnetic interactions and the nature of chemical bonding in the copper DL-alanine complex.

Experimental

The Cu(II)-DL-alanine complex was prepared by a known method [3]. The complex crystallized as the monohydrate with the following composition

Cu [CH₃CH(NH₂)COO]₂ · H₂O (257.73). Calcd. C 27.96; H 5.47; N 10.87; Cu 24.65. Found C 28.60; H 5.24; N 10.78; Cu 25.00%.

Density 2.37 g cm⁻³.

The optical absorption of the complex in aqueous solution has been studied using a Cary-14 automatic recording spectrophotometer in the region 13330–28570 cm⁻¹. A 10⁻³ mol dm⁻³ solution in a pyrex capillary tube was used for the ESR study of the solution. The glass sample was prepared by dissolving the complex in a glycerine-water mixture with a glycerine to water ratio of 3 : 2 and cooling it to 77 K in a quartz tube. A Varian X-band V4502-12 reflection type ESR spectrometer with a multipurpose V4531 cavity with 100 kHz field modulation was used for the ESR study. A proton probe combined with a Hewlett Packard frequency counter was used for field measurement. A Varian temperature control unit was used for low temperature work. The magnetic susceptibility of the complex was measured by the Faraday method employing a single pan Mettler analytical balance (Type-H 16GD) with a least count of 10⁻⁵ g.

Theoretical

Bonding Parameters

The copper amino acid complex investigated here has a square planar D_{4h} symmetry [4]. The $2s$, $2p_x$, $2p_y$ and $2p_z$ orbitals of each of the four ligands are available to form molecular orbitals with the $3d$ orbitals of the central copper ion. The expressions for these orbitals have been derived [5] in terms of α , α' , β_1 and β where α and α' represent the covalent or ionic character of in-plane sigma bonding, and β_1 and β represent in-plane and out-of-plane π -bonding, respectively. It has been shown [5] that $\alpha^2 = 1$ indicates that the bond is 100% ionic, whereas $\alpha^2 = 0.5$ 100% covalent character.

The spin HAMILTONIAN for Cu(II) in a field of D_{4h} symmetry is given as

$$\mathcal{H} = \beta_0 [g_{\parallel} H_z S_z + g_{\perp} (H_x S_x + H_y S_y)] + A_{\parallel} S_z I_z + A_{\perp} (S_x I_x + S_y I_y) \quad (1)$$

KIVELSON and NEIMAN [5], assuming that FERMI's hyperfine constant is proportional to the covalence parameter, derived a relationship between the bonding parameters α , α' , β_1 , β and the magnetic parameters g_{\parallel} , g_{\perp} , A_{\parallel} , A_{\perp} as well as the transition energies $E_{xy} - E_{x^2-y^2}$ and $E_{xz} - E_{x^2-y^2}$. Thus, if one can obtain g_{\parallel} , g_{\perp} , A_{\parallel} , A_{\perp} , $E_{xy} - E_{x^2-y^2}$ and $E_{xz} - E_{x^2-y^2}$, then α , α' , β_1 and β can be determined. But recently ROCKENBAUER [6] has shown that the above assumption is not true and therefore the different bonding parameters have been evaluated from the modified expression [6] of KIVELSON and NEIMAN.

Linewidth

KIVELSON [7], following the formulation of KUBO and TOMITA [8], developed the theory of linewidth in solution. Later on WILSON and KIVELSON [9] have shown that the linewidth T_2^{-1} is given by

$$T_2^{-1} = (A + A') + BM + CM^2 + DM^3 \quad (2)$$

where the linewidth parameters A , B , C , D have their usual meaning [9] and A' is called the residual linewidth due to unspecified mechanisms. The spin-rotational relaxation mechanism has been found to be the most important of these mechanisms. ATKINS and KIVELSON [10], following HUBBARD's theory [11], gave the following expression for the linewidth due to this mechanism

$$\alpha_{RS} = \frac{2}{\sqrt{3}} \frac{\hbar}{\beta_0 g} \frac{1}{12\pi r^3} (\Delta g_{\parallel}^2 + 2\Delta g_{\perp}^2) \frac{kT}{\eta} \quad (3)$$

where

$$\Delta g_{\parallel} = g_{\parallel} - 2.0023, \quad \Delta g_{\perp} = g_{\perp} - 2.0023$$

η is the viscosity of the solution, r the molecular radius of the equivalent rotating sphere in the solution and the remaining symbols have their usual meaning. KIVELSON [12] has also calculated the contribution of electric field fluctuation mechanisms after VAN VLECK [13] and ORBACH [14], as applied to liquids, but only the ORBACH process was found to be useful.

Results and Discussion

Optical Absorption Study

The experimental optical absorption curve of the complex in solution, a plot between optical density D and wavenumber σ , has a non-Gaussian form as shown in Fig. 1. It was analyzed [15, 16] into three Gaussian curves, each of which corresponds to a single transition. The measured values of different parameters like line position σ (10^3 cm^{-1}), half linewidth δ (10^3 cm^{-1}), optical density D , molar absorbance ϵ ($\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$), and oscillator strength f for experimental as well as analyzed curves are shown in Table I.

The analyzed bands have been found to be of the 'forbidden' type since they are quite weak ($\epsilon < 10^3$). Such absorption bands are observed only in the case of Cu(II) complexes but not in the case of the free ion. This shows that the transitions responsible for these bands take place between the levels caused by the field of the ligands [17]. Thus the analyzed band positions convey important information about the symmetry of the crystal field at the Cu(II) ion in the complex. In octahedral symmetry only one band, whereas in a field of tetragonal symmetry three bands are possible because of the splitting of

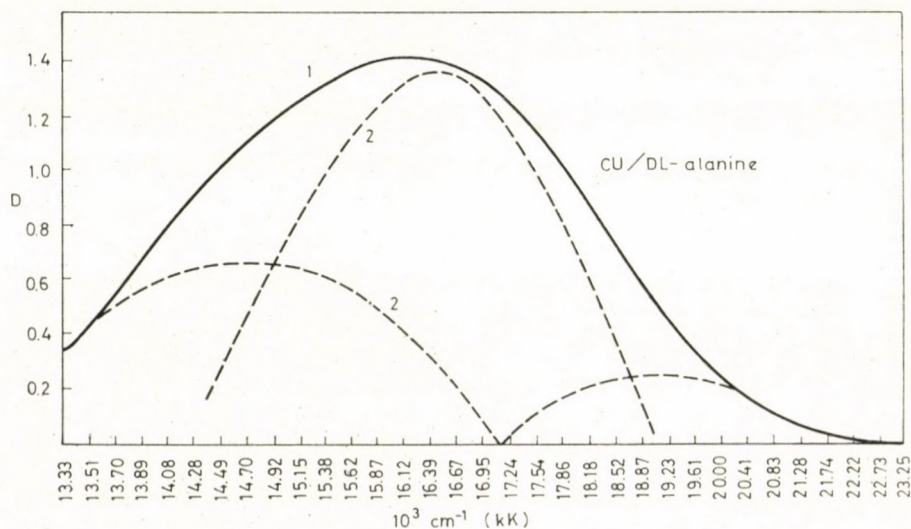


Fig. 1. Experimental (1) and analyzed (2) optical bands of Cu/DL-alanine in solution

Table I
Parameters obtained from the optical absorption study of the complex

		σ	δ	D	ϵ	$f \times 10^4$	σ_1/σ_2
Cu/DL-alanine	Experimental band	16.29	2.34	1.43	51.6	11.11	
	Component bands						
	1	19.23	1.54	0.25	9.2	1.30	1.16
	2	16.57	1.54	1.36	49.2	6.97	
3	14.87	1.54	0.68	24.4	3.45		

the energy levels. BJERRUM [18] has shown that the ratio σ_1/σ_2 is 1 for octahedral symmetry and the value reduces from 2 to 1.67 on going from a square planar to a square pyramidal structure. σ_1/σ_2 for copper nitrate in water and ammonia is found to be 1.33 and the structure is distorted octahedral. This ratio is slightly more than 1 for a tetragonal complex. In our case the ratio σ_1/σ_2 is 1.16 suggesting a tetragonal symmetry of ligands around the Cu(II) ion. The X-ray crystal structure data of Cu/DL-alanine [4] show that the copper atom is at the center of symmetry and is surrounded by two oxygen and two nitrogen atoms in a distorted square. The octahedron is completed by a long Cu—O₅ bond (276 p.m.), thus forming a tetragonal structure. Therefore the symmetry predicted on the basis of the ratio σ_1/σ_2 obtained experimentally is satisfied.

Following OWEN's work [19], the cubic field splitting parameter Δ has been calculated taking the ground state as $d_{x^2-y^2}$ and the optical excitation energies as $\sigma_1 = d_{x^2-y^2} \rightarrow d_{xz,yz}$, $\sigma_2 = d_{x^2-y^2} \rightarrow d_{xy}$ and $\sigma_3 = d_{x^2-y^2} \rightarrow d_{z^2}$. The value of Δ obtained for the complex investigated is 13.54 kK which is in agreement with both the theoretical and experimental observations for similar complexes [20]. This justifies the level arrangement assumed here.

ESR Study

The ESR spectra of the Cu(II)-DL-alanine complex in polycrystalline, glassy and solution states are given in Fig. 2. For the sake of convenience, the result of each will be discussed separately.

Polycrystalline Study

The polycrystalline spectrum has shown seven points of inflection and hence three g values, g_1 , g_2 and g_3 . All the three g values have been measured with the help of KNEUBUHL's [21] method. The lineshape has been determined

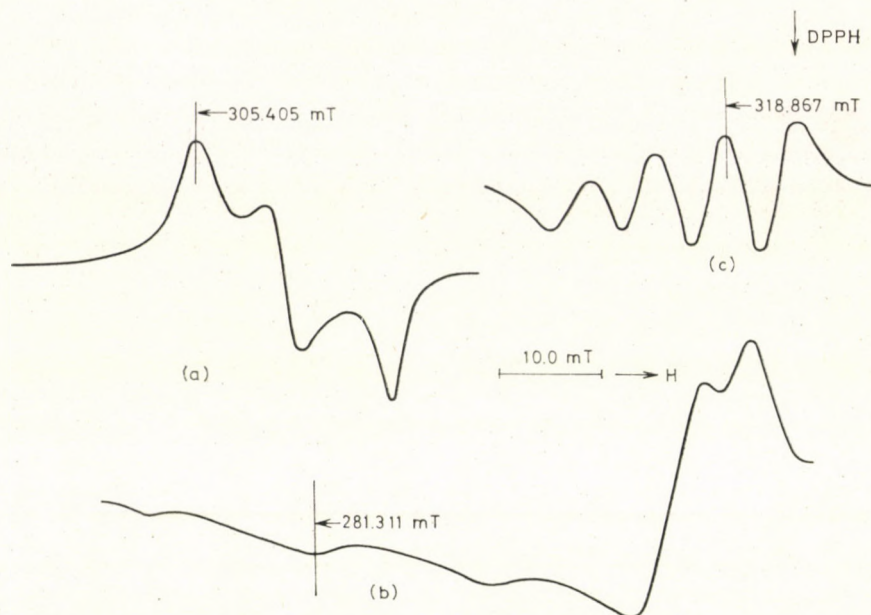


Fig. 2. Experimental ESR spectra of Cu/DL-alanine in (a) Polycrystalline, (b) Glassy and (c) Dissolved state

and found to be Lorentzian. The peak-to-peak linewidth has been measured, which is larger than for the parent copper compound [21]. The results are given in Table II.

Table II

Parameters obtained from polycrystalline sample study

Sample		g_1	g_2	g_3	g	ΔH_{PP} (mT)
$\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$	$g_{\perp} =$	2.080	$g_{\parallel} =$	2.270	2.143	5.774
Cu/DL-alanine		2.054	2.126	2.183	2.121	19.256

The change in g -values from the parent compound, as seen in Table II, is due to some change in the spin-orbit coupling constant λ_0 and the energy gap between the excited and ground states ΔE . However, a small change in ΔE will not affect g much and, therefore, a reduction in λ_0 due to covalency [22] seems to be mainly responsible for the decrease in g -values. This indicates a greater covalency in the complex. Moreover, the decrease in g -values may also be ascribed to exchange effects.

The change in linewidth is mainly due to the change in spin-lattice, dipole-dipole and exchange interactions [23]. In copper salts, spins are loosely

coupled to lattice vibrations [24] and so spin-lattice interaction will not affect the width of the line. Thus the width of the line will mainly be controlled by dipole-dipole and exchange interactions. It is obvious that after complex formation the copper ions are diluted, decreasing thereby the dipolar and exchange interactions. But the decrease in exchange will be due to its exponential form [25] and so the broadening of the line is observed. Anyway, such reduction in exchange could not bring any change in the shape of the line.

A definite and quantitative interpretation of the changes in linewidth can be provided using different linewidth theories [8, 26, 27]. The values obtained for different parameters from above theories are shown in Table III.

From Table III it is seen that $(\Delta H_{1/2})_{\text{exp}}$ is smaller than $(\Delta H_{1/2})_{\text{calc}}$. This is due to exchange coupling. The calculated values of dipolar width and

Table III

Computed values of mean ion distance, linewidth, dipolar width, exchange frequency and exchange integral

Sample	Mean ion distance r^2 (pm)	VAN VLECK Theory		ANDERSON—WEISS Theory		KUBO—TOMITA Theory		Exchange integral $ J $ (cm ⁻¹)
		Linewidth		Dipolar width	Exchange frequency	Dipolar width	Exchange frequency	
		$(\Delta H_{1/2})_{\text{exp}}$ (mT)	$(\Delta H_{1/2})_{\text{cal}}$ (mT)	$\omega_D^2 \times 10^{-18}$ (rad ² · s ⁻²)	$\omega_E \times 10^{-9}$ (rad · s ⁻¹)	$\omega_D^2 \times 10^{-9}$ (rad ² s ⁻²)	$\omega_E \times 10^{-9}$ (rad s ⁻¹)	
CuSO ₄ · 5 H ₂ O	520	5.000	41.416	14.96	17.02	10.66	50.67	0.15
Cu/DL-alanine	570	16.670	42.075	15.71	5.35	11.19	15.92	0.02

$$* \Delta H_{1/2} = \text{Half width at half power points} = \sqrt{3} \frac{\Delta H_{\text{PP}}}{2} \text{ (for Lorentzian shape)}$$

exchange frequency have decreased as compared to the copper salt. Moreover, the reduction in exchange narrowing is faster than that in dipolar width and thus it is inferred that the reduction in exchange is the principal cause of broadening here.

Glass Study

KIVELSON and NEIMAN [5] predicted eight (four weak and four strong) lines for copper complexes in glasses. However, our complex gave four weak lines and only one strong line. The magnetic parameters g_{\parallel} , g_{\perp} , A_{\parallel} and A_{\perp} for the complex have been determined employing the method of VANNGARD and ASSA [28] and are given in Table IV. The values of different bonding parameters evaluated [6] using the above magnetic parameters are shown in Table V.

Table IV
Parameters obtained for glassy state*

	$g_{ }$	g_{\perp}	Δg	g	$(10^9 A_{ } \text{ s}^{-1})$	$(10^9 A_{\perp} \text{ s}^{-1})$
Cu/DL-alanine	2.255	2.058	0.197	2.123	3.19	0.28

* $\nu = 9131$ MHz.

Table V
Bonding parameters for the copper (II) complex

	α^2	α'^2	β_1^2	β^2
Cu/DL-alanine	0.79	0.29	0.87	0.90

It is seen from Table V that α^2 or β_1^2 or β^2 is less than 1 but greater than 0.5, which shows that the bonding in the complex is fairly covalent. The value of β^2 is greater than β_1^2 suggesting that the bonding of the central metal to the ligands occurs mainly in the molecular plane. A fairly covalent nature of the complex is also in agreement with the results of optical study [5]. The values of the bonding parameters obtained here are of the same order of magnitude as found for other copper complexes of similar nature [9, 25, 29].

Furthermore, the study of the complex in glassy state giving two values of g indicates an axial symmetry of the ligands, whereas the polycrystalline study shows a rhombic one since the spectra gave three values of g . The rhombic g -values in polycrystalline state have been ascribed to the spin-exchange interaction effect between the dissimilar Cu(II) ions [1]. Moreover, tetragonal molecular g -values can be estimated from the rhombic g -values of the crystal bulk by considering the crystal structure and the effect of the above spin exchange interaction. The values are, $g_{||} = 2.251$ and $g_{\perp} = 2.054$.

Solution Study

The aqueous solution study of the complex showed four hyperfine lines corresponding to $I = 3/2$ for copper. The individual hyperfine lines are not completely symmetric and also have different intensities. The spectral line can be represented [9] by the equation

$$\omega_0 = g_0 \beta_0 H / \hbar + aM + \frac{1}{2} \hbar a^2 [I(I+1) - M^2] / g_0 \beta_0 H \quad (4)$$

where ω_0 is the microwave frequency in rad/s, g_0 the isotropic g -value, a the isotropic hyperfine splitting constant and the rest of the symbols have their

usual meaning. The values of g_0 and a obtained using the method of WILSON and KIVELSON [9] are 2.077 and $1.25 \times 10^9 \text{ s}^{-1}$, respectively.

The absolute sign of a has not been determined. However, from Eq. (4), if the $M = -3/2$ line is assumed to be at a lower field than the $M = 3/2$ line, a should be negative. But here a positive value of a has been considered because the experimental linewidth parameter B comes out to be positive and the theoretical value of B can be positive only when a is positive.

The theoretical values of the linewidth parameters have been determined from Eqs (5–8) used by MISRA and SHARMA [9]. The experimental parameters ($A + A'$), B , C and D have been obtained by solving simultaneously four equations similar to Eq. (2), each corresponding to one hyperfine linewidth. The experimental A' is then obtained by subtracting the calculated A from the experimental ($A + A'$). The different calculated linewidth parameters, τ_R and α_{RS} values are shown in Table VI while the parameters obtained from experimental linewidths are given in Table VII. The data on Cu/DL-aspartic acid [9] have also been given in these tables for the purpose of comparison.

The only adjustable parameter in the computations of linewidth parameters is r , the molecular hydrodynamic radius. The value of this parameter was adjusted in such a way that it should give the best agreement between experimental and calculated parameters B and C . The calculated and experimentally obtained linewidths along with the r value are given in Table VIII. The moment of inertia of Cu/DL-alanine complex along the symmetry axis perpendicular to the plane of ligands and passing through the copper nucleus has been calculated [30] equal to $1654.80 \times 10^{-16} \text{ a.m.u. cm}^2$ by taking the

Table VI

Calculated linewidth parameters, τ_R^* and α_{RS}
($T = 300 \text{ K}$, $\eta_{\text{water}} = .01002 \text{ poise}$)

	A (mT)	B (mT)	C (mT)	D (mT)	τ_R (10^{-11} s)	α_{RS} (mT)
Cu/DL-alanine	0.2557	0.1494	0.0097	0.00027	0.591	8.5908
Cu/DL-aspartic acid	0.6047	0.3414	0.0195	0.00061	1.007	11.0000

$$* \tau_R = \frac{4}{3} \pi r^3 \eta / kT$$

Table VII

Experimentally obtained linewidth parameters

	$A + A'$ (mT)	A' (mT)	B (mT)	C (mT)	D (mT)
Cu/DL-alanine	3.2664	3.0107	0.1688	0.2023	-0.0272
Cu/DL-aspartic acid	3.3656	2.7608	0.3106	0.1799	-0.1866

Table VIII

Experimental and calculated linewidth along with the hydrodynamic radius

	M	ΔH_{exp} (mT)	ΔH_{cal} (mT)	$\Delta H_{\text{exp}} - \Delta H_{\text{cal}}$ (mT)	r (pm)
Cu/DL-alanine	3/2	3.883	.514	0.369	180
	1/2	3.398	3.344	0.054	
	-1/2	3.236	3.194	0.042	
	-3/2	3.560	3.062	0.497	

bond distances from crystal structure data [4] which gives the radius of an equivalent sphere to be 253 pm. The value 180 pm obtained here for this complex does not seem to be too low considering the uncertainties associated with the estimation of magnetic parameters and also the approximation in applying Eq. (2). The value of r found for copper acetylacetonate in toluene [9] was 335.7 pm. Acetylacetonate is a larger molecule than alanine and so a smaller value of r for Cu/DL-alanine is reasonable.

KIVELSON [12] gave expressions for three important electric field fluctuation mechanisms which contribute to experimental linewidth. For the complex studied here the contributions (in mT) are as follows:

VAN VLECK direct	= 0.3
VAN VLECK RAMAN	= 2.9
ORBACH	= 56.0
Unexplained experi- mental extreme hyperfine linewidth in case of Cu/DL- alanine	= 23.9

It appears from above results that these processes are inadequate to account for the unexplained experimental linewidth. Only the ORBACH process gives some hopeful results.

It is observed from Table VI that the calculated parameters A and B are quite comparable and a large residual linewidth is obtained. This is due to the fact that the first term in the expressions of A and B is very significant and comes out nearly of the same order of magnitude. The linewidth contribution α_{RS} due to spin-rotational relaxation mechanism is sufficiently large. This might be so because the HUBBARD theory [11], which is the basis of calculation of α_{RS} , best applies to large molecules where strong intermolecular anisotropic interactions are present with the solvent molecules [9] and also rotations are not relatively free or inertial [14]. The deviation of calculated linewidths

from the experimental data is more in extreme lines. One of the reasons may be that the linewidth parameters B and C are not of different signs.

From the above it can be concluded that the agreement between theory and experiment is not as good as was found by KIVELSON [9] for vanadyl acetylacetonate in chloroform. This is perhaps because the theory holds best for small values of $|b/\omega_0|$ and $|\Delta\nu/\nu|$. In our case the values of $|b/\omega_0|$ and $|\Delta\nu/\nu|$ are 0.03 and 0.10, respectively, compared to 0.007 and 0.02 for vanadyl acetylacetonate. The values of $|b/\omega_0|$ and $|\Delta\nu/\nu|$ in our case are similar to the values 0.01 and 0.10 obtained for copper acetylacetonate in chloroform [9]. Furthermore, the Eq. (2) is a second order expression which may not hold as well for Cu^{2+} as for VO^{2+} due to larger anisotropies in the Cu^{2+} magnetic parameters, causing poor agreement between theory and experiment.

Magnetic Susceptibility Study

The apparatus for measuring the magnetic susceptibility of the complex has been calibrated with the help of standard substances $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$ and $\text{Hg}[\text{Co}(\text{CNS})_4]$, having susceptibilities 5.85×10^{-6} and 16.44×10^{-6} cgs units, respectively. The susceptibility thus measured has been corrected for the diamagnetism of different diamagnetic groups and atoms in the complex molecule [31]. This corrected susceptibility has been used for the determination of experimental effective dipole moment [31]. The theoretical susceptibility of the complex has also been evaluated. The results obtained are given in Table IX.

Table IX

The data on susceptibility and magnetic moment together with diamagnetic correction at room temperature ($T = 300 \text{ K}$)

	Experimental χ/gm (10^{-6} cgs)	Diamagnetic correction D/gm (10^{-6} cgs)	$\chi_{\text{theoret}}/\text{gm}$ (10^{-6} cgs)	$\chi_{\text{correct}}/\text{gm}$ (10^{-6} cgs)	μ_{e} (B.M.)
Cu/DL-alanine	4.96	0.42	5.46	5.38	1.83

On account of D_{4h} symmetry of the crystal field and energy level scheme as given here, BLEANEY *et al.* [32] and OWEN [19] obtained the following expressions for the magnetic moments along and normal to the tetragonal axis:

$$\begin{aligned} \mu_{\parallel}^2 &= 3 \left[1 - \frac{4\lambda_0 p_1^2}{\Delta_1} \right] + \left[\frac{24kT p_1^2}{\Delta_1} \right] \\ \mu_{\perp}^2 &= 3 \left[1 - \frac{\lambda_0 p_2^2}{\Delta_2} \right] + \left[\frac{6kT p_2^2}{\Delta_2} \right] \end{aligned} \quad (5)$$

where

$$\Delta_1 = E_{xy} - E_{x^2-y^2}, \Delta_2 = E_{xz,yz} - E_{x^2-y^2}$$

$$p_1^2 = \alpha^2 \beta_1^2 \quad \text{and} \quad p_2^2 = \alpha^2 \beta^2$$

For the evaluation of $\mu_{||}$ and μ_{\perp} ; α , β and β_1 have been taken from the glass study, whereas Δ_1 and Δ_2 from the optical absorption study of the complex. Average dipole moment μ_c has been determined from the relation

$$\mu_c^2 = \frac{\mu_{||}^2 + 2\mu_{\perp}^2}{3} \quad (6)$$

The results thus obtained are shown in Table X. The experimental dipole moment has also been given for the purpose of comparison.

Table X

Dipole moment data using two methods, their difference and percent change

	$\mu_{ }$ B.M.	μ_{\perp} B.M.	μ_c B.M.	μ_e B.M.	$\mu_e - \mu_c$ B.M.	\pm % change
Cu/DL-alanine	1.90	1.77	1.82	1.83	+0.01	0.6

It is observed from Table X that there is a good agreement between the experimental and calculated μ values at room temperature. Thus the assumed $d_{x^2-y^2}$ ground state for the complex studied seems to be appropriate. The experimental magnetic moment value of 1.83 B. M. for the complex is greater than the corresponding value of 1.45 B. M. reported for copper acetate monohydrate, which consists of isolated ion pairs with $r_{ij} = 260$ pm and $|J| = 300$ cm⁻¹ [31]. The present complex with r_{ij} and $|J|$ as given in Table III cannot be expected to have isolated ion pairs and thus the difference in the magnetic moments is explained. The confirmation of this conclusion comes from X-ray crystallographic data [4] of the complex. Therefore, dimer formation as suggested by JEZOWSKA-TRZEBIATOWSKA *et al.* [2] in other copper amino acid complexes does not seem to be valid here.

Conclusion

The combined study of optical absorption and magnetic susceptibility has shown that the complex investigated has a crystal field of tetragonal symmetry and the ground state is $d_{x^2-y^2}$. The polycrystalline phase ESR study has shown that the lineshape is Lorentzian and a larger linewidth of the com-

plex than the parent compound is due to a greater decrease in exchange as compared to dipolar interaction on complexation. The glass and optical absorption study indicates that there is a definite bonding between the central metal ion and the ligands and that the in-plane bonding is fairly covalent in comparison with the out-of-plane π -bonding. The linewidth study in solution revealed that a better fit of theoretical results with the experimental one can be obtained by accounting for the contributions of significant mechanisms such as spin-rotational relaxation mechanism or ORBACH process. A good agreement between the effective magnetic moment values from two methods indicates that both methods, macroscopic and microscopic, are equally valid for such systems. Thus all the three studies presented here are complementary to each other and are useful to provide important information about the physico-chemical nature of the complex as well as about the magnetic and non-magnetic interactions existing between the metal ion and the ligands.

*

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AROMATIZATION OF 3 β -CHLORO-5,7 β -DIBROMO- -5 α -CHOLESTAN-6-ONE

SHORT COMMUNICATION

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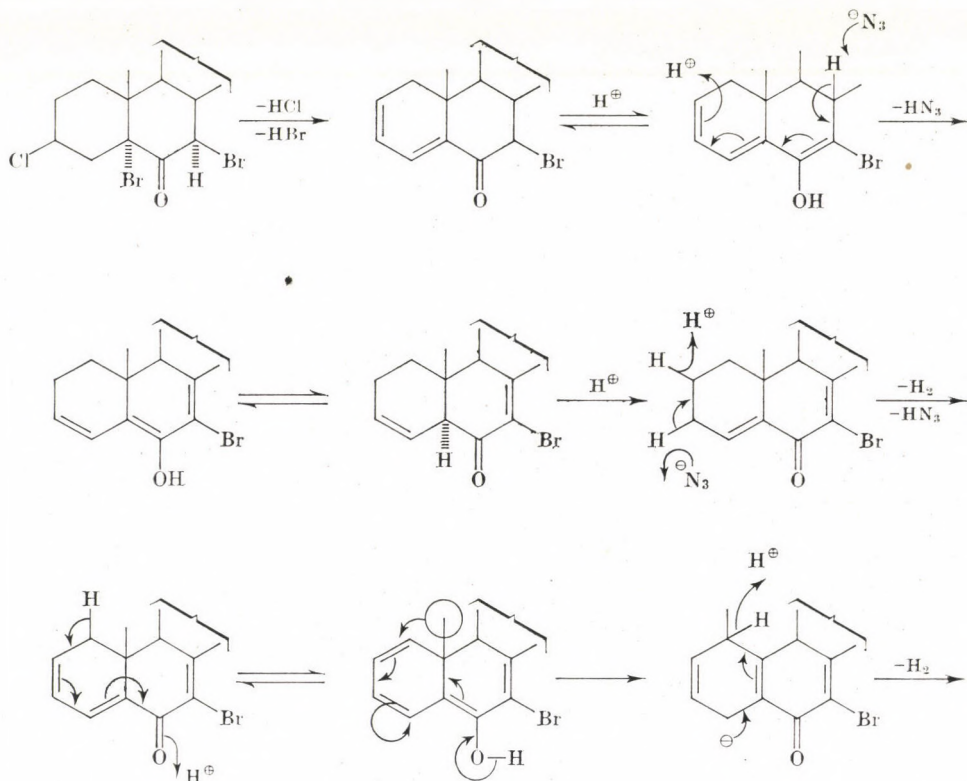
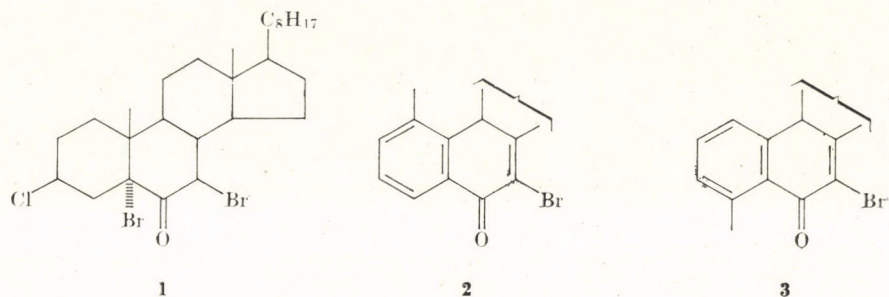
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During our investigation on the transformation of steroidal ketones to corresponding lactams and tetrazoles [1, 2, 3], we treated 3 β -chloro-5,7 β -dibromo-5 α -cholestan-6-one (**1**) in benzene with sodium azide —H₂SO₄ and heated the reaction mixture on a water bath for 15 h. After usual work-up of the reaction mixture and column chromatography over silica gel, a single compound, m.p. 128 °C was obtained. Contrary to our expectations this compound was shown to be the ring-*A* aromatized ketone **2**.

This structure of the compound melting at 128 °C is compatible with its spectral properties. Its IR spectrum had peaks at 1685 (conjugated >C=O), 1585 (>C=C< aromatic) [4] and 680 cm⁻¹ (C—Br). The presence of a carbonyl chromophore conjugated with carbon-carbon double bond was further revealed by its UV spectrum (255 nm and 290 nm). The ¹H-NMR spectrum of compound **2** gave signals at δ 7.92 d, d (1 H, *J* = 8 Hz, *o*-coupled, and *J* = 2 Hz, *m*-coupled C₄-H), 7.3 m.c. (2 H, C₂-H and C₃-H), 2.4 s (C₁-CH₃), 0.75 (C₁₃-CH₃), 1.0 and 0.87 (other methyl protons). The appearance of signals in the downfield region (δ 7.92–7.3 integrating for 3 protons) strongly supported the presence of aromatized ring *A*. Two possible structures **2** and **3** can be suggested for the compound of m.p. 128 °C. A distinction between these two structures **2** and **3** was made with help of the NMR data. The signal at δ 7.92 (1 H) is clearly due to a proton beta to the C₆-keto group as in the case of **2**; the alternate structure **3**, where the beta position to the carbonyl is occupied by a methyl group, would be expected to give a multiplet for 3 protons in the region around δ 7.0. On the basis the compound melting at 128 °C has been identified as **2**.

Experimental

The m.p. is uncorrected. The UV spectrum was determined in 95% ethanol with a Beckman DK₂ spectrophotometer. The IR spectrum was recorded in KBr with a Perkin—Elmer 237 spectrophotometer. The NMR spectrum was obtained in CDCl₃ on a Varian A60 instrument with Me₄Si as the internal standard (s = singlet; d,d = double doublet; m.c. = multiplet centred at).



Reaction of 1 with sodium azide — H₂SO₄

A mixture of 1 [5] (1.0 g), dry benzene (25 mL) and conc. sulphuric acid (3 mL) was heated to a temperature of 80–90 °C and sodium azide (200 mg) was added gradually, with stirring. The reaction mixture was kept at this temperature for 15 h and then poured onto crushed ice. The benzene layer was separated and the aqueous layer was extracted several times with chloroform. The combined extracts were washed with sodium bicarbonate solution (5%) and water and dried over anhydrous sodium sulfate. The solvents were removed under reduced pressure; the semi-solid thus obtained was chromatographed over silica gel (20.0 g).

Elution with light petroleum ether (8 : 1) (15 mL fractions) yielded 7-bromo-1-methyl-19-nor-cholesta-1,3,5(10),7-tetraen-6-one (**2**), recrystallized from light petroleum (630 mg), m.p. 128 °C. C₂₇H₃₇OBr. Calcd. C 70.89; H 8.09. Found C 70.67; H 8.00%.

*

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ÜBER DIE SPEKTROGRAPHISCHEN EIGENSCHAFTEN DER KAPILLARELEKTRODEN, III*

ANWENDUNG VON MITTELSPANNUNGSFUNKENENTLADUNG

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Es wurde die Anwendungsmöglichkeit der Mittelspannungsfunkenentladung in Verbindung mit der spektrochemischen Anregung der Lösungen in Kapillarelektroden untersucht. Die Optimierungen waren auf die Verbesserung der optimalen Untergrundschwärzung, des Signal/Rauschen-Verhältnisses und des Parameters der analytischen Eichgeraden gerichtet.

Einleitung

Die Kapillarelektroden wurden bis jetzt fast ausschließlich in Verbindung mit der Abreißbogen-Anregung angewendet [1–3]. Bei diesen Versuchen wurde die Leistungsfähigkeit dieser Anregungsart nach den erreichten Werten der relativen Empfindlichkeit (Parameter B_X), der relativen Genauigkeit (Präzision) der Konzentrationsbestimmung (Parameter $s_{c_{x,r}}$) und den Nachweisgrenzen (Parameter c_L) beurteilt. Die gegebenen Wertungsparameter reichten für die Bestimmung von Haupt- und Nebenkomponten aus [4, 5], aber bei der Bestimmung von Spurenelementen [5, 6] wurde die gewünschte durchschnittliche Nachweisgrenze von $20 \mu\text{g} \cdot \text{mL}^{-1}$ entweder nur gerade oder aber auch nicht annähernd erreicht. Da aber diese Methode günstige Genauigkeitswerte aufweist, wurden für die Bestimmungen der Neben- und einiger Spurenelemente in auf Membranfiltern [7] aus der Luft ausfiltrierten Staubteilchen, die Kapillarelektroden angewendet. Um das Nachweisvermögen weiter zu verbessern wurde für die Anregung anstatt der Wechselstrombogen ein Mittelspannungsfunke eingesetzt.

Experimenteller Teil

Die durch Optimierungsversuche als optimal ermittelten allgemeinen experimentellen Versuchsbedingungen sind in Tabelle I angegeben. In Tabelle II sind die verwendeten Spektrallinien zusammen mit deren wichtigsten, der Literatur entnommenen [8] Parametern angeführt.

* II. Mitteilung: *Acta Chim. (Budapest)*, **48**, 203 (1966)

Tabelle I

Allgemeine Arbeitsbedingungen und Anregungsbedingungen

Spektrograph	Gitterspektrograph PGS-2, C. Zeiss-Jena, DDR $m = 2$; $D = 0,365 \cdot 10^{-6}$
Wellenlängenbereiche	1. von 240 nm bis 320 nm 2. von 300 nm bis 380 nm
Abbildungsart	dreilinsige mit Zwischenabbildung
Zwischenblende	5,0 mm
Spaltbreite	0,040 mm
Elektrodenart	Graphit, VEB Elektrokarbon, Topolčany, ČSSR
Trägerelektrode	SU-404 mit Teflon-Reservoir
Gegenelektrode	SU-202
Elektrodenabstand	4,0 mm
Emulsionsart	Orwo, DDR; WU-3
Entwickler	Orwo, DDR; F-43, 10 Minuten bei 20 °C
Anregungsart	Mittelspannungsfunkenanregung
Anregungsquelle	BIG-300; Ungarn
Primärspannung	420 V
Primärintensität	7 A
Dämpfungswiderstand	15,5 Ohm
Kapazität	3 μ F
Selbstinduktion	75 mH
Zündungszahl	100 pro Sekunde
Expositionszeit	120 Sekunden; 4×30 s unter Nachfüllung des Reservoirs mit neuen analysierenden Lösung
Mikrophotometer	G-II, C. Zeiss-Jena, DDR
Vergößerung	16 \times
Spalthöhe	14,0 mm
Spaltbreite	0,20 mm

Die gemessenen Schwärzungswerte wurden aufgrund der I -Transformationsoperation [9] in die I -Werte und manchmal auch in die relativen Intensitätswerte I mit dem Unterprogramm "TRANSL" umgerechnet [10]. Die notwendigen Transformationsparameter wurden wiederum rechnerisch mittels des Programms DEPALT G/K-M-78 ermittelt [11]. Für die Optimierung der Expositionszeit sowie für die Untersuchung der Proportionalität zwischen den Linienintensitäten und den zugehörigen Untergrundintensitäten wurden die Beziehungskurven [12, 13] herangezogen. Für diese Berechnungen wurde das Programm ECC-F-72 [14] verwendet. Für die Ermittlung der Parameter der analytischen Eichgeraden wurde eine Minimalisierungsprozedur [15] in Form des Rechenprogramms CANCAL ACL-MO-78 [16] angewendet, welches gleichzeitig auch durch statistische Testprüfungen die ganze Prozedur kontrolliert. Die Werte der Nachweisgrenzen, Garantiegrenzen der Reinheit sowie die zugehörigen Standardabweichungen wurden mit Hilfe des Rechenprogramms NG-LM-71, welches die Rechensequenz [17] berücksichtigt, ermittelt.

Bei den analytischen Arbeiten wurden zwei bis sechs Membranfilter in Salpetersäure (1 : 4) aufgelöst. Diese Lösung wurde nach Abdampfung des überflüssigen Anteils in einem 50 mL Meßkolben aufgefüllt. Die Zahl der verwendeten Membranfilter wurde so gewählt, daß die Staubmenge maximal 50 mg und minimal 10 mg betrug.

Die Parameter der optimierten Eichgeraden sind zusammen mit den Werten der Nachweis- und Garantiegrenzen der Reinheit in Tabelle III angegeben.

Diskussion

In der Emissionsspektrochemie muß die Optimierung [18] einer gegebenen analytische Aufgabe vor allem zwei Faktoren berücksichtigen. Es ist die durchschnittliche Untergrundschwärzung und das Signal/Rauschen-Ver-

Tabelle II

Verwendete Spektrallinien und deren Parameter

Element	Wellenlänge in nm	Intensität im Cu-Bogen	Ionisations- potential in kJ · mole ⁻¹	Anregungspotential in kJ · mole ⁻¹
Al I	256,798	240	578	466
Al I	257,510	480		466
Al I	266,039	200		459
Co I	252,136	4 300	759	478
Co I	257,435	960		516
Co I	341,234	6 700		401
Co I	347,402	8 000	653	401 353 597
Cr II	267,716	1 800		572
Cr II	283,563	250		500
Cr I	298,647	2 100	745	591
Cu I	261,837	400		365
Cu I	327,396	25 000		486
Fe I	248,815	2 600	760	402
Fe I	302,107	1 600		348
Fe I	344,061	4 000		428
Mg I	279,553	10 000	737	409
Ni I	300,363	2 200		438
Ni I	301,200	3 700		352
Ni I	341,476	8 200	716	551
Pb I	261,418	7 000		554
Pb I	280,199	10 000		419
Pb I	368,348	14 000	907	751
Zn I	334,502	1 400		432
Pd I	276,309	1 900		488
Pd I	302,791	1 500	804	448
Pd I	324,270	11 000		448
Pd I	325,164	2 700		488

Doublett

Bemerkung: der Umrechnungsfaktor [22] für 1 kJ · mole⁻¹ ist 0,01036 eV (SI-Einheiten!)

hältnis. Erstens ist es erwünscht, mit solchen Spektren zu arbeiten, die im ganzen aktuellen Wellenlängenbereich eine optimale Untergrundschwärzung aufweisen. Dadurch kann man die geringste Untergrundintensitätsfluktuationen erreichen, die letzten Endes das Nachweisvermögen anhebt. Die Steigerung des Nachweisvermögens kann aber auch durch Optimierung der Signal/Rauschen-Verhältnisse erreicht werden.

Bei der endgültigen Auswahl der analytischen Linienpaare, die zur Konzentrationsbestimmung herangezogen werden, sind unbestritten die Parameter der aufgestellten analytischen Eichgeraden die entscheidendsten Werte. Dabei ist der Koeffizient der Bestimmtheitsmaße $R\%$ ($R = r^2 \cdot 100$) nur ein Hilfswert und stellt das Maß der Erschöpfung des Optimierungsvermögens der Methode dar. Entscheidende Werte sind aber die Richtungstangente der Eichgeraden und die relative Genauigkeit der Konzentrationsbestimmung sowie die Linearität.

Tabelle III
Parameter der optimierten analytischen Eichgeraden

Linienpaar	Bestimmtheitsmaß [%]	Parameter $B_X \pm s_{B_X}$	Relative Genauigkeit [%]	Testprüfungen		Nachweisgrenze [$\mu\text{g} \cdot \text{mL}^{-1}$]	Garantiegrenze [$\mu\text{g} \cdot \text{mL}^{-1}$]
				$t_{B_X} = 1$	t_{LIN}		
Al 257,5 Pd 276,5	95,6	$0,86 \pm 0,04$	$\pm 19,0$	⊖	⊕	$15,4 \pm 7,0$	$31,7 \pm 15,3$
Co 341,1 Pd 325,1	98,9	$0,99 \pm 0,04$	$\pm 13,4$	⊕	⊕	$4,0 \pm 1,0$	$7,0 \pm 2,0$
Cr 267,7 Pd 276,5	99,2	$1,25 \pm 0,03$	$\pm 11,3$	⊖	⊕	$1,6 \pm 0,2$	$2,8 \pm 0,4$
Cu 327,1 Pd 324,3	92,6	$1,29 \pm 0,09$	$\pm 32,4$	⊖	⊕		
Fe 302,1 Pd 296,3	99,5	$1,12 \pm 0,03$	$\pm 10,3$	⊖	⊕	$1,1 \pm 0,1$	$2,2 \pm 0,3$
Mg 279,6 Pd 302,8	97,8	$0,99 \pm 0,04$	$\pm 22,4$	⊕	⊕		
Ni 300,4 Pd 276,3	99,5	$0,91 \pm 0,02$	$\pm 13,2$	⊖	⊕	$0,4 \pm 0,04$	$0,5 \pm 0,07$
Pb 280,2 Pd 276,3	97,8	$1,01 \pm 0,03$	$\pm 17,9$	⊕	⊕	$9,8 \pm 3,8$	$27,0 \pm 10,0$
Zn 334,5 Pd 324,3	96,0	$0,84 \pm 0,05$	$\pm 54,8$	⊖	⊕	$0,9 \pm 0,5$	$2,0 \pm 1,1$

Optimierung der Expositionszeit

Die Optimierung der spektrochemischen analytischen Methoden verlangt vor allem die Festlegung der günstigsten Expositionszeit. Dies ist durch die Fahrspetrogrammtechnik [19] zu erreichen. Bei dieser Optimierung müssen jedoch zwei Faktoren berücksichtigt werden: das Signal/Rauschen-Verhältnis sowie die optimale Untergrundschwärzung. Die Optimierung der erstgenannten Erscheinung kann anhand der Abhängigkeit (1) durchgeführt werden. Diese Funktionsabhängigkeit weist entweder einen ständig steigenden Charakter auf, oder aber einen sättigungsartigen Verlauf eventuell mit einem flachen Maximum.

$$\sum_1^Q \frac{(I_{X,L+U,i} - I_{X,U,i})}{I_{X,U,i}} = f\left(\sum_1^Q t_i\right) \quad (1)$$

Dabei stellt i die Folge und Q die Endzahl der Fahrspetrogrammschritte dar. Die Funktionsabhängigkeit (2), die eine Hilfsfunktion ist,

$$\sum_1^Q I_{X,L,i} = \sum_1^Q (I_{X,L+U,i} - I_{X,U,i}) = f\left(\sum_1^Q t_i\right) \quad (2)$$

veranschaulicht die Abänderungen der Nettointensitätswerte in Abhängigkeit der Exposition t_i . Die Entscheidung bei der Wahl der Expositionszeit läßt für den Verlauf mit stetig steigender Tendenz eine so lange Exposition zu, bis man die optimale Untergrundschwärzung erreicht. Dagegen ist beim Maximumverlauf die Erreichung des Maximum maßgebend.

Die Festlegung der optimalen Untergrundschwärzung wurde anhand der von DOERFFEL und DEMUTH [20] empfohlenen Gleichung (3) ermittelt:

$$S_{U,opt} = 0,183 \cdot \gamma \quad (3)$$

Das aber bedeutet, daß dieser Wert, ebenso wie der γ -Wert, wellenlängenabhängig [9] ist. Diese Tatsache, dadurch daß die γ -Werte oberhalb von 310 nm eine steigende Tendenz aufweisen, bedeutet, daß der Wert $S_{U,opt}$ oberhalb von 310 nm wiederum einen steigenden Charakter besitzen wird. Die so ermittelten $S_{U,opt}$ Werte wurden jedoch für die weitere Bearbeitung konsequent in die relativen Intensitätswerte $I_{U,opt}$ umgerechnet.

Die Festlegung der endgültigen optimalen Expositionszeiten ist in den Abbildungen 1 und 2, die für Al und Pb gelten, veranschaulicht. Aus diesen Abbildungen ist ersichtlich, daß gleichzeitig mit der Erreichung der optimalen Untergrundintensitätswerte $I_{U,opt}$ in der Funktionsabhängigkeit (4),

$$\sum_1^Q I_{X,U,i} = f \left(\sum_1^Q t_i \right) \quad (4)$$

auch das erwartete Maximum der Funktion (1) eintrat. Die Linien der anderen Elemente haben sich mit Ausnahme der Fe 344,1- und Ni 341,5-Linien, ganz ähnlich wie die Al- und Pb-Linien verhalten. Bei den genannten zwei Linien

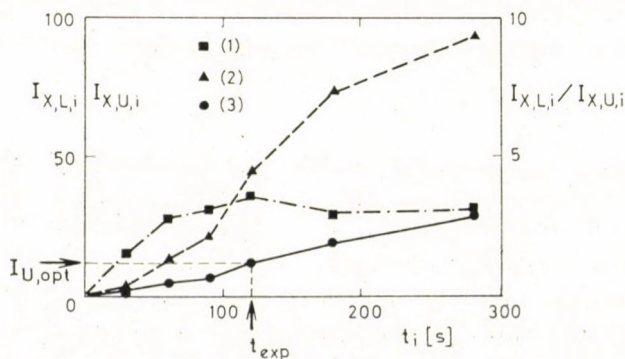


Abb. 1. Graphische Darstellung des Verlaufs der Abhängigkeiten (1), (2) und (4); Spektrallinie: Al 257,5. (1) Funktionsabhängigkeit (1); (2) Funktionsabhängigkeit (2); (3) Funktionsabhängigkeit (4)

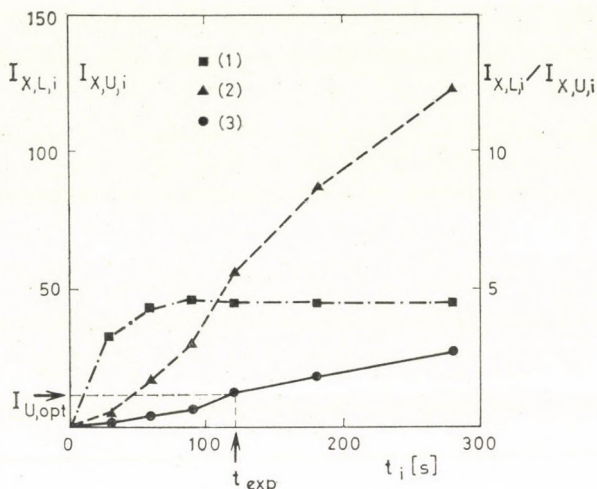


Abb. 2. Graphische Darstellung des Verlaufs der Abhängigkeiten (1), (2) und (4); Spektrallinie: Pb 261,4. (1) Funktionsabhängigkeit (1); (2) Funktionsabhängigkeit (2); (3) Funktionsabhängigkeit (4)

(Fe und Ni) wurde schon vor dem Maximum der Funktion (1), u. zw. 30 Sekunden früher, die optimale Untergrundintensität erreicht. Dieses Phänomen kann den in diesem Wellenlängenbereich schon bemerkbaren Molekülbanden zugeschrieben werden.

Nachträglich wurde auch die Proportionalität zwischen den Nettointensitäten $I_{X,L}$ der analytischen Elemente und den zugehörigen Untergrundintensitäten $I_{X,U}$ auf Grund einer Normierung geprüft und graphisch dargestellt. Die graphischen Darstellungen (Abb. 3 und 4) veranschaulichen die Funktionsabhängigkeit (5) wiederum für die Al- und Pb-Linien.

$$\left[\frac{\sum_1^Q I_{X,L,i}}{I_{X,L,Q}} \cdot 100 \right] = f \left[\frac{\sum_1^Q I_{X,U,i}}{I_{X,U,Q}} \cdot 100 \right]. \quad (5)$$

Die Elemente wie Al (Abb. 3), Cr, Mg und teilweise auch Fe und Ni weisen nach einer 120 Sekunden langen Expositionszeit gewisse Störungen der Entfaltung der proportionalen Erhöhung der Nettointensitäten und deren Untergrundintensitäten auf. Dagegen ist bei allen weiteren Linien von Cu, Pb (Abb. 4) und Zn in der Gesamtexpositionszeit bis zu 290 Sekunden der proportionale Verlauf erreicht. Die diskutierten Abhängigkeiten haben also die 120 Sekunden lange Expositionszeit (4×30 Sekunden) als die optimale Expositionszeitspannweite für alle analytische Elemente bestätigt.

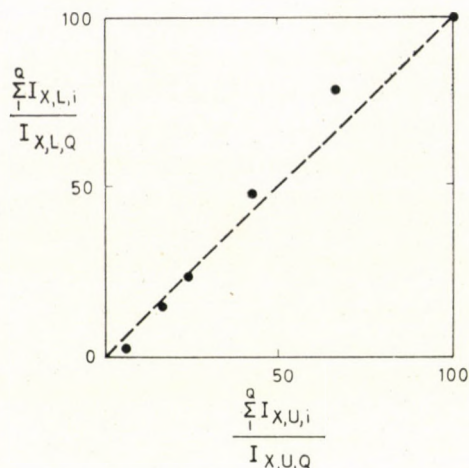


Abb. 3. Graphische Darstellung des Verlaufs der Funktionsabhängigkeit (5); Linie: Al 257,5

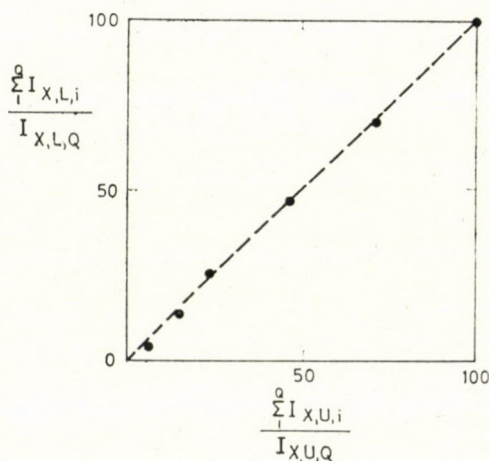


Abb. 4. Graphische Darstellung des Verlaufs der Funktionsabhängigkeit (5); Linie: Pb 261,4

Bewertung der analytischen Eichgeraden

Anhand der Vorexperimente und der diskutierten Teiloptimierungen wurden unter den endgültigen experimentellen Bedingungen (Tab. I) die analytischen Eichgeraden aufgestellt. An die zuverlässigen Eichgeraden wurden von vornherein folgende Anforderungen gestellt: die experimentellen $\Delta Y_{i,j}$ -Werte müssen mindestens für 1,5 Ordnungslängen der Konzentrationswerte einen signifikant linearen Verlauf aufweisen, und zwar mindestens mit 99% iger statistischer Sicherheit; bei einer Linienpaar-Auswahlmöglich-

keit sollen diese Linienpaare bevorzugt werden, die mindestens 95%ige Bestimmtheitsmaße erreichen; schließlich soll möglichst der B_X -Parameterwert, — die Richtungstangente der Eichgeraden —, die die relative Empfindlichkeit der Methode darstellt, für die Atomlinien entweder gleich oder kleiner als Eins sein, und zwar wiederum mit 99%iger statistischer Sicherheit.

Die bei Beachtung dieser Richtlinien erhaltenen Ergebnisse sind in Tabelle III angegeben. Hier soll erwähnt werden, daß nicht alle Kombinationen der in der Tabelle II angegebenen analytischen Linien und Bezugslinien

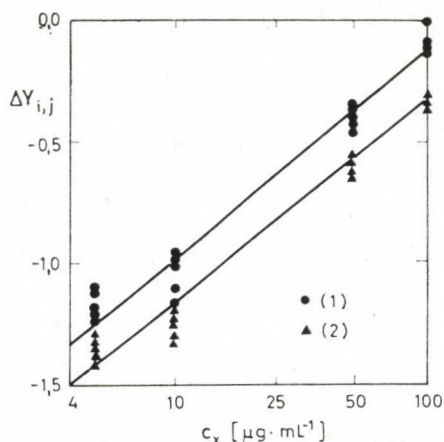


Abb. 5. Analytische Eichgeraden: (1) Linienpaar Al 257,5/Pd 276,3; (2) Linienpaar Al 257,5 Pd 302,8

die oben festgelegten Auswahlkriterien erfüllen. Die Kombinationen der Al 256,8 und Al 266,0 Linien mit den Pd-Linien haben wegen der schwachen Intensitäten der Al-Linien ganz ungünstige Nachweisgrenzen ergeben. Bei der Endbewertung wurde die Kombination Al 257,5/Pd 276,3 gewählt (Abb. 5), da diese Linienkombination die günstigste Nachweisgrenze aufwies. Aus ganz ähnlichen Gründen mußte auf die Linien Co 257,4, Cr 283,6 und Cu 261,8 verzichtet werden. Der Untergrund der Linien Co 347,4, Cr 298,7 (Abb. 6), Ni 341,5 und Pb 368,3 (Abb. 7) war durch die systematische Struktur gekennzeichnet, was nicht nur die Bestimmung von Nachweisgrenzen in Frage gestellt, sondern auch die Linearität der Eichgeraden durch Störpegel gestört hat. Dagegen war die Ni 300,4 Linie frei von Selbstabsorptionserscheinungen und wies dadurch einen annehmbaren relativen Genauigkeitswert der Konzentrationsbestimmung auf (Abb. 8). Die Linien Co 252,1, Fe 248,8 und Pb 261,4 (Abb. 9) wiesen schon deutliche Selbstabsorptionserscheinungen ($B_X \doteq 0,5$ bis $0,8$) auf und dadurch eignen sie sich weniger zur analytischen Anwendung. Für die Pb-Bestimmung

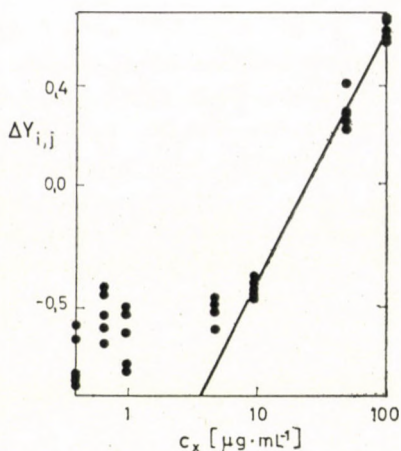


Abb. 6. Analytische Eichgerade des Linienpaars Cr 298,5/Pd 257,5 nach der Begrenzung des Konzentrationsintervalls

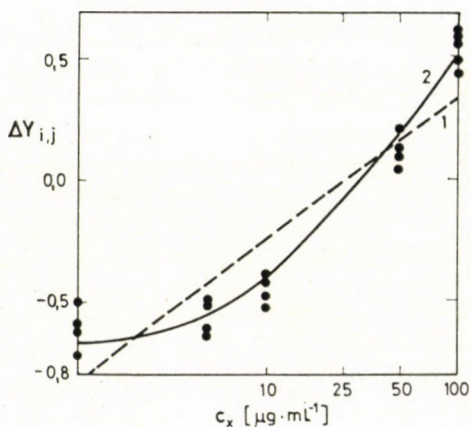


Abb. 7. Analytische Eichgerade des Linienpaars Pb 368,3/Pd 325,2; (1) berechneter Linearverlauf, falsche Eichgerade; (2) graphisch konstruierte, nichtlineare Eichgerade

eignete sich am besten das Linienpaar Pb 280,2/Pd 276,3 (Abb. 10). Schliesslich haben die analytischen Linien Fe 244,1 und Ni 301,2 ungünstige relative Genauigkeitswerte der Konzentrationsbestimmung ($s_{c_{x,r}} \doteq \pm 30\%$) ergeben und deswegen wurden ihre Linienkombinationen aus der Auswahl weggelassen.

Alle endgültig ausgewählten Linienpaare (Tab. III) weisen einen signifikant linearen Verlauf auf, und zwar mindestens mit einer 99%igen statistischen Sicherheit, sowie ein Bestimmtheitsmaß, das mit Ausnahme der Cu-Linie immer größer als 95% war. Dies gilt immer für den Konzentrationsintervall von $5 \mu\text{g} \cdot \text{mL}^{-1}$ bis $100 \mu\text{g} \cdot \text{mL}^{-1}$. Der Parameter B_X erreicht nur bei den Linienpaaren Co/Pd, Mg/Pd und Pb/Pd den idealen Wert ($B_X \doteq 1$). Das bedeu-

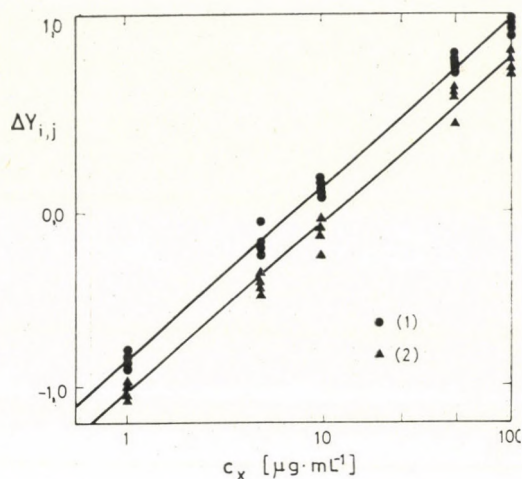


Abb. 8. Analytische Eichgeraden: (1) Liniennpaar Ni 300,4/Pd 276,3; (2) Liniennpaar Ni 300,4/Pd 302,8

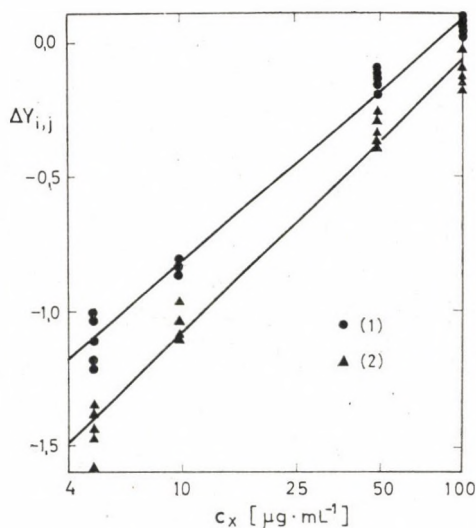


Abb. 9. Analytische Eichgeraden: (1) Liniennpaar Pb 261,4/Pd 276,3; (2) Liniennpaar Pb 261,4/Pd 302,8

tet aber, daß bei allen anderen Liniennpaaren theoretisch die Möglichkeiten einer Verbesserung der Leistungsparameter besteht, aber höchstwahrscheinlich nur auf Kosten der Einengung der aktuellen Konzentrationsspannweite der Eichgeraden, hauptsächlich dann, wenn auch gleichzeitig am "Blindwert" oder "Störpegel" eine Korrektur vorgenommen wird. Bei dem Liniennpaar Cr/Pd

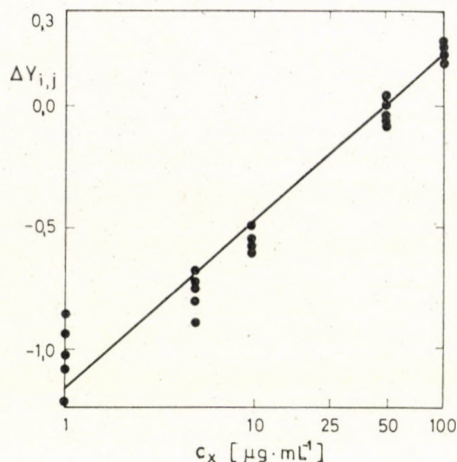


Abb. 10. Analytische Eichgerade des Linienpaars Pb 280,2/Pd276,3

überrascht der erreichte, den Zahlenwert Eins wesentlich überschreitende B_X -Wert nicht, da die Cr II 267,7 Linie eine Ionenlinie ist. Dagegen werden die ungünstigen B_X -Werte des Cu/Pd-Linienpaars wahrscheinlich entweder durch die unterschiedlichen spektrochemischen Eigenschaften des schwärflüchtigen Pd und leichtflüchtigen Cu hervorgerufen oder aber es handelt sich um einen nichtidentifizierten "Störpegel" bei der Cu-Linie.

Die erreichten relativen Genauigkeitswerte der Konzentrationsbestimmung schwanken im Durchschnitt um den Wert $\pm 15\%$. Dadurch liegen sie für die Lösungsmethoden [1–3] der Emissionsspektrochemie gerade am Rande der akzeptablen Werte [21]. Dagegen liegen die Nachweisgrenzen, mit Ausnahme von Al und Pb, unter $4 \mu\text{g} \cdot \text{mL}^{-1}$. Überraschend niedrig ist der Wert von $0,9 \mu\text{g} \cdot \text{mL}^{-1}$ für Zn, aber leider wird diese günstige Nachweisgrenze von einem keinesfalls annehmbaren relativen Genauigkeitswert begleitet. Für die Mg-Linien wurde die Nachweisgrenze nicht berechnet, da Mg in Staubproben entweder ein Nebenelement oder aber ein Hauptelement darstellt. Die Ermittlung der Nachweisgrenzen für die Cu-Linien wurde durch mehrere Faktoren verhindert; hauptsächlich haben die Verunreinigungen in anderen für die Eichung benutzten sog. spektralreinen Chemikalien ungünstige Bedingungen geschaffen.

Schlußfolgerungen

Die Untersuchung der Anwendung der Mittelspannungsfunkenanregung für die Kapillarelektroden hat bestätigt, daß diese Anregungsart zur Verbesserung des Nachweisvermögens beitrug, Allerdings geht diese Verbesserung mit einer Abnahme der relativen Genauigkeit der Konzentrationsbestimmung

einher. Die untersuchte Methode eignet sich für die Neben- und Spurenelementbestimmung bis ca $4 \mu\text{g} \cdot \text{mL}^{-1}$. Die Unterschiede in den Ionisationspotentialen und Anregungspotentialen der analytischen Elemente und der Bezugs-elemente bringen bei Mehrkomponentenanalysen mit Mittelspannungsfunkenanregung bei weitem nicht so große Schwierigkeiten wie bei der Bogenanregung von elektrisch nichtleitenden Pulverproben mit sich.

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THE EFFECT OF THIOUREA AND ITS DERIVATIVES ON HYDROGEN OVERVOLTAGE AT THE DROPPING GALLIUM ELECTRODE

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The effect of thiourea and its derivatives on hydrogen overvoltage at the dropping gallium electrode has been investigated in perchloric acid solutions. It has been established that the thiourea derivatives investigated increase the rate of the hydrogen evolution reaction, and their catalytic action increases in the order SMTU < TU < < DMTU < DETU < TMTU at more negative potential values ($\eta < -0.7$ V). It is assumed that the catalytic action of the additives can be explained by their adsorption at the electrode surface and by the formation under the participation of H_3O^+ ion of a surface complex, the discharge of which requires a lower activation energy, than the discharge of H_3O^+ .

The effect of urea, thiourea and selenourea on hydrogen overvoltage measured at the gallium electrode has been reported in our earlier communication [1]. The catalytic effect of the said compounds on electrolytic hydrogen evolution increases in the order urea < thiourea < selenourea. An investigation of the effect of the substituted derivatives of the above additives on the rate of hydrogen evolution at the liquid gallium electrode in dependence on the nature and position of the substituents seemed to be of interest. Though selenourea has the highest catalytic effect, owing to its instability, it seemed more suitable to investigate the stable thiourea derivatives, similarly of important catalytic action, easy to handle and well known from electrochemical point of view. Thus, e.g. in conjunction with the corrosion inhibitors of iron several *N*-substituted derivatives have been investigated, and a relationship was found between the efficiency of inhibition and the size of the substituting groups [2].

Experimental

Investigations were carried out using the experimental and evaluation methods described in [1] at the dropping electrode prepared from gallium of 99.9999% purity, in perchloric acid solutions containing different thiourea derivatives. The perchloric acid solution was prepared from 70% perchloric acid of analytical grade (Merck) with bidistilled water, and the following additives were used: twice recrystallized thiourea (TU) manufactured by Reanal; twice recrystallized *N,N'*-dimethyl thiourea (DMTU). *N,N'*-diethyl thiourea (DETU); *N,N'*-tetramethyl thiourea (TMTU); *S*-methyl thiourea (SMTU) manufactured by Merck.

The $\eta - \lg j$ curves plotted from current density (j) – overvoltage (η) value-pairs, obtained from experimental data measured in solutions containing $1 \text{ mol/dm}^3 \text{ HClO}_4 + X$

mol/dm³ additive, are shown in Figs 1–4. As can be seen from Fig. 1, in the solutions containing 1 mol/dm³ HClO₄ + 10⁻⁴ mol/dm³ additive, the rate of hydrogen evolution increases in the presence of the additives (at $\eta = \text{const}$) in the order SMTU < TU < DETU < TMTU, as compared to the value measured in pure perchloric acid solution. The slope of the straight sections of the polarization curves (b) changes between 0.068 and 0.093 V. In the more negative potential range the $\eta - \lg j$ curves deviate from the straight line, the value of $\frac{\partial \eta}{\partial \lg j}$ increases, which presumably can be attributed to the desorption of the additives. The potential value at which the curve deviates from the straight line, falls in the case of *N*-substituted derivatives within the range from -0.65 V to -0.75 V, while in the cases of TU and SMTU this value is close to -0.8 V.

To elucidate the relationship between the concentration of the additives and the hydrogen evolution reaction, the polarization curves have been recorded for the single additives in 1 mol/dm³ perchloric acid solutions of various additive concentrations (10⁻⁶ to 10⁻² mol/dm³). This is illustrated in Fig. 2, showing the $\eta - \lg j$ curves measured in perchloric acid for six

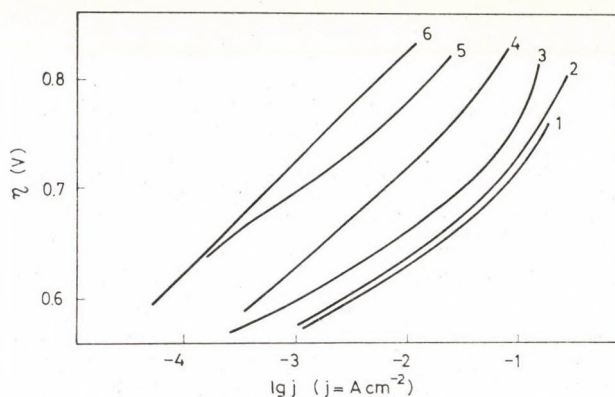


Fig. 1. $\eta - \lg j$ curves at the dropping gallium electrode in 1 mol/dm³ HClO₄ + 10⁻⁴ mol/dm³ additive solutions, ① TMTU; ② DETU; ③ DMTU; ④ TU; in ⑤ 1 mol/dm³ HClO₄ + 5.7 · 10⁻⁴ mol/dm³ SMTU solution, in ⑥ 1 mol/dm³ HClO₄ solution

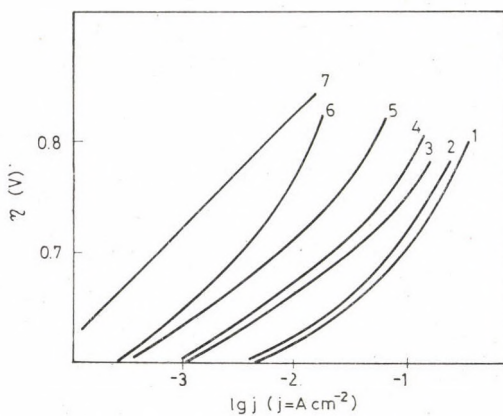


Fig. 2. $\eta - \lg j$ curves at the dropping gallium electrode in 1 mol/dm³ HClO₄ + DMTU solution of different concentrations, ① 3.6 · 10⁻²; ② 7.1 · 10⁻³; ③ 1.1 · 10⁻⁴; ④ 6.4 · 10⁻⁵; ⑤ 1.1 · 10⁻⁵; ⑥ 1.0 · 10⁻⁶ mol/dm³ DMTU, ⑦ in 1 mol/dm³ HClO₄ solution

different DMTU concentrations. It can be seen from the figure that the rate of hydrogen evolution increases with an increase in additive concentration. In the case of 10^{-6} to 10^{-2} mol/dm³ additive, the slope of the polarization curve varies between 0.120 and 0.116 V at potential values of $\eta > -0.75$ V, but at $\eta \approx -0.75$ V it diverts from the straight line. $\eta - \lg j$ curves of similar course have been obtained in the presence of TU and DETU of various concentrations, $\Delta \lg j$ increasing also in these latter two cases with increasing additive concentration.

As can be seen from Fig. 3, in the presence of TMTU the pattern of the $\eta - \lg j$ curves is somewhat different from the aforementioned. It can be noted from the figure that in the additive concentration range from 10^{-5} to 10^{-2} mol/dm³ the catalytic action (already relatively strong at an additive concentration of 10^{-5} mol/dm³) slightly changes on a further increase in concentration. Curves measured in perchloric acid solutions containing 10^{-2} and 10^{-3} mol/dm³ TMTU intersect. Depending on the concentration of the additive, the deviation of the polarization curves from the straight line falls into the potential interval $\eta = -0.70$ to -0.75 V, and is shifted with decreasing TMTU concentration towards more negative potentials. The slope of the curves varies between 0.068 and 0.105 V. The anomaly observed in the concentration

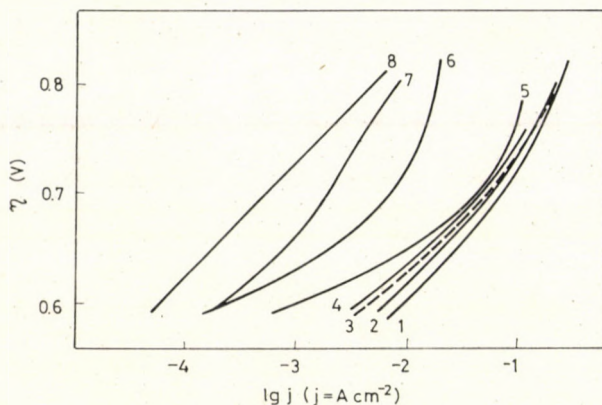


Fig. 3. $\eta - \lg j$ curves at the dropping gallium electrode in 1 mol/dm³ HClO₄ + TMTU solution of different concentrations, ① $1.0 \cdot 10^{-1}$; ② $1.0 \cdot 10^{-2}$; ③ $1.0 \cdot 10^{-3}$; ④ $4.3 \cdot 10^{-4}$; ⑤ $1.15 \cdot 10^{-5}$; ⑥ $1.15 \cdot 10^{-6}$; ⑦ $1.2 \cdot 10^{-7}$ mol/dm³ TMTU, ⑧ in 1 mol/dm³ HClO₄ solution

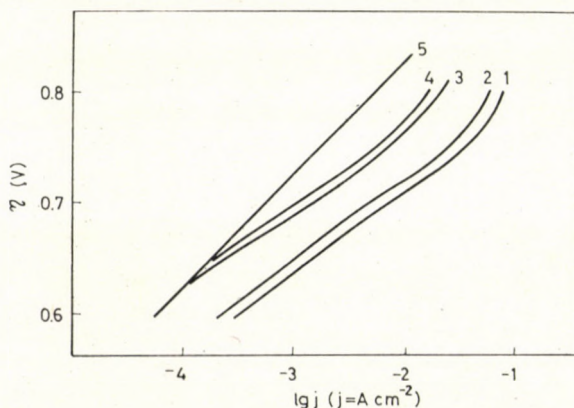


Fig. 4. $\eta - \lg j$ curves at the dropping gallium electrode in 1 mol/dm³ HClO₄ + SMTU solution of different concentrations, ① $2.2 \cdot 10^{-2}$; ② $1.8 \cdot 10^{-2}$; ③ $1.35 \cdot 10^{-3}$; ④ $5.7 \cdot 10^{-4}$ mol/dm³ SMTU; in ⑤ 1 mol/dm³ HClO₄ solution

dependence of the polarization curves obtained in the presence of TMTU additive can be presumably explained by multilayer adsorption due to the different molecular structure of this additive from that of the other additives (DMTU, DETU, TU).

In the presence of SMTU polarization curves of different course than those measured in the presence of *N*-substituted thiourea derivatives are obtained. As can be seen from Fig. 4, the effect of this additive on the rate of hydrogen evolution differs most essentially in so far from that of *N*-substituted thiourea derivatives and of thiourea that at low SMTU concentrations ($1.25 \cdot 10^{-3}$ to $5.7 \cdot 10^{-4}$ mol/dm³) and at potential values of $\eta > -0.70$ V the change of reaction rate decreases with a shift of the potential in the positive direction, to attain at $\eta = -0.66$ V the value measured in pure acid solution.

This different behaviour may be due to the fact that of all the TU derivatives investigated SMTU is the sole ionic compound in acid solution, and the solution contains (SMTUH)⁺ ions formed by protonation, the adsorption of which diminishes at the electrode surface with a shift of the potential in positive direction.

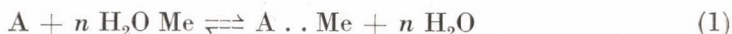
Interpretation of the Results

The slope of the polarization curves measured in the presence of TU derivatives is at potentials more positive than -0.65 to -0.75 V near parallel to the curves measured in pure perchloric acid solution at the liquid gallium electrode, which indicates that the rate determining step of the hydrogen evolution reaction is also in the presence of the additives investigated the charge transfer.

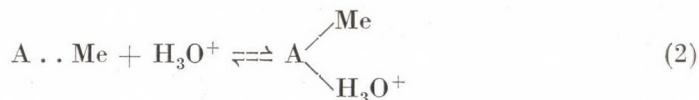
According to our assumption the additives investigated (A) exert their catalytic action by adsorption at the electrode surface and by the formation

of a surface complex $A \begin{matrix} \diagup \text{Me} \\ \diagdown \text{H}_3\text{O}^+ \end{matrix}$ under participation of the H_3O^+ ions, the discharge of which requires a lower activation energy than the discharge of H_3O^+ .

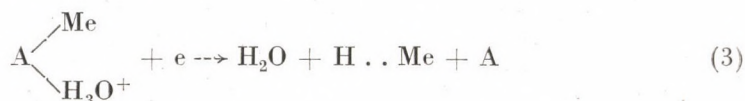
The first step of the mechanism assumed is the adsorption



which is followed by the formation of the surface complex



The discharge of the surface complex, the rate determining step of the catalytic process, may be the step



Current density measured (j) is the sum of two parallel processes, the catalytic step according to (3) and the rate of the direct process $\text{H}_3\text{O}^+ + e \rightarrow$.

The surface coverage of the electrode with respect to the assumed complex $[\text{MeA H}_3\text{O}^+]$ is θ , while the rate of process (3) is $j_K\theta$ (where j_K is the rate of the catalytic process if $\theta = 1$), at the uncovered surface the direct discharge of H_3O^+ proceeds at a current density of j_0 , the rate of this step is $j_0(1 - \theta)$. The current density measured can be described with the following equation:

$$j = j_0(1 - \theta) + j_K\theta \quad (4)$$

For the elucidation of the relationship between the concentration and the catalytic action of the additive the function $\theta = f(c)$ ought to be known. The concrete form of the function is not known, and as first step it is assumed that the adsorption of catalyst A can be described with Langmuir isotherm:

$$c_A K = \frac{\theta}{1 - \theta} \quad (5)$$

where c_A is the catalyst concentration in the bulk of the solution, and K is the equilibrium constant of adsorption.

From equations (4) and (5) we have:

$$\frac{1}{(j - j_0)} = \frac{K}{c_A(j_K - j_0)} + \frac{1}{(j_K - j_0)} \quad (6)$$

If the adsorption of the catalysts can be described by a Langmuir isotherm, then the plotting of the pairs of values $j - c_A$ belonging together in the coordinate system $1/(j - j_0) - 1/c_A$ must give a straight line.

On plotting in the above way the value pairs belonging together in the case of the additives investigated, with the exception of SMTU, a straight line is obtained only in the region of low concentrations. At higher concentrations, the curves deviate, depending on the nature of the additive, indicating that the Langmuir isotherm is not suitable for the description of the compounds investigated, presumably because it does not take into consideration the interaction of the particles adsorbed at the electrode surface.

More suitable for the description of the relationship between the concentration and the catalytic action of the additives are isotherms taking into account the interaction of the particles of the adsorbate. An isotherm of this kind is Frumkin isotherm or other isotherms taking into consideration the interactions mentioned [3].

Using Frumkin isotherm

$$B c_A = \frac{\theta}{1 - \theta} \exp[-2a\theta] \quad (7)$$

(where B takes into consideration the equilibrium constant of adsorption, a the interaction between the adsorbed particles), substituting Eq. (7) into

Eq. (4), rearranging the equation, and assuming that $j_K \gg j_0$, after logarithmic transformation the equation

$$\lg(j - j_0) = \lg j_K B + \lg c_A + \lg(1 - \theta) + 2a\theta \quad (8)$$

is obtained, which has at low coverage, $\theta \approx 0$, the simplified form

$$\lg(j - j_0) \approx \lg j_K B + \lg c_A \quad (9)$$

At constant potential values j_K , j_0 and B are constant, so that at the simplifying conditions used in (9) $\lg(j - j_0)$ changes linearly with $\lg c_A$. At higher concentrations, when $\theta \neq 0$ the terms $\lg(1 - \theta)$ and $2a\theta$ can not be any more neglected with increasing θ , and the curve $\lg(j - j_0) - \lg c_A$ deviates from the straight line, $\lg(1 - \theta)$ taking into consideration the decrease in number of the free sites, and $2a\theta$ the interaction between the molecules at the electrode surface.

To control the correctness of the assumed relationships between the catalytic action and the adsorption of the additives, the respective pairs of values $\lg(j - j_0)$ and $\lg c_A$ have been plotted at constant potential $\eta = -0.70$ V for the single thiourea derivatives. As shown by Fig. 5, in the case of TU derivatives points determined by the pairs of values $\lg(j - j_0) - \lg c_A$, calculated from data measured at low concentrations lie along a straight line, while at higher concentrations the points do not lie, with the exception of SMTU, along a straight line, the curve approaches a saturation value.

The concentration value (c^*), at which the curve deviates from the straight line obtained at low concentrations, depends on the adsorptive capability of the additive. The lower is the concentration at which this devia-

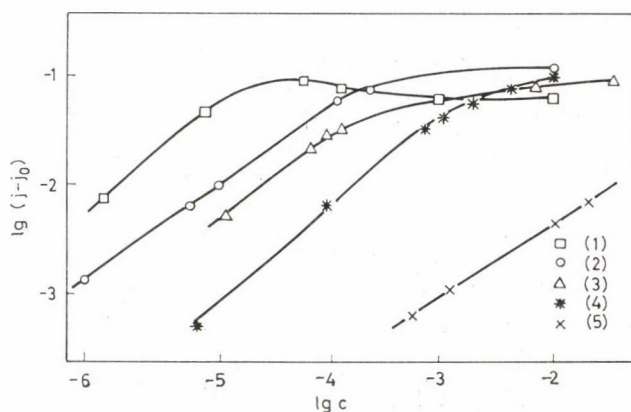


Fig. 5. $\lg j - \lg c$ curves of thiourea derivatives in 1 mol/dm³ perchloric acid solution at $\eta = -0.74$ V overvoltage: ① TMTU, ② DETU, ③ DMTU, ④ TU and ⑤ SMTU

tion occurs, the higher is the adsorptive capability of the given additive, the interaction between the adsorbed additive molecules. $\lg c^*$ values characteristic of adsorptive capability are summarized in Table I.

In the case of SMTU, related $\lg(j - j_0) - \lg c_A$ values calculated from data measured lie along a straight line, in the concentration range investigated

Table I

	$\varphi = -0.74$ V		$\varphi = -0.70$ V	
	$j^* \left[\frac{\text{A}}{\text{cm}^2} \right]$	$\lg c^*$	$j^* \left[\frac{\text{A}}{\text{cm}^2} \right]$	$\lg c^*$
SMTU	0.03	—	0.01	—
TU	0.09	-2.79	0.07	-3.11
DMTU	0.12	-3.21	0.06	-3.57
DETU	0.15	-4.49	0.08	-4.13
TMTU	0.52	-4.82	0.16	-4.82

the curve does not deviate, indicating that in this case the value of Θ is so small that equation (9) can be applied.

On the $\lg(j - j_0) - \lg c_A$ curve plotted on the basis of data measured for TMTU, small local maximum appear in the 10^{-6} to 10^{-5} concentration range (Fig. 5), which presumably are due to the multilayer adsorption of the given compound. The magnitude of the maximum decreases with increasing potential.

The quantity j_K in equation (4) is proportional to the catalysis constant of reaction (3), and is thus suitable for the comparison of the catalytic activity of the additives at constant potential. j_K values were calculated by plotting the values obtained from experimental data according to Eq. (5) in the coordinate system $1/(j - j_0) - 1/c_A$, and by extrapolating to $1/c_A \rightarrow 0$ value the straight section obtained at low concentrations, corresponding to the validity of Langmuir isotherm. j_K values calculated from the axial intersect obtained are summarized in Table I. It will be noted from data in the Table that in the potential range investigated j_K increases with a shift of the potential in negative direction. The order of the j_K values of the additives depends on the potential, being in the potential range $\varphi > -0.70$ V SMTU < DMTU < TU < DETU < < TMTU, while at potential values of $\varphi < -0.70$ V in the order SMTU < < TU < DMTU < TMTU is obtained. The change in the order of the catalytic action of DMTU and TU can be explained by the different dependence of their j_K values on the potential.

The order of the $\lg c^*$ values, characteristic of the adsorption capability of the additives, is also dependent on the potential, in the interval $\varphi < -0.70$ V they decrease in the order SMTU > TU > DMTU > DETU > TMTU, while

in the potential interval $\varphi > -0.70$ V, similarly as in the case of j^* , the value of $\lg c^*$ too changes in the order $SMTU > DMTU > TU > DETU > TMTU$.

It can be seen from the aforesaid that the catalytic action of additives changes parallel to their adsorption capability. In the evaluation of the results it must be taken into consideration that the c^* values have been obtained from data of kinetic measurements too, so that they are characteristic rather of the adsorption conditions of the transitory complexes. For the comparison of adsorption capability and catalytic action, data characteristic of adsorption (θ , B , a) would be needed, which are independent of the data of kinetic measurements.

The elucidation of the relationships between the adsorption capability, catalytic action and molecular structure of additives requires also further investigations.

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AZIDO-BARBITURATE, I

DARSTELLUNG VON BARBITURSÄUREDERIVATEN MIT EINER
AZIDOGROPPE IN STELLUNG 5

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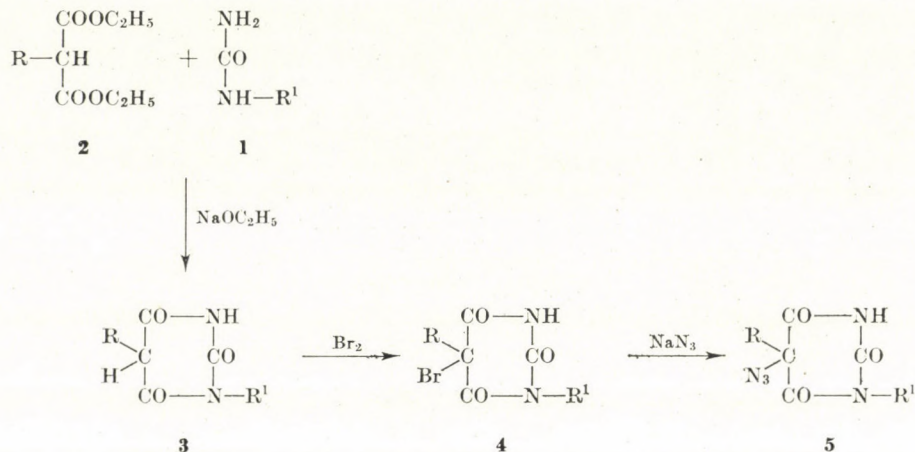
Zur Veröffentlichung angenommen am 29. Juli 1980

Die 5-Azidobarbiturate (5) wurden auf zwei Reaktionswegen dargestellt: 5-Brombarbiturate wurden einerseits mit Natriumazid umgesetzt, andererseits wurde ein eine Azidogruppe enthaltendes Malonsäurederivat mit Harnstoff oder substituiertem Harnstoff in Anwesenheit von Natriumäthylat umgesetzt. Nach vorläufigen pharmakologischen Untersuchungen besitzen die Azidoverbindungen mit einer sekundären Butylgruppe eine bedeutende krampfhemmende Wirkung.

Die pharmakologischen und klinischen Untersuchungen der von Morphin und seinen Derivaten hergestellten Azidoverbindungen [1, 2] zeigten, dass der Einführung der Azidogruppe in das Molekül eine günstige Wirkung zukommt. Diese Resultate veranlassten uns, Barbitursäurederivate herzustellen, die eine Azidogruppe enthalten. In der vorliegenden Mitteilung wird über die Herstellung von Azidobarbituraten berichtet, welche jeweils in Stellung 5 eine Azidogruppe enthalten. Das andere Wasserstoffatom in Stellung 5 wurde meistens durch eine apolare Gruppe ersetzt, die in als wirksam bekannten Barbitursäurederivaten vorkommt. Nach demselben Prinzip verfahren wir bei der Herstellung von 5-Azidobarbituraten (5g-k) die an einem der Stickstoffatome des Barbituratringes auch einen Substituenten besaßen. Die Synthese von 5-Azidobarbituraten wurde auf zweierlei Reaktionswegen verwirklicht:

Auf dem klassischen Reaktionswege [3] wurden aus monosubstituiertem Malonsäurediäthylester (2) und Harnstoff (1, R¹=H) oder substituiertem Harnstoff (1, R¹=CH₃ oder C₆H₅) in Anwesenheit von Natriumäthylat in Stellung 5 monosubstituierte Barbitursäurederivate (3) dargestellt, die bei der Einwirkung von elementarem Brom die 5-Brom-, 5-R-, 1-R¹-Barbitursäuren (4) lieferten. Die Reaktion von (4) mit Natriumazid ergab die 5-Azido-, 5-R-, 1-R¹-Barbitursäuren (5). In Übereinstimmung mit Literaturdaten [4–7] wurde gefunden, dass die 5-monosubstituierten Barbitursäurederivate an der Luft, hauptsächlich in Anwesenheit von Wasser zu 5-Hydroxy-, 5-R-, 1-R¹-Barbitursäuren oxydiert werden. Die ziemlich weiten Grenzen der in der Literatur

* Korrespondenz bitte an diesen Autor richten.

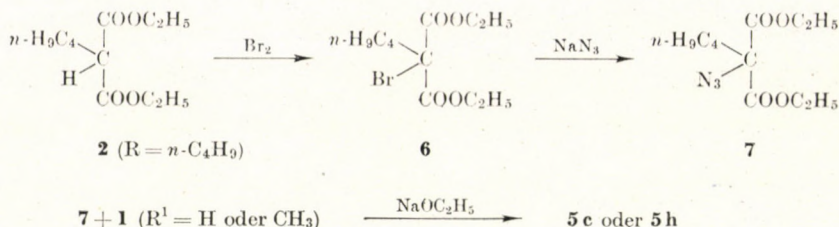


3, 4, 5	R	R ¹	3, 4, 5	R	R ¹	3, 4, 5	R	R ¹
a	CH ₃	H	e	<i>iso</i> -C ₄ H ₉	H	h	<i>n</i> -C ₄ H ₉	CH ₃
b	C ₂ H ₅	H	f	C ₆ H ₅	H	i	<i>sek</i> -C ₄ H ₉	CH ₃
c	<i>n</i> -C ₄ H ₉	H	g	CH ₃	CH ₃	j	C ₂ H ₅	C ₆ H ₅
d	<i>sek</i> -C ₄ H ₉	H				k	<i>sek</i> -C ₄ H ₉	C ₆ H ₅

angegebenen Schmelzpunkte der einzelnen Verbindungen **3** können damit im Zusammenhang stehen. Bei mehreren Verbindungen wurde während der Trocknung eine Verfärbung beobachtet. Die Rohprodukte von **3** wurden deshalb bei der Bromierungsreaktion ohne vorangegangene Reinigung eingesetzt. Die 5-Brombarbiturate (**4**) wurden teils in organischem Medium, teils in Wasser dargestellt. Im letzteren Falle wurden bessere Ausbeuten erhalten, wenn vor der Zugabe des Broms dem Wasser eine HBr-Lösung zugefügt wurde. Wegen der Zersetzlichkeit [8, 9] der 5-Phenyl-5-brombarbitursäure (**4f**) wurde diese Verbindung nach Isolierung aus dem Reaktionsansatz ohne Reinigung sofort der Azidolyse unterworfen, um 5-Phenyl-5-azidobarbitursäure zu gewinnen. Diese Methode wurde auch bei anderen Verbindungen von **5** angewendet.

Die Azidolyse wurde in einem Gemisch von einem mit Wasser mischbarem Lösungsmittel und Wasser durchgeführt. Die Reaktion verlief bei Siedetemperatur im allgemeinen in einigen Stunden. Am Ende der Reaktion wurde das im Überschuss eingesetzte Natriumazid durch Ansäuern in Azoimid überführt, welches infolge seines niedrigen Siedepunktes leicht zu entfernen ist. Das Ansäuern schien auch daher naheliegend, weil am Ende der Reaktion teilweise die Bildung des Natriumsalzes von 5-Azidobarbituraten (**5**) eintrat. Nach dem zweiten Reaktionsweg wurde *n*-Butylmalonsäureäthylester

(2, R = *n*-C₄H₉) bromiert und aus dem so gewonnenen Brom-*n*-butylmalonester (6) Azido-*n*-butylmalonester (7) nach der Vorschrift von FORSTER und MÜLLER [10] dargestellt.



Durch Reaktion von (7) mit Harnstoff (1, R¹ = H) oder *N*-Methylharnstoff (1, R¹ = CH₃) erhält man in Anwesenheit von Natriumäthylat die 5-Azido-5-*n*-butylbarbitursäure (5c) bzw. die 5-Azido-5-*n*-butyl-1-methylbarbitursäure (5h).

Die Toxizität der intravenös verabreichten 5-Azido-barbiturate (5) war im Mäuseversuch im allgemeinen wesentlich kleiner als die der Barbiturate [11]. Gewisse Vertreter der Verbindungsklasse besitzen sedative, andere aber eine krampfhemmende Wirkung. Was die letztere Wirkung betrifft, so sind die sek-Butyl-substituierten Verbindungen von Bedeutung (5d, 5i, 5k) [11].

Die krampfhemmende Wirkung der 5-Azido-5-*sek*.butylbarbitursäure war nahezu identisch mit der der 5-Ethyl-5-phenylbarbitursäure [12].

Experimenteller Teil

Schmelzpunkte wurden mit einem Büchi-Gerät bestimmt, IR-Spektren mit dem Gerät Perkin—Elmer 177 aufgenommen. Jedes 5-Azido-barbiturat (5) zeigte eine für die Azidogruppe charakteristische Bande um 2100 cm⁻¹.

Elementaranalysen wurden im Organisch-chemischen Institut der Lajos-Kossuth-Universität durchgeführt.

Allgemeines Verfahren zur Herstellung von 5-Azido-barbituraten (5) aus 5-Brombarbituraten (4)

0,1 Mol 4 wird in 50 oder 60%-igem warmen wässrigem Aceton aufgelöst und mit einer Lösung von 7,2 g (0,11 Mol) NaN₃ in 50 mL 50%-igem warmem Aceton versetzt. Das Reaktionsgemisch wurde 0,5 bis 4 Stdn. am Rückfluss erhitzt und danach auf 30–35 °C abgekühlt. Der Ansatz wurde unter dem Abzuge mit 10%-iger Salzsäure auf einen pH-Wert von 2 bis 3 angesäuert und anschliessend auf 1–5 °C abgekühlt. Das ausgeschiedene Produkt wurde filtriert, getrocknet und umkristallisiert. Fiel beim Abkühlen kein Niederschlag aus, so wurde das Aceton abgedampft. Azido-barbiturate konnten in einigen Fällen aus den Mutterlauge nach Abdestillieren des Acetons zusätzlich gewonnen werden.

5-Azido-5-methylbarbitursäure (5a)

3a und 4a wurden nach dem Verfahren von PETERS [13] gewonnen.

Ausbeute an 3a: 40,8%, Schmp.: 201–202 °C. Lit. [13]: 200–202 °C.

Rohausbeute an 4a: 66,1%, Schmp.: 189–191,5 °C. Lit. [13]: 186,5–188 °C; Lit. [14]: 190 °C.

4a wurde mit einem 50%-igen Überschuss an NaN_3 in 60 proz. wässrigem Aceton 2 h am Rückfluss erhitzt. 66% des zu erwartenden **5a** fielen aus, weitere Mengen an **5a** konnten nach Verdampfen des Acetons isoliert werden. Es wurde aus 50%-igem Äthanol, danach aus Wasser umkristallisiert. Ausbeute 81,9%, Schmp.: 189–190 °C.

$\text{C}_5\text{H}_5\text{N}_5\text{O}_3$ (183,1). Ber.: C 32,8; H 2,75; N 38,2. Gef.: C 33,5; H 2,79; N 38,2%.

5-Azido-5-ethylbarbitursäure (5b)

3b wurde durch Erhitzen der äthanolischen Lösung von Äthylmalonester, Harnstoff und Natriumäthylat im Molverhältnis von 1 : 1, 5 : 2 während 6 h am Rückfluss. Nach dem Abkühlen des Kondensationsansatzes wurde das Na-Salz von **3b** abfiltriert, das nach Ansäuern **3b** ergab. Rohausbeute 54,6%, Schmp.: 188–190,5 °C. In der Literatur sind Werte zwischen 185° und 197° angegeben [3, 15–17]. Sofort nach Bestimmung des Feuchtigkeitsgehaltes wurde **3b** bei 35–40 °C in der Weise bromiert, dass der wässrigen Aufschlämmung von **3b** vor der Zugabe des Broms eine 48%-ige HBr-Lösung zugefügt wurde, deren Volumen 10% des Volumens des zugegebenen Wassers ausmacht. **4b** wurde aus Essigsäureäthylester umkristallisiert. Ausbeute: 75,4%, Schmp.: 202–204 °C. In der Literatur sind Werte zwischen 202 und 208 °C angegeben [5, 13, 14, 16].

5b wurde nach der allgemeinen Vorschrift mit einer Reaktionsdauer von 4 h dargestellt. Umkristallisation aus Äthanol, Aceton und Dichloräthan, Ausbeute 77,1%, Schmp.: 167–169 °C.

$\text{C}_6\text{H}_7\text{N}_5\text{O}_3$ (197,2). Ber.: C 36,6; H 3,58; N 35,5. Gef.: C 36,8; H 3,68; N 35,3%.

5-Azido-5-n-butylbarbitursäure (5c)

Darstellung von 5c aus 4c

3c wurde aus *n*-Butylmalonester und Harnstoff wie **3b** dargestellt. **3c** wurde ohne Reinigung im Gemisch von Wasser und HBr-Lösung zu **4c** bromiert. Nutschfeuchtes, rohes **4c** wurde in Methanol in 24 h sowie im Aceton-Wasser-Gemisch in 4 h zu **5c** umgesetzt. **5c** kristallisiert aus Äthanol oder Dichloräthan. Rohausbeute an **3c** 84,5%, Schmp.: 194–198 °C. Die Literaturwerte liegen im Bereich von 192–215 °C [15,17–20]. Rohausbeute an **4c** 91,6%, Schmp.: 90–96 °C. *Lit.* [14]: 109 °C, *Lit.* [19]: 114 °C.

Ausbeute an **5c** 43,2%, Schmp.: 150–151 °C.

$\text{C}_8\text{H}_{11}\text{N}_5\text{O}_3$ (225,2). Ber.: C 42,7; H 4,92; N 31,1. Gef.: C 42,6; H 4,96; N 31,7%.

Darstellung von 5c aus *n*-Butyl-azidomalonester (7)

n-Butyl-brommalonester (**6**) wurde aus *n*-Butylmalonester nach der Vorschrift von DOX und YODER [19] hergestellt. Ausbeute an **6** 81,5%, K_p : 115–117 °C, $n_D^{20} = 1,4528$.

7 wurde analog der Vorschrift von FORSTER und MÜLLER [10] für Äthyl-azidomalonester hergestellt, ein kleiner Teil von rohem **7** wurde fraktioniert. Ausbeute: 70,6%, $K_{p,3,5}$: 101–102 °C, $d_4^{20} = 1,114$, $n_D = 1,4420$. Im IR-Spektrum deutliche Absorption bei 2100 cm^{-1} . Nach Kochen mit Lauge konnte kein Bromgehalt nachgewiesen werden.

Aus 4,6 g (0,2 gAtom) Na und 0,11 dm^3 wasserfreiem Äthanol wurde eine Natriumäthylat-Lösung dargestellt. Hierzu wurden 9 g (0,15 Mol) Harnstoff (**1**) und 25,7 g (0,1 Mol) rohes **7** gegeben. Der Ansatz wurde 5 h am Rückfluss erhitzt, anschließend auf Raumtemperatur abgekühlt, auf Eiswasser gegossen und der pH-Wert mit Salzsäure auf 3 eingestellt. Der ausgefallene Niederschlag wurde abgesaugt, getrocknet und zweimal aus Äthanol sowie einmal aus Dichloräthan umkristallisiert. Ausbeute an **5c** 19,5%, Schmp.: 150–151 °C. Das Produkt zeigte keine Schmp.-Depression mit aus **4c** gewonnenem **5c**.

5-Azido-5-*sek*-butylbarbitursäure (5d)

3d wurde aus *sek*-Butylmalonester und Harnstoff wie **3b** dargestellt. Es wurde aus 50%-igem Äthanol umkristallisiert. Sowohl das gereinigte als auch das frisch hergestellte rohe, feuchte **3d** wurden in wässrigem Medium zu **4d** bromiert, welches aus wässrigem Äthanol, Essigsäureäthylester und Äthanol umkristallisiert wurde.

Ausbeute an **3d** 55,7%, Schmp.: 195–197 °C. Die Literaturwerte schwanken zwischen 193 und 199 °C [18, 21, 22].

Ausbeute an **4d** 74,1%, Schmp.: 174–176 °C.

$C_8H_{11}BrN_2O_3$ (263,1). Ber.: C 36,5; H 4,22; Br 30,4; N 10,7. Gef.: C 36,9; H 4,22; Br 29,6; N 10,9%.

5d wurde nach dem allgemeinen Verfahren mit einer Reaktionsdauer von 4 h dargestellt und aus Äthanol und Aceton umkristallisiert. Ausbeute: 60,7%, Schmp.: 131–132 °C.

$C_8H_{11}N_5O_3$ (225,2). Ber.: C 42,7; H 4,92; N 31,1. Gef.: C 41,9; H 5,08; N 32,0%.

5-Azido-5-isobutylbarbitursäure (5e)

3e wurde aus Isobutylmalonester und Harnstoff wie **3b** dargestellt. Das rohe, feuchte **3e** wurde in der üblichen Weise sofort zu **4e** umgesetzt. Das feuchte Rohprodukt von **4e** wurde mit einem 40%-igen Überschuss an NaN_3 sofort der Azidolyse in 50%-igem wässrigem Aceton unterworfen. Reaktionsdauer 4 h. Das rohe **5e** wurde nach Trocknung mit der zwanzigfachen Menge an CCl_4 ausgekocht. Das in der Hitze ungelöste, abgenutzte **5e** wurde aus 50%-igem Äthanol umkristallisiert. Rohausbeute an **3e** 85%, Schmp.: 239–242 °C. In *Lit.* [23] sind 235–236 °C angegeben.

Rohausbeute an **4e** 73%, Schmp.: 162–163 °C. Ausbeute an **5e** 65%, Schmp.: 137–138 °C.

$C_8H_{11}N_5O_3$ (225,2). Ber.: C 42,7; H 4,92; N 31,1. Gef.: C 42,3; H 5,05; N 30,5%.

5-Azido-5-phenylbarbitursäure (5f)

Es wurde versucht, **3f** durch Hydrolyse der aus Phenylcyanessigsäure-äthylester und Guanidin darstellbaren 2,4-Diimino-5-phenylbarbitursäure zu gewinnen, doch war die Umsetzung der 2-ständigen Iminogruppe nach längerer Reaktionsdauer nur unvollständig. Die Kondensation des Phenylcyanessigsäure-äthylesters mit Harnstoff und die anschließende saure Hydrolyse der 4-Imino-5-phenylbarbitursäure ergab wegen des schlechten Wirkungsgrades der Kondensation nur 4,8% an **3f**. Das durch Reaktion von Phenylmalonensäure-diäthylester und Harnstoff gewonnene rohe **3f** wurde nach Trocknung mit der 4-fachen Menge an Äthanol ausgekocht und der in der Hitze unlösliche Teil abgenutzt und aus Wasser umkristallisiert.

Ausbeute an **3f** 40,3%, Schmp.: 260–263 °C. In der Literatur findet man Werte zwischen 250 und 263 °C [17, 24–27]. **3f** wurde in wässrigem HBr 1 h bei 10–12 °C bromiert. Rohausbeute an **4f** 90,4%, Schmp.: 202–204 °C. *Lit.* [26, 28]: 204–206 °C.

Das feuchte Rohprodukt von **4f** wurde sofort mit NaN_3 umgesetzt. In die Lösung von 13 g (0,2 Mol) NaN_3 in 37 mL Wasser wurden in fünf Portionen insgesamt 11,3 g (0,04 Mol) auf Trockensubstanz bezogenes **4f** eingetragen. Nach erfolgter Zugabe bei Raumtemperatur wurde die Lösung mit 72 mL Methanol versetzt und 4,5 h am Rückfluss erhitzt. Der auf Raumtemperatur abgekühlte Ansatz wurde unter dem Abzuge mit Salzsäure versetzt und in offenem Gefäß über Nacht stehengelassen. Es wurde dann auf 5–10 °C abgekühlt, filtriert, mit Wasser gewaschen und getrocknet. Das erhaltene **5f** 8,8 g = 89,7% wurde mit Äther ausgekocht und noch warm filtriert. Das nicht in Lösung gehende Produkt wurde aus 50% Äthanol, danach aus Acetonitril umkristallisiert. Schmp.: 210–211 °C.

$C_{10}H_7N_5O_3$ (245,2). Ber.: C 49,0; H 2,88; N 28,6. Gef.: C 49,1; H 3,07; N 28,8%.

5-Azido-1,5-dimethylbarbitursäure (5g)

Das Gemisch von Methylmalonensäure-diäthylester, Methylharnstoff und Natriummethylat im Molverhältnis von 1 : 1,05 : 1,1 Äthanol wird 12 h zum Sieden erhitzt. **3g** wurde wie **3b** isoliert und das feuchte Produkt aus 50%-igem Äthanol umkristallisiert. Ausbeute an **3g** 51,7%, Schmp.: 168–169 °C. Die Literaturwerte liegen zwischen 169 und 173 °C [29–31].

3g wurde sowohl in Wasser als auch in Chloroform zu **4g** umgesetzt und aus 50%-igem Äthanol umkristallisiert. Ausbeute an **4g** 75,7% in wässrigem Medium Schmp.: 94–95 °C.

$C_6H_7BrN_2O_3$ (235,0). Ber.: Br 34,0. Gef.: Br 32,7%.

4g wurde in 60%-igem wässrigem Aceton mit einem 100%-igen Überschuss an NaN_3 3 h zum Sieden erhitzt. **5g** wurde nach Verdampfen des Acetons isoliert und aus 50%-igem Äthanol, danach aus Wasser umkristallisiert. Ausbeute 59,3%, Schmp.: 109–110 °C.

$C_6H_7N_5O_3$ (197,2). Ber.: C 36,6; H 3,58; N 35,5. Gef.: C 36,8; H 3,61; N 35,2%.

5-Azido-5-*n*-butylbarbitursäure (5h)

3h wurde aus *n*-Butylmalonester und *N*-Methylharnstoff wie **3b** dargestellt. Das nach üblicher Aufarbeitung des Reaktionsgemisches erhaltene Na-Salz wurde in Wasser gelöst und angesäuert. Das anfangs ölige **3h** wurde über Nacht fest. Die Mutterlauge wurde nicht weiter zwecks Gewinnung von zusätzlichen Mengen aufgearbeitet. Rohausbeute von **3h** 45,4%, Schmp.: 55–56 °C. *Lit.* [32]: 60–62 °C. Nach Isolierung wurde das noch feuchte **3h** sofort in wässrigem Medium zu **4h** bromiert. Rohausbeute an **4h** 75,0%, Schmp.: 96–97 °C.

Das feuchte Rohprodukt von **4h** wurde mit einem 100%-igen Überschuss an NaN_3 in 50%-igem wässrigem Aceton in der Hitze 4 h umgesetzt. Beim Ansäuern fällt **5h** ölig an, das beim Stehen kristallin wird. Umkristallisation aus Äther und 30% Methanol. Ausbeute 68,0%, Schmp.: 76–77 °C.

$\text{C}_9\text{H}_{13}\text{N}_5\text{O}_3$ (239,2). Ber.: C 45,2; H 5,48; N 29,3. Gef.: C 45,4; H 5,38; N 30,0%.

Darstellung von **5h** aus **7**

Die Kondensation von fraktioniertem *n*-Butyl-azidomalonester **7** und *N*-Methylharnstoff in dem bei der Darstellung von **5c** angegebenen Molverhältnis ergab **5h** in einer Ausbeute von 35,2%. Schmp.: 77 °C, keine Schmp.-Depr. mit aus **4h** gewonnener Substanz.

5-Azido-5-*sek*-butyl-1-methylbarbitursäure (5i)

3i wurde aus *sek*-Butylmalonester und *N*-Methylharnstoff wie **3b** dargestellt. Rohausbeute an **3i** 68,4%, Schmp.: 80–83 °C. Ein kleiner Teil von **3i** wurde aus Wasser umkristallisiert, Schmp.: 86–86,5 °C. *Lit.* [33]: 89–90 °C.

Das rohe **3i** wurde sowohl in Wasser als auch in CHCl_3 bromiert. **4i** stellt in beiden Fällen eine amorphe Masse dar, welche nach dem allgemeinen Verfahren mit einem 100%-igen Überschuss an NaN_3 in 2 h zu **5i** umgesetzt wurde. Nach Ansäuern und Abdestillieren des Acetons blieb eine formbare Masse zurück, die beim Stehen in Kühlschrank dest wurde. Das rohe **5i** wurde aus Äthanol, danach aus Wasser umkristallisiert. Ausbeute von **5i** bezogen auf **3i**: 37,1%. Schmp.: 132,5–134,5 °C.

$\text{C}_9\text{H}_{13}\text{N}_5\text{O}_3$ (239,2). Ber.: C 45,2; H 5,48; N 29,3. Gef.: C 45,5; H 5,52; N 29,3%.

5-Azido-5-äthyl-1-phenylbarbitursäure (5j)

3j und **4j** wurden nach dem Verfahren von ASPELUND und LINDH [34] dargestellt.

Ausbeute an **3j** 62,3%, Schmp.: 185–187 °C. *Lit.* [17, 34]: 185–186,5 °C.

Ausbeute an **4j** 84,0%, Schmp.: 133–134 °C. *Lit.* [34]: 137–138 °C.

$\text{C}_{12}\text{H}_{11}\text{BrN}_5\text{O}_3$ (311,1). Ber.: Br 25,7. Gef.: 26,0%.

Ein **4j** und NaN_3 im Molverhältnis 1 : 0,95 enthaltendes Gemisch wurde in 60%-igem Aceton 1 h zum Sieden erhitzt. Das rohe **5j** wurde aus einem Äthanol und Benzin im Verhältnis 1 : 2 enthaltenden Gemisch umkristallisiert; Ausbeute 77,9%, Schmp.: 160–161 °C.

$\text{C}_{12}\text{H}_{11}\text{N}_5\text{O}_3$ (272,3). Ber.: C 52,8; H 4,06; N 25,6. Gef.: C 53,0; H 4,21; N 26,2%.

5-Azido-5-*sek*-butyl-1-phenylbarbitursäure (5k)

3k wurde aus *sek*-Butylmalonester und *N*-Phenylharnstoff wie **3b** hergestellt. Das Äthanol wurde aus dem Reaktionsansatz abdestilliert. Der Destillationsrückstand wurde bei 10 °C in Wasser gelöst und das rohe **3k** mit Salzsäure ausgefällt. Das rohe **3k** wurde bei Temperaturen unter 10 °C in 1*n* NaOH-Lösung aufgenommen und mit Äther extrahiert. Die wässrige Phase wurde abgetrennt bei Temperaturen unter 10 °C mit Salzsäure angesäuert; Ausbeute an **3k** 72,8%, Schmp.: 159–160 °C.

$\text{C}_{14}\text{H}_{16}\text{N}_2\text{O}_3$ (260,3). Ber.: C 64,6; H 6,20; N 10,8. Gef.: C 64,5; H 6,40; N 10,9%.

3k wurde sowohl in Wasser als auch in CHCl_3 bromiert. **4k** wurde in beiden Fällen als amorphe Masse erhalten, die mit einem 100%-igen Überschuss an NaN_3 in 60% wässrigem Aceton 4 h der Azidolyse unterworfen wurde. Nach Ansäuern und Abkühlen des Reaktionsgemisches erhält man eine Substanz, die sich nicht als Azidoderivat erwies. Aus der Mutterlauge wurde das Aceton abgedampft. Nach Abkühlen und Abnutschen wurde die erhaltene Substanz aus Benzol umkristallisiert; die hierbei ausgefallene Substanz war wiederum kein

Azidoderivat. **5k** wurde nach Eindampfen der benzolischen Mutterlauge erhalten. Es wurde zuerst aus 50%-igem Äthanol, dann aus CCl_4 umkristallisiert. Die auf **3k** bezogene Ausbeute von **5k** beträgt 25,6%, Schmp.: 121–122 °C.

$\text{C}_{14}\text{H}_{15}\text{N}_5\text{O}_3$ (301,3). Ber.: C 55,8; H 5,02; N 23,2. Gef.: C 55,5; H 4,95; N 22,8%.

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AZIDO-BARBITURATE, II

HERSTELLUNG VON BARBITURSÄUREDERIVATEN MIT EINER AZIDOGROPPE AM SUBSTITUENTEN

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Die bei Siedetemperatur in wässrig-organischem Medium ausgeführte Umsetzung von am Substituenten ein Halogenatom enthaltenden Barbitursäurederivaten mit Natriumazid ergibt Azidobarbiturate. Nach vorläufigen pharmakologischen Prüfungen hat die 5-Phenyl-5-(2-hydroxy-3-azidopropyl) barbitursäure (**10a**) eine beträchtliche gefässerweiternde Wirkung.

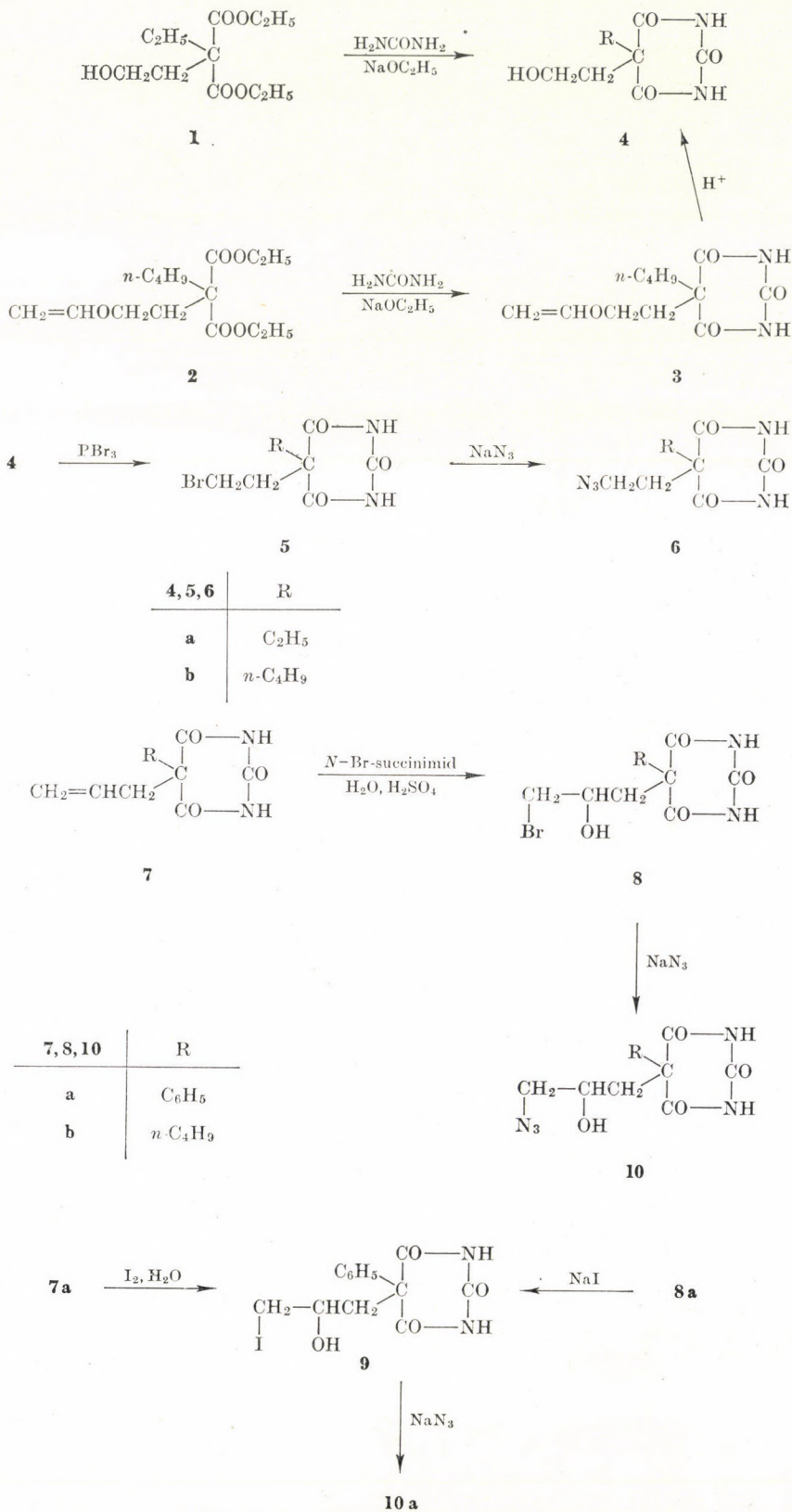
SMISSMAN und WIRTH beschreiben [1] Barbitursäurederivate die am Substituenten eine Azidogruppe tragen. Die Autoren stellten 5-Phenyl-5-(3-azidopropyl) barbitursäure als Zwischenprodukt zur Herstellung von 5-Phenyl-5-(3-aminopropyl) barbitursäure dar. In der vorausgehenden Mitteilung [2] synthetisierten wir mit der gleichen Zielsetzung Barbiturate, die am Substituenten eine Azidogruppe tragen. Die 5-Alkyl-5-(2-hydroxyäthyl) barbitursäuren (**4a**, R = C₂H₅; **4b**, R = n - C₄H₉) wurden auf dem in der Literatur angegebenen Wege nach folgendem Schema dargestellt [3, 4].

SKINNER und HERDNER machten darauf aufmerksam [5], dass der Austausch der OH-Gruppe in der 2-Hydroxyäthyl-gruppierung mit HBr mit der Spaltung des Barbituratringes einhergehen kann. Im Laufe der Herstellung von 2-Bromäthylbarbituraten (**5**) probierten wir mehrere Methoden aus, wobei die Umsetzung mit HBr niedrige Ausbeuten ergab; dagegen erzielten wir zufriedenstellende Ergebnisse bei der Anwendung von PBr₃.

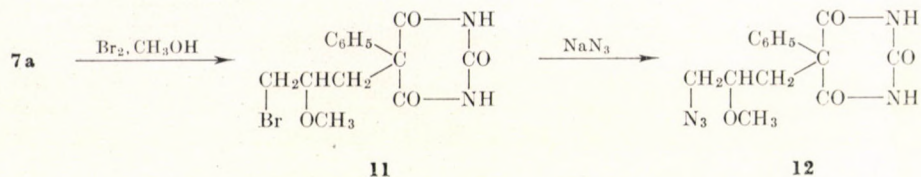
Die 5-Phenyl-5-(2-hydroxy-3-brompropyl) barbitursäure (**8a**) und die 5-Phenyl-5-(2-hydroxy-3-iodpropyl) barbitursäure (**9**) wurden aus 5-Phenyl-5-allylbarbitursäure (**7a**) auf den geschilderten, bekannten Wegen hergestellt. **9** wurde auch mit einem Gemisch von KIO₃ und KI sowie mit Iod in wässrigem Milieu aus **7a** hergestellt. Im ersteren Falle erzielten wir bessere Ausbeuten. **9** wurde auch aus **8a**, und zwar durch Halogenaustausch hergestellt.

Die 5-n-Butyl-5-(2-hydroxy-3-brompropyl) barbitursäure (**8b**) wurde nach dem Verfahren von WIRTH [6] zur Herstellung von **8a** aus 5-n-Butyl-5-allylbarbitursäure (**7b**) hergestellt.

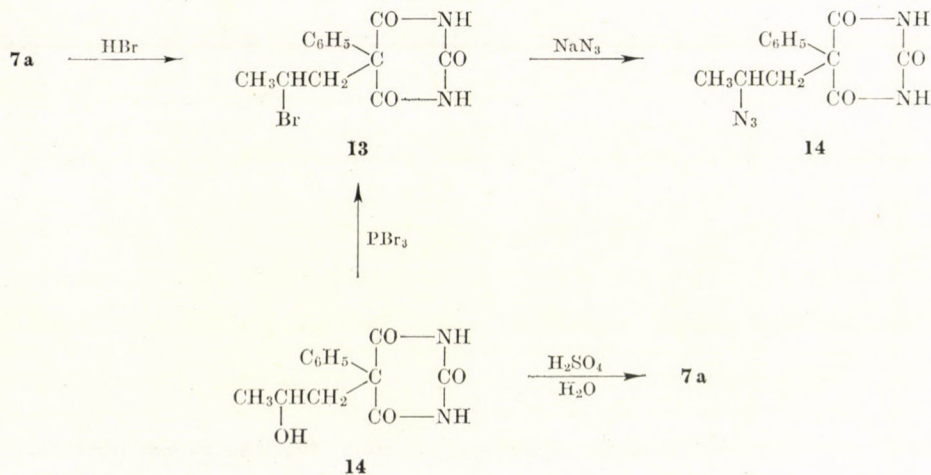
* Korrespondenz bitte an diesen Autor richten.



Die 5-Phenyl-5-(2-methoxy-3-brompropyl)barbitursäure (**11**) wurde aus **7a** mit Brom in Methanol nach dem Verfahren von SMISSMANN und Mitarbeitern [8] hergestellt.

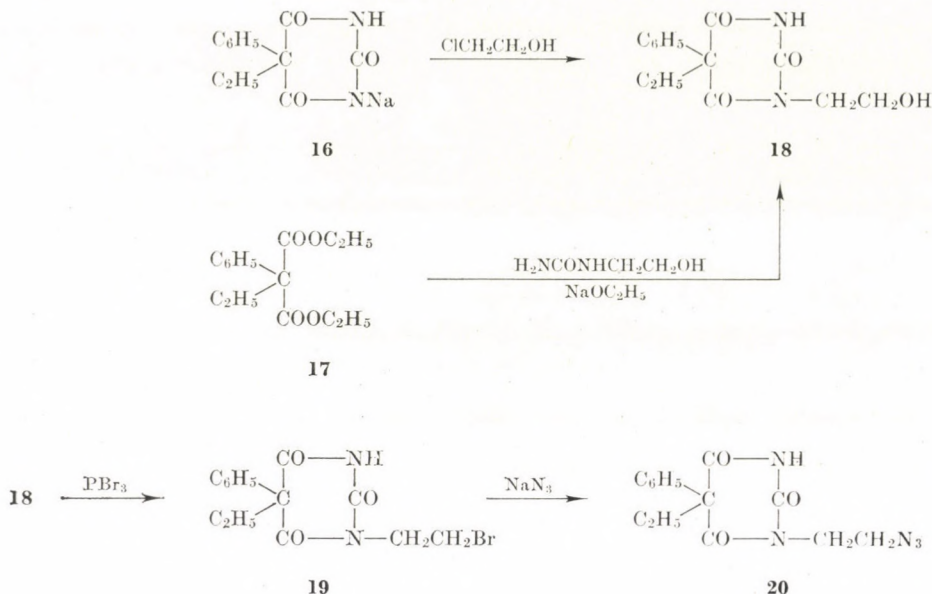


Die 5-Phenyl-5-(2-brompropyl) barbitursäure (**13**) wurde einerseits durch Anlagerung von HBr an die Doppelbindung von **7a**, andererseits durch die Reaktion von 5-Phenyl-5-(2-hydroxypropyl) barbitursäure (**14**) mit PBr₃ hergestellt.



Aus 5-Phenyl-5-äthylbarbitursäure-Na (**16**) stellten wir nach der Publikation von HENZE und SPURLOCK [9] mit Äthylenchlorhydrin die 1-(2-Hydroxy-äthyl)-5-phenyl-5-äthylbarbitursäure dar.

Die Reaktion von Phenyl-äthylmalonsäure-diäthylester (**17**) mit *N*-(2-Hydroxyäthyl) harnstoff lieferte in Anwesenheit von Natriumäthylat ebenfalls **18**, aus dem wir durch Einwirkung von PBr₃ die 1-(2-Bromäthyl) 5-phenyl-5-äthylbarbitursäure (**19**) gewannen. Die Umsetzung der Halogenverbindungen (**5a**, **5b**, **8a**, **8b**, **9**, **11**, **13**, **19**) mit einem Überschuss an NaN₃ ergab die entsprechenden Azidobarbiturate (**6a**, **6b**, **10a**, **10b**, **12**, **15**, **20**). Als Lösungsmittel wurden Gemische von Acetonitril und Wasser sowie Aceton-Acetonitril-Wasser verwendet. Solange sich **10a** und **10b** leicht gebildet hatten, trat die Umsetzung bei **12** und **15** erst nach langer Reaktionsdauer und mit grossem Überschuss an NaN₃ ein. Die nach dem Verfahren von SKINNER und LYMAN [10] herge-



stellte 5-(Chlormethyl)-5-äthylbarbitursäure lieferte mit einem grossen Überschuss an nach NELLES [11] aktiviertem NaN_3 in einem Cellosolv-Wasser-Gemisch bei Siedetemperatur erst nach 20 h ein IR-spektroskopisch nachweisbares Azidoderivat. Die Isolierung der reinen 5-(Azidomethyl)-5-äthylbarbitursäure ist uns bisher nicht gelungen. Hier sei vermerkt, dass nach unseren Erfahrungen die Schmelzpunkte von **10a** und **10b** schwanken. Es war besonders bei **10a** augenfällig, dass bei der Durchführung der Schmelzpunktbestimmungen unter völlig identischen Bedingungen die Änderung normalerweise bei einer abweichenden Temperatur eintrat, was sich meistens innerhalb von 2°C abspielte.

Nach den bisher zur Verfügung stehenden Daten der pharmakologischen Testverfahren [12] besitzt die 5-Phenyl-5-(2-hydroxy-3-azidopropyl) barbitursäure **10a** eine bemerkenswerte gefässerweiternde Wirkung.

Experimenteller Teil

Schmelzpunkte unkorrigiert: Büchi; IR: Perkin-Elmer 177: Jedes Azidobarbiturat zeigte eine Bande bei 2100 cm^{-1} .

5-Äthyl-5-(2-hydroxyäthyl)barbitursäure (4a)

Der (2-Hydroxyäthyl)äthylmalonsäure-diäthylester (**1**) und die daraus erhaltene 5-Äthyl-5-(2-hydroxyäthyl) barbitursäure (**4a**) wurden nach dem Verfahren von SHONLE und Mitarbeitern [3] dargestellt. **4a** wurde aus 50%-igem Äthanol umkristallisiert. Ausbeute an **1** 28,3%, Kp.₆: $128-130^\circ$. Lit. [3]: Kp.₆: $128-131^\circ\text{C}$. Ausbeute an **4a** 62,9%, Schmp.: $178-180^\circ$. Lit. [4]: 176°C , Lit. [3]: 178°C .

5-Äthyl-5-(2-bromäthyl)barbitursäure (5a)

Beim Erhitzen von **4a** in 48%-igem HBr trat eine Zersetzung auf. Eine anfangs bei 0 °C, anschliessend bei Raumtemperatur durchgeführte Reaktion ergab nur eine Ausbeute von 38%. — Das Gemisch von 10 g (0,05 Mol) **4a** und 40,6 g (0,15 Mol) PBr₃ wurde 1,5 h bei einer Badtemperatur von 110 °C gehalten. Die auf 70 °C abgekühlte Reaktionslösung wurde mit 85 mL Äthanol versetzt und über Nacht im Kühlschrank stehengelassen. Es wurde abgesehen und aus 50%-igem wässrigem Äthanol umkristallisiert. Ausbeute 6,8 g; 52%, Schmp.: 161–162 °C. *Lit.* [13]: 164–165 °C.

5-Äthyl-5-(2-azidoäthyl) barbitursäure (6a)

Der Lösung von 1,3 g (0,02 Mol) NaN₃ in 25 mL 60%-iger wässriger Acetonlösung werden 2,6 g (0,01 Mol) **5a** zugefügt. Nach 2-stündigem Erhitzen am Rückfluss wird der Ansatz auf etwa 35 °C abgekühlt, der pH-Wert auf 3 eingestellt und das Aceton abdestilliert. Nach Abkühlen auf 1–5 °C wurde die ausgefallene Substanz abfiltriert und getrocknet. Es wurde zuerst aus einem Äthanol und Benzin im Verhältnis 1 : 9 enthaltendes, anschliessend aus 30%-igem wässrigem Methanol umkristallisiert. Ausbeute 0,8 g; 35%, Schmp.: 151–152,5°.

C₈H₁₁N₃O₃ (225,2). Ber.: C 42,7; H 4,92; N 31,1. Gef.: C 42,5; H 4,74; N 30,9%.

5-n-Butyl-5-(2-azidoäthyl)barbitursäure (6b)

2 und das daraus erhaltene **3** und **4b** wurden nach dem Verfahren von CRETCHER und Mitarb. [4] hergestellt. Nach der Isolierung wurde **3** durch Kochen mit Säure sofort in **4b** überführt, woraus mit PBr₃ **5b** gewonnen wurde, das wir aus 50%-igem wässrigem Äthanol umkristallisierten. **5b** wurde mit einem 100%-igem Überschuss an NaN₃ in 60%-igem wässrigem Aceton 6 h zum Sieden erhitzt. Es wurde aus einem Äthanol und Benzin im Verhältnis 1 : 2 enthaltenden Gemisch und danach aus 30%-igem wässrigem Methanol umkristallisiert. Ausbeute an **2** 54,5%, Kp.: 124–127 °C; *Lit.* [4]: Kp.: 165°. Ausbeute an **4b** bezogen auf **2**: 32%, Schmp.: 146–147 °C. *Lit.* [4, 14, 15]: 147–149 °C.

Ausbeute an **5b** 40,5%, Schmp.: 151–152 °C, *Lit.* [16]: 153,5 °C. Ausbeute an **6b** 32,7%, Schmp.: 113–114 °C.

C₁₀H₁₅N₃O₃ (253,3). Ber.: C 47,4; H 5,97; N 27,7. Gef.: C 48,0; H 6,21; N 26,9%.

5-Phenyl-5-allylbarbitursäure (7a)

Durch Reaktion von Phenyl-allyl-cyanessigsäure-äthylester (Kp.₅: 132–134 °C, $n_D^{20} = 1,5058$, $d_4^{20} = 1,0545$) mit Guanidin wurde 5-Phenyl-5-allyl-2,4-diimino-barbitursäure hergestellt, die bei der sauren Hydrolyse **7a** lieferte. Umkristallisiert wurde aus Wasser. Ausbeute: 70,7%, Schmp.: 154–155,5 °C. *Lit.* [17]: 154–155 °C.

5-Phenyl-5-(2-hydroxy-3-brompropyl)barbitursäure (8a)

Die Verbindung wurde durch Reaktion von **7a** mit N-Bromsuccinimid und Schwefelsäure in Dioxan nach WIRTH [6] gewonnen. Das trockene Rohprodukt von **7a** wurde in dreifacher Menge Aceton ausgekocht und der Rückstand getrocknet. Ausbeute 82,6%, Schmp.: 139–140 °C. *Lit.* [6]: 240–241 °C.

5-Phenyl-5-(2-hydroxy-3-iodpropyl)barbitursäure (9)

9 wurde aus **7a**, KIO₃ und KI in mit Schwefelsäure angesäuertem Wasser nach dem Verfahren von BOBRANSKI und Mitarb. [7] hergestellt. Ausbeute 75,6%, Schmp.: 230–231 °C Zersetzung. *Lit.* [7]: 223–225 °C.

C₁₃H₁₃IN₂O₄ (388,2). Ber.: C 40,2; H 3,37; I 32,7; N 7,22. Gef.: C 40,6; H 3,30; I 33,0; N 7,24%.

Die Reaktion von **7a** mit elementarem Iod in Wasser nach der Vorschrift von BOBRANSKI und Mitarb. [18] lieferte **9** mit einer Ausbeute von 32,7%. Das Gemisch von **8a** und NaI wurde 24 h zum Sieden erhitzt, wobei **9** mit einer Ausbeute von 56,8% erhalten wurde. Die auf drei verschiedenen Wegen dargestellten Substanzen führten gegenseitig zu keiner Schmp-Depression.

5-Phenyl-5-(2-hydroxy-3-azidopropyl)barbitursäure (10a)

10a wurde sowohl aus **9** als auch aus **8a** mit nahezu gleicher Ausbeute erhalten. Das Gemisch von **8a** und NaN_3 im Molverhältnis 1 : 4 wurde in 60%-igem Aceton 6 h zum Sieden erhitzt, das Gemisch von **9** und NaN_3 im Molverhältnis 1 : 4 dagegen 1 h in 60%-igem Acetonitril. Ausbeute 30%. Für **10a** wurde kein bestimmter Zersetzungspunkt gefunden: im Bereich von 190 und 225 °C findet man auch unter gleichen Bedingungen immer bei anderen Temperaturen ein 2°-Intervall, in dem eine schnelle Änderung eintritt.

$\text{C}_{13}\text{H}_{13}\text{N}_5\text{O}_4$ (303,3). Ber.: C 51,5; H 4,32; N 23,1. Gef.: C 52,4; H 4,54; N 23,0%.

5-n-Butyl-5-allylbarbitursäure (7b)

Das Gemisch von *n*-Butyl-allylmalonsäure-diäthylester [3], Harnstoff und Natriumäthylat im Molverhältnis von 1 : 1,5 : 2 wurde 3 h in Äthanol zum Sieden erhitzt. Nach Abdampfen des Äthanols wurde der Rückstand in Eiswasser gelöst und das Produkt mit Salzsäure ausgefällt. Umkristallisation aus Wasser, Ausbeute 65,5%, Schmp.: 126,5–127,5 °C. *Lit.* [3]: 125–125,5 °C. *Lit.* [19]: 128 °C.

-n-Butyl-5-(2-hydroxy-3-brompropyl)barbitursäure (8b)

8b wurde aus **7b**, wie für **8a** beschrieben, hergestellt. Das Rohprodukt wurde aus Essigsäure-äthylester und Äthanol umkristallisiert, ausbeute 68,7%, Schmp.: 222,5–223 °C.

$\text{C}_{11}\text{H}_{17}\text{BrN}_5\text{O}_4$ (321,2). Ber.: C 41,1; H 5,34; Br 24,9; N 8,72. Gef.: C 41,6; H 5,22; Br 24,9; N 8,70%.

5-n-Butyl-5-(2-hydroxy-3-azidopropyl)barbitursäure (10b)

8 g (0,025 Mol) **8b** und 3,25 g (0,05 Mol) NaN_3 wurden in 50 mL 60%-igem wässrigem Aceton und 30 mL Acetonitril 6 h zum Sieden erhitzt. Der auf 40 °C abgekühlte Ansatz wurde mit 10% Salzsäure auf pH 3 eingestellt. Nach dem Abdampfen der Lösungsmittel wurde das Rohprodukt abgenutscht und aus Wasser umkristallisiert. Ausbeute 61%. Die bei der Schmelzpunktsbestimmung von **10a** beobachteten Erscheinungen traten auch bei **10b** auf: meistens wurde ein Schmp. von 211–212 °C gefunden.

$\text{C}_{11}\text{H}_{17}\text{N}_5\text{O}_4$ (283,3). Ber.: C 46,6; H 6,05; N 24,7. Gef.: C 46,4; H 5,78; N 23,8%.

5-Phenyl-5-(2-methoxy-3-brompropyl)barbitursäure (11)

Die Verbindung wurde aus **7a** mit methanolischer Bromlösung nach der Methode von SMISSMANN und Mitarb. [8] dargestellt. **11** wurde aus Äthylacetat umkristallisiert. Ausbeute 71,8%, Schmp.: 209–210 °C. *Lit.* [8]: 209–209,5 °C.

5-Phenyl-5-(2-methoxy-3-azidopropyl)barbitursäure(12)

11 und NaN_3 wurden im Molverhältnis von 1 : 5 wird in 60%-igem wässrigem Acetonitril 24 h zum Sieden erhitzt. Das Produkt wurde durch Lösen in Lauge und Fällen mit Säure und anschließende Kristallisation aus Wasser gereinigt. Ausbeute 51,2%. Schmp.: 170–171 °C.

$\text{C}_{14}\text{H}_{15}\text{N}_5\text{O}_4$ (317,3). Ber.: C 53,0; H 4,77; N 22,1. Gef.: C 52,2; H 4,67; N 21,6%.

5-Phenyl-5-(2-brompropyl)barbitursäure (13)

13 wurde aus **7a** mit HBr in Eisessig nach dem von KONIECZNY [21] für die Darstellung der 5,5-Bis-(2-brompropyl)barbitursäure angegebenen Verfahren gewonnen und aus Äthanol umkristallisiert. Ausbeute 58,7%, Schmp.: 221–222 °C, *Lit.* [20]: 221–222 °C. Aus **14** wurde mit PBr_3 ebenfalls **13** auf die für **5a** beschriebene Weise hergestellt. Ausbeute 61,1%, Schmp.: 221–222 °C, keine Schmp.-Depr. mit aus **7a** hergestelltem **13**.

5-Phenyl-5-(2-hydroxypropyl)barbitursäure (14)

14 wurde aus **7a** mit konz. Schwefelsäure nach der Vorschrift von SMISSMANN und Mitarb. [22] dargestellt und aus Wasser umkristallisiert. Ausbeute 59,8%, Schmp.: 228–230 °C, *Lit.* [22]: 229–231 °C.

5-Phenyl-5-(2-azidopropyl)barbitursäure (15)

Das Gemisch von **13** und NaN_3 im Molverhältnis von 1 : 5 wurde in 70%-igem wässrigem Acetonitril 20 h zum Sieden erhitzt. Das Rohprodukt wurde aus Wasser umkristallisiert. Ausbeute 21,9%, Schmp.: 180–180,5 °C.

$\text{C}_{13}\text{H}_{13}\text{N}_3\text{O}_3$ (287,3). Ber.: C 54,4; H 4,56; N 24,4. Gef.: C 54,7; H 4,57; N 24,2%.

1-(2-Hydroxyäthyl)-5-phenyl-5-äthylbarbitursäure (18)

Die Verbindung wurde aus **16** und Äthylenchlorhydrin nach der Vorschrift von HENZE und SPURLOCK [9] hergestellt. Ausbeute 21,4%, Schmp.: 145–146 °C, *Lit.* [9, 23]: 145–145,5 °C. **18** wurde ebenfalls aus Phenyl-äthylmalonester (**17**), *N*-(2-Hydroxyäthyl) harnstoff (Schmp.: 95 °C, Darstellung nach CHARLTON und DAY [24]) und Natriumäthylat (Molverhältnis 1 : 1,1 : 1,5) in Äthanol durch 11 stündiges Kochen dargestellt. Ausbeute 10%, Schmp.: 145–146 °C; keine Schmp.-Depression mit der aus **16** dargestellten Substanz.

1-(2-Bromäthyl)-5-phenyl-5-äthylbarbitursäure (19)

Die Verbindung wurde nach dem Verfahren von HENZE und SPURLOCK [9] aus **18** durch Einwirkung von PBr_3 gewonnen. Ausbeute 79,1%, Schmp.: 126–128,5 °C, *Lit.* [9]: 127,5–128,5 °C.

1-(2-Azidoäthyl)-5-phenyl-5-äthylbarbitursäure (20)

19 und NaN_3 wurden im Molverhältnis von 1 : 2 in 60%-igem wässrigem Aceton zum Sieden erhitzt, der pH-Wert auf 3 eingestellt und das Aceton abgedampft. Die abgeschiedene Masse wurde in Äther aufgenommen und in Petroläther eingetropfelt. Das Produkt wurde aus 70%-igem wässrigem Methanol umkristallisiert. Ausbeute 76,6%, Schmp.: 91–92 °C.

$\text{C}_{14}\text{H}_{15}\text{N}_5\text{O}_3$ (301,3). Ber.: C 55,8; H 5,02; N 23,2. Gef.: C 56,5; H 5,12; N 23,3%.

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MIXED LIGAND COMPLEXES OF METAL THIOCYANATES WITH 2,2'-DIPYRIDYL AND 1,10-PHENANTHROLINE

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A new class of mixed ligand complexes of metal thiocyanates with 2,2'-dipyridyl and 1,10-phenanthroline were synthesized and subjected to chemical analysis, IR studies and magnetic measurements. The investigations provide evidence for the formation of high spin 1 : 1 : 4 (M : L : SCN) in case of Co(II), Ni(II) and Mn(II) and 1 : 1 : 2 (M : L : SCN) mixed complexes in case of Cu(II), Cd(II) and Zn(II), respectively.

Introduction

SCHILT [1] has prepared a large number of mixed cyanide complexes of Fe(II) and Fe(III) in which one ligand is 1,10-phenanthroline or 2,2'-dipyridyl *e.g.* $[\text{Fe}(\text{CN})_2(\text{phen})_2]$ and $[\text{Fe}(\text{CN})_2(\text{dipy})_2]$.

Similar type of mixed thiocyanate complexes of Fe(II) have been reported by DRIVER and WALKER [2] *e.g.* $[\text{Fe}(\text{SCN})_2(\text{phen})_2]\text{H}_2\text{O}$ and $[\text{Fe}(\text{SCN})_2(\text{dipy})_2]$.

The present investigation was planned to extend our knowledge on mixed metal thiocyanate complexes using 1,10-phenanthroline and 2,2'-dipyridyl as the other ligands. With this aim in view some new mixed ligand thiocyanate complexes of 1,10-phenanthroline and 2,2'-dipyridyl with Cd(II), Co(II), Mn(II), Ni(II), Cu(II) and Zn(II) were prepared, subjected to chemical analysis, IR studies and magnetic measurements.

Experimental

Solutions

Cobalt, nickel, manganese, copper, cadmium and zinc sulphates of AnalaR (grade B.D.H) were used to prepare aqueous alcoholic solutions in 25% ethanol of these metal salts.

2,2'-dipyridyl (B.D.H), 1,10-phenanthroline monohydrate (Merck) and ammonium thiocyanate of A.R. grade were used to prepare aqueous alcoholic (4 : 1) solutions in 25% ethanol. All solutions were 0.05 M.

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Table I
Chemical analysis and magnetic measurement

Name of the compound, and formula	Colour	Metal %		C %	
		Calc.	Found	Calc.	Found
1	2	3	4	5	6
1. $[\text{Cu}(\text{C}_{10}\text{H}_8\text{N}_2)(\text{SCN})_2]$ Dithiocyanato mono-(2,2'-dipyridyl) copper(II)	Green	18.94	19.11	42.91	42.72
2. $[\text{Cu}(\text{C}_{12}\text{H}_8\text{N}_2)(\text{SCN})_2]$ Dithiocyanato mono-(1,10-phenanthroline) copper(II)	Green	17.67	17.48	46.72	46.51
3. $(\text{NH}_4)_2[\text{Mn}(\text{C}_{10}\text{H}_8\text{N}_2)(\text{SCN})_4]$ Diammonium tetrathiocyanato mono-(2,2'-dipyridyl)manganese (II)	Light yellow	11.47	11.51	35.08	35.21
4. $(\text{NH}_4)_2[\text{Mn}(\text{C}_{12}\text{H}_8\text{N}_2)(\text{SCN})_4]$ Diammonium tetrathiocyanato mono-(1,10-phenanthroline) manganese(II)	Light yellow	10.92	11.02	38.17	38.22
5. $[\text{Cd}(\text{C}_{10}\text{H}_8\text{N}_2)(\text{SCN})_2]$ Dithiocyanato mono-(2,2'-dipyridyl) cadmium(II)	White	29.24	29.36	37.46	37.44
6. $[\text{Cd}(\text{C}_{12}\text{H}_8\text{N}_2)(\text{SCN})_2]$ Dithiocyanato mono-(1,10-phenanthroline) cadmium(II)	White	27.52	27.61	41.14	41.21
7. $(\text{NH}_4)_2[\text{Co}(\text{C}_{10}\text{H}_8\text{N}_2)(\text{SCN})_4]$ Diammonium tetrathiocyanato mono-(2,2'-dipyridyl) cobalt(II)	Brown	12.20	12.31	34.79	34.82
8. $(\text{NH}_4)_2[\text{Co}(\text{C}_{12}\text{H}_8\text{N}_2)(\text{SCN})_4]$ Diammonium tetrathiocyanato mono-(1,10-phenanthroline) cobalt(II)	Brown	11.62	11.84	37.87	38.11
9. $[\text{Zn}(\text{C}_{10}\text{H}_8\text{N}_2)(\text{SCN})_2]$ Dithiocyanato mono-(2,2'-dipyridyl) zinc(II)	White	19.38	19.18	42.68	43.01
10. $[\text{Zn}(\text{C}_{12}\text{H}_8\text{N}_2)(\text{SCN})_2]$ Dithiocyanato mono-(1,10-phenanthroline) zinc(II)	White	18.09	18.13	46.49	45.99
11. $(\text{NH}_4)_2[\text{Ni}(\text{C}_{10}\text{H}_8\text{N}_2)(\text{SCN})_4]$ Diammonium tetrathiocyanato mono-(2,2'-dipyridyl) nickel(II)	Grey	12.16	12.11	34.80	34.62
12. $(\text{NH}_4)_2[\text{Ni}(\text{C}_{12}\text{H}_8\text{N}_2)(\text{SCN})_4]$ Diammonium tetrathiocyanato mono-(1,10-phenanthroline) nickel(II)	Grey	11.59	11.62	37.90	38.11

Preparation of the complexes

The metal-2,2-dipyridyl or -1,10-phenanthroline complex was obtained by mixing metal and 2,2'-dipyridyl or 1,10-phenanthroline in the ratio 1 : 3 or 1 : 2, depending upon the nature of the metal. A freshly prepared solution of ammonium thiocyanate was added slowly to the

data of the mixed ligand complexes

H %		N %		S %		μ_{eff} in Bohr magnetons
Calc.	Found	Calc.	Found	Calc.	Found	
7	8	9	10	11	12	13
2.38	2.43	16.69	16.69	19.07	19.13	2.09
2.22	2.08	15.57	15.71	17.80	17.91	2.05
3.34	3.44	23.38	23.19	26.72	26.84	5.88
3.18	3.16	22.27	22.19	25.45	25.55	5.89
2.08	2.10	14.57	14.69	16.65	16.68	diamagnetic
1.95	2.02	13.71	13.92	15.67	15.49	diamagnetic
3.31	3.32	23.19	23.05	26.50	26.42	5.22
3.16	3.27	22.09	21.98	25.25	25.27	5.19
2.37	2.33	16.60	17.16	18.97	19.24	diamagnetic
2.21	2.24	15.50	15.62	17.71	17.65	diamagnetic
3.31	3.17	23.20	23.08	26.52	26.81	3.46
3.16	3.21	22.10	22.31	25.26	25.12	3.46

hot solution of the metal-2,2'-dipyridyl or metal-1,10-phenanthroline complex, till complete precipitation occurred. The solution was left to cool at room temperature for 2-3 hours. The precipitate was filtered, washed first with distilled alcohol for the removal of 2,2'-dipyridyl or 1,10-phenanthroline, then with distilled water to remove thiocyanate ion.

Finally the precipitate was dried at 50-60 °C.

Chemical analysis

Elemental analysis for C, H and N was performed in Microanalytical Laboratories, I.I.P. Dehra Dun, water of crystallization was determined by heating the sample at 105 °C. Sulphur was estimated by CARIUS' method [3].

In order to determine metal contents a known amount of isolated complex was decomposed with *conc.* nitric acid. The acid was neutralized with sodium carbonate and the neutral solution was subjected to gravimetric analysis [3].

Cobalt was measured as cobalt anthranilate, manganese, zinc and cadmium as ammonium phosphates, nickel as nickel dimethyl glyoxime and copper as cuprous thiocyanate.

The results of chemical analysis are summarized in Table I.

The magnetic susceptibility was measured at room temperature on a Gouy balance consisting of semi-micro Mettler balance for suspending and weighing the sample in a magnetic field of 8.5×10^3 Gauss generated by an electromagnet (4 amp, 100 volts, UNISCO, India) fed from A.C. mains.

On the basis of magnetic moment the following information regarding the structure of these complexes is obtained.

The magnetic moment values of the complexes under investigation fall under two categories: the octahedral complexes of Co, Mn and Ni, with μ_{eff} values between 3.46 and 5.89 B.M., and the square planar complexes of Cu with μ_{eff} values of 2.05 and 2.09 B.M. The Zn and Cd complexes were diamagnetic.

In the case of high spin octahedral complexes under study magnetic moments are of the same order as reported by other workers, for example, DRIVER and WALKER (*loc. cit.*) found the magnetic moment value of the complex $[\text{Fe}(\text{SCN})_2(\text{dipy})_2]$ to be 5.22 B.M. and MOORE [4] got the spin only value of 5.9 B.M. for the high spin Mn(II) complexes. The existence of high spin octahedral mixed complexes synthesized by us, therefore, indicated in the light of the above observations.

The results are summarized in Table I.

IR Studies

Lattice water is known to give absorption bands in the region of 3550–3200 (asymmetric and symmetric O–H stretching modes) and in the region of 1630–1600 cm^{-1} (H–O–H bending mode) [5].

The complexes isolated do not show any peak in this region.

Inorganic thiocyanates have been found to absorb in the range of 2130–2020 cm^{-1} [6]. The C–N stretching frequency is shifted towards higher value on coordination. The complexes under investigation show stretching bands in the region of 2040–2080 cm^{-1} confirming the presence of thiocyanate in these complexes.

The infrared spectra of a large number of 1,10-phenanthroline and 2,2'-dipyridyl [7] complexes have been reported. It has been found that the spectra of the free ligands undergo slight modification on coordination. In particular the ring frequencies (1600–1000 cm^{-1}) tend to undergo small but observable shifts to higher wave numbers. The bands corresponding to these ligands shift towards higher wave numbers in the spectra of the investigated complexes.

In the spectra of 2,2'-dipyridyl two bands of the free ligand at 995 cm^{-1} and 759 cm^{-1} have been suggested. The former peak shifts to 1010 cm^{-1} and the latter 10–20 cm^{-1} higher in the complexes [8]. All the complexes of 2,2'-dipyridyl under discussion show these bands shift to above 1000 and 760 cm^{-1} thereby confirming the presence of 2,2'-dipyridyl in them.

It has been established by X-ray analysis [9] that metals of the first transition series form M–N bonds in thiocyanate complexes. Accordingly in our complexes M–N peaks are found in every complex. Two types of metal-nitrogen peaks are observed *i.e.*, due to nitrogen of dipyridyl or phenanthroline or due to thiocyanate.

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PLATINUM METAL COMPLEXES OF CYCLOALKYL DITHIOCARBAMATES

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The complexes of ruthenium(III), rhodium(III), palladium(II), osmium(IV), osmium(III), iridium(III) and platinum(II) with sodium salts of cyclopentyl (NaCPD) and cycloheptyl (NaCHD) dithiocarbamic acids have been synthesized and characterized on the basis of elemental analyses, conductance measurements, spectral (electronic and vibrational) and magnetic moment data. Various ligand field (10 Dq), nephelauxetic (B , C and β) and single electron repulsion parameters (Δ_1 , Δ_2 and Δ_3) have also been calculated. The nephelauxetic parameters are indicative of strong covalency in the metal ligand bond.

Introduction

There is a growing interest in the chemistry of transition metal complexes of sulphur donor ligands on account of their encouraging anticancer, antiviral and antifungal activities [1–3]. Dithiocarbamates too belong to such class of ligands. A large number of dithiocarbamate complexes are known [4, 5], yet no report is available on transition metal complexes of cyclopentyl and cycloheptyl dithiocarbamates. Since, any change in the group attached to nitrogen may affect the spectral properties of complexes, it is considered worthwhile to investigate the magnetic and spectral properties of platinum metal complexes with these ligands. It has also been observed that the carcinostatic, antiviral and antifungal activities of metal chelates can be markedly affected by minor changes in the ligand [1, 2]. Therefore, such a study appears to be essential before any viable relation between the structure and carcinostatic, antiviral and antifungal activities of metal chelates can be laid out. This paper reports the synthesis and characterization of ruthenium(III), rhodium(III), palladium(II), osmium(IV), osmium(III), iridium(III) and platinum(II) complexes of cyclopentyl and cycloheptyl dithiocarbamates.

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Experimental

The ligands have been synthesized by the general method suggested by GILMAN and BLATT [6]. The platinum metal salts used were procured from Johnson Matthey Chemicals, London.

The complexes have been prepared as follows:

Ruthenium(III), rhodium(III) and iridium(III) complexes

All these complexes have been obtained by adding an aqueous solution of appropriate metal chloride to the sodium salt of dithiocarbamate dissolved in water in 1 : 3 molar ratio at room temperature. The precipitate was filtered, washed with distilled water and dried over P_4O_{10} .

Osmium(IV) complexes

The tetrakis(dithiocarbamato)-complex of osmium(IV) can be prepared by the reaction of $(NH_4)_2OsCl_6$ with sodium salt of the respective dithiocarbamic acid in a 1 : 5 molar ratio in aqueous methanol and was obtained as a dark green crystalline precipitate after a reaction time of about four hours. The precipitate was filtered and washed with aqueous methanol and dried over P_4O_{10} in vacuum.

Osmium(III) complexes

Trisdithiocarbamato complexes of these ligands are prepared by refluxing respective tetrakis complex in tetrahydrofuran for about ten hours.

Palladium(II) and platinum(II) complexes

The aqueous solution of palladium chloride or potassium tetrachloroplatinate was added to an aqueous solution of sodium salt of appropriate dithiocarbamate in 1 : 2 molar ratio. The orange/yellow precipitate obtained was washed with distilled water and dried over P_4O_{10} .

Analytical procedures and physical measurements

The metal content of the complexes was determined by standard gravimetric method. Nitrogen was estimated by Kjeldahl method and sulphur as barium sulphate. The carbon and hydrogen analyses were carried out at C. D. R. I., Lucknow.

Infrared spectra were recorded in solid state (KBr-Pellets) in the region 4000—200 cm^{-1} on a Perkin—Elmer-621 grating spectrophotometer. The electronic spectra of these complexes in acetone were run on a Perkin—Elmer 4000 \AA and visible range Russian C Ø 10 spectrophotometer. Magnetic measurements were carried out by Gouy's method using mercury tetrathiocyanatocobaltate(II) as a calibrant. Conductance measurements were made in nitrobenzene at 30.00 ± 0.05 °C on a Beckmann Conductivity Bridge Model No. RC-18A. Molecular mass determinations were carried out ebullioscopically in benzene using a Gallenkamp (U.K.) ebulliometer.

Results and Discussion

Some physical properties of the complexes are listed in Table I. Elemental analyses of these complexes indicate 1 : 4 for Os(IV), 1 : 3 for Ru(III), Rh(III), Ir(III) and Os(III) and 1 : 2 for Pd(II) and Pt(II) metal to ligand stoichiometry. All these complexes are soluble in benzene, acetone, chloroform, *N,N'*-dimethyl formamide and nitrobenzene. Molar conductance of 10^{-3} M solution of all these complexes indicate the nonelectrolytic nature of the complexes. From molecular mass measurements, it is concluded that these complexes are monomeric.

Magnetic moments and electronic spectra

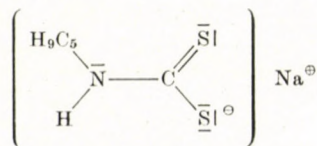
Ruthenium(III) complexes

The magnetic moment of (tris)dithiocarbamate derivatives of ruthenium(III) lies in the range 1.80–1.85 B. M. at room temperature, which are appreciably lower than the spin-value, (2.10 B. M.) of the free ion. This value

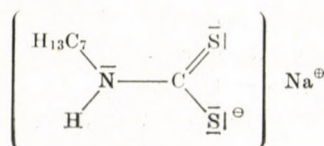
Table I
Analytical data of platinum metal complexes*

Complex	Colour	De-comp. temp. °C	Found (calcd) %					Mol. wt. Found (calcd)
			C	H	N	S	M	
Ru(CPD) ₃	Dark brown	200	36.8 (37.1)	4.8 (5.1)	7.1 (7.2)	32.8 (33.0)	16.9 (17.3)	560 (581.1)
Ru(CHD) ₃	Dark brown	180	43.1 (43.3)	6.1 (6.3)	6.1 (6.3)	28.5 (28.8)	15.0 (15.2)	650 (665.1)
Rh(CPD) ₃	Orange	155	36.7 (37.0)	4.6 (5.1)	7.1 (7.2)	32.3 (32.5)	17.4 (17.6)	570 (582.9)
Rh(CHD) ₃	Orange	150	42.9 (43.1)	6.1 (6.3)	6.0 (6.3)	28.6 (28.8)	15.2 (15.4)	652 (666.9)
Pd(CPD) ₂	Orange	155	33.2 (33.8)	4.1 (4.7)	6.5 (6.6)	30.0 (30.0)	24.6 (24.9)	420 (626.4)
Pd(CHD) ₂	Yellow	155	39.5 (39.8)	5.4 (5.8)	5.6 (5.8)	26.3 (26.5)	21.6 (22.0)	476 (482.4)
Os(CPD) ₄	Green	220	34.2 (34.6)	4.5 (4.8)	6.2 (6.7)	30.6 (30.8)	22.6 (22.9)	815 (830.2)
Os(CHD) ₄	Green	175	40.5 (40.7)	5.2 (5.9)	5.7 (5.9)	27.0 (27.1)	19.7 (20.2)	932 (942.2)
Os(CPD) ₃	Red	180	32.1 (32.2)	4.1 (4.5)	6.2 (6.3)	28.4 (28.6)	28.0 (28.4)	667 (670.2)
Os(CHD) ₃	Red	175	38.0 (38.2)	5.4 (5.6)	5.2 (5.6)	25.1 (25.4)	25.2 (25.2)	742 (754.2)
Ir(CPD) ₃	Orange yellow	220	31.8 (32.1)	4.2 (4.5)	6.1 (6.2)	28.4 (28.6)	28.6 (28.6)	659 (672.2)
Ir(CHD) ₃	Orange yellow	165	37.6 (38.1)	5.1 (5.5)	5.4 (5.5)	25.2 (25.4)	25.0 (25.4)	747 (756.2)
Pt(CPD) ₂	Yellow	205	27.5 (28.0)	3.6 (3.9)	5.2 (5.4)	24.5 (24.8)	37.7 (37.9)	508 (515)
Pt(CHD) ₂	Yellow	160	33.1 (33.6)	4.5 (4.9)	4.8 (4.9)	22.4 (22.4)	34.0 (34.1)	568 (571)

* where, NaCPD =



and NaCHD =



calculated by employing the spin-orbit coupling constant of the free ion has been logically found higher than the spin-only value 1.73 [7a]. This lowering may be due to the presence of low symmetry ligand fields. However, the possibility of these complexes being polymeric is ruled out because in such cases the electron interaction of the metal atoms through direct exchange or superexchange phenomenon is quite severe and results in a very low magnetic moments [7]. The electronic spectra of the complexes show bands at *ca.* 13 000–14 000, 17 000–18 000 and 21 000–21 500 cm^{-1} . The positions of these bands (Fig. 1) are comparable to other ruthenium(III) complexes possessing octahedral stereochemistry [8–10]. The ground state of ruthenium(III) in octahedral field is ${}^2T_{2g}$ and accordingly the bands may be assigned [8a] to ${}^4T_{1g} \leftarrow {}^2T_{2g}$, ${}^4T_{2g} \leftarrow {}^2T_{2g}$ and ${}^2T_{1g}$, ${}^2A_{2g} \leftarrow {}^2T_{2g}$ transitions in an increasing order of energy. The values of different ligand field and nephelauxetic param-

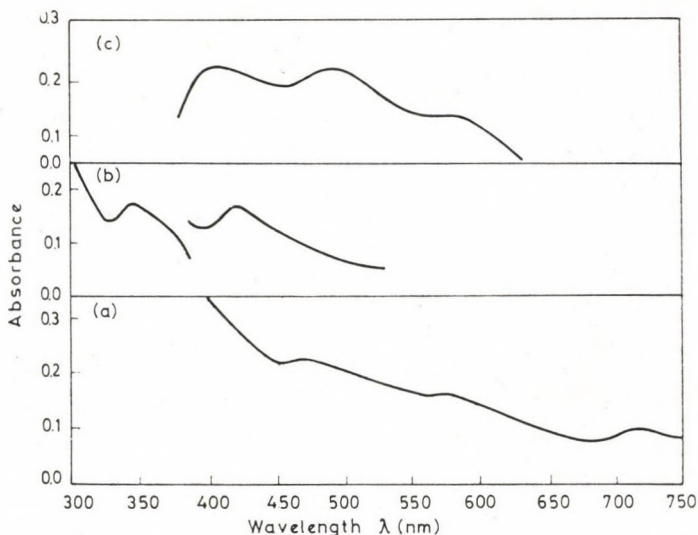


Fig. 1. Absorption spectra of (a) $\text{Ru}(\text{CHD})_3$, (b) $\text{Rh}(\text{CHD})_3$, (c) $\text{Pt}(\text{CHD})_2$ in acetone

eters (Table II) also support the pseudo octahedral stereochemistry [8] for these complexes. The ratio ν_2/ν_1 are in the range 1.25–1.28 in very good agreement with the literature data [11, 12]. The considerable decrease in the value of Racah interelectronic parameter B from that of the free ion value suggests strong covalent bonding between the ligand and the central atom [8]. The overall effect of some covalent bonding will be an increase in the observed value of $10 Dq$, or Δ , high value of Δ being usually associated with considerable electron delocalization, that means covalent bonding [8].

Table II
Magnetic moments and electronic spectral data of platinum metal complexes

Complex	Bands observed	Assignments		10 Dq	B	C	β	Δ eH. BM (300 K)
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
Ru(CPD) ₃	13 200 17 000 21 000	$^4T_{1g} \leftarrow ^2T_{2g}$ $^4T_{2g} \leftarrow ^2T_{2g}$ $^2T_{1g}, ^2A_{2g} \leftarrow ^2T_{2g}$	1.28	23 075	475	2125	0.76	1.80
Ru(CHD) ₃	14 000 17 500 21 500	-do-	1.25	24 499	437	2125	0.70	1.85
Rh(CPD) ₃	23 000 28 000	$^1T_{1g} \leftarrow ^1A_{1g}$ $^1T_{2g} \leftarrow ^1A_{1g}$	1.21	24 248	312	1248	0.43	Diamag
Rh(CHD) ₃	23 800 29 000	-do-	1.21	24 300	325	1300	0.45	Diamag
Ir(CPD) ₃	27 200 29 000 32 500	$^1T_{1g} \leftarrow ^1A_{1g}$ $^1T_{2g} \leftarrow ^1A_{1g}$ C.T.	1.06	27 648	112	448	0.17	Diamag
Ir(CHD) ₃	27 500 29 400 31 500	-do-	1.06	27 972	118	472	0.18	Diamag
Os(CPD) ₄	25 300 33 000	— C.T.	—	—	—	—	—	Diamag
Os(CHD) ₄	25 800 34 500	— C.T.	—	—	—	—	—	Diamag
Os(CPD) ₃	32 000	— C.T.	—	—	—	—	—	1.63
Os(CHD) ₃	32 500	— C.T.	—	—	—	—	—	1.67
			Δ_1		Δ_2	Δ_3		
Pd(CPD) ₂	19 000 22 800 27 000	$^1A_{2g} \leftarrow ^1A_{1g}$ $^1B_{1g} \leftarrow ^1A_{1g}$ $^1E_g \leftarrow ^1A_{1g}$	21 100		5900	3675		Diamag
Pd(CHD) ₂	19 500 23 000 27 500	$^1A_{2g} \leftarrow ^1A_{1g}$ $^1B_{1g} \leftarrow ^1A_{1g}$ $^1E_g \leftarrow ^1A_{1g}$		21 600	5600	3975		Diamag
Pt(CPD) ₂	16 000 19 000 24 000	$^1A_{2g} \leftarrow ^1A_{1g}$ $^1B_{1g} \leftarrow ^1A_{1g}$ $^1E_g \leftarrow ^1A_{1g}$		18 100	5100	4475		Diamag
Pt(CHD) ₂	17 000 20 500 25 000	-do-		19 100	5600	3975		Diamag

Rhodium(III) and iridium(III) complexes

The tris(dithiocarbamato)-derivatives of rhodium(III) and iridium(III) are of low spin type (t_g^6) and are found to be diamagnetic.

The electronic spectra of these complexes show bands at *ca.* 23 000—24 000 and 28 000—29 000 cm^{-1} Rh(III) and at *ca.* 27 000—27 500, 29 000

and 31 000–32 500 cm^{-1} Ir(III). The bands positions (Fig. 1) are similar to those reported with sulphur donor ligands possessing pseudo octahedral stereochemistry [8, 13, 14] and accordingly, the first two bands in both cases may be assigned to ${}^1T_{1g} \leftarrow {}^1A_{1g}$ and ${}^1T_{2g} \leftarrow {}^1A_{1g}$ transitions in an increasing order of energy. The bands at somewhat higher energy in iridium derivatives *ca.* 31 000–32 500 cm^{-1} can be attributed to a charge transfer transition [15, 16]. The electronic spectra of these complexes are further rationalized in terms of ligand field (10 Dq) and interelectronic repulsion parameters (*B* and *C*). The values of these parameters (Table II) are consistent with those normally observed for pseudooctahedral complexes of trivalent rhodium and iridium possessing sulphur donor atoms [13]. The ratio ν_2/ν_1 , is 1.21 for the rhodium complexes and 1.06 for the iridium complexes in very good agreement with the literature data [8a]. The *B* value is 45–43% of the free ion value in rhodium complexes and 18–17% of the free ion value in iridium complexes. This fact suggests that it is a considerable orbital overlap with strong covalency in the metal ligand σ -bond.

Osmium(III) and osmium(IV) complexes

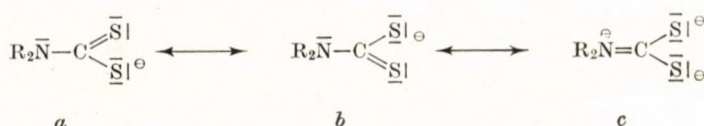
The magnetic moment of tris(dithiocarbamato)-derivative of Os(III) lies at *ca.* 1.6–1.7 B. M. at room temperature, whereas the Os(IV) complexes are diamagnetic. The electronic spectra of osmium(IV) complexes show intense absorption at *ca.* 25 000–26 000 and 35 000 cm^{-1} while osmium(III) complexes show intense band at *ca.* 32 000 cm^{-1} . All these bands are undoubtedly charge transfer in origin. Low energy spin forbidden transitions may be observed [8] in the osmium complexes. These all are dominated by charge transfer bands.

Palladium(II) and platinum(II) complexes

The palladium(II) and platinum(II) complexes are diamagnetic. The electronic spectra of these complexes show band in the regions 16 000–17 000, 19 000–20 500 and 24 000–25 000 cm^{-1} for Pt(II), and 19 000–19 500, 22 500–23 000 and 27 000–27 500 cm^{-1} for Pd(II). The position of these bands (Fig. 1) are comparable with the square planar palladium(II) and platinum(II) complexes [8, 13, 14, 17]. The ground state of square planar complex is ${}^1A_{1g}$ and accordingly, the bands observed for these complexes may be assigned to ${}^1A_{2g} \leftarrow {}^1A_{1g}$, ${}^1B_{1g} \leftarrow {}^1A_{1g}$ and ${}^1E_g \leftarrow {}^1A_{1g}$ transitions in increasing order of energy. By assuming a value of $F_2 = 10$, $F_4 = 600 \text{ cm}^{-1}$ for the Slater Condon interelectronic repulsion parameters, it is possible to calculate [8, 18] A_1 , A_2 and A_3 the single electron parameters. These values also support the proposed stereochemistry for palladium(II) and platinum(II) complexes.

Vibrational spectral studies

Infrared spectral studies have not been carried out in detail, since it is quite difficult to assign the bands being most of them highly coupled. The structure of dithiocarbamates can be represented by the following formalism:



The extent to which resonance form (c) contributes to the structure and its effects on the physical chemical properties of the complexes has been extensively studied [19]. NAKAMOTO concluded [20] that resonance form (c) does indeed contribute to the structure to a considerable extent. The monodentate and/or bidentate nature of the dithiocarbamate ligand is decided by the (C-S) stretching frequency. In case of bidentate behaviour a single strong band appears in the region $965-1000\text{ cm}^{-1}$, while a doublet is expected in the region $1000 \pm 70\text{ cm}^{-1}$ in the monodentate behaviour [21-24]. Except Os(IV) appearance of only one strong band in the region $980-1005\text{ cm}^{-1}$

Table III
 Characteristic IR bands for platinum metal complexes (cm^{-1})

Compounds	$\nu(\text{C}\cdots\text{N})$	$\nu(\text{C}\cdots\text{S})$	$\nu(\text{M}-\text{S})$
NaCPD	1490s	990s, 1000s	—
NaCHD	1980s	990s, 1005s	—
Ru(CPD) ₃	1505s	1005s	345w
Ru(CHD) ₃	1505s	1000s	350w
Rh(CPD) ₃	1500s	995s	335w
Rh(CHD) ₃	1495s	1005s	325w
Pd(CPD) ₂	1505s	985s	330w
Pd(CHD) ₂	1510s	990s	345w
Os(CPD) ₄	1495s	995s	345w
Os(CHD) ₄	1490s	1000s	340w
Os(CPD) ₃	1500s	980s	380w
Os(CHD) ₃	1495s	990s	375w
Ir(CPD) ₃	1495s	1005s	320w
Ir(CHD) ₃	1500s	990s	325w
Pt(CPD) ₂	1505s	975s	300w
Pt(CHD) ₂	1500s	985s	315w

strongly supports the bidentate nature of the ligands in these complexes, while in case of Os(IV) complex some additional bands are observed at *ca.* 1420, 1265 and 995 cm^{-1} suggesting monodentate behaviour of the ligands [25]. This indicates that tetrakis-derivatives of Os(IV) contain both monodentate and bidentate dithiocarbamate ligands. The ureid band (C—N) near 1490 cm^{-1} is very characteristic for the dithiocarbamates. The frequency of this band lies between that for C—N (1250—1350 cm^{-1}) and C=N (1640—1690 cm^{-1}) which suggests that this band possesses some double bond character [19, 26]. In all these complexes this band shifts to higher frequency ($\sim 20 \text{ cm}^{-1}$) also indicating the bidentate behaviour of the dithiocarbamates [27]. Coordination through sulphur has been confirmed by the appearance of new bands in the far infrared in the ruthenium(III), rhodium(III), palladium(II), osmium(IV), osmium(III), iridium(III) and platinum(II) complexes at *ca.* 350, 330, 340, 350, 370, 320 and 320 cm^{-1} regions which may be assigned to ν (M—S) vibrations, respectively. Characteristic I.R. bands have been listed in Table III.

*

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HETEROCYCLIZATION WITH IMINIUM CHLORIDES, III

SYNTHESIS OF 3,4-DIHYDRO-(1*H*)-1,3,4-BENZOTRIAZEPINE-2,5-DIONES

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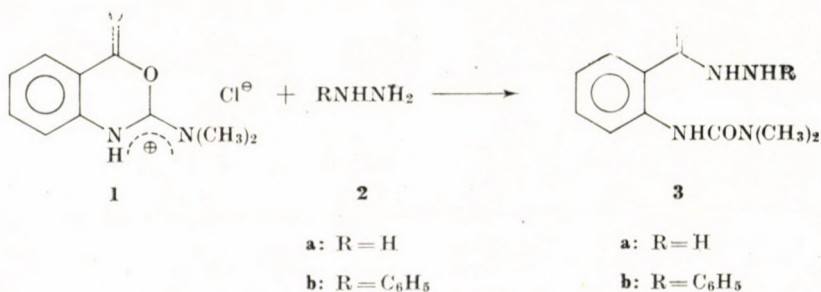
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A new route to the title compounds has been developed. 3,4-Dihydro-3-methyl-(1*H*)-1,3,4-benzotriazepine-2,5-dione was prepared by treating 2-dimethylammonio-(4*H*)-3,1-benzoxazine-4-one chloride with methylhydrazine and cyclizing the 2-dimethylcarbamoylanthraniloylhydrazide with heating. Two reports on the synthesis of a number of 3,4-dihydro-(1*H*)-1,3,4-benzotriazepine-2,5-diones are shown to be in error. These routes give actually 3-amino-2,4-(1*H*,3*H*)-quinazolinodiones.

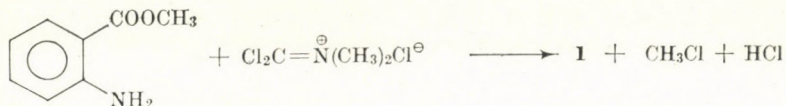
In recent years much research work has been devoted to the preparation of benzodiazepines. Of the six classes known, the most important compounds are 1,4-benzodiazepines, some of which are in current use as psychoterapeutic agents. Owing to this fact, increasing synthetic effort has been made lately to prepare the benzotriazepine ring system, too. Of the six possible classes of benzotriazepines only three ones, benzo-1,3,4-, 1,2,5- and 1,3,5-triazepines have been studied to date. While the two former classes are well known in the literature [1, 2], benzo-1,3,5-triazepines are documented in few instances [3]. In this paper we report specifically on the preparation of 3,4-dihydro-(1*H*)-1,3,4-benzotriazepine-2,5-diones.

The new route developed in this research seems to be, besides PEET's work [4], the only unequivocal way of synthesizing this class of compounds. Our synthesis — in accordance with PEET's results — has allowed us to examine critically two reported routes and also the products obtainable by these reactions and described as the title compounds.

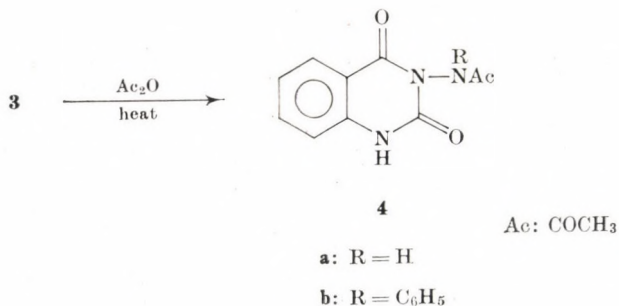
Treatment of 2-dimethylammonio-(4*H*)-3,1-benzoxazine-4-one chloride (1) with hydrazines (2) gave 2-dimethylcarbamoylanthraniloylhydrazides (3a, b).



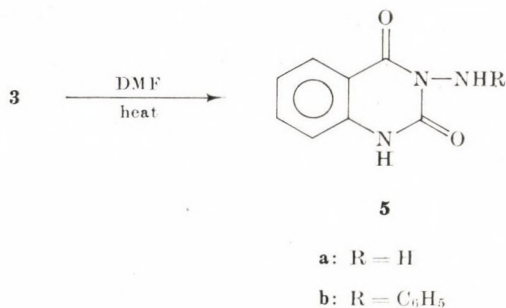
Compound **1** is readily available from the reaction of methyl anthranilate and phosgene immonium chloride [(dichloromethylene)-dimethylammonium chloride]:*



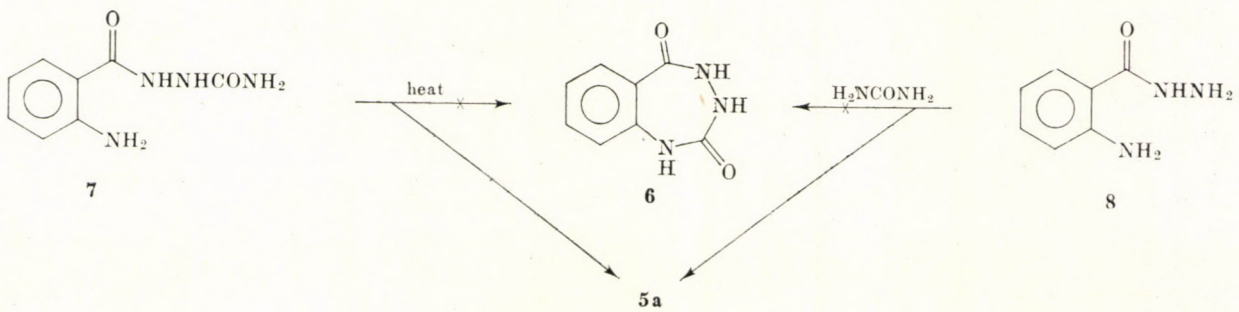
Compound **1** is very reactive even under mild conditions. In alcohol, with two equivalents of the hydrazine or in the presence of a base — for instance sodium acetate — **3a, b** are formed in good yields (80–90%) at room temperature. Cyclization of **3** was accomplished by short boiling in Ac_2O or DMF. Compounds **4a** and **4b**, prepared in Ac_2O , were acetylated in the 3-position and were found to possess six-membered rings in both cases.



In DMF there was a slight hope of the formation of benzo-1,3,4-triazepine — at least in the case of **3a** — but compounds **5**, similarly to **4**, were 3-amino-2,4-(1*H*,3*H*)-quinazolidinediones [6]:

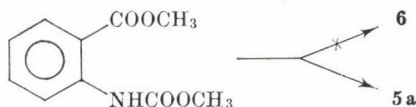


* For a survey of the preparation and reactions of phosgene immonium chloride, see Ref. [5].



LANGIS and CHAREST [7] reported two methods for the preparation of 3,4-dihydro-(1H)-1,3,4-benzotriazepine-2,5-diones (**6**). They stated that cyclization of 2-aminobenzoyl semicarbazide (**7**) at reflux temperature, or the refluxing of 2-aminobenzoylhydrazine (**8**) with urea, in decalin gave **6**. PEET *et al.* [4] recently examined this claim and established that neither of these reactions produced a seven-membered ring, but the products were quinazoline-2,4-diones (**5**).

Our work does support PEET's statement; we have also prepared the product from **7** and **8** according to LANGIS and CHAREST's method, and found it to be identical in all respects with our compound **5a**. We also found, in accordance with PEET, that a recent U.S. patent by BALEY [8] referring to the preparation of the title compounds must also be faulty. This general method involves the condensation of alkyl *N*-carboxyanthranilates with hydrazines:



The intermediate of this reaction is probably the corresponding hydrazide — similar to **3a** — which can cyclize only to the thermodynamically favoured, more stable six-membered ring; therefore this kind of ring closure is not suitable for the preparation of benzo-1,3,4-triazepines. It means that the structures of the compounds described as benzo-1,3,4-triazepines in the literature, prepared by the three methods mentioned above, are largely doubtful.

When the N-1 atom in the hydrazide is protected by alkylation, the unwanted ring closure can be avoided, and the formation of the seven-membered ring can be achieved.

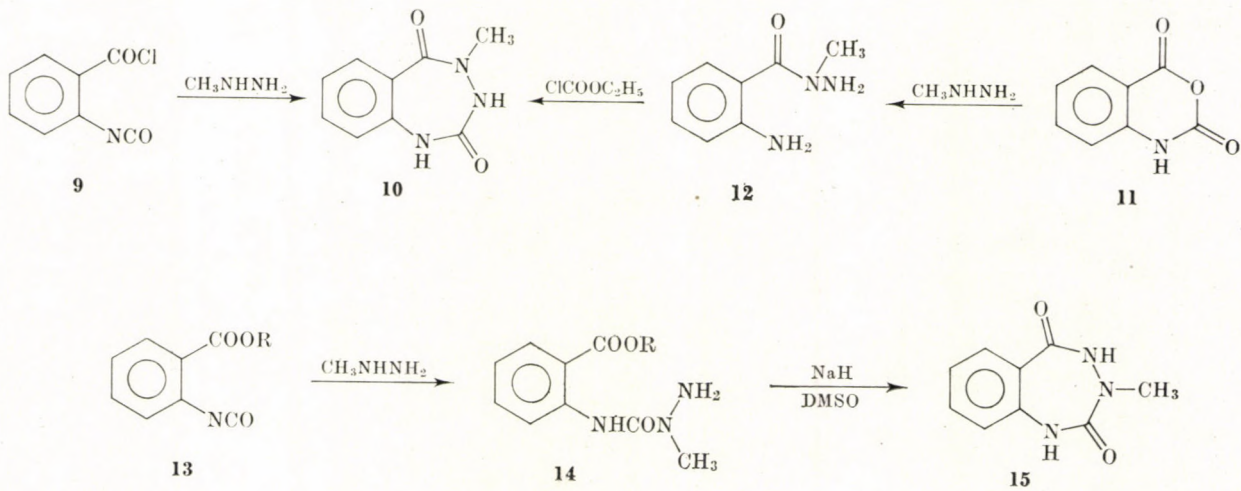
PEET and SUNDER [4, 9] have developed some new routes, but the yields are generally low.

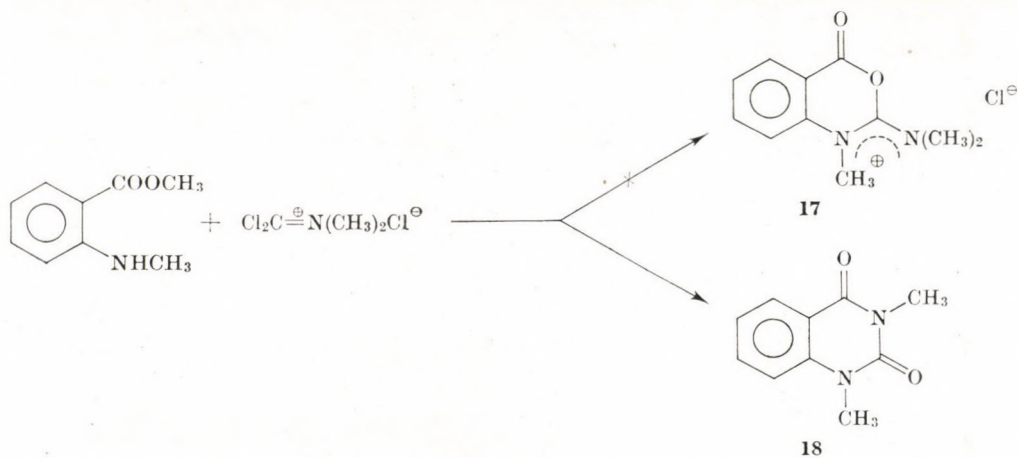
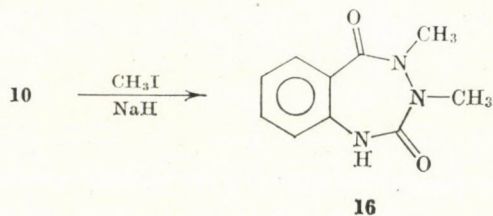
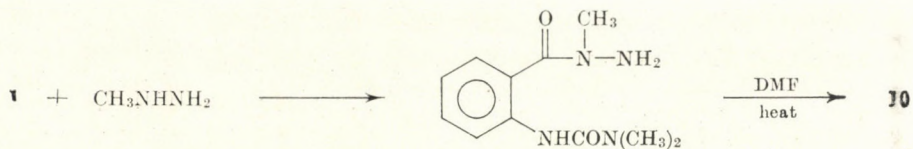
When methylhydrazine is used, acylation takes place mostly on the nitrogen atom attached to the methyl group, resulting in the required structure, **10**.

Our method is analogous, but it seems to be more convenient than the former ones (simple reagents, short reaction times, good yields):

Compound **10** can be selectively methylated at the 3-position with NaH and MeI in DMF to give **16**, which proved to be identical with the compound described in the literature [4, 10].

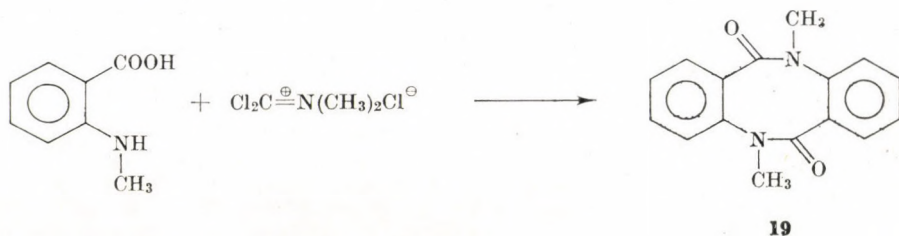
Preparation of the isomeric 1,4-dimethyl derivatives was attempted by a reaction route similar to **1** → **3** → **4**, starting from methyl *N*-methylantranilate, through 1-methyl-2-dimethylammonio-(4H)-3,1-benzoxazine-4-one chloride (**17**), according to the equation below.





This attempt failed, since instead of 17, the product was 18. Compound 17 probably rearranged with ring opening, followed by cyclization with *N*-acylation and elimination of methyl chloride.

It is interesting to remark that *N*-methylantranilic acid behaved in quite a different manner, because self-condensation took place resulting in a dibenzodiazocine derivative (19):



Experimental

2-Dimethylammonio-(4H)-3,1-benzoxazine-4-one chloride (1)

(Dichloromethylene)-dimethylammonium chloride (phosgene immonium chloride)* (16.25 g; 0.1 mole) and 15.1 g (0.1 mole) of methyl anthranilate were boiled in methylene chloride until gas evolution ceased. The white solid product was filtered off, washed with ether and dried in a desiccator to obtain 18.4 g (81%) of **1**, m.p. 211–213 °C (d.).

$C_{10}H_{11}N_3O_2Cl$ (226.47). Calcd. C 52.90; H 4.86; N 12.36; Cl⁻ 15.68. Found C 53.12; H 4.87; N 12.38; Cl⁻ 15.75%.

IR (KBr): ν_{CO} 1815 cm^{-1} ; $C=N^+$ 1680 cm^{-1} .

NMR (TFA): δ_{NMe_2} 3.39s (3H), 4.35s (3H); ArH 7.5–7.75m (2H), 7.98t (1H), 8.22d (1H), $J_0 = 8$ Hz.

2-Dimethylcarbamoylethraniloylhydrazides (3a, b)

Compound **1** (2.26; 0.01 mole) and the hydrazine (0.02 mole) in 10 mL of ethanol were allowed to stand at room temperature for 3 h. The solution was then diluted with water, whereupon a white solid precipitated, which was filtered off and recrystallized from EtOH.

3a: 1.63 g (73%), 2-*N,N*-dimethylureidobenzhydrazide, m.p. 158–160 °C (d.), then 282–283 °C.

$C_{10}H_{14}N_4O_2$ (222). Calcd. C 54.05; H 6.31; N 25.21. Found C 53.83; H 6.59; N 24.92%.

IR (KBr): ν_{CO} 1665, 1645 cm^{-1} ; ν_{NH} 3400–3200 cm^{-1} .

NMR ($CDCl_3$): δ_{NMe_2} 3.10s (6H); ArH 6.86t (1H), 7.2–7.4m (2H), 8.24d (1H), $J_0 = 8$ Hz; NH 4.10 bs (2H), 10.16 bs (1H).

3b: 2.55 g (86%), 2-(*N,N*-dimethylureido)-benzoylphenylhydrazine, m.p. 153–155 °C (d.), then 230–231 °C.

$C_{16}H_{18}N_4O_2$ (298). Calcd. C 64.40; H 6.04; N 18.77. Found C 64.18; H 5.97; N 18.34%.

IR (KBr): ν_{CO} 1665, 1640 cm^{-1} ; ν_{NH} 3360, 3300–3250 cm^{-1} .

NMR ($CDCl_3$): δ_{NMe_2} 2.98s (6H); ArH 6.75–6.95m (4H), 7.1–7.3m (3H), 7.52d (1H), 8.19d (1H), $J_0 = 8$ Hz; NH 6.25d (1H), 9.10d (1H), $J_{NHNH} = 4$ Hz, 10.05s (1H).

3-Amino-(1H,3H)-quinazoline-2,4-diones

3a, b (0.005 mole) was boiled in 10 mL of DMF for 1 h. The solution was poured into water, the resulting solid was filtered off, washed with ethanol, and recrystallized from DMF.

5a: 0.81 g (94%), 3-amino-(1H,3H)-quinazoline-2,4-dione, m.p. 289–291 °C (*lit.* [13] m.p. 291–293 °C).

$C_8H_7N_3O_2$ (177.15). Calcd. C 54.20; H 3.95; N 23.75. Found C 54.38; H 3.49; N 24.19%.

IR (KBr): ν_{CO} 1730, 1650 cm^{-1} ; NH 3320, 3250–2700 cm^{-1} .

MS (*m/e*): M^+ 177 (63.6%), 146 (100%), 92 (11.6%), 90 (13.6%).

Preparation of 5a according to LANGIS and CHAREST [7]

(A) 2-Aminobenzoylhydrazine (1.5 g; 0.01 mole), urea (0.6 g; 0.01 mole) and decalin (15 mL) were refluxed for 5 h. On cooling a solid precipitated, which was collected, washed with ethanol and recrystallized from DMF to afford 1.45 g (86%) of **5a**, m.p. 288–290 °C.

(B) 2-Aminobenzoyl semicarbazide (2.0 g; 0.01 mole) was refluxed in decalin (15 mL) for 4 h, to yield 0.89 g (50%) of **5a**, m.p. 287–289 °C (DMF).

5b: 1.06 g (85%), 3-anilino(1H,3H)-quinazoline-2,4-dione, m.p. 230–231 °C.

$C_{14}H_{11}N_3O_2$ (253.26). Calcd. C 66.30; H 4.35; N 16.60. Found C 66.55; H 4.54; N 16.25%.

IR (KBr): ν_{CO} 1740, 1670 cm^{-1} ; ν_{NH} 3260, 3200–2800 cm^{-1} .

MS (*m/e*): M^+ 253 (100%), 146 (79.6%), 120 (11.7%), 92 (19.2%), 91 (27.7%).

* Phosgene immonium chloride was prepared by VIEHE's method, by the chlorination of tetramethylthiuram disulfide in methylene chloride at 40 °C.

3-Acetamino-(1H,3H)-quinazoline-2,4-diones

Compound **3a, b** (0.005 mole) was boiled in acetic anhydride (10 mL) for 10 min. On cooling crystals precipitated, which were collected, washed with ether and dried.

4a: 0.96 g (87%), 3-acetamino-(1H,3H)-quinazoline-2,4-dione, m.p. 278–280 °C.

$C_{10}H_9N_3O_3$ (219). Calcd. C 54.85; H 4.11; N 19.18. Found C 54.68; H 4.21; N 19.35%.

IR (KBr): ν CO 1745, 1700, 1680 cm^{-1} ; ν NH 3500, 3280 cm^{-1} .

MS (*m/e*): M^+ 219 (11%), 177 (97%), 146 (100%), 92 (9.5%), 90 (8.3%).

4b: 1.22 g (84%), 3-acetanilido-(1H,3H)-quinazoline-2,4-dione, m.p. 236–239 °C.

$C_{16}H_{13}N_3O_3$ (295.10). Calcd. C 65.05; H 4.41; N 14.25. Found C 64.03; H 4.68; N 14.98%.

IR (KBr): ν CO 1745, 1700, 1675 cm^{-1} ; ν NH 3290 cm^{-1} .

NMR ($CDCl_3 + CD_3OD$ 1 : 1): CH_3CO 2.18s (3H); ArH 6.95–7.6m (6H), 7.7m (2H), 7.95dd (1H), $J_0 = 8$ Hz, $J_m = 2$ Hz.

MS (*m/e*): M^+ 295 (6.6%), 253 (100%), 146 (61.2%), 119 (17.4%), 92 (15.6%), 91 (20.9%).

3,4-Dihydro-4-methyl-(1H)-1,3,4-benzotriazepine-2,5-dione (10)

Compound **1** (3.25 g; 0.02 mole) and methylhydrazine (1.85 g; 0.06 mole) were stirred in 20 mL ethanol for 3 h. After evaporation of the solvent the residue was triturated with ethyl acetate to remove the hydrochloride salt of methylhydrazine. The filtrate was evaporated to dryness. An oily substance remained which was taken up in 10 mL of DMF, boiled for 1 h and poured into water. The white solid which precipitated was filtered off and dried in air to obtain 3.05 g (79%) of **10**, m.p. 262–264 °C. (*lit.* [4] m.p. 266–267 °C).

$C_9H_9N_3O_2$ (191.12). Calcd. C 56.50; H 4.71; N 22.05. Found C 56.03; H 4.82; N 22.83%.

IR (KBr) ν CO 1730, 1680 cm^{-1} ; ν NH 3250, 3180 cm^{-1} .

NMR (TFA): δ NCH₃ 3.67s (3H); ArH H-1 7.15d ($J = 8$ Hz), H-2 7.64t ($J = 8$ Hz), H-3 7.39t ($J = 8$ Hz), H-4 7.94d ($J = 8$ Hz); NH 8.00 wide (1H), 8.57s (1H).

MS (*m/e*): M^+ 191 (38.8%), 162 (15.5%), 146 (100%), 92 (9.1%), 90 (14.1%).

3,4-Dihydro-3,4-dimethyl-(1H)-1,3,4-benzotriazepine-2,5-dione (16)

To a stirred mixture of 0.33 g (0.011 mole) of NaH (80%) in 10 mL of DMF there was added 1.9 g (0.01 mole) of **10**. After dissolution, 1 mL of methyl iodide was slowly added, with ice cooling. The reaction mixture was stirred for 3 h at room temperature, then poured into water and extracted with CH_2Cl_2 . The organic layer was dried ($MgSO_4$) and concentrated to give an oil which solidified on rubbing with ether: 1.2 g (58%), m.p. 185–186 °C (*lit.* [10] m.p. 189–190 °C).

IR (KBr): ν CO 1710, 1650 cm^{-1} ; ν NH 3250 cm^{-1} .

NMR ($DMSO-d_6$): δ CH₃ 2.90s (3H), 3.20s (3H); ArH 8.01–7.0m (4H); NH 9.71s (1H).

1,3-Dimethyl-(1H,3H)-quinazoline-2,4-dione (18)

(Dichloromethylene)-dimethylammonium chloride (1.63 g; 0.01 mole) and 1.65 g (0.01 mole) of methyl *N*-methylantranilate were refluxed in dichloroethane (10 mL) for 2 h. On cooling a white solid precipitated, which was collected, washed with ether and dried to obtain 1.45 g (76%) of **18**, m.p. 162–164 °C (*lit.* [10] m.p. 165–166 °C).

$C_{10}H_{10}N_2O_2$ (190.20). Calcd. C 63.12; H 5.27; N 14.75. Found C 63.00; H 5.35; N 14.98%.

IR (KBr): ν CO 1715, 1665 cm^{-1} .

NMR ($CDCl_3$): δ NMe 3.45s (3H), 3.58s (3H); ArH 7.15t (2H), 7.55d (1H), 8.1d (1H).

5,11-Dimethyldibenzo[*b, f*]1,5-diazocine-6,12-dione (19)

(Dichloromethylene)-dimethylammonium chloride (1.63 g; 0.01 mole) and 1.52 g (0.01 mole) of *N*-methylantranilic acid were stirred in 10 mL dichloroethane at 40 °C for 2 h. The solvent was evaporated in vacuum and the oily residue was triturated with water to yield 0.6 g (23%) of **19**, m.p. 203–205 °C (EtOAc) (*lit.* [12] m.p. 206–207 °C).

$C_{16}H_{14}N_2O_2$ (266.30). Calcd. C 72.16; H 5.29; N 10.52. Found C 71.95; H 5.29; N 10.07%.

IR (KBr): ν CO 1665, 1655 cm^{-1} .

NMR ($CDCl_3$): δ NMe 3.44s (6H); ArH 7.23dt (8H).

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ANODIC DISSOLUTION OF METALS, I

KINETICS OF THE DISSOLUTION PROCESS INVOLVING TWO, AND THREE CONSECUTIVE CHARGE TRANSFER STEPS

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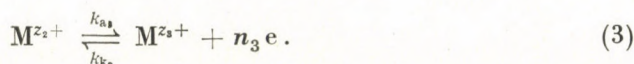
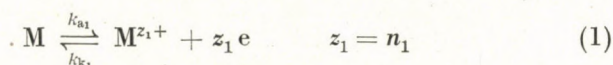
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Methods are surveyed by means of which it can be decided whether the dissolution of a metal *via* several charge transfer steps in series is a two- or a three-step mechanism. The information relevant to the decision of this question is furnished by the rate constant of the second reaction step. These rate constants can be calculated from polarization curves, or from data gathered using a rotating ring disc electrode in the experiments.

The ionization of metals, and the reduction of metal ions can proceed *via* (a series of) charge transfer steps, one following the other [1, 2]. In the literature we find several methods described [2, 3, 6] by means of which it can be decided whether or not a given electrode process is a series of charge transfer reactions. Most often the methods described consist of the analysis of polarization curves [2, 3] or of the interpretation of experimental data gathered by means of rotating ring disc electrodes [4, 5, 6]. With the help of these an unequivocal statement about the occurrence of serial charge transfer can be made in most of the cases. If the metal ion stable in the solution carries three positive charges it is sometimes impossible unequivocally to say whether the overall process consists of two or of three charge transfer reactions in series. In the case of indium, for instance, it is proven [7] that its anodic dissolution is a series of charge transfers: the intermediary In^+ ions are detectable. However, no definite conclusion concerning the further oxidation of the In^+ ions, *viz.* whether one or two charge transfer steps will occur, could be drawn [7].

Therefore, in this paper, we intend to summarize the electrochemical methods by means of which it is possible to decide whether electrode processes analogous to the one mentioned proceed over two, or over three charge transfer steps in series. In what follows we restrict our discussions to the anodic processes which take place on the metal electrode, *i.e.* to the anodic dissolution of metals.

What we shall study are the electrode processes



In Eqs (1), (2), and (3) we refer to the k_{a_i} anodic and the k_{k_i} cathodic rate constants ($i = 1, 2, 3$) which are functions [2] of electrode potential ε , viz.

$$k_{a_i} = k'_{a_i} \exp \frac{\alpha_i n_i F \varepsilon}{RT} \quad (4)$$

$$k_{k_i} = k_{k_i} \exp - \frac{(1 - \alpha_i) n_i F \varepsilon}{RT} \quad (5)$$

where k'_{a_i} and k'_{k_i} stand for the rate constants when $\varepsilon = 0$ (their value depends on the reference electrode used); α_i is the transfer factor of the i^{th} step; n_i is the number of charges transferred with the i^{th} step; z_i is the number of charges on the ions, F is the Faraday constant, R is the molar gas constant; and T is the thermodynamic temperature.

Next, we find the equation of the polarization curve (the correlation between current density j and potential ε of the electrode) for the processes (1), (2), and (3) which take place at the electrode. In the calculations we suppose that the kinetics of these processes are affected by charge transfer and diffusion only. In an earlier paper [6] we have already mentioned that, in general, the equation that should describe the polarization curve of a process that consists of more than two charge transfers cannot be written in a clear-cut, explicit form because the curve is too complicated. Therefore in what follows we propose to deal with the anodic dissolution only of the metal and suppose that the electrolyte solution does not contain ions of the metal being dissolved. This latter supposition is an important simplification of the equations that describe the polarization curves.

In the conditions as here described, the anodic current density j that passes the electrode made of metal M can be given as the flux of the electric charges conducted off the surface, in other words, as the rate of diffusion [2] of ions M^{z_1+} , M^{z_2+} , and M^{z_3+} ,

$$j = z_1 X_1 c_{1,0} + z_2 X_2 c_{2,0} + z_3 X_3 c_{3,0} \quad (6)$$

where $c_{1,0}$, $c_{2,0}$, and $c_{3,0}$ symbolize the concentrations at the surface of the

electrode metal M, respectively, of the ions M^{z_1+} , M^{z_2+} , and M^{z_3+} , and X_i stands for the rate constant of the diffusion

$$X_i = \frac{F D_i}{\delta_i} \quad (7)$$

where D_i and δ_i are, respectively, the diffusion coefficient and the thickness of the diffusional layer. If work with the rotating disc electrode is done

$$X_i = 0.62 F D_i^{2/3} \nu^{-1/6} (2\pi f)^{1/2} = X_i' f^{1/2} \quad (8)$$

where ν is the kinematic viscosity, and f is the r.p.m. of the rotating electrode.

The unknown concentration figures $c_{1,0}$, $c_{2,0}$ and $c_{3,0}$ in Eq. (6) can be calculated on the basis of the material balance involving the ions M^{z_1+} , M^{z_2+} , and M^{z_3+} . For the stationary state we can write [2] the three equations which follow.

$$\frac{k_{a_1}}{n_1} - \left(\frac{k_{k_1}}{n_1} + \frac{k_{a_2}}{n_2} \right) c_{1,0} + \frac{k_{k_2}}{n_2} c_{2,0} = X_1 c_{1,0} \quad (9)$$

$$\frac{k_{a_2}}{n_2} c_{1,0} - \left(\frac{k_{k_2}}{n_2} + \frac{k_{a_3}}{n_3} \right) c_{2,0} + \frac{k_{k_3}}{n_3} c_{3,0} = X_2 c_{2,0} \quad (10)$$

$$\frac{k_{a_3}}{n_3} c_{2,0} - \frac{k_{k_3}}{n_3} c_{3,0} = X_3 c_{3,0} \quad (11)$$

The correlation between rate constants, which depend on electrode potentials according to Eqs (4) and (5) and on current density j , and X_i can be constructed on the basis of Eqs (6), (9), (10), and (11), viz.

$$j = \frac{k_{a_1} \left[z_1 X_1 + A_2 \left(z_2 + \frac{n_3 A_3}{X_2 + A_3} \right) \right]}{z_1 X_1 + k_{k_1} + z_1 A_2} \quad (12)$$

where

$$A_2 = \frac{k_{a_2}}{n_2 + \frac{k_{k_2}}{X_2 + A_3}} \quad (13)$$

$$A_3 = \frac{k_{a_3}}{n_3 + \frac{k_{k_3}}{X_3}} \quad (14)$$

The magnitude mutually related to the rate constants in Eq. (12) can be widely different; in such instances this expression become much more simple. The rate constants, in relation to each other, can be regulated since k_{a_i} and k_{k_i} depend, according to Eqs (4) and (5) on the electrode potential ε ; X_i is unaffected by the electrode potential and is sensitive only to the hydrodynamic conditions of the solution and is proportional to the square root of the r.p.m. in the case of a rotating disc electrode [cf. Eq.(8)]. By means of Eq. (12) we can find those proportions of the rate constants at which proportions a straight line is plotted for the polarization curves in an ε vs $\lg j$ coordinate system. The b coefficients of the Tafel-lines thus obtained allow to draw conclusions concerning the mechanism of the process in many cases.

A scrutiny of Eq. (12) will reveal that, under the conditions here defined, the ε vs $\lg j$ correlation will be linear if the kinetics of the anodic dissolution is governed by the diffusion of the ions M^{z_1+} , M^{z_2+} , and M^{z_3+} .

1) If the diffusion of ion M^{z_1+} off the metal surface into the solution proceeds much more rapidly than its further oxidation, *i.e.* when

$$X_1 \gg A_2 \quad (15)$$

and when

$$A_2 \ll k_{k_1} \gg X_1 \quad (16)$$

and thus practically an equilibrium in respect of reaction step (1) is attained, then the kinetics of the anodic dissolution of the metal is determined by the diffusion of ions M^{z_1+} into the solution, and, according to Eq. (12)

$$j = z_1 X_1 \frac{k_{a_1}}{k_{k_1}}. \quad (17)$$

Eqs (4) and (5) being taken into consideration, the correlation between electrode potential and the logarithm of current density j can be formulated as follows.

$$\varepsilon = \frac{RT}{z_1 F} \ln \frac{k'_{k_1}}{k'_{a_1}} - \frac{RT}{z_1 F} \ln z_1 X_1 + \frac{RT}{z_1 F} \ln j \quad (18)$$

Then, according to Eq. (18), if $z_1 = 1$ then the b coefficient of the Tafel-line has the value of 59.2 mV, at 25 °C. When a rotating disc electrode is used, the alteration of its r.p.m. alters the value of j at constant potential, and alters the value of ε at constant current density. According to Eqs (17) and (8), at constant electrode potential current density is proportional to $f^{1/2}$, Eqs (18) and (8) show that ε changes linearly with $\lg f$ when j is constant, and if $z_1 = 1$ the coefficient of $\lg f$ is -29.6 mV at 25 °C.

2) If the condition contrary to criterion (15) is realized, i.e. if

$$X_1 \ll A_2 \quad (19)$$

and if, along with the validity of Eq. (16) it is true that

$$X_2 \gg A_2 \quad (20)$$

and

$$k_{k_2} \gg X_2 \quad (21)$$

then the kinetics of the anodic dissolution of metal M is determined by the diffusion of ions M^{z_2+} into the solution, and according to Eq. (12)

$$j = z_2 \frac{k_{a_1} k_{a_2}}{k_{k_1} k_{k_2}} X_2 \quad (22)$$

In view of Eqs (4) and (5), for the ε vs $\ln j$ correlation we have

$$\varepsilon = \frac{RT}{z_2 F} \ln \frac{k'_{k_1} k'_{k_2}}{k'_{a_1} k'_{a_2}} - \frac{RT}{z_2 F} \ln z_2 X_2 + \frac{RT}{z_2 F} \ln j \quad (23)$$

Then, if $z_2 = (z_1 + n_2) = 2$, the coefficient b of the Tafel-line is 29.6 mV, at 25 °C.

3) If conditions according to Eqs (16), (19) and (21) are fulfilled, further if

$$X_2 \ll A_3 \quad (24)$$

and

$$k_{k_3} \gg X_3 \quad (25)$$

then, according to Eq. (12)

$$j = z_3 \frac{k_{a_1} k_{a_2} k_{a_3}}{k_{k_1} k_{k_2} k_{k_3}} X_3 \quad (26)$$

In view of Eqs (4) and (5), for the ε vs $\ln j$ correlation we have

$$\varepsilon = \frac{RT}{z_3 F} \ln \frac{k'_{k_1} k'_{k_2} k'_{k_3}}{k'_{a_1} k'_{a_2} k'_{a_3}} - \frac{RT}{z_3 F} \ln z_3 X_3 + \frac{RT}{z_3 F} \ln j \quad (27)$$

Herefrom, when $z_3 = 3$, the coefficient b of the Tafel-line is 19.7 mV, at 25 °C.

Like at 1) also in cases 2) and 3) j is proportional to $f^{\frac{1}{2}}$ when electrode potential is constant, and there is a similar correlation between ε and $\lg f$.

In the foregoing parts we considered those cases in which the kinetics of the anodic process of three consecutive charge transfers is governed solely by the diffusion of ion M^{z_1+} , M^{z_2+} , and M^{z_3+} . Then there is a linear correlation between ε and $\lg j$. Based upon the coefficient b of this linear correlation, further, based upon the consequences of the variation of r.p.m. in the case of a rotating electrode, conclusions in respect to the rate-determining step can be deduced, or in respect of the question whether the oxidation of the metal M at the surface of the electrode gives the ion M^{z_1+} , M^{z_2+} or M^{z_3+} . However, only one section of the polarization curve represents pure diffusion polarization, at low anodic polarization, as a rule. The criteria discussed render it obvious that when anodic polarization is enhanced the occurrence of pure diffusion polarization cannot be expected. Therefore in this case experimental data allow to conclude which of the possible intermediates is produced but not to conclude whether the process consists of two or more steps. Thus, for instance, at the anodic dissolution of indium in perchloric acid there is, suitable conditions prevailing, in the polarization curve a section that reveals pure diffusion polarization, with a b coefficient of 60 mV [8]. Consequently we find, according to Eq. (18) that the oxidation of indium at the electrode gives only In^+ ions.

We wish to note, however, that Tafel-lines alone, which refer to pure diffusion polarization, do not unmistakably reveal whether or not anodic dissolution proceeds *via* stepwise mechanism, since such straight lines can emerge also when parallel, not stepwise, processes occur.

Under suitable conditions a linear correlation is possible also when pure transfer polarization occurs. In the course of electrode reactions (1), (2), and (3) no effect by diffusion is exerted when

$$\left. \begin{array}{l} \text{a. } X_1 \ll A_2 \\ \text{b. } X_2 \ll A_3 \\ \text{c. } X_3 \gg k_{k_3} \end{array} \right\} \quad (28)$$

When this condition is fulfilled we have for j the expression, deduced from Eq. (12)

$$j = \frac{z_3 k_{a_1} k_{a_2} k_{a_3}}{z_1 k_{a_2} k_{a_3} + n_2 k_{k_1} k_{a_3} + n_3 k_{k_1} k_{k_2}} \quad (29)$$

4) According to Eq. (29), at slightly positive potentials, where k_{k_1} and k_{k_2} predominate over k_{a_2} and k_{a_3} , the terms which contain k_{a_3} in the denominator can be neglected and we may write

$$j = \frac{z_3 k_{a_1} k_{a_2}}{n_3 k_{k_1} k_{k_2}} k_{a_3} \quad (30)$$

With Eqs (4) and (5) in mind we deduce from Eq. (30) that

$$\varepsilon = \frac{RT}{(z_2 + \alpha_3 n_3) F} \ln \frac{n_3 k'_{k_1} k'_{k_2}}{z_3 k'_{a_1} k'_{a_2} k'_{a_3}} + \frac{RT}{(z_2 + \alpha_3 n_3) F} \ln j \quad (31)$$

In this case the coefficient b of the Tafel-line, with $\alpha_3 = 0.5$, and $z_1 = n_2 = n_3 = 1$ ($z_2 = 2$), is 23.6 mV, at 25 °C.

5) In consequence of a shift towards positive voltages of the electrode potential, only k_{k_1} will become much greater than k_{a_2} and k_{a_3} ; k_{k_2} and k_{k_3} will become much smaller than these. Thus all the terms except that which contains k_{k_1} can be neglected in the denominator of Eq. (29) and

$$j = \frac{z_3 k_{a_1} k_{a_2}}{n_2 k_{k_1}} \quad (32)$$

With Eqs (4) and (5), we have

$$\varepsilon = \frac{RT}{(z_1 + \alpha_2 n_2) F} \ln \frac{n_2 k'_{k_1}}{k'_{a_1} k'_{a_2}} + \frac{RT}{(z_1 + \alpha_2 n_2) F} \ln j \quad (33)$$

Thus in such a case the coefficient b of the Tafel-line, when $\alpha_2 = 0.5$ and $z_1 = n_2 = 1$, is 39.4 mV, at 25 °C. In the case when $z_1 = 1$ and $n_2 = 2$, $b = 29.6$ mV. Accordingly, in the course of the anodic dissolution of a metal for which $z_3 = 3$, this is a three-step process when the Tafel coefficient b is about 40 mV, and is a two-step process when b is about 30 mV. Thus there we have a criterion by which it can be in principle decided whether the anodic dissolution of indium proceeds via two, or three, charge transfers in series. Uncertainties are encountered with this method when figures between 30 and 40 mV are found for coefficient b .

6) When anodic polarization is great, the terms which contain cathodic rate constants can be neglected and thus

$$j = \frac{z_3}{z_1} k_{a_1} \quad (34)$$

According to Eq. (4) we have

$$\varepsilon = \frac{RT}{z_1 \alpha_1 F} \ln \frac{z_1}{z_3 k'_{a_1}} + \frac{RT}{z_1 \alpha_1 F} \ln j \quad (35)$$

Tafel-coefficient in this case is 118.3 mV at 25 °C and with $z = 1$ and $\alpha_1 = 0.5$.

Accordingly, when pure charge transfer polarization occurs as the Tafel-lines are plotted, then coefficient b allows, in principle, deduction concerning

stepwise mechanisms, respectively, concerning the question whether the process consists of two or of three consecutive charge transfer steps. However, the inaccuracy of the determination of coefficient b , respectively, the fact that α_1 might deviate from the figure 0.5, cause that often no definite conclusion in respect to the mechanism of the process can be drawn.

All this tends to show that the second step in the reaction formula (1)–(3) carries that information which enables us to decide whether the process is one of two charge transfers or one of three. Therefore every kinetic information which is (discernibly) affected by k_{k_2} or by k_{a_2} is, in principle, suitable to help us to solve this problem. With this in mind, when even diffusion and transfer polarizations are in evidence together, the task we set ourselves can be accomplished. Thus, if phase (2) is the impeded step within the (1)–(3) process and if the conditions which are obtained are

$$A_2 \simeq z_1 X_1 \ll k_{k_1}, \quad X_2 \ll A_3 \gg k_{k_2} \quad (36)$$

then from Eq. (12) we deduce

$$j = \frac{k_{a_1}}{k_{k_1}} \left(z_1 X_1 + \frac{z_3}{n_2} k_{a_2} \right) \quad (37)$$

or

$$j = \frac{z_3}{n_2} \frac{k_{a_1} k_{a_2}}{k_{k_1}} + z_1 \frac{k_{a_1}}{k_{k_1}} X' f^{\frac{1}{2}} \quad (38)$$

In other words, polarization curves can be plotted for a rotating disc electrode of the metal M at various r.p.m. and constant potentials, and a diagram j vs $f^{\frac{1}{2}}$ subsequently constructed on the basis of these data will give a straight line, the intersection of this with the axis will represent correlation (32). The quotient of intersection and slope of the straight line will be

$$C = \frac{z_3}{n_2 z_1} X' k_{a_1} = \frac{z_2}{n_2 z_1} X' k'_{a_2} \exp \frac{\alpha_2 n_2 F \varepsilon}{RT} \quad (39)$$

$\lg C$ -figures plotted in function of ε will give a straight line, and its slope informs about the value of $\alpha_2 n_2$. For instance, at 25 °C, if $z_3 = 3$, $\alpha_2 = 0.5$, and $n_2 = 1$ (three-step mechanism), then the slope is 118.3 mV; if, with these conditions but with $n_2 = 2$ (two-step mechanism) the slope is 59.2 mV. Thus a well interpretable criterion is available for to settle our question, provided that the conditions according to Eq. (36) are fulfilled.

It follows that for a decision to be reachable in the question of the number of steps involved in this mechanism practically only those experimental data can be utilized which have been found when the impeded step of the process was the further oxidation of the M^{z_1+} ions (*cf.* the case discussed at 5). With

this insight here gained we now consider how the use of a rotating ring disc electrode (RRDE) [6] contributes to the elucidation of the mechanism.

As known, the products formed on the disc of the electrode can be determined by voltametry on the ring electrode. If the disc of the RRDE is the metal M and step (2) in the sequence (1)–(3) is impeded, then the concentration of the M^{z_1+} ion will increase on the surface of the disc. The I_R limiting diffusion current of the oxidation of M^{z_1+} to M^{z_2+} can be measured on the ring electrode and we may expect that the intensity of this current will be affected by the rate constant of reaction step (2).

Therefore, in what follows, we propose to study how I_R depends on the kinetical parameters of the process (1)–(3). If, as a condition mentioned before, the solution does not contain ions of metal M [6],

$$I_R = r_1^2 \pi (n_2 + n_3) X_1 N c_{10} \quad (40)$$

where r_1 is the radius of the disc electrode, N is the geometrical factor of the RRDE, and c_{10} is the concentration of the M^{z_1+} ion at the surface of the disc electrode. On the basis of Eqs (6), (9), (10), and (40), the following expression of I_R is possible

$$I_R = \frac{(z_3 - z_1) X_1 N I}{z_1 X_1 + \frac{k_{a_2} \left(z_2 X_2 + \frac{z_2}{n_3} \frac{X_2}{X_3} k_{k_3} + \frac{z_3}{n_3} k_{a_3} \right)}{n_2 X_2 + \frac{n_2}{n_3} \frac{X_2}{X_3} k_{k_3} + \frac{n_2}{n_3} k_{a_3} + k_{k_2} + \frac{k_{k_2} k_{k_3}}{n_3 X_3}} \quad (41)$$

where $I = r_1^2 \pi j$, the current passing through the disc. If, in accord with the criteria mentioned before, the reaction step (2) (charge transfer) is impeded, *i.e.* the rate constant k_{a_2} of the step (3) is great in relation to k_{k_2} , X_2 , and k_{k_3} , and the removal of the M^{z_3+} ions off the metal surface is not hindered, then Eq. (41) can be rewritten as

$$I_R = \frac{(z_3 - z_1) X_1 N I}{z_1 X_1 + \frac{z_3}{n_2} k_{a_2}} \quad (42)$$

In the comparatively simple correlation (42) we have k_{a_2} , and this magnitude can be utilized in answering of the question raised before.* If we

* Eq. (42) is considerably simplified also when reaction step (3) is the most impeded one. Then also a simple correlation emerges by means of which it can be decided, in principle, from data for I_R and I whether two or three charge transfer steps constitute the overall process. In this instance, however, I_R is unmeasurably small. Under these conditions M^{z_2+} ions will accumulate at the surface of the disc electrode, and the oxidation of these may generate a well recordable limiting current. The magnitude of this current does not depend on the rate constants of step (2).

suppose that the oxidation of M^{z_1+} to M^{z_3+} occurs in one step, *i.e.* that $n'_2 = n_2 + n_3$ and that in Eq. (41) $k_{a_3} = k_{k_3} = 0$, ($z_3 = z_2$), then from Eq. (41) we deduce

$$I_R = \frac{n'_2 X_1 N I}{z_1 X_1 + \frac{z_2 X_2 k_{a_2}^*}{n'_2 X_2 + k_{k_2}^*}} \quad (43)$$

where $k_{a_2}^*$ and $k_{k_2}^*$ are rate constants, respectively, of the oxidation of M^{z_1+} to M^{z_2+} , and of its opposite process. In the first the apparent transfer coefficient is $n'_2 \alpha_2$, in the second this is $(1 - \alpha_2)n'_2$. Studies of the anodic dissolution of indium show that $z_3 = 3$, $n_2 = 1$, and $n'_2 = 2$.

With Figure 1 we illustrate, by means of Eqs (12) and (41), curves for ε vs $\lg I$, and $\lg I_R$ vs $\lg I$ correlations calculated with parameters arbitrarily selected, and which satisfy the conditions prescribed for Eqs (42) and (43). As expressed by the data, curves 1 and 3 pertain to the three one-electron steps in series, curves 2 and 4 refer to the one-electron and the subsequent two-electron process. The shapes of the polarization curves do not show essential deviations, but the $\lg I$ vs $\lg I_R$ curves conspicuously differ from each other. In the case of the three-step mechanism, when there is a high current density on the disc electrode, the curve runs parallel to the abscissa; in the case of a two-step mechanism the curve turns back towards the abscissa. It can be shown that, under the circumstances here obtained, the curve $\lg I_R$ vs $\lg I$ cannot run parallel to the abscissa unless a three-step process occurs. Thus we have a proof for a three-step process. The reverse, unfortunately does not

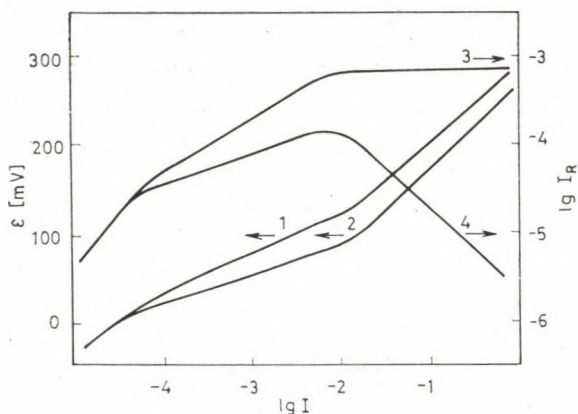


Fig. 1. Polarization curves calculated (Curves 1 and 2); correlation $\lg I_R$ vs $\lg I$ (Curves 3 and 4). $k'_{a_1} = 10^{-3} \frac{A}{dm^2}$, $k'_{a_2} = k_{a_2}^* = 10^3 A dm mole^{-1}$, $k'_{a_3} = 10^9 A dm mole^{-1}$, $k'_{k_2} = 10^4 A dmole^{-1}$, $k_{k_2}^* = 0$, $k_{k_3} = 0$, $f = 100$ r.p.m., $\alpha_1 = \alpha_2 = \alpha_3 = 0.5$, $D = 10^{-7} dm^2 s^{-1}$, $\nu = 10^{-4} dm^2 s^{-1}$, $t = 25^\circ C$, $N = 0.1$, $z_1 = 1$, $n_2 = n_3 = 1$ (for Curves 1, and 3), $n'_2 = 2$ (for Curves 2 and 4)

hold true: a turn of the curve towards the abscissa does not prove the occurrence of a two-step mechanism because this phenomenon may be provoked by the passivation of the disc electrode, or in the case of limit current, by complex formation [9] if this occurs during anodic dissolution.

In fact, at high anodic polarization Eq. (34) describes the polarization curve for both cases, *i.e.*

$$I = r_1^2 \pi \frac{z_3}{z_1} k_{a_1}$$

Herefrom, and from Eq. (42), and taking into account of Eqs (4) and (5), we have for the case just discussed

$$I_R = 2r_1^2 \pi X_1 N \frac{k'_{a_1}}{k'_{a_2}} \exp \frac{(\alpha_1 - \alpha_2) F \varepsilon}{RT} \quad (44)$$

Thus if $\alpha_1 = \alpha_2$ then I_R does not change with ε nor with the current intensity on the disc electrode.

Under similar conditions it follows from Eq. (43) that

$$I_R = r_1^2 \pi X_1 N \frac{k'_{a_1}}{k'_{a_2}} \exp \frac{(\alpha_1 - 2\alpha_2) F \varepsilon}{RT} \quad (45)$$

Therefore, since $\alpha_1 < 2\alpha_2$, I_R must diminish with ε , *i.e.* with the increase of anodic current intensity on the disc electrode.

On the polarization curves here calculated three linear sections emerge. In the $b = 59$ mV section for low current density the kinetics of the (1)–(3) overall process is determined by the diffusion of ions M^+ ; in the section for higher current densities step (2), at still higher ones step (1) governs (*cf.* the cases discussed in paragraphs 1), 5), and 6)).

The data obtainable by RRDE-technique can be interpreted also in another way [4, 6]. Then the correlation (42) allows us to write

$$\frac{I}{I_R} = \frac{z_1}{n'_2 N} + \frac{z_3 k_{a_2}}{n_2 n'_2 N X'_1} f^{-\frac{1}{2}}. \quad (46)$$

Accordingly, when $\frac{I}{I_R}$ is plotted as a function of $f^{-\frac{1}{2}}$ at constant potential on the disc, for a three-step mechanism always a straight line emerges [*cf.* Eq. (8)]. The slope of this straight line allows the apparent transfer factor $\alpha_2 n_2$ of the second step in the process (1)–(3) to be determined. When a two-step process occurs, we deduce from correlation (43) that

$$\frac{I}{I_R} = \frac{z_1}{n'_2 N} + \frac{z_2 X_2 k_{a_2}^*}{(n'_2 X_2 + k_{k_1}^*) n'_2 N X_1} \quad (47)$$

It can be seen that no straight line results in the $\frac{I}{I_R}$ vs $f^{-\frac{1}{2}}$ diagram, at a constant potential [6]. Experimental points approach the abscissa. As straight line results only if $X_2 \gg k_{k_2}$ i.e. at high r.p.m. of the electrode or if sufficiently high positive potentials are applied. Accordingly, when $\frac{I}{I_R}$ vs $f^{-\frac{1}{2}}$ curves turn towards the abscissa this suggests that a two-step mechanism is at work. If the condition previously mentioned is fulfilled, Eq. (47) assumes a form similar to Eq. (46), viz.

$$\frac{I}{I_R} = \frac{z_1}{n'_2 N} + \frac{z_2 k_{a_2}^*}{n'_2{}^2 N X'_1} f^{-\frac{1}{2}}. \quad (48)$$

Otherwise stated: when $\frac{I}{I_R}$ figures at constant potential are plotted in function of $f^{-\frac{1}{2}}$ a straight line results, the slope of which denotes the apparent transfer factor $n'_2 \alpha_2$ of the oxidation of M^{z_1+} ion to the final product. Since $\alpha_2 n_2 < \alpha_2 n'_2$, it can be deduced on the basis of these apparent transfer factors whether a three-step or a two-step mechanism occurs.

Correlations (46) and (48) can be written also in the following form:

$$\frac{I}{I_R} = A + B f^{-\frac{1}{2}} \quad (49)$$

The straight lines $\frac{I}{I_R}$ vs $f^{-\frac{1}{2}}$ severally pertinent to various electrode potentials give the numeral values of B at various potentials. B , since in it k_{a_2} , respectively, $k_{a_2}^*$ are included, is an exponential function of electrode potentials:

$$B = B' \exp \frac{n_2 \alpha_2 F \varepsilon}{RT} \quad (50)$$

where, for a three-step process

$$B' = \frac{z_3 k'_{a_2}}{n_2 n'_2 N X'_1}$$

and for a two-step process

$$B' = \frac{z_2 k_{a_2}^*}{n'_2 N X'_1}$$

From (50) we get

$$\varepsilon = \frac{RT}{n_2 \alpha_2 F} \ln B' + \frac{RT}{n_2 \alpha_2 F} \ln B \quad (51)$$

Accordingly, if $z_3 = 3$, $\alpha_2 = 0.5$ and ε is plotted as a function of $\ln B$, then in the case of a three-step mechanism ($n_2 = 1$) the coefficient of $\ln B$, at room temperature, is 118 mV, in the case of a two-step mechanism ($n_2 = 2$) this is 59 mV.

The method here suggested was utilized in an attempt to find out whether the anodic dissolution of indium in perchlorate medium is a two- or a three-step process. The result of this attempt will be described in a subsequent paper.

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INDEX

PHYSICAL AND INORGANIC CHEMISTRY

Bonding Parameters and ESR Hyperfine Linewidth of the Cu(II)-DL-Alanine Complex, B. N. MISRA, R. KRIPAL	101
The Effect of Thiourea and its Derivatives on Hydrogen Overvoltage at the Dropping Gallium Electrode, K. SZABÓ, M. TAKÁCS	131
Mixed Ligand Complexes of Metal Thiocyanates with 2,2'-Dipyridyl and 1,10-Phenanthro- line, W. U. MALIK, P. P. BHARGAWA, M. M. SIDDIQUI	155
Platinum Metal Complexes of Cycloalkyl Dithiocarbamates, S. KUMAR, N. K. KAUSHIK Anodic Dissolution of Metals, I. Kinetics of the Dissolution Process Involving Two, and Three Consecutive Charge Transfer Steps, L. KISS, J. FARKAS	161 181

ORGANIC CHEMISTRY

Reaction of Lead(IV)acetate with Steroidal 6-Oximino Compounds, SHAFIULLAH, H. ALI, SHAMSUZZAMAN	97
Aromatization of 3 β -Chloro-5,7 β -dibromo-5 α -cholestan-6-one (Short Communication), SHAFIULLAH, H. ALI, SHAMSUZZAMAN	115
Azidobarbiturates, I. Synthesis of Barbituric Acid Derivatives Containing Azido Group in Position 5, GY. TÓTH, S. MAKLEIT (in German)	139
Azidobarbiturates, II. Synthesis of Barbituric Acid Derivatives Containing Azido Group in the Substituent, GY. TÓTH, S. MAKLEIT (in German)	147
Heterocyclization with Iminium Chlorides, III. Synthesis of 3,4-Dihydro-(1H)-1,3,4-benzo- triazepine-2,5-diones, I. BITTER, L. SZŐCS, L. TÓKE	171

ANALYTICAL CHEMISTRY

On Spectrographic Characteristics of Capillary Electrodes, III. Use of Medium Voltage Spark Discharge, M. MATHERNY, M. ONDÁŠOVÁ (in German)	119
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CYCLODEXTRIN COMPLEX OF A VOLATILE INSECTICIDE (DDVP)

L. SZENTE and J. SZEJTLI*

(Chinoin Pharmaceutical and Chemical Works, Biochemical Research Laboratory, Budapest)

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O,O-Dimethyl-2,2-dichlorovinyl phosphate (DDVP) is a moderately volatile liquid of powerful insecticidal effect. Its inclusion complex with β -cyclodextrin is a stable crystalline substance, which has practically no gas effect, but a much more persistent contact effect than free DDVP.

Introduction

In an earlier paper SZEJTLI and BÁNKY [1] reported the catalytic decomposition of Trichlorfon (*O,O*-dimethyl-1-hydroxy-2,2,2-trichloroethylphosphonate), with the elimination of hydrochloric acid, in aqueous solution in the presence of β -cyclodextrin. The product of this decomposition was a crystalline inclusion complex consisting of *O,O*-dimethyl-2,2-dichlorovinyl phosphate (DDVP) and β -cyclodextrin. DDVP is a moderately volatile and relatively rapidly decomposing liquid and a powerful insecticide. Under the action of water, but especially of alkali, it decomposes to glycolic acid, dichloroacetaldehyde and inorganic phosphate.

The preparation of a crystalline β -cyclodextrin complex of DDVP may be of interest for two reasons: by complexation a non volatile, stable preparation can be obtained which preserves its activity for a long period [2], and the complexing reaction can also be utilized to remove DDVP, a substance with high environmental hazards [3] from the mother liquors of Trichlorfon production.

Since the profitable industrial production of β -cyclodextrin has become a reality similar to DDVP many other active principles (pesticides) can be potentially stabilized and formulated by inclusion complex formation. In this paper we describe some chemical and biological characteristics of the β -cyclodextrin complex of DDVP.

Materials and Methods

DDVP: purity over 99% (Chinoin).

β -cyclodextrin: moisture content 13.3% (Chinoin).

The DDVP content of the complex was determined by elementary analysis, colorimetry

* To whom correspondence should be addressed.

[4] and gas chromatography. The parameters of gas chromatography were as follows: column 10% UCW 982; injector temperature 200 °C; temperature of FID detector 250 °C; temperature program 5 °C/min; carrier gas N₂; flow rate 20 mL/min. Retention time of DDVP was 3.10 min. The crystalline inclusion complex was subjected to X-ray powder diffractometry on a Philips PW 1060 instrument. Thermoanalytical studies were carried out with a Du Pont 990 type analyser.

Preparation of the complex

To a solution of β -cyclodextrin (10.0 g) in distilled water, maintained at 65 °C, a solution of DDVP (1.95 g) in 96% ethanol (10 mL) was added dropwise, with intensive stirring. After the completion of addition, the mixture was gradually cooled during a period of 5 h, with constant stirring, to room temperature. Crystallization of the complex set in at 45 ± 2 °C. The mixture was then allowed to stand in a refrigerator for 12 h, filtered, and the product dried at room temperature. The crystalline DDVP- β -cyclodextrin complex (10.8 g) contained 16.3% DDVP, equivalent to 1 : 1 DDVP/ β -cyclodextrin molar ratio. The yield was 90.7% calculated for β -cyclodextrin and 88.7% for DDVP.

Characterization of the inclusion complex

The DDVP- β -cyclodextrin complex is a white crystalline powder without a characteristic melting point. Complex formation was supported by the X-ray powder diffractogram (Fig. 1) which was significantly different from that of β -cyclodextrin crystallized under identical conditions. Since the guest molecule is a liquid, the formation of a new crystal phase is an indirect proof of complex formation [5].

Turbidity measurements also substantiate inclusion complex formation [6]. This method is based on the different crystallization behaviour of the complex and of β -cyclodextrin under identical conditions (Fig. 2).

The high stability of the DDVP- β -cyclodextrin complex is indicated by the fact that in a stream of humid air only 2–3% of the initial DDVP content is lost after 6 days at 25 °C. At the same time neat DDVP evaporated up to 96% after three days. (Determination of the liberated DDVP was carried out by colorimetry [4], Fig. 3).

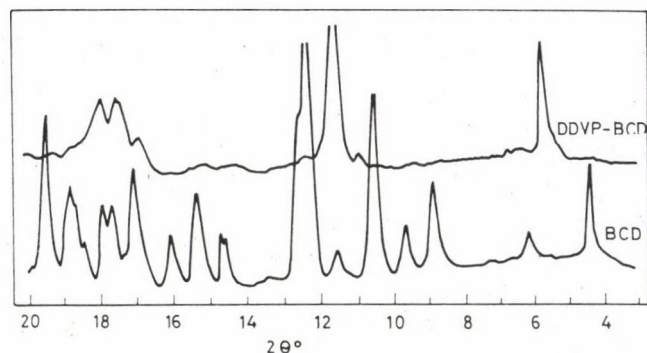


Fig. 1. X-Ray powder diffractograms of β -cyclodextrin and of its complex with DDVP

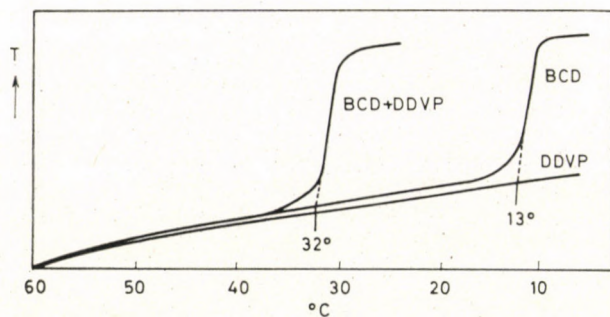


Fig. 2. Turbidity curves of β -cyclodextrin and of its complex with DDVP

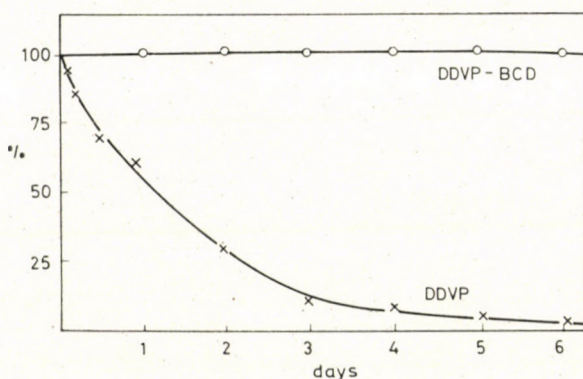


Fig. 3. Release of DDVP in a stream of humid air from complexed and uncomplexed DDVP

Thermal stability of the complex was tested by the method of thermo-fractionation (TAS method [5, 7, 8]). The sample to be examined (20 mg of the complex and a mechanical mixture of β -cyclodextrin and DDVP equivalent to the DDVP content of the complex) was heated from 60 °C to 300 °C in a glass vial with a capillary end. The end of the capillary was placed in front of a TLC plate and thus the evaporate emerging from the capillary at a given temperature was adsorbed giving individual spots on the adsorbent layer (Silicagel G, Sil-G-UV₂₅₄, MN-Co, 0.25 mm thickness). After development of the chromatogram in a 1 : 1 mixture of petroleum ether (b.p. 40–60 °C) and ethyl acetate, the spots were detected in UV light of 254 μ m. The mechanical mixture released detectable amounts of DDVP at as low as 60–80 °C; from 100 °C on decomposition products appeared and there was a continuous release of DDVP up to 220 °C.

In contrast, the inclusion complex started to liberate DDVP only at 100–120 °C and products of thermal decomposition (three components) appeared at 160 °C only. From this temperature on the release of DDVP became faster and was continuous up to 200 °C (Figs 4a and 4b).

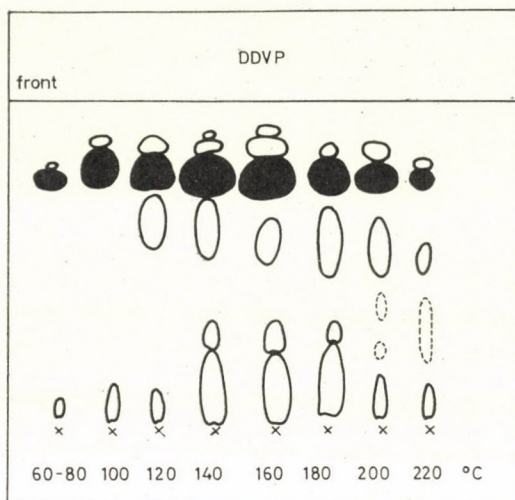


Fig. 4a. TAS chromatogram with a mechanical mixture of DDVP and β -cyclodextrin (the black spot is DDVP)

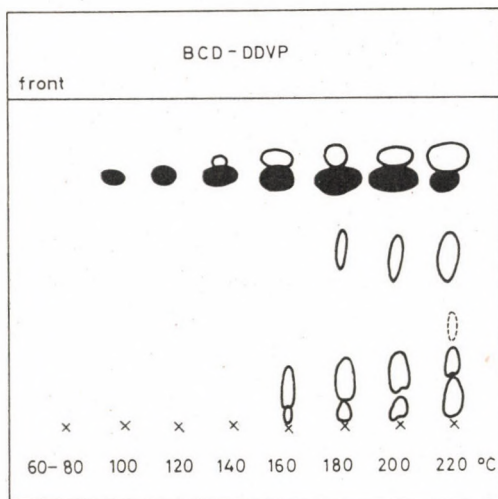


Fig. 4b. TAS chromatogram with DDVP- β -cyclodextrin complex

According to thermoanalytical studies, the decomposition of free DDVP sets in at relatively low temperatures, and up to 250 °C there is a continuous loss of material totalling to about 90% weight loss. The remaining 10% decomposes at a much lower rate. It is interesting to note that when complexed with β -cyclodextrin, β -cyclodextrin itself starts to decompose at a temperature about 100 °C lower than in the pure state. Probably the acid degradation product of DDVP catalyze

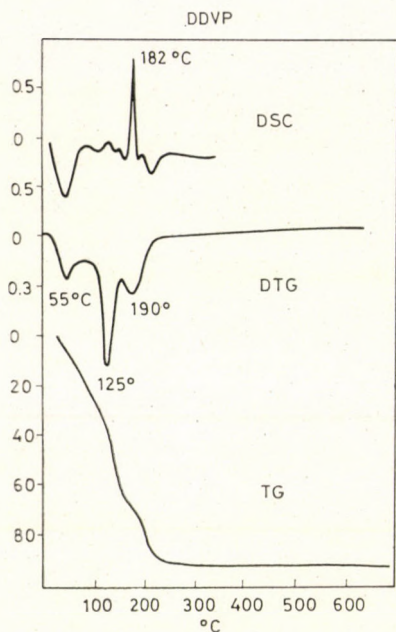


Fig. 5a. Thermoanalytical curves of DDVP

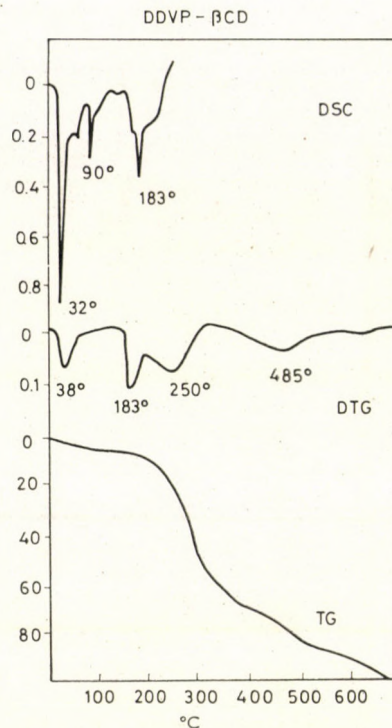


Fig. 5b. Thermoanalytical curves of DDVP-β-cyclodextrin complex

the degradation of β-cyclodextrin. On the other hand, as shown by the TG curve, the release of complexed DDVP is much slower (Figs 5a and 5b). These facts provide satisfactory evidence for the formation of a true complex.

Comparative acute toxicity studies

The acute toxicity values of free DDVP and its complex with β-cyclodextrin were determined in mice, using intravenous administration.

DDVP:

For males LD₅₀ (24–168 h) 84.14 mg/kg (deviation 71.29–99.29 mg/kg).

For females LD₅₀ (24–168 h) 80.52 mg/kg (deviation 65.92–95.35 mg/kg).

DDVP-β-cyclodextrin complex:

For males LD₅₀ (24–168 h) 138.63 mg/kg (deviation 120.99–158.85 mg/kg).

For females LD₅₀ (24–168 h) 123.31 mg/kg (deviation 109.12–139.34 mg/kg).

The data refer to the DDVP content of the complex.

In vivo resorption studies with labelled DDVP

In vivo resorption of DDVP labelled with ^{32}P (Amersham) and of its inclusion complex was studied on female CFY rats. The substances were given orally as a homogenizate in aqueous solution containing 20% of dextrane. After

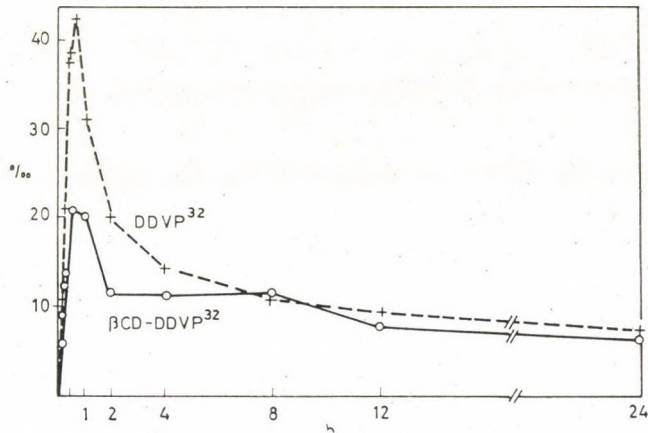


Fig. 6. Resorption of labelled DDVP and its complex in rats

administration, at intervals samples of blood were withdrawn; the blood radioactivity levels were determined and expressed as promille values [9]. Complex formation somewhat retards resorption and this may explain the increase in the LD_{50} values (Fig. 6).

Comparative studies of insecticidal activity

Test insects: dried bean beetle (*Acanthoscelides obtectus*)
 American cockroach (*Blabera fasca gigantea*)
 forest maybeetle (*Melolontha melolontha*)
 larvae of the I and II stage
 larvae of wire worm species (*Agriotes sp.*)
 larvae of house fly (*Musca domestica*)

Dose ranges for the inclusion complex and for control DDVP were 1–0.0156% and 0.025–0.00156%, respectively, with 5 doses for each. The usual Petri-dish method was applied; doses of the test substances were placed into etched glass dishes. Three parallels were made with each series, 20 animals were

placed into each dish. Deterioration stages of the experimental animals were recorded.

As it is apparent from Table I, the gas effect of the complex is much lower than that of free DDVP; 0.1% of the latter killed 80% of dried bean beetles within 20 min, while the complex killed only 38%. After two days, however,

Table I

Comparison of the effect of DDVP and of its complex with β -cyclodextrin on dried bean beetles
Concentration (based on DDVP): 0.1%

Contact time in min	Deterioration, %							
	DDVP				DDVP β -CD			
	after				after			
	1	2	3	4 days	1	2	3	4 days
20	80	—	—	—	38	12	—	—
60	90	—	—	—	75	15	15	12
300	92	—	—	—	90	70	55	35
1440	99	30	28	20	95	93	91	84

Concentration (based on DDVP): 0.01%

Contact time in min	Deterioration, %							
	DDVP				DDVP β -CD			
	after				after			
	1	2	3	4 days	1	2	3	4 days
20	12	—	—	—	6	—	—	—
60	35	—	—	—	25	—	—	4
300	55	—	—	—	45	65	23	30
1440	70	—	—	—	94	90	87	82

DDVP did not kill a single beetle even after 300 min contact time, whereas the complex even then killed 70% of the beetles. Other data of Table I also demonstrate that concerning its instantaneous effect the complex is much less effective than free DDVP, but the former is much better when the duration of the effect is considered. At 0.01% DDVP concentration the differences in duration are even more conspicuous.

Table II demonstrates that with free DDVP after 12 days the 50% killing effect cannot be attained anymore in the soil, while with the complex, applying 48 h contact time, this can be achieved even after 48 days. Another observation was that in dry soils the complex was rather ineffective, but an increase of the moisture content of the soil, for instance by irrigation, resulted in higher effec-

Table II

Comparison of the effect of DDVP and of its β -cyclodextrin complex in the soil on the larvae type L_1 and L_2 of forest maybeetle and on the larvae of wire worm and house fly

Period after application	Time required to achieve ED ₅₀	
	Complex	DDVP
1 day	43 min	31 min
12 days	59 min	less than 50%
20 days	14 h	less than 50%
25 days	38 h	no effect
48 days	47 h	no effect
117 days	less than 50%	no effect

tivity. The probable explanation is that under the effect of water the DDVP-cyclodextrin complex dissociates, but no DDVP is released from the dry complex.

*

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THERMOCHEMICAL ASPECTS OF ANION-EXCHANGE REACTIONS, III

CALORIMETRIC AND EQUILIBRIUM STUDIES OF ANION EXCHANGE REACTIONS INVOLVING ORGANIC IONS

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Ion-exchange equilibria of the oxalic, maleic and fumaric acid anions were studied on chloride form strongly basic anion exchange resin. Equilibrium and calorimetric measurements were made in aqueous solution, at 25 °C to obtain the thermochemical parameters of the exchange reaction. The chloride form resin shows a pronounced selectivity only for the monovalent maleic acid anion, whereas the rest of the studied species are not adsorbed preferentially by the resin. The selectivity for the monovalent maleinate anion can be explained if we realize the ability of that ion to form a strong intramolecular hydrogen bond. Due to this bond formation the hydration ability of the ion is dramatically decreased which, in turn, markedly influences the distribution of the ion between the two phases. The free energy of the system is lowered considerably when this poorly hydrated species is transferred into the resin phase where the relative permittivity is much lower than that of the aqueous solution phase. This case is an example of the systems where the selectivity is not governed by the interactions in the resin phase. The relatively small enthalpy and entropy changes of the exchange reactions indicate also the lack of a strong resin phase interaction.

Introduction

In our previous articles thermochemical data have been reported for the heat of exchange of the hydroxide and orthophosphate anions on chloride form strongly basic anion exchange resin [1a and b]. The present article is concerned with the exchange reaction of the mono- and bivalent anions of the oxalic, maleic and fumaric acids on the same type and form of the resin that was used previously.

The above systems are interesting for several reasons. For the separation of the organic acids anion-exchange chromatography has been used widely [2]. There is, no general rule, however, for prediction of the selectivity (*i.e.* elution) order for the organic ions. The selectivity is a result of a number of interactions and an adequate judgement of the governing interaction is not always obvious. Thermochemical parameters of the exchange reaction or structural data for the distributing species may be useful in the prediction or interpretation of the selectivity.

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Experimental

1. Selection of the useful pH-range

The domain of pH where the distribution of the acid anions can be studied has been judged from the mole fraction distribution diagram of the oxalic (H_2Ox), maleic (H_2M), and fumaric (H_2F) acids. From Fig. 1 appears that if $pH > 8$ then all the studied acids are present in a fully ionised form in the solution. The ion-exchange distribution of the bivalent acid anions

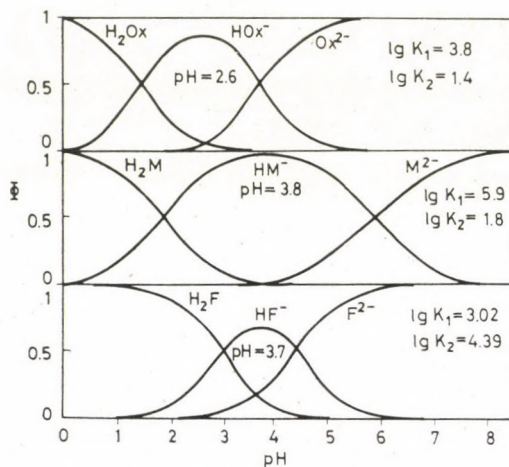


Fig. 1. The mole fraction distribution diagrams of the investigated acids. The K protonation constants are taken from Ref. [3]

can therefore be studied if care is taken to maintain the pH above eight in the equilibrium solution.

From the curves in Fig. 1 appears too that the mole fraction of the monovalent oxalic and maleic acid anions approaches almost 1 at $pH = 2.6$ and 3.8 , respectively. For the fumaric acid, however, it reaches only about 0.7 at its maximum; the rest being none and fully dissociated acid. The HF^-/Cl^- exchange reaction therefore can not be studied without serious interference.

2. Ion-exchange resin and chemicals

Dowex 1 \times 8 has been prepared and its capacity has been determined as described before [1a]. The maleic (Schuchardt München), fumaric- and oxalic acids (Reanal, Budapest) were reagent grade chemicals.

3. Solutions

For the monovalent acid anions (Y^-) the Y^-/Cl^- exchange reaction was studied as a function of the resin composition at total normality 0.1 ($TN = c_{Y^-}z_Y + c_{Cl^-}z_{Cl}$). From 0.1 mol/dm³ maleic acid and sodium chloride stock solutions mixed solutions (500 cm³) were prepared by mixing the appropriate volumes of the stock solutions. In the mixed solutions the equivalent fraction of the acids ($x_Y = c_Y z_Y / TN$) were set to 0.1, 0.2, 0.3, 0.5, 0.7, 0.8 and 0.9 (in the case of mono/monovalent exchange equivalent and mole fractions are, of course, equal). The pH of the 500 cm³ mixed solutions were set to the appropriate value (in the $H_2Ox-NaCl$ mixtures to 2.6 in the $H_2M-NaCl$ mixtures to 3.8) by addition of solid potassium hydroxide.

The exchange reaction, Y^{2-}/Cl^- was studied at 0.1 and at 0.01 total normalities. For these investigations 0.05 mol/dm³ acid and 0.1 mol/dm³ sodium chloride stock solutions were prepared and mixed to obtain the same equivalent fractions as in the case of the mono/mono-

valent exchange. The pH of these solutions were set between 8 and 10. For the measurements at total normality 0.01 the above solutions were diluted with water and their pH was adjusted when it was necessary.

4. Equilibrium measurements

Known quantities of the resin (~ 0.5 g) were weighed into 100 cm³ glass stoppered flasks and to them was added exactly 100 cm³ of the stock or mixed solutions using a pipette. The flasks were left overnight for equilibration at 25 ± 0.1 °C in a thermostatic bath. Before separation and analysis of the equilibrium phases the pH of the solution phase has been measured by a calibrated glass electrode. For the calculation of the composition of the phases in equilibrium aliquot samples were taken both from the original and from the equilibrium solutions (v_{ao} , v_{ae}). The chloride content of the samples were titrated with 0.05 mol/dm³ Hg(NO₃)₂ [4]. From the burette readings (v_o , v_e) the equivalent fractions in the solution (x) and in the resin phases (\bar{x}) have been calculated by the following equations:

$$x_{Cl} = \frac{fN}{TN} \frac{v_e}{v_{ae}}; \quad x_Y = 1 - x_{Cl}$$

$$\bar{x}_Y = \frac{fNV}{Cw} \left(\frac{v_e}{v_{ae}} - \frac{v_o}{v_{ao}} \right); \quad \bar{x}_{Cl} = 1 - \bar{x}_Y.$$

Here $f \cdot N$ is the exact normality of the titrant, TN and V are the total normality and the volume of the solution phase (100 cm³), C and w are the capacity (3.161 mequiv/g) and the weight of the resin (~ 0.5 g).

The calculated equivalent fractions were used to construct the ion-exchange isotherms as well as for the calculation of the thermodynamic equilibrium constants.

5. The calorimeter and the calorimetric measurements

The reaction vessel of the calorimeter was an original LKB (Sweden) product while the thermostat and the associated electronics were built by us. The detailed description of the instrument will be given elsewhere [5]. The overall performance of the calorimeter was checked by the method of IRVING and WADSÖ [6] and the heat of the THAM-HCl reaction (-29.723 kJ mol⁻¹) was reproducible within 0.2 per cent.

The technique used for the determination of the enthalpy of the exchange reaction was the same as described before [1a].

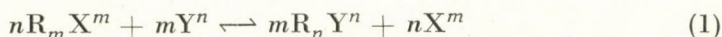
Results and Discussion

The results of the equilibrium measurements can be represented in terms of ion-exchange isotherms. For the studied reactions these are shown in Fig. 2.

In Fig. 2a the isotherm shows that the adsorption of the monovalent oxalate anion is not preferred by the chloride form resin. In the case of the heterovalent exchange the distribution of the ions is strongly influenced by the phenomenon of the electroselectivity and that makes the bonding of the bivalent oxalate anion preferred as the total normality of the solution increases Fig. 2b.

On the contrary to the case of the monovalent oxalate anion the chloride form resin shows a high affinity for the maleate anion (HM⁻) as it is demonstrated by Fig. 2c. Isotherms for the bivalent maleate and fumarate anions, Figs 2d and e demonstrate again the above mentioned effect of the electroselectivity.

For an adequate assessment and comparison of the selectivity of the reactions the thermodynamic equilibrium constants should be calculated and used. For the ion-exchange reaction (1)



the thermodynamic equilibrium constant is defined as

$$K^T = \frac{[\bar{a}(Y)]^m [a(X)]^n}{[a(X)]^n [a(Y)]^m} \quad (2)$$

In the two phases the activities are defined in two different manner in eqn. (2). In the resin phase $\bar{a} = f\bar{x}$ in the solution phase, however, $a = \gamma m$. As can be seen two different standard states are adopted in the two phases. The solid phase will be considered as a mixture of two hydrated salts $R_m X^m$ and $R_n Y^n$ as components. When the resin is entirely in X^m -form, $\bar{x}(X) = 1$, then the activity coefficient defined in mole fraction base equal to 1, when it is entirely in the Y^n -form, $\bar{x}(Y) = 1$, then $f(Y) = 1$. In contrary to this convention in the solution phase we retained the standard state normally used in the electrochemistry of solutions *i.e.* the activity coefficient, γ is defined on molality base and is

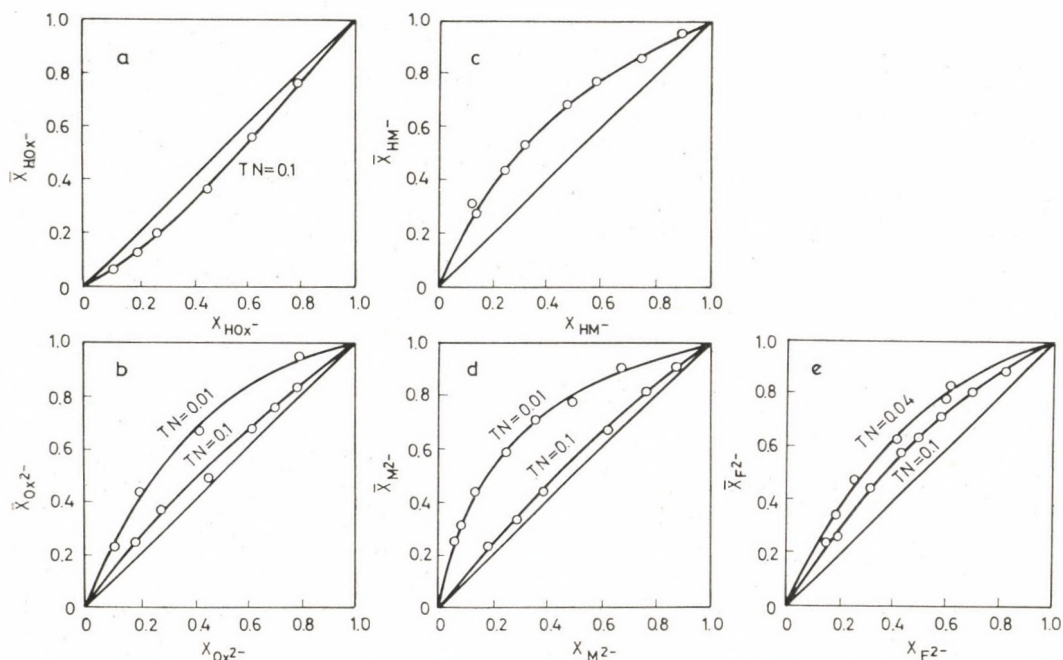


Fig. 2. Ion-exchange isotherms at 25 °C for the studied equilibria; a, HOx⁻/Cl⁻; b, Ox²⁻/Cl⁻; c, HM⁻/Cl⁻; d, M²⁻/Cl⁻; e, F²⁻/Cl⁻

equal to 1 in a 1 molal solution which is, of course, not a real but a hypothetical standard state.

If the equivalent fraction in the solution phase is defined as $x = zc/TN$ and this is put in the activity expression then after substitution the activities into eqn. (2) we obtain:

$$K^T = K'_x \frac{[f(Y)]^m}{[f(X)]^n}, \quad (3)$$

where

$$K'_x = \frac{[\bar{x}(Y)]^m [x(X)]^n}{[\bar{x}(X)]^n [x(Y)]^m} \cdot \frac{[\gamma(X)]^n}{[\gamma(Y)]^m} \cdot \frac{n^m}{m^n} \cdot TN^{n-m}. \quad (4)$$

Eqn. (4) contains only experimentally accessible quantities although the ratio of the solution phase activity coefficients can only be estimated for the studied systems. In lack of a better approximation the DAVIES-equation [7] has been used to estimate the above activity ratio.

When K' is calculated from the equilibrium measurements then, as it is usually observed, it depends on the degree of conversion of the resin, *i.e.* on the equivalent fraction of the counter ions ($\bar{x}(\text{Cl})$ or $\bar{x}(Y)$). These functions are shown on $\lg K'$ vs. \bar{x}_{Cl} diagrams in Fig. 3.

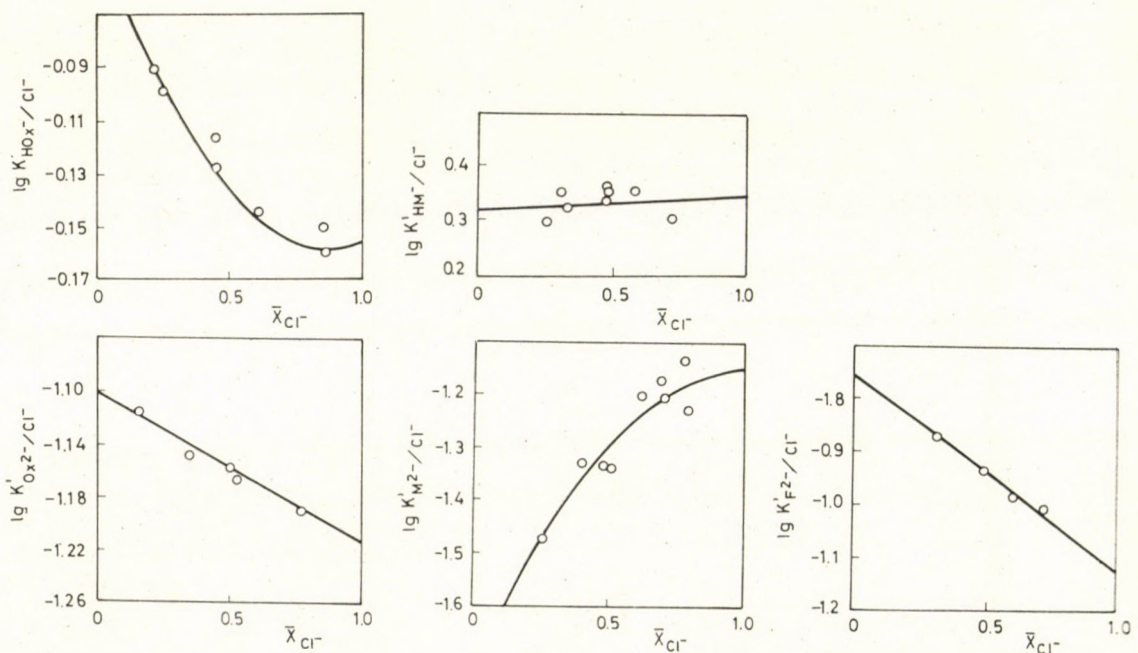


Fig. 3. Dependence of the selectivity coefficient, K' on the composition of the resin phase for the HOx^-/Cl^- , $\text{OX}^{2-}/\text{Cl}^-$, HM^-/Cl^- , $\text{M}^{2-}/\text{Cl}^-$, and for the $\text{F}^{2-}/\text{Cl}^-$ systems

If for the choice of the components and standard states the above convention is accepted then the evaluation of K^T is possible by the method of FREEMAN [8]. This method uses the concept of excess free energies to equate the deviations from ideality whereby a simultaneous calculation of the equilibrium constant and the activity coefficients are made possible. For the calculation of the thermodynamic equilibrium constant the following equation was derived by FREEMAN:

$$RT \ln K' = RT \ln K^T - \sum_{\nu=0}^{N'} G_{\nu} [-(2\bar{x}_{\text{Cl}} - 1)^{\nu+1} + 2\nu\bar{x}_{\text{Cl}}(1 - \bar{x}_{\text{Cl}})(2\bar{x}_{\text{Cl}} - 1)^{\nu-1}] \quad (5)$$

The experimental values of $\ln K'$ are to be fitted parametrically to the equation above using as many terms in the summation as the precision requires ($\nu = 0 \dots N$). The application of a least square procedure yields the values of K^T and the G_{ν} fitting parameter. FREEMAN proved too that the G_{ν} parameter describes the course of $\ln f(\text{Cl})$ and $\ln f(\text{Y})$ as a function of $\bar{x}(\text{Cl})$ and these functions are given by the following equations:

$$RT \ln f(\text{Cl}) = z_{\text{Cl}}(1 - \bar{x}_{\text{Cl}})^2 \sum_{\nu=0}^N G_{\nu} [2(\bar{x}_{\text{Cl}} - 1)^{\nu} + 2\nu\bar{x}_{\text{Cl}}(2\bar{x}_{\text{Cl}} - 1)^{\nu-1}] \quad (6)$$

$$RT \ln f(\text{Y}) = z_{\text{Y}}\bar{x}_{\text{Cl}} \sum_{\nu=0}^N G_{\nu} [(2\bar{x}_{\text{Cl}} - 1)^{\nu} - 2\nu(1 - \bar{x}_{\text{Cl}})(2\bar{x}_{\text{Cl}} - 1)^{\nu-1}] \quad (7)$$

The calculated thermodynamic equilibrium constants are given in Table I and as an application of eqns (6 and 7) the calculated activity coefficient functions are shown for the HOx^-/Cl^- and $\text{Ox}^{2-}/\text{Cl}^-$ systems in Fig. 4.

From the calculated equilibrium constants the free energy of the exchange, ΔG° was obtained by using the

$$\Delta G^{\circ} = - \frac{1}{z_{\text{Cl}} z_{\text{Y}}} RT \ln K^T$$

relationship. These data are also given in Table I.

Table I
Thermochemical data for the studied exchange reactions

Y^{n-}	K^T	ΔG°	ΔH	ΔS
		KJ equiv ⁻¹		JK ⁻¹ equiv ⁻¹
HOx^-	0.753	+0.70	+3.58	+ 1
Ox^{2-}	0.107	+2.77	+6.35	+13
HM^-	2.150	-1.85	-5.51	-12
M^{2-}	0.045	+3.84	+7.80	+13
F^{2-}	0.119	+2.64	+8.11	+18

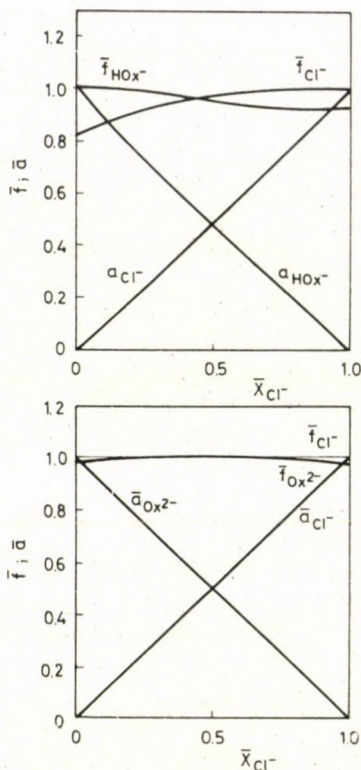


Fig. 4. The calculated activity and activity coefficient functions for the HOx^-/Cl^- and Ox^{2-}/Cl^- systems

From the calorimetric measurements the enthalpy change corresponding to a given degree of the resin conversion was evaluated in the same way as was described in the first part of this series, see eqn. (7) in Ref. [1a]. The enthalpy change of the reactions were measured at different values of the resin conversion and these results are shown in Fig. 5.

In order to get proper standard enthalpy values the experimental data should be corrected with the difference in the relative apparent molal heat contents ($\Delta\varphi$) of the acid and sodium chloride solutions. The φ values are obtained from the measurement of the heat of dilution. In our cases, however, the process of dilution is inevitably accompanied by a change in the pH of the solution therefore the result would be a sum of the heat of dilution and that of the protonation or deprotonation of studied anion. No correction has therefore been applied for the obtained ΔH figures. These corrections, however, amounts to only a few tenths in terms of kJ/equiv therefore neither the ΔH nor the $(\Delta H - \Delta G)/T = \Delta S$ values would be significantly influenced by these corrections.

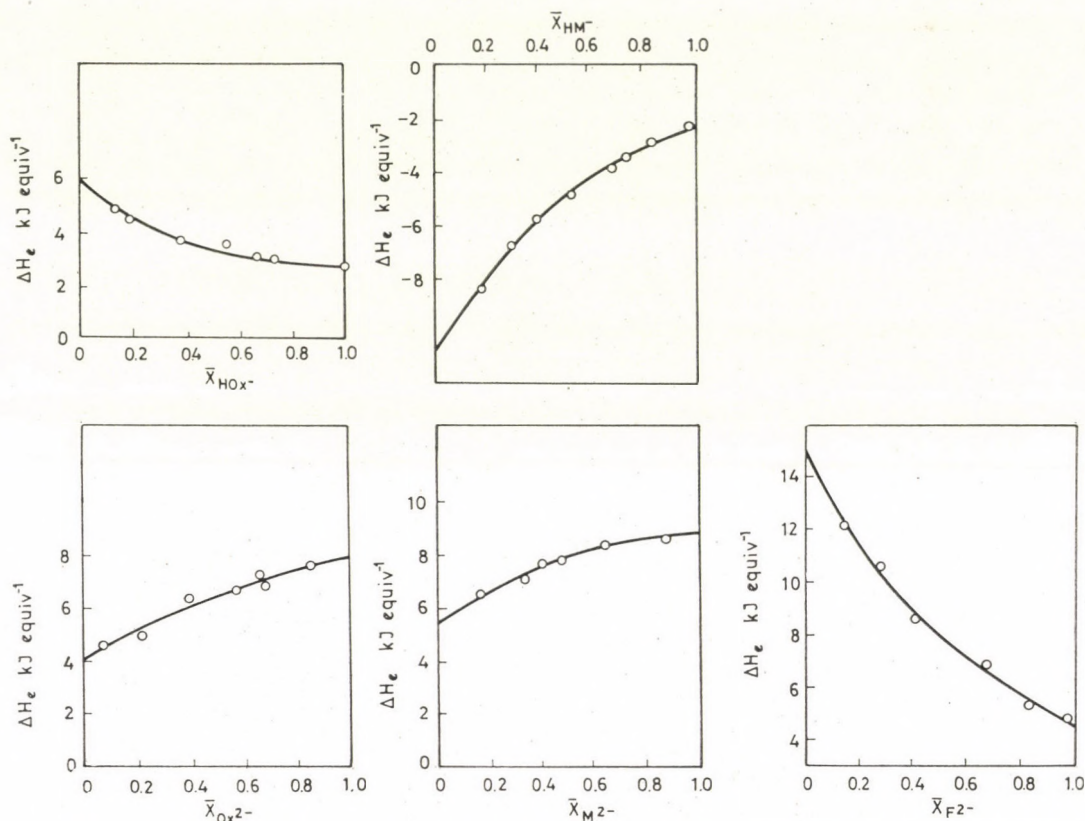


Fig. 5. Variation of the heat of exchange as a function of the resin composition for the studied systems

From a comparison of the thermodynamic data in Table I appears that with the exception of the MH^-/Cl^- system the free energy changes are positive for the rest of the studied reactions. These positive free energy values originate solely from the unfavourable (positive) enthalpy change because the entropy values are otherwise favourable (positive) in sign.

From the thermochemical parameters one would like to conclude for the type of the interaction that is responsible for the observed (high or low) selectivity. As a first approach to this end one may use the principles applied for the interpretation of the stability constants of the complex formation reactions.

When complexes formed in aqueous solution are studied then the different types of bonding are reflected in the values of the ΔH° and ΔS° of the complexation reaction. From a large body of data it became possible to make the following generalizations [9].

In the case of essentially electrostatic bonding, mostly realized between hard acceptor and donor, the complex formation is due to a large gain of entropy

while the enthalpy change generally counteracts the reaction. The ordered water structure around the donor and acceptor molecules will serve as a source of entropy. When complexes are formed this structure will be more or less broken down and this process is followed by an increase in entropy.

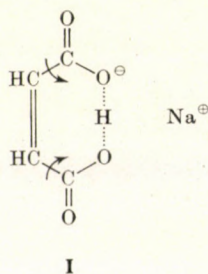
In the case of essentially covalent bonding, realized between very soft acceptor and donor, the complex formation is due to a large decrease of enthalpy accompanying the formation of the covalent bond.

The value of ΔH° thus seems to provide a good measure of covalency of the bond between the donor and the acceptor. The more negative ΔH° the stronger is generally the covalent bond.

In the field of the ion exchange these principles may work *e.g.* in the case of a weak acid cation exchange but the application of these guide lines to the anion exchange would be either very formal or may lead to very far-fetched comparisons.

For the studied reactions the thermochemical parameters do not show to any specific mode of the above mentioned interactions. The source of interaction that governs selectivity should therefore be found not within the resin phase but rather in the solution phase.

Out of the investigated anions the chloride-form exchanger shows only preference for the monovalent maleinate anion MH^- . The interaction that may lead to this exceptional selectivity is the ability of this ion to form intramolecular hydrogen bond.



This interaction dramatically decreases the polarising ability of the single negative charge being smeared over a very large species. A well known consequence of this interaction is the low solubility of the NaHM in water. The poorly hydrated HM^- ion is therefore transferred into the resin phase. The free energy of the systems is thereby considerably lowered because the relative permittivity of the solid phase is lower than that of the aqueous phase.

When the acid is fully ionised then the ionic repulsion between the carboxylate groups cause a large rotation around the $\text{C}-\text{C}$ single bond (shown by arrows in formula I) which prevents the formation of a strong intramolecular hydrogen bond [10]. This distortion leads to a higher degree of hydration of

the M^{2-} ion which is manifested in the lower value of the selectivity coefficient. The latter structural information became evident from the single crystal diffraction studies of the Na_2M . These studies also revealed that there are no similar distortions in the case of H_2M and KHM which makes the $O \dots H \dots O$ bond fairly stable.

Similar explanations, of course, do not apply either to the fumaric acid where the $C=C$ double bond fixes the carboxylate groups in a trans position or to the oxalic acid where the $C-C$ single bonds allows free rotation of the groups.

The presented examples show again that the anion exchange is a fairly complex phenomenon and selectivity is unlikely to be explained by a simple resin-phase dominated electrostatic interaction.

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CARBOHYDRATE METHYL ETHERS, X*

HYDROGENOLYSIS OF BENZYLIDENE ACETALS
SYNTHESIS OF MONO- AND DI-*O*-METHYL ETHERS OF L-ARABINOSE

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Preparation methods of 2-, 3- and 4-mono-*O*-methyl-, as well as 2,3-, 2,4- and 3,4-di-*O*-methyl-L-arabinose are described starting from *exo* and *endo* benzyl 3,4-*O*-benzylidene- β -L-arabinopyranoside, respectively. $^1\text{H-NMR}$ and GLC data are presented.

Introduction

D- and L-Arabinose are sugars frequently occurring in nature as the components of plant polysaccharides [1] and plant glycosides; first of all as the carbohydrate component of saponines [2]. The methyl ethers of D- and L-arabinose are essential standard compounds in the structural examination of polysaccharides, saponine glycosides and oligosaccharides containing arabinose. Various methods are known for the syntheses of arabinose methyl ethers starting from different compounds [3]. In the present paper a facile route is described for the synthesis of all the mono- and di-*O*-methyl ethers of L-arabinose using the *exo*- and *endo*-isomers of benzyl 3,4-*O*-benzylidene- β -L-arabinopyranoside as starting material.

Results and Discussion

The benzylidene acetals of glycopyranosides, involving *cis axial-equatorial* hydroxyl groups, may form two stereoisomers. The absolute configuration of the isomers (called *exo* or *endo*, according to the steric position of the phenyl group) can be determined by $^1\text{H-NMR}$ [4–6] and $^{13}\text{C-NMR}$ spectroscopic [7–8] methods.

On hydrogenolysis of the *exo*-isomers of dioxolane-type benzylidene acetals with $\text{LiAlH}_4\text{-AlCl}_3$, the reagent attacks the *axial* oxygen atom of the dioxolane skeleton and the product contains *equatorial O*-benzyl and *axial* free hydroxyl groups. In the case of the *endo*-isomers, the point of attack by the reagent is on the *equatorial* oxygen atom and products with *axial O*-benzyl and *equatorial* free hydroxyl group are formed [9–16].

* For Part IX, see Ref. [11].

Methylation of benzyl *exo*-3,4-*O*-benzylidene-(1) and benzyl *endo*-3,4-*O*-benzylidene- β -L-arabinopyranoside (2) [16], using KUHN's procedure [17], resulted in crystalline 3 and syrupy 4, respectively. The structures of both compounds were substantiated by $^1\text{H-NMR}$ investigation and it was established that the methylation reaction was not accompanied by isomerization of the dioxolane skeleton. The benzylidene proton of 3 and 4 appeared at $\delta = 6.20$ and $\delta = 5.90$ ppm, respectively.

Hydrogenolysis of 3 with $\text{LiAlH}_4\text{-AlCl}_3$ gave a 74 : 26 mixture (GLC) of the 3-*O*-benzyl- (5) and 4-*O*-benzyl isomers (6). The separation of 5 and 6, or their acetates, by chromatography remained unsuccessful.

On hydrogenolysis compound 4 gave a 7 : 93 mixture of 5 and 6, from which compound 6 was isolated in the crystalline state.

We have shown that the hydrogenolysis of dioxolane-type benzylidene acetals is a completely stereospecific reaction. The presence of the by-product may be explained by isomerization caused by chloroalane [16]. The rate of isomerization depends on the configuration of the dioxolane ring, hence these results support our earlier observation, namely the *endo*-isomers of the benzylidene acetals of arabinopyranosides always react with higher stereoselectivity than the corresponding *exo*-isomers. It is also worthy of note that the 2,4-disubstituted analogues are better crystallizable than the 2,3-disubstituted compounds.

Acid hydrolysis of 4 resulted in benzyl 2-*O*-methyl- β -L-arabinopyranoside (7). Methylation of 8, 10, 6, 13 and 15 [16], using KUHN's procedure, gave the two dibenzyl monomethyl analogues (9 and 11) and the three monobenzyl dimethyl derivatives (12, 14 and 16).

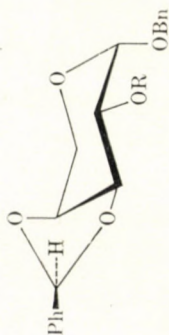
The catalytic hydrogenation of 7, 9, 11, 12, 14 and 16 gave the corresponding three mono- (17, 18 and 19) and three dimethyl L-arabinoses (20, 21 and 22), respectively, which were purified by column chromatography.

The purity of the blocked analogues 3, 4, 6, 7, 9, 11, 12, 14 and 16 was checked by GLC examinations, and the retention index I_T^{UCW} [18] of these compounds was determined.

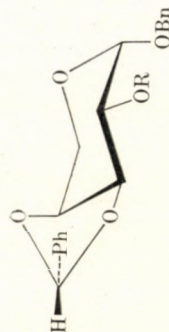
TLC examination of the free methyl ethers has shown that of the monomethyl ethers the 2-*O*-methyl derivative exhibits the highest mobility, whereas 4-*O*-methyl-L-arabinose has the lowest R_f value. A similar rule has been observed for the dimethyl ethers, the 2,3-di-*O*-methyl ether exhibiting the highest R_f and the 3,4-di-*O*-methyl-L-arabinose the lowest R_f value.

Experimental

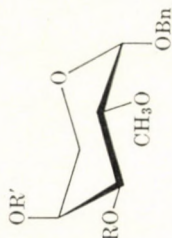
M.p.'s were determined on a Kofler hot-stage apparatus and are uncorrected. Optical rotations were measured with a Perkin-Elmer 241 automatic polarimeter; equilibrium values are given in 17-22. All published $[\alpha]_D$ values given in the experimental part are taken from Ref. [3]. $^1\text{H-NMR}$ spectra were obtained on a JEOL MH-100 (100 MHz) instrument using



1 R = H

3 R = CH₃

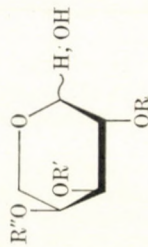
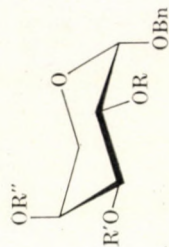
2 R = H

4 R = CH₃

5 R = Bn, R' = H

6 R = H, R' = Bn

7 R = R' = H

17 R = CH₃, R' = R'' = H18 R = R'' = H, R' = CH₃19 R = R' = H, R'' = CH₃20 R = R' = CH₃, R'' = H21 R = R'' = CH₃, R' = H22 R = H, R' = R'' = CH₃

8 R = R'' = Bn, R' = H

9 R = R'' = Bn, R' = CH₃

10 R = R' = Bn, R'' = H

11 R = R' = Bn, R'' = CH₃12 R = R' = CH₃, R'' = Bn

13 R = R'' = H, R' = Bn

14 R = R'' = CH₃, R' = Bn

15 R = Bn, R' = R'' = H

16 R = Bn, R' = R'' = CH₃Ph = C₆H₅—Bn = C₆H₅—CH₂—

TMS as internal standard. GLC was performed with a Hewlett—Packard 5840 A instrument. Columns: (a) 2% OV-101 100—200 mesh, with 20 mL/min He gas; (b) 10% UCW 982 on Gas Chrom Q 80—100 mesh, 120 cm \times 2.16 mm ID stainless steel, 4 ft, 225° isothermal, with 20 mL/min N₂ gas; (c) 10% UCW 982 on Gas Chrom Q 80—100 mesh, 120 cm \times 2.16 mm ID stainless steel, 4 ft, 250° isothermal, with 20 mL/min N₂ gas. TLC examination was carried out on DC-Alurolle Kieselgel 60F 254 (Merck), detection with 50% sulfuric acid. For column chromatographic separation Kieselgel G (Merck) was used with solvent systems (A) petroleum ether-ethyl acetate (7 : 3); (B) dichloromethane-methanol (8 : 2).

Benzyl *exo*-3,4-*O*-benzylidene-2-*O*-methyl- β -L-arabinopyranoside (3)

To a solution of benzyl *exo*-3,4-*O*-benzylidene- β -L-arabinopyranoside (1, 2.00 g) in dry DMF (30 mL) methyl iodide (1.90 mL) and silver oxide (1.90 g) were added in two portions and the solution was stirred at room temperature for 10 h. It was then diluted with dichloromethane (150 mL), filtered, the filtrate was washed with 5% sodium cyanide solution (2 \times 30 mL) and water (3 \times 30 mL), dried over Na₂SO₄ and concentrated. Traces of DMF were removed by vacuum distillation. The syrupy residue was dissolved in dichloromethane (100 mL), washed with water, dried and concentrated to give 2.02 g (96.8%) of a product. Recrystallization from hexane (50 mL) gave pure **3** (1.13 g; 54.2%), m.p. 58—60 °C, $[\alpha]_D^{+160}$ (*c* = 0.99, chloroform), $R_f(A)$ 0.62, $R_T(c)$ 3.71 min, I_{250}^{UCW} 2551.

NMR (in CDCl₃): δ = 7.55—7.20 ppm (m, 10H, 2 Ph), 6.20 (s, 1H, PhCH), 5.06 (d, 1H, H-1), 4.83—4.48 (m, 3H, PhCH₂ and H-3), 4.22—4.10 (m, 1H, H-4), 3.96 (d, 2H, H-5_a, 5_c), 3.60—3.40 (m, 1H, H-2), 3.54 (s, 3H, OCH₃).

Benzyl *endo*-3,4-*O*-benzylidene-2-*O*-methyl- β -L-arabinopyranoside (4)

Methylation of benzyl *endo*-3,4-*O*-benzylidene- β -L-arabinopyranoside (2, 2.0 g) as described above for the preparation of **3** gave syrupy **4** (1.96 g; 93.9%), $[\alpha]_D^{+171}$ (*c* = 1.85, chloroform), $R_f(A)$ 0.62, $R_T(c)$ 3.47 min, I_{250}^{UCW} 2521.

NMR (in CDCl₃): δ = 7.60—7.20 ppm (m, 10H, 2 Ph), 5.90 (s, 1H, PhCH), 4.97 (d, 1H, H-1), 4.66 (q, 2H, PhCH₂), 4.40—4.16 (m, 2H, H-3 and H-4), 4.04 (d, 2H, H-5_a, 5_c), 3.50—3.32 (m, 1H, H-2), 3.42 (s, 3H, OCH₃).

Ring cleavage of benzyl *exo*-3,4-*O*-benzylidene-2-*O*-methyl- β -L-arabinopyranoside

To a solution of **3** (1.70 g) in 1 : 1 dichloromethane-ether (40 mL) LiAlH₄ (380 mg) was added. After heating to 45 °C a solution of AlCl₃ (1.33 g) in ether (10 mL) was added, and the mixture was stirred at 45 °C for 5 min. After cooling, the excess of LiAlH₄ was decomposed by the addition of ethyl acetate (5 mL) and Al(OH)₃ was precipitated by the addition of water (10 mL). The organic layer was decanted and the residue extracted with ether (2 \times 30 mL). The combined organic layers were washed with water (2 \times 20 mL), dried over Na₂SO₄ and concentrated to give a 74 : 26 mixture (1.60 g; 94.1%) of benzyl 3-*O*-benzyl-2-*O*-methyl- (**5**) and benzyl 4-*O*-benzyl-2-*O*-methyl- β -L-arabinopyranoside (**6**): $R_T(a)$ 4.35 and 5.03 min.

Ring cleavage of benzyl *endo*-3,4-*O*-benzylidene-2-*O*-methyl- β -L-arabinopyranoside

Hydrogenolysis of **4** (1.70 g) was carried out as described above for **3** to give a 7 : 93 mixture (1.58 g; 92.9%) of **5** and **6**. Recrystallization from cyclohexane gave pure **6** (980 mg; 57.6%), m.p. 73—74 °C, $[\alpha]_D^{+184}$ (*c* = 1.97, chloroform), $R_T(b)$ 10.84 min, I_{250}^{UCW} 2583.

NMR (in CDCl₃): δ = 7.60—7.15 ppm (m, 10H, 2 Ph), 5.04 (d, 1H, H-1), 4.64 and 4.63 (2q, 4H, 2 PhCH₂), 4.02 (m, 1H, H-3), 3.82—3.68 (m, 3H, H-4, H-5_a, 5_c), 3.54 (dd, 1H, H-2), 3.37 (s, 1H, OCH₃), 2.61 (d, 1H, HO-3), after the addition of D₂O 4.02 (dd, 1H, H-3), the doublet at 2.61 ppm disappeared. $J_{1,2}$ = 3.5 Hz, $J_{2,3}$ = 9.4 Hz, $J_{3,4}$ = 2.8 Hz.

Benzyl 2-*O*-methyl- β -L-arabinopyranoside (7)

A solution of **4** (2.08 g) in ethanol (40 mL) and 0.1 N sulfuric acid (40 mL) was boiled for 4 h. The hot solution was neutralized with BaCO₃, filtered and concentrated to obtain 1.49 g (96.5%) of **7**, which was purified by column chromatography (C) to give pure **7** (980 mg;

63.4%). Recrystallization from cyclohexane gave 540 mg (35%), m.p. 74–76 °C, $[\alpha]_D +241^\circ$ ($c = 0.92$, chloroform), $R_f(B)$ 0.77 $R_T(b)$ 1.66 min, I_{225}^{UCW} 1957.

NMR (in $CDCl_3$): $\delta = 7.50-7.20$ ppm (m, 5H, Ph), 5.05 (d, 1H, H-1), 4.63 (q, 2H, PhCH₂), 4.09–3.87 (m, 2H, H-3 and H-4), 3.75 (d, 2H, H-5_a, 5_e), 3.63–3.43 (m, 1H, H-2), 3.33 (s, 3H, OCH₃), 3.21 (s, 2H, HO-3 and HO-4).

Benzyl 2,4-di-*O*-benzyl-3-*O*-methyl- β -L-arabinopyranoside (9)

To a solution of benzyl 2,4-di-*O*-benzyl- β -L-arabinopyranoside (8) in dry DMF (15 mL) silver oxide (0.78 g) and methyl iodide (0.78 mL) were added in two portions and the mixture was stirred at room temperature for 96 h. At the 48th hour further amounts of silver oxide (0.39 g) and methyl iodide (0.39 mL) were added. The mixture was diluted with dichloromethane, filtered, washed with 5% sodium cyanide solution (2 \times 20 mL) and water (3 \times 20 mL), dried over Na₂SO₄ and concentrated. The traces of DMF were removed by vacuum distillation to obtain 1.03 g (94.8%) of the product. Its purification was carried out by column chromatography (A) to give syrupy 9 (670 mg; 61.7%), $[\alpha]_D +132^\circ$ ($c = 1.67$, chloroform), $R_f(A)$ 0.56, R_T 15.70 min (c), I_{250}^{UCW} 3087.

NMR (in $CDCl_3$): $\delta = 7.60-7.20$ ppm (m, 15H, 3 Ph), 4.90 (d, 1H, H-1), 4.80–4.42 (3q, 6H, 3 PhCH₂), 4.04–3.60 (m, 5H, skeleton protons), 3.43 (s, 3H, OCH₃).

Benzyl 2,3-di-*O*-benzyl-4-*O*-methyl- β -L-arabinopyranoside (11)

Benzyl 2,3-di-*O*-benzyl- β -L-arabinopyranoside (10, 1.05 g) was methylated as described above for the preparation of 9 to give 900 mg (82.8%) of a crude product. Its purification by column chromatography (A) gave syrupy 11 (540 mg; 49.7%), $[\alpha]_D +110^\circ$ ($c = 1.40$, chloroform), $R_f(A)$ 0.47, $R_T(c)$ 13.05 min, I_{250}^{UCW} 3022.

NMR (in $CDCl_3$): $\delta = 7.50-7.20$ ppm (m, 15H, 3 Ph), 4.88 (d, 1H, H-1), 4.80–4.46 (3q, 6H, 3 PhCH₂), 3.98–3.90 (m, 2H, H-3 and H-4), 3.71 (d, 2H, H-5_a, 5_e), 3.56–3.48 (m, 1H, H-2), 3.43 (s, 3H, OCH₃).

Benzyl 4-*O*-benzyl-2,3-di-*O*-methyl- β -L-arabinopyranoside (12)

To a solution of 6 (860 mg) in dry DMF (15 mL) silver oxide (0.78 g) and, in two portions, methyl iodide (0.78 mL) were added. After stirring at room temperature for 24 h, 0.39 g of silver oxide and 0.39 mL of methyl iodide were added, and the mixture was stirred for additional 24 h. Work-up in the usual manner gave 890 mg (99.4%) of crude 12, which was recrystallized from cyclohexane (9 mL) to obtain 540 mg (60.3%), m.p. 69–71 °C, $[\alpha]_D +169^\circ$ ($c = 3.14$, chloroform), $R_f(A)$ 0.39, $R_T(b)$ 9.14 min, I_{225}^{UCW} 2515.

NMR (in $CDCl_3$): $\delta = 7.50-7.20$ ppm (m, 10H, 2 Ph), 5.02 (d, 1H, H-1), 4.69 and 4.65 (2q, 4H, 2 PhCH₂), 3.84–3.52 (m, 5H, skeleton protons), 3.41 (s, 6H, 2-OCH₃ and 3-OCH₃).

Benzyl 3-*O*-benzyl-2,4-di-*O*-methyl- β -L-arabinopyranoside (14)

To a solution of benzyl 3-*O*-benzyl- β -L-arabinopyranoside (13, 825 mg) in dry DMF (15 mL) silver oxide (1.56 g) and, in two portions, methyl iodide (1.56 mL) were added, and the mixture was stirred at room temperature for 96 h. In the 48th hour more silver oxide (0.78 g) and methyl iodide (0.78 mL) were added. Work-up in the usual manner gave 890 mg (99.4%) of 14, which was purified by column chromatography (A) to obtain 600 mg (67%) syrupy product, $[\alpha]_D +136^\circ$ ($c = 0.42$, chloroform), $R_f(A)$ 0.37, $R_T(b)$ 7.92 min, I_{225}^{UCW} 2475.

NMR (in $CDCl_3$): $\delta = 7.50-7.20$ ppm (m, 10H, 2 Ph), 5.00 (d, 1H, H-1), 4.90–4.50 (2q, 4H, 2 PhCH₂), 3.96–3.62 (m, 5H, skeleton protons), 3.46 and 3.42 (2s, 6H, 2-OCH₃ and 4-OCH₃).

Benzyl 2-*O*-benzyl-3,4-di-*O*-methyl- β -L-arabinopyranoside (16)

Methylation of benzyl 2-*O*-benzyl- β -L-arabinopyranoside (15, 825 mg) was carried out as described above for the preparation of 14. Purification of the crude product by column chromatography (A) resulted in pure syrupy 16 (610 mg; 68.2%), $[\alpha]_D +137^\circ$ ($c = 1.60$, chloroform), $R_f(A)$ 0.24, R_T 7.64 min (b), I_{225}^{UCW} 2459.

NMR (in CDCl_3): $\delta = 7.50\text{--}7.20$ ppm (m, 10H, 2 Ph), 4.83 (d, 1H, H-1), 4.65 and 4.63 (2q, 4H, 2 PhCH_2), 3.96–3.68 (m, 5H, skeleton protons), 3.51 and 3.42 (2s, 6H, 3- OCH_3 and 4- OCH_3).

2-O-Methyl-L-arabinose (17)

A suspension of 10% PdC catalyst (150 mg) in ethanol (20 mL) was saturated with hydrogen gas for 15 min. After the addition of a solution of **7** (720 mg) in ethanol (20 mL) the mixture was hydrogenated at room temperature for 5 h. The catalyst was filtered off and the filtrate concentrated to give 500 mg of crude **17**, which was purified by column chromatography (B) to obtain pure **17** (310 mg; 66.7%), syrup, $[\alpha]_{\text{D}} +85^\circ$ ($c = 0.98$, water), *lit.* $[\alpha]_{\text{D}} +100^\circ$ (water), $R_f(B)$ 0.42.

3-O-Methyl-L-arabinose (18)

Hydrogenation of **9** (880 mg) as described above for the preparation of **17** (150 mg, 10% PdC, 40 mL of ethanol, 10 h) gave **18** (390 mg) which was purified by column chromatography (B) to give pure syrupy **18** (210 mg; 63.2%), $[\alpha]_{\text{D}} +86^\circ$ ($c = 1.95$, water), *lit.* $[\alpha]_{\text{D}} +96^\circ$, $+110^\circ$ (water), $R_f(B)$ 0.42 and 0.38.

4-O-Methyl-L-arabinose (19)

Compound **11** (510 mg) was hydrogenated in ethanol (40 mL) in the presence of 10% PdC (100 mg) for 5 h to give 220 mg of **19** which was purified by column chromatography (B) to obtain pure syrupy **19** (130 mg; 67.5%), $[\alpha]_{\text{D}} +101^\circ$ ($c = 1.97$, water), *lit.* $[\alpha]_{\text{D}} +132 \pm 2^\circ$ (water), $R_f(B)$ 0.37.

2,3-Di-O-methyl-L-arabinose (20)

Compound **12** (450 mg) was hydrogenated in ethanol (35 mL) in the presence of 10% PdC for 6 h to give 210 mg of **20**. Purification of the product by column chromatography (B) gave syrupy **20** (110 mg; 49.2%), $[\alpha]_{\text{D}} +22^\circ$ ($c = 1.09$, chloroform), $+86^\circ$ ($c = 0.66$, water), *lit.* $[\alpha]_{\text{D}} +101^\circ$, $+107^\circ$ (water), $R_f(B)$ 0.66.

2,4-Di-O-methyl-L-arabinose (21)

A mixture of **14** (410 mg), 10% PdC (100 mg) in ethanol (35 mL) was hydrogenated for 6 h to give crude **21** (220 mg) which was purified by column chromatography (B) to yield 110 mg (54.0%) of syrupy **21**, $[\alpha]_{\text{D}} +36^\circ$ ($c = 0.94$, chloroform), $+99^\circ$ ($c = 0.76$, water), *lit.* $[\alpha]_{\text{D}} +118^\circ$, $+129^\circ$ (water), $R_f(B)$ 0.65.

3,4-Di-O-methyl-L-arabinose (22)

To a solution of **16** (300 mg) in ethanol (35 mL) 10% PdC (100 mg) was added and the mixture was hydrogenated for 10 h to give 150 mg of **22**, which was purified by column chromatography (B) to obtain pure syrupy **22** (80 mg; 53.6%), $[\alpha]_{\text{D}} +115^\circ$ ($c = 1.24$, chloroform), $+135^\circ$ ($c = 0.40$, water), *lit.* $[\alpha]_{\text{D}} +104^\circ$, $+116^\circ$, $+125^\circ$ (water), $R_f(B)$ 0.62.

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SYNTHESIS OF PEPTIDES CONTAINING D-GLUCOSAMINIC ACID, II*

SYNTHESIS OF SOME TRI- AND HEXAPEPTIDES

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Using the azide method of fragment condensation, the acetates of the tripeptides glycyalanyl-4,6-*O*-benzylideneglucosaminic amide, glycy-4,6-*O*-benzylideneglucosaminylalanine amide, 4,6-*O*-benzylideneglucosaminylglycyalalanine amide and that of the hexapeptide 4,6-*O*-benzylideneglucosaminylglycyalanyl-4,6-*O*-benzylideneglucosaminylglycyalanyl amide have been synthesized.

In the previous paper it was reported that, according to our investigations, in the synthesis of peptides containing D-glucosaminic acid (H-GA-OH), which can be regarded as an analogue of serine, it is advisable to use the 4,6-*O*-benzylidene derivative (H-BEGA-OH) to prevent lactonization.

When in the peptide to be prepared the H-BEGA-OH is in C-terminal position, the azide method was found to be the most favourable for the construction of the peptide bonds. In the present paper syntheses of tri- and hexapeptides containing H-BEGA-OH are described. The purpose of the work was primarily the preparation of such tripeptides, and the examination of their physical and chemical properties, which contained the H-BEGA-OH at different (C-terminal, N-terminal and intermediate) positions. The other two amino acids were glycine and alanine. The syntheses of the three tripeptides and their amides were accomplished as outlined in Figs 1–3.

The coupling into tripeptides of the intermediates prepared and described earlier [1], was effected by the azide method in DMF in all three cases. Occasionally some difficulties were encountered during the usual processing of the reaction mixture owing to the poor solubility of the BEGA-containing tripeptide esters. For example, the solubility of Z-BEGA-Gly-Ala-OMe was found to be particularly low in ethyl acetate, thus a suspension had to be processed.

In the next step, the peptide esters were to be converted into the amides to make them suitable for the prospective biological examinations. The ammonolysis could be effected smoothly and in satisfactory yields (73–65%) in the

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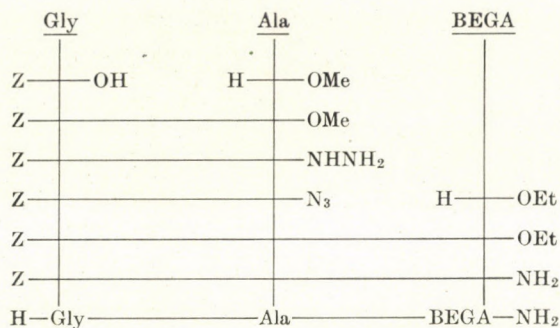


Fig. 1

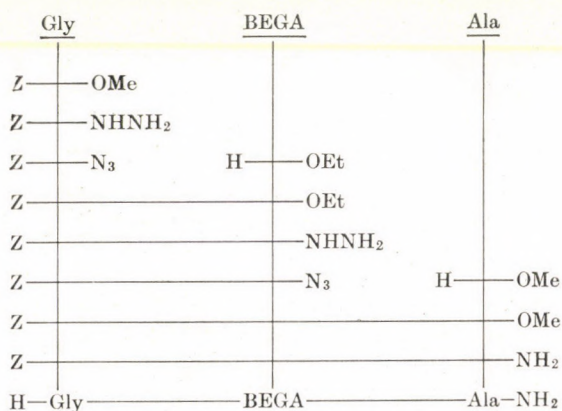


Fig. 2

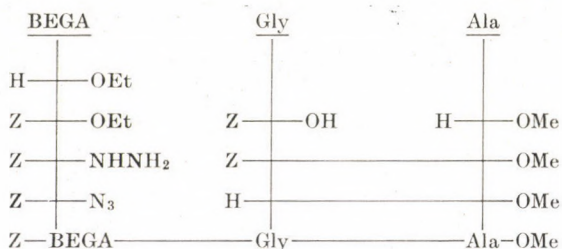


Fig. 3

case of Z-Gly-BEGA-Ala-OMe and Z-Gly-Ala-BEGA-OEt; the products readily crystallized from 50% aqueous alcohol. The preparation of Z-BEGA-Gly-Ala-NH₂, however, could not be achieved in this way, since treatment of the corresponding ester with ammonia gave a substance contaminated with an unknown by-product (or by-products) defying purification. Therefore, this tripeptide amide was synthesized by the reactions outlined in Fig. 4.

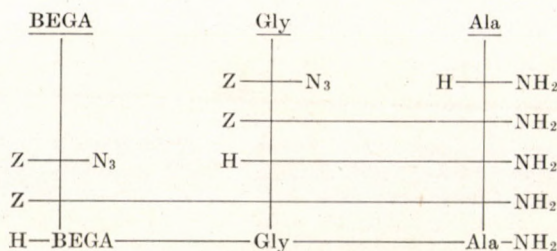


Fig. 4

Since the tripeptide was obtained in this manner in a satisfactory yield (71%), the method was adapted to the synthesis of H-Gly-BEGA-Ala-NH₂, too.

Removal of the carbobenzyoxy protective group from the tripeptide amides was achieved by catalytic hydrogenolysis, since preliminary tests indicated non-desirable decomposition processes on the effect of HBr in glacial acetic acid. In the hydrogenolysis acetic acid was used as the acid, since hydrochloric acid might cause partial cleavage of the benzylidene group. The tripeptide amides are very scarcely soluble in cold methanol or aqueous methanol hence the hydrogenolysis was effected first in DMF solutions. Later it was recognized that the reaction can also be accomplished in alcoholic suspensions to give the acetates of the free tripeptides. Their recrystallization by means of cold solvents resulted in chromatographically homogeneous products.

After the successful syntheses of tripeptides, the preparation of a hexapeptide containing 4,6-*O*-benzylideneglucosaminic acid was tried and realized by the azide method. The hexapeptide to be synthesized was Z-BEGA-Gly-Ala-BEGA-Gly-Ala-NH₂, obtainable by coupling of the fragments Z-BEGA-Gly-Ala-N₃ and H-BEGA-Gly-Ala-NH₂. The Z-BEGA-Gly-Ala-NHNH₂ was prepared from the corresponding ester in a satisfactory yield (83%). The coupling was effected in DMF solution. In the next step the solvent was removed in vacuum (27 Pa) and the residual jelly product was isolated by centrifuging. The pure, amorphous hexapeptide was obtained in nearly 50% yield.

The synthesis of the hexapeptide was attempted also by the activated ester method, using pentachlorophenyl ester. It had been found earlier that Z-BEGA-OH containing a free carboxyl group could not be converted into the activated PCP ester, since considerable lactonization took place on the effect of DCC. Therefore Z-BEGA-Gly-Ala-OH was chosen as the model compound. First, pentachlorophenol was allowed to react with DCC in DMF, then the solution was mixed with a solution of the protected tripeptide in DMF at 0 °C. The weight of the DCU which precipitated during the reaction was nearly identical with the calculated amount. However, on repeated purification of the product the pure substance could be isolated only in 28% yield, which indicates the occurrence of considerable side reactions.

In the next step the active ester was allowed to react with H-BEGA-Gly-Ala-NH₂ in DMF, in the usual manner. After processing, the hexapeptide amide was obtained in 45% yield; the m.p., IR spectrum and *R_f* values were identical with those of the product prepared by the azide coupling method. The optical rotations of the amorphous products (from azide method $[\alpha]_D^{20} = -32^\circ$, from active ester method $[\alpha]_D^{20} = -26.5^\circ$, in DMF, *c* = 2%) indicated that the coupling with the active ester was accompanied by racemization.

The main results of the present investigation can be summarized as follows:

(a) Gly-Ala-BEGA-OEt, BEGA-Gly-Ala-OMe and Gly-BEGA-Ala-OMe tripeptide esters and their amide derivatives were prepared by the azide method of fragment condensation and the acetate of BEGA-Gly-Ala-BEGA-Gly-Ala-NH₂ hexapeptide amide was also obtained in this way.

(b) In addition to the acid-sensitivity of peptides containing 4,6-*O*-benzylideneglucosaminic acid side reaction(s) may appear during the alkaline (NH₃) treatment of the tripeptide carrying H-BEGA-OH in *N*-terminal position.

(c) The peptides containing H-BEGA-OH are poorly soluble in the non-polar solvents commonly used in peptide chemistry; this can probably be attributed to the presence of hydroxyl groups.

(d) In the synthesis of the hexapeptide amide by the activated ester method, a significant racemization was observed as compared with the hexapeptide synthesized by the azide fragment condensation technique. This is probably due not to the method but to the special behaviour of the tripeptides participating in the reaction.

Experimental

M.p.'s were determined on a Büchi-Tottoli apparatus and are uncorrected. IR spectra were recorded in KBr pellets (Perkin-Elmer Model 457). The *R_f* values were determined using the ascending technique of thin-layer chromatography in the following solvent systems: (1) EtOAc : AcOH : MeOH : H₂O = 3 : 0.7 : 0.7 : 0.5. (2) *t*-BuOH : AcOH : H₂O = 2 : 2 : 1; (3) EtOAc : HCOOH : H₂O = 3 : 1 : 1; (4) EtOAc : *i*-PrOH : Py : H₂O = 3.5 : 1 : 0.7 : 0.7; (5) MeOH : CHCl₃ : (Me)₂CO : NH₃ = 2.5 : 1 : 1.5 : 1; (6) BuOH : AcOH : (Me)₂CO = 4 : 1 : 1. For the detection of the spots ninhydrin or chlorotolidine were used. All compounds were analyzed for C, H, N, with results of at least 0.4% accuracy.

I. Preparation of tripeptide esters

Z-Glycyl-4,6-*O*-benzylideneglucosaminic acid hydrazide

Z-Glycyl-4,6-*O*-benzylideneglucosaminic acid ethyl ester [1] (12.55 g; 25 mmoles) was dissolved in anhydrous ethanol (175 mL) with gentle heating, and 98% hydrazine hydrate (4.5 mL) was added to the solution which was then refluxed for 1 h. After cooling, the mixture was allowed to stand at room temperature for 12 h, whereupon the product partly separated from the solution. It was then kept in a refrigerator for a few hours, the solid was filtered off, washed with a mixture of anhydrous alcohol and anhydrous ether, and dried in a vacuum desiccator over P₂O₅ and paraffin chips; a white crystalline substance (12 g; 98%) with m.p. 192–193 °C was obtained. The product was suitable for use in coupling reactions without further purification. After recrystallization from a mixture of DMF and acetonitrile (1 : 5), the m.p. of the substance of analytical grade purity was 196–197 °C (d).

Z-Glycyl-4,6-O-benzylideneglucosaminylalanine methyl ester

A solution of Z-glycyl-4,6-O-benzylideneglucosaminic acid hydrazide (10 g; 20 mmoles) in DMF (80 mL) was cooled to -10°C ; 6*N* hydrochloric acid (65 mmoles), then a solution of NaNO_2 (1.75 g; 25 mmoles) in water (5 mL) were added, with stirring, at -15 – -20°C . The solution of -10°C temperature was stirred for 10 min, then cooled again to -20°C and it was added in small portions to a mixture of alanine methyl ester hydrochloride (8.5 g; 61 mmoles), DMF (100 mL) and triethylamine (34.5 mL; 250 mmoles) cooled to -20°C . The addition was completed in 20 min, then the solution was stirred at 0°C and at room temperature for 1 h each, and refrigerated for 16 h. In the next step the solvent was evaporated in vacuum on a bath of 30°C , the last traces were removed by distillation with benzene. The pale yellow oily crystalline mass was dissolved in a mixture of 20% NaCl solution (400 mL) and ethyl acetate (375 mL) cooled to 0°C . After separation, the aqueous phase washed twice with ethyl acetate, the combined ethyl acetate solution was washed with 20% NaCl solution, dried over Na_2SO_4 , filtered, the solvent was evaporated in vacuum and the residue crystallized from 50% alcohol to obtain a pure substance (7.0 g, 61%) m.p. 107 – 108°C .

IR: CO(OR) 1740 cm^{-1} , Amide I 1650 cm^{-1} , Amide II 1535 cm^{-1} .

TLC: R_f : 0.88.

Z-4,6-O-Benzylideneglucosaminylglycylalanine methyl ester

A solution of Z-4,6-O-benzylideneglucosaminyl hydrazide (7.6 g; 17.5 mmoles) [2] in DMF (50 mL) was allowed to react in the presence of 6*N* hydrochloric acid (9.5 mL; 48 mmoles) first with a solution of NaNO_2 (1.5 g, 21 mmoles) in water (5 mL), then with a solution of glycylalanine methyl ester HBr [3] (12.5 g, 52 mmoles) and triethylamine (14.8 mL) in DMF (100 mL), under the conditions given above. After the accomplishment of coupling, the solvent was removed in vacuum, the residue dissolved in a mixture of 25% NaCl (3100 mL) and ethyl acetate (3250 mL) and the insoluble part was filtered off. (On the basis of the m.p. and the TLC test, it is also a tripeptide.) The ethyl acetate fraction was processed as usual. The evaporation residue and the substance filtered off were combined and crystallized from 50% alcohol to obtain a pure substance (5.0 g, 50%) m.p. 187°C .

IR: CO(OR) 1720 , Amide I 1660 cm^{-1} , Amide II 1535 cm^{-1} .

TLC: R_f : 0.74.

Z-Glycylalanyl-4,6-O-benzylideneglucosaminic acid ethyl ester

A solution of Z-glycylalanine hydrazide [4] (7.5 g; 25.6 mmoles) in DMF (75 mL) was allowed to react first with a solution of NaNO_2 (2.05 g; 30 mmoles) in water (5 mL) in the presence of 6*N* hydrochloric acid (80 mmoles), then with a solution of 4,6-O-benzylideneglucosaminic acid ethyl ester hydrochloride (7.3 g; 21 mmoles) in DMF (40 mL) in the presence of triethylamine (11.5 mL; 80 mmoles), under the conditions given above. After completing the coupling reaction, the solution was evaporated to dryness to obtain a pale yellow crystalline syrup. This was dissolved in a mixture of 20% NaCl (200 mL) and ethyl acetate (200 mL); after the separation of the two phases, the aqueous fraction was washed with ethyl acetate three times, the combined organic phase was washed with 20% NaCl solution and dried over Na_2SO_4 . The solution was evaporated to dryness in vacuum and the residue crystallized from a mixture of ethyl acetate and petroleum ether to obtain the pure product (9.3 g; 77%) m.p. 150 – 151°C .

IR: CO(OR) 1730 cm^{-1} , Amide I 1650 cm^{-1} , Amide II 1535 cm^{-1} .

TLC: R_f : 0.77.

II. Preparation of the protected peptide amides**Z-Glycyl-4,6-O-benzylideneglucosaminic amide**

Z-Glycyl-4,6-O-benzylideneglucosaminic acid ethyl ester [1] (1.1 g; 2.2 mmoles) was dissolved, with cooling, in cold, saturated methanolic ammonia (25 mL). The mixture was allowed to react in a bomb tube at room temperature for 48 h, then it was evaporated to dryness in vacuum on a bath of maximum 30°C temperature. The slightly sticky foamy residue was thoroughly rubbed with petroleum ether, filtered, washed with petroleum ether and dried in

a vacuum desiccator over P_2O_5 and paraffin chips. Recrystallization from 50% alcohol gave the pure amide (0.8 g; 80%), m.p. 197 °C.

IR: Amide I 1695 (Z) cm^{-1} , 1655 cm^{-1} , 1610 cm^{-1} , Amide II 1540 and 1500 cm^{-1} .

Z-Glycylalanyl-4-6-O-benzylideneglucosaminyl amide

Z-Glycylalanyl-4,6-O-benzylideneglucosaminic acid ethyl ester (1.15 g; 2 mmoles) was allowed to react with methanolic ammonia as described above and the mixture processed to obtain the product (0.71 g; 65%), m.p. 166 °C.

IR: Amide I 1710 cm^{-1} , 1685 cm^{-1} , 1670 cm^{-1} , Amide II 1540 cm^{-1} .

Z-Glycyl-4,6-N-benzylideneglucosaminylalanine amide

(a) *Ammonolysis method.* Z-Glycyl-4,6-O-benzylideneglucosaminylalanine methyl ester (1.0 g; 1.75 mmole) was allowed to react with methanolic ammonia as described above. The reaction mixture was worked up and the product crystallized from anhydrous alcohol to obtain the amide (0.65 g; 63%), m.p. 218 °C (d.).

IR: Amide I 1670 cm^{-1} , 1645 cm^{-1} , Amide II 1535 cm^{-1} .

(b) *Coupling method.* A solution of Z-glycyl-4,6-O-benzylideneglucosaminic acid hydrazide (10.0 g; 20.5 mmoles) in DMF (80 mL) was allowed to react, in the presence of 6*N* HCl (65 mmoles), first with a solution of $NaNO_2$ (1.7 g; 24.7 mmoles) in water (3 mL), then with a solution of alanine acetate (3.3 g; 22.5 mmoles) in DMF (100 mL) and with triethylamine (12.2 mL; 87.5 mmoles) under the conditions described above. After the accomplishment of coupling, the solvent was removed in vacuum on a bath of 35–40 °C temperature, the semi-crystalline residue was rubbed with a mixture of 20% NaCl solution (80 mL) and ethyl acetate (100 mL) in a mortar, the jelly material was isolated by centrifuging and the purification procedure was then repeated. The crystalline substance obtained in this way was filtered off, washed with ethyl acetate (2 × 25 mL), 20% NaCl (2 × 25 mL) solution then with water (4 × 25 mL), and after drying it was recrystallized from 50% alcohol to obtain 8.0 g (73%) of the amide, m.p. 218 °C (d.).

TLC: R_f^1 : 0.88; R_f^2 : 0.88; R_f^3 : 0.86.

Z-4,6-O-Benzylideneglucosaminylglycylalanine amide

A solution of Z-4,6-O-benzylideneglucosaminic acid hydrazide [2] (8.5 g; 20 mmoles) in DMF (50 mL) was allowed to react in the presence of 6*N* HCl (12 mL; 64.5 mmoles) first with a solution of $NaNO_2$ (1.68 g; 24.25 mmoles) in water (3 mL), then in the presence of triethylamine (12.2 mL; 87 mmoles) with a solution of glycylalanine amide-HCl [3] (4.1 g; 22.5 mmoles) in DMF (75 mL), under the conditions described above. When the coupling was complete, the solution was evaporated to dryness. The remaining white crystalline material was rubbed with a mixture of ethyl acetate (50 mL) and 20% NaCl solution (30 mL) in a mortar, filtered and the purification procedure was repeated. The solid product was washed on the filter with ethyl acetate (2 × 25 mL), 20% NaCl solution (2 × 20 mL) and with water (4 × 25 mL). A white substance difficult to filter was obtained; after drying it was crystallized from 90 parts of 70% alcohol to obtain the pure product (7.7 g; 71%) m.p. 246–247 °C (d.).

TLC: R_f^1 : 0.95; R_f^2 : 0.85; R_f^3 : 0.95.

III. Preparation of the free peptide amides

1,6-O-Benzylideneglucosaminylglycylalanine amide acetate

Z-4,6-O-Benzylideneglucosaminylglycylalanine amide (1 g; 1.83 mmole) was suspended in anhydrous methanol (150 mL), anhydrous acetic acid (0.11 mL; 1.83 mmole) was added, and the mixture was hydrogenated in the presence of 10% Pd/C catalyst (0.1 g) until the evolution of CO_2 ceased (about 6 h). The catalyst was filtered off, washed with anhydrous $NeOH$ (2 × 10 mL), the combined filtrate was evaporated to dryness in vacuum, the crystalline residue washed with ether (8 × 10 mL) and dried in vacuum to obtain 0.8 g (93%) of the product.

TLC: R_f^1 : 0.42; R_f^2 : 0.47.

The substance, found to be pure by elemental analysis, was used in the further coupling processes.

Glycylalanyl-4,6-*O*-benzylideneglucosaminic amide, acetic acid salt

Z-Glycylalanyl-4,6-*O*-benzylideneglucosaminic amide (2.0 g; 2.67 mmoles) in anhydrous methanol (150 mL) and in anhydrous acetic acid (0.21 mL; 3.67 mmoles) in the presence of 10% Pd/C (0.1 g) was subjected to hydrogenolysis in the above-described manner. The evaporation residue was triturated with anhydrous ether (3×10 mL), the crystalline product filtered off, washed with anhydrous ether (3×10 mL) and dried in vacuum to give 1.7 g (99%) of the product. The melting point was not characteristic, it varied according to the mode of drying.

TLC: R_f^1 : 0.27; R_f^2 : 0.57; R_f^3 : 0.44; R_f^4 : 0.25.

Glycyl-4,6-*O*-benzylideneglucosaminylalanine amide, acetic acid salt

Z-Glycyl-4,6-*O*-benzylideneglucosaminylalanine amide (1g; 1.83 mmole) was subjected to hydrogenolysis in anhydrous methanol (150 mL) in the presence of anhydrous acetic acid (0.21 mL) and Pd/C (0.2 g), as above. The evaporation residue was washed with dry ether (8×10 mL), filtered off and dried in vacuum to obtain 0.85 g (99.0%) of the product, m.p. 138–140 °C.

TLC: R_f^1 : 0.42; R_f^2 : 0.31.

4,6-*O*-Benzylideneglucosaminic acid amide hydrochloride

4,6-*O*-Benzylideneglucosaminic acid ethyl ester hydrochloride (3.46 g; 10 mmoles) was dissolved in saturated ammoniacal methanol (60 mL) and the mixture was allowed to react in a bomb tube for 48 h. The solvent was then removed in vacuum without heating, the residue was dissolved in anhydrous methanol (100 mL) and the solvent removed again under mild conditions. This procedure was repeated three times. The residue was dissolved in warm methanol (30 mL), clarified with carbon and mixed with anhydrous ether (50 mL) adding the solution in portions, under vigorous stirring and scratching of the flask. The substance which separated on cooling was filtered off with suction, washed with a solvent mixture (1 part of methanol + 9 parts of dry ether) (2×10 mL) and dried; the purification procedure was then repeated. The product was 2.4 g (74.0%), m.p. 180–181 °C (d.).

TLC: R_f^1 : 0.72; R_f^2 : 0.67; R_f^3 : 0.89.

IV. Preparation of the hexapeptide**Z-4,6-*O*-Benzylideneglucosaminylglycylalanyl-4,6-*O*-benzylideneglucosaminylglycylalanine amide***Azide method***Z-4,6-*O*-Benzylideneglucosaminylglycylalanine hydrazide**

Z-4,6-*O*-benzylideneglucosaminylglycylalanine methyl ester (3.9 g; 7 mmoles) was dissolved in anhydrous ethanol (46 mL), hydrazine hydrate (1.26 mL) was added, and the colourless, water-clear solution was refluxed for 1 h. A white product started to separate slowly after about 45 minutes. The mixture was allowed to stand at room temperature for 24 h, then it was refrigerated for 1 h. The product was then filtered off, thoroughly washed with small portions of a mixture of alcohol and ether (2 : 3), and dried in a vacuum desiccator. A white crystalline substance was obtained (3.25 g; 83%), m.p. 200–205° (d.).

IR: the ester band at 1770 cm^{-1} disappeared.

Coupling

A solution of Z-4,6-*O*-benzylideneglucosaminylglycylalanine hydrazide (1.68 g; 3 mmoles) in DMF (15 mL) was allowed to react in the presence of 1.61 mL (9.66 mmoles) 6*N* HCl first with a solution of NaNO₂ (0.234 g; 3.4 mmoles) in a minimum amount of water, then, in the presence of triethylamine (1.8 mL; 13.1 mmoles), with a solution of 4,6-*O*-benzylideneglucosaminylglycylalanine amide acetic acid salt (1.58 g; 3.37 mmoles) in DMF (15 mL), under the conditions described above. After the accomplishment of coupling, the solution

was evaporated to dryness in vacuum on a bath of maximum 30 °C temperature. The last traces of the solvent were carefully removed by distillation with benzene, then the somewhat yellowish, sticky residue was suspended in a mixture of ethyl acetate (50 mL) and 20% NaCl solution (20 mL) and it was thoroughly rubbed. The product was isolated by centrifuging and the purification procedure was repeated. Finally, the solid was washed on the filter with water (30 mL), ethyl acetate (30 mL) and petroleum ether (30 mL). After drying in vacuum, the resulting pure product (1.3 g; 46%) had m.p. 204–206 °C (with decomposition).

TLC: R_f^1 : 0.845; R_f^2 : 0.82; R_f^3 : 0.87; R_f^4 : 0.86.

Activated ester method

Z-4,6-O-Benzylideneglucosaminylglycylalaninepentachlorophenyl ester

Dicyclohexylcarbodiimide (0.412 g; 2 mmoles) and pentachlorophenol (0.798 g; 3 mmoles) were dissolved in DMF (20 mL) at 0 °C. The solution was stirred for 20 min, then Z-BEGA-Gly-AlaOH (1.1 g; 2 mmoles) dissolved in DMF (10 mL) was added to the slightly opaque solution, in one portion, at 0 °C. The mixture was then stirred at 0 °C for 3 h and allowed to stand at room temperature for 17–18 h. By the next day the DCU separated and the colour of the solution became pale yellow. DCU was filtered off, washed with some dioxane and the filtrate was evaporated to dryness in vacuum (27 Pa) on a bath of 30–32 °C temperature; the last traces of the solvent were removed with benzene.

The somewhat sticky solid was triturated with petroleum ether (2 × 20 mL) at 50 °C then filtered off. The yellowish white product was crystallized first from 35 parts of methanol, then from 40 parts of ethanol to yield the pure compound (0.45 g; 28.5%), m.p. 182–184 °C.

TLC: R_f^3 : 0.89.

Coupling

The acetic acid salt of 4,6-O-benzylideneglucosaminylglycylalanine amide (0.28 g; 0.63 mmole) dissolved in DMF (5 mL) was mixed first with triethylamine (0.1 mL; 0.65 mmole) then with Z-BEGA-Gly-Ala-OPCP (0.5 g; 0.63 mmole, in 2 mL of DMF) under stirring. After standing for 24 h, the solvent was evaporated in vacuum; its last traces were removed with benzene. The white sticky crystalline residue was rubbed with ethyl acetate (2 × 8 mL), filtered off, suspended in water (5 mL), mixed with a further amount of water (10 mL) and the crude product was isolated by centrifuging. This was dried and crystallized from 20 parts of butanol saturated with water to obtain the pure product (0.15 g; 45%), m.p. 204–206 °C (with decomposition). The chromatogram of the substance was identical with that of the compound prepared by the azide method.

Acetic acid salt of 4,6-O-benzylideneglucosaminylglycyl-alanyl-4,6-O-benzylideneglucosaminylglycylalanine amide

Z-BEGA-Gly-Ala-BEGA-Gly-Ala-NH₂ (0.25 g; 0.267 mmole) was dissolved in anhydrous dimethylformamide (1 mL) and the solution was diluted with anhydrous methanol (40 mL). First, anhydrous acetic acid (0.018 mL; 0.29 mmole, methanolic stock solution) was added to the solution, then it was hydrogenated in the presence of 10% Pd/C (0.1 g) at 25 °C until the evolution of CO₂ ceased. The solution was filtered and the solvent evaporated in vacuum on a bath of maximum 25 °C temperature; traces of DMF were removed by treatment with benzene as usual. The white product was triturated with anhydrous ether (3 × 3 mL) and dried in vacuum to obtain a microcrystalline powder (0.21 g; 91%), m.p. 126–150 °C (d.).

TLC: R_f^1 : 0.42.

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CYCLODEXTRIN INCLUSION COMPLEXES OF 2-CHLOROETHYL PHOSPHONIC ACID

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Crystalline complexes of 2-chloroethyl phosphonic acid with α -, β - and γ -cyclodextrins have been prepared in 80, 60–70 and 65% yield, calculated for cyclodextrins, respectively; the content of 2-chloroethyl phosphonic acid was 20–25%, 12% and 15%, respectively, corresponding to a molar ratio of ~ 2 moles, ~ 1.2 mole and ~ 1.5 mole per 1 mole of the cyclodextrin, respectively.

The crystalline structure of the products was proved by X-ray powder diffraction diagrams, the fact of complex formation by DSC, TEA and TG or DTG.

Decomposition of 2-chloroethyl phosphonic acid (Ethephon, Ethrel, Maturit, Rol-fruct, *etc.*) gives rise to ethylene, which exerts a hormon-like effect on plants. At a concentration of a few ppm ethylene enhances the intensity of respiration in plants, increases the level of ATP, and accelerates thereby ripening. It also reduces the starch content of the leaves and increases the activity of chlorophyllase, and has thus a defoliating effect. Ethylene is therefore used increasingly in agriculture for accelerating ripening and for defoliation [1, 2].

2-Chloroethyl phosphonic acid [$\text{Cl}-\text{CH}_2-\text{CH}_2-\text{P}=\text{O}(\text{OH})_2$] is a hygroscopic crystalline substance of m.p. 72–76 °C. It is marketed as a 30–50% aqueous solution adjusted to pH 2, since decomposition sets in beyond pH 3. These commercial solutions also contain various by-products formed during manufacturing (phosphoric acid, phosphoric acid esters *etc.*).

Earlier we had recognized [3] that under the effect of cyclodextrin Trichlorfon (*O,O*-dimethyl-1-hydroxy-2,2,2-trichloro-ethyl phosphonate) was converted to DDVP (*O,O*-dimethyl-2,2-dichlorovinyl phosphate). In the present work we investigated whether the decomposition of 2-chloroethyl phosphonic acid would also be catalyzed by cyclodextrin.

Measuring the ethylene evolved during the decomposition of 2-chloroethyl phosphonic acid in a Warburg apparatus, we observed that after an initial slight decomposition the acceleration of the reaction stopped (at pH values beyond 4) and in the presence of cyclodextrin the decomposition of 2-chloroethyl phosphonic acid was incomplete in aqueous solution. This finding suggested that cyclodextrin may form a stable complex with this compound. Interaction between β -cyclodextrin and 2-chloroethyl phosphonic acid is supported by Fig. 1. During the cooling of a 5% solution of β -cyclodextrin, the precipita-

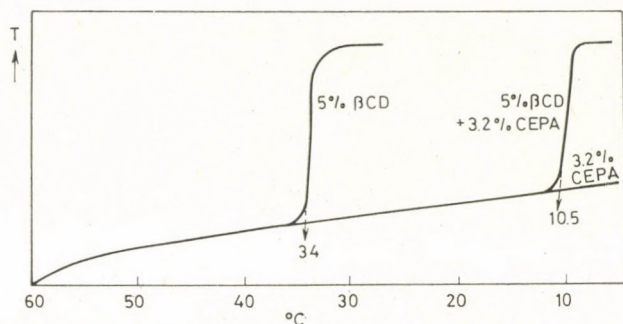


Fig. 1. Turbidity curves recorded during the cooling of solutions of β -cyclodextrin, 2-chloroethylphosphonic acid and the complex of the two. Cooling time 3 h (CEPA = 2-chloroethyl phosphonic acid)

tion of crystals began at 34 °C; in the presence of 3.2% of 2-chloroethyl phosphonic acid crystallization started only at 10.5 °C. Such a significant difference in the temperature of crystallization is diagnostic for complex formation [4]. Under suitable conditions also the crystalline complexes of 2-chloroethyl phosphonic acid with α -, β - and γ -cyclodextrin could be prepared.

The cyclodextrin complexes of 2-chloroethyl phosphonic acid are crystalline materials containing 10–30% of the active principle. Their composition, as it is general with inclusion complex, is not stoichiometric. Such complexes are readily soluble in water and their solution is only slightly acidic and therefore less corrosive than 2-chloroethyl phosphonic acid solutions marketed at present. The biological effects of complexed 2-chloroethyl phosphonic acid are the same as those of the uncomplexed compound, but complexation modifies both the resorption in plants and the rate of decomposition. In this way a retarded ethylene effect can be achieved. Detailed studies in this respect will be published elsewhere [5].

Owing to the relatively low price of β -cyclodextrin, complexes formed with this host are of primary importance for practical applications. In respect of molecular dimensions, however, the ideal complexing agent for 2-chloroethyl phosphonic acid is α -cyclodextrin; a higher guest molecule content can be attained with this complexing agent, than with β -cyclodextrin. This study mainly concerns the preparation and investigation of the α -cyclodextrin complex of 2-chloroethyl phosphonic acid; after a realization of the industrial production of α -cyclodextrin this complex is expected to find application in the agriculture.

Experimental

All materials used, *i.e.* α -, β - and γ -cyclodextrin, and Rol-fruit (a solution containing 40% of 2-chloroethyl phosphonic acid) were the products of Chinoin (Hungary).

Preparation of the α -cyclodextrin-2-chloroethyl phosphonic acid complex

To a 50% aqueous solution of α -cyclodextrin an equal volume of Rol-fruct solution containing 40% of 2-chloroethyl phosphonic acid was added with intensive stirring at 80 °C. Stirring was continued while cooling the solution with ice-water; then the solution was allowed to stand in a refrigerator overnight. The small crystals which precipitated were filtered off and dried over solid potassium hydroxide. The product was a non-hygroscopic pale green material which could be readily pulverized. The yield based on the weight of α -cyclodextrin was 104%. As shown by determination according to VOLHARD [6], the complex contained no chloride ion; after hydrolysis with 1N KOH for 1 h the bound chlorine content was found, by VOLHARD's method to be 7.03%; this corresponds to 5.55% ethylene and 28.6% 2-chloroethyl phosphonic acid content in the complex. In molarity this is equivalent to 2.7 mole of 2-chloroethyl phosphonic acid per mole of α -cyclodextrin. In a Warburg apparatus in an alkaline medium 745 μ l ethylene was released by 20 mg of the complex, which corresponded to 4.6% ethylene and 23% 2-chloroethyl phosphonic acid, *i.e.* 2 mole of 2-chloroethyl phosphonic acid per mole of α -cyclodextrin. Since ethylene is somewhat soluble in aqueous alkali, its quantity cannot be exactly determined; the determination based on the chlorine content seems to be more reliable.

One g of a complex prepared as described above releases under suitable conditions 37.25 ml of ethylene gas.

Figures 2 and 3 demonstrate the thermoanalytical behaviour of the 2-chloroethyl phosphonic acid- α -cyclodextrin complex. In Fig. 2 the DSC (differential scanning calorimetry), DTG (differential thermogravimetry) and TG (thermogravimetry) curves are shown; Fig. 3, in turn, presents the TEA (thermal evolution analyzer) curves. The DSC curves represent enthalpy changes, DTG curves weight changes and the TEA curves show the organic material carried away by a stream of nitrogen and detected by flame ionization. Thus when during decomposition an organic material is transferred to the gas phase, this becomes apparent from the TEA curve. Loss of inorganic material is not detected by the TEA curves, but is shown

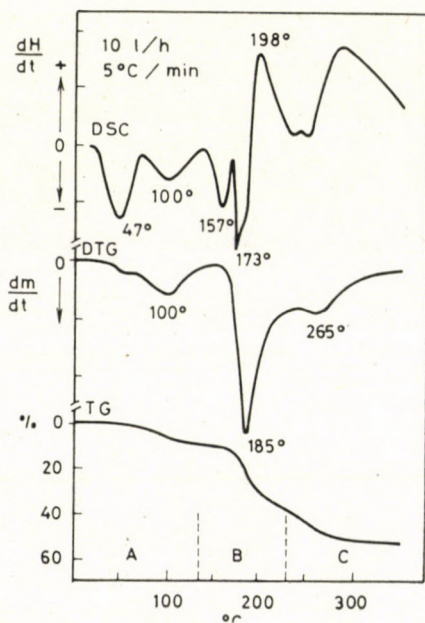


Fig. 2. Thermoanalytical curves of the α -cyclodextrin complex of 2-chloroethyl phosphonic acid DSC (differential scanning calorimetry), (7.44 mg, in an air stream of 10 liter/h.; 5 °C/min); TG (thermogravimetry) and DTG (differential thermogravimetry) curves were recorded on a Du Pont 990 Thermo Analyzer (6.68 mg)

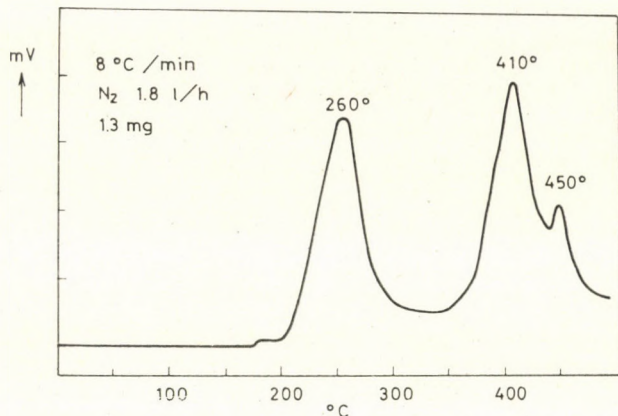


Fig. 3. TEA (Thermal evolution analyzer) curves of the α -cyclodextrin complex of 2-chloroethyl phosphonic acid, recorded on a Du Pont 916 Thermal Evolution Analyzer (8 °C/min; N₂ stream 1.8 liter/h; 1.3 mg)

by the DTG curve. If there is no loss of material, only melting or other phase transition, then this is indicated by the DSC curve.

According to the thermoanalytical curves, the processes caused by heating of the complex occur in three phases. In the first phase, ("A") i.e. up to 140 °C, the sample loses 10% of water. Loss of absorbed water is characterized by a peak at 47 °C, whereas loss of

Table I

Characteristic X-ray reflections (2 Θ° values, cursive figures represent the most intense peaks) of the cyclodextrins and their 2-chloroethyl phosphonic acid complexes

α -CD	α -CD complex	β -CD	β -CD complex	γ -CD	γ -CD complex
5.2	—	4.6	4.6	5.1	—
9.7	—	6.3	—	6.2	—
11.8	—	9.0	—	—	7.3
12.0	12.0	9.8	9.8	11.2	11.6
13.5	13.3	10.7	10.7	12.5	12.2
14.3	—	11.7	—	14.0	14.3
15.2	—	12.5	12.5	—	14.8
15.8	—	—	13.7	15.5	15.7
—	17.6	14.8	14.7	16.5	16.4
20.1	20.1	15.5	15.5	17.0	17.0
—	20.9	16.2	16.2	18.0	17.7
21.7	—	17.2	17.3	18.9	18.6
		17.8	17.8	—	19.3
		18.8	18.5	—	20.3
		—	19.0		
		19.8	19.6		

water of crystallization indicated by a peak at 100 °C. Endothermic peaks on the DSC curve at 157 and 173 °C ("B") correspond to the melting of the sample and to its decomposition, respectively. The melt is dark, indicating that decomposition already sets in during melting, but as shown by the TEA curve, the release of volatile organic material, probably of ethylene, only starts at about 170 °C. Intensive loss of organic material can be identified by a peak at 260–265 °C, this probably corresponds to the release of the total amount of ethylene. Total caramelization and charring of cyclodextrin and finally its burning starts at about 350 °C and is completed at about 600 °C ("C").

Decomposition of α -cyclodextrin proper takes place in the range of 300–350 °C. In this temperature range hardly any loss of weight was observed with the complex.

The preparation of the β -cyclodextrin complex of 2-chloroethyl phosphonic acid is similar to the process described above. The yield based on β -cyclodextrin is 60–70%, the content of bound chlorine (according to VOLHARD) is 3%, which corresponds to 2.4% ethylene and 12% 2-chloroethyl phosphonic acid, that is to 1.15 mole of 2-chloroethyl phosphonic acid per mole of β -cyclodextrin. Based on the volume of ethylene released in a Warburg apparatus, the molar ratio was found 1.2 mole per mole β -cyclodextrin.

The γ -cyclodextrin complex of 2-chloroethyl phosphonic acid can be prepared in a similar way giving a yield of 65% calculated for γ -cyclodextrin. The bound chlorine content of the complex was found to be 5.3%, corresponding to 4.3% ethylene and 21.2% chloroethyl phosphonic acid, and to a composition of 2.4 mole per mole γ -cyclodextrin.

Complex formation was further supported by the non-identity of the X-ray powder diffraction patterns with those of the parent cyclodextrins crystallized under the same conditions. In Table I the $2\theta^\circ$ values of the significant peaks in the X-ray powder diagrams of cyclodextrins, as well as of their complexes with 2-chloroethyl phosphonic acid, are compiled. The formation of a new crystal lattice is apparent in both cases, in other words, significant differences indicating complex formation can be observed.

Kinetics of decomposition

20 mg of an α -cyclodextrin complex prepared as described above, containing 23% 2-chloroethyl phosphonic acid was placed in the bulbs of a Warburg apparatus. Into the side arm of each bulb buffer solution (2 mL) was pipetted. After having reached thermal equilibrium the gauge tubes were closed, and the buffer solutions poured into the bulbs. The complex dissolved immediately. Measurements were carried out at three different pH values (6.64, 8.04 and 11.0) and at three different temperatures (27, 37, and 47 °C). At suitable intervals the amount of ethylene evolved was recorded and corrected for atmospheric pressure. The theoretical volume of ethylene expected from 20 mg substance was 745 μ l, which guaranteed satisfactory accuracy of the measurements.

Relating the actual volume of evolved gas to the theoretical limit, the degree of decomposition of 2-chloroethyl phosphonic acid was calculated. First-order rate constants calculated graphically from the logarithmic plots.

The decomposition of uncomplexed 2-chloroethyl phosphonic acid was studied similarly. For this purpose 10 mg of a Rol-fruct solution containing 40% 2-chloroethyl phosphonic acid was weighed into the bulb of the Warburg apparatus and decomposed at the pH and temperature values described above.

Logarithmic first-order rate constants plotted against the reciprocal values of the absolute temperatures gave straight lines for the different pH values in the case of the uncomplexed acid, but not for its cyclodextrin complex. At 27 °C cyclodextrin somewhat accelerates, but at higher temperatures it retards the decomposition. The difference, however, is insignificant and therefore it can be expected that in solution the biological effect of complexed 2-chloroethyl phosphonic acid will be the same as that of the uncomplexed material.

*

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THE ROLE OF CATALYST SURFACE AND STRUCTURE OF MOLECULES IN METAL CATALYSIS*

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As a development of catalyst theory we introduced a few years ago the principle of catalytic system [1]. This was based upon such experimental facts that confirmed: the catalytic surface for a given reaction is formed by a catalyst together with the reactant molecules. In this respect the role of hydrogen bears a special importance by forming the catalytic effect of metals, *i.e.* the extent and route of the catalytic reaction is strongly influenced by the presence and quantity of hydrogen, thereby the activity and selectivity of a catalytic reaction is controlled by hydrogen.

I. The Effect of Hydrogen

As a result of the work carried out in the last few years the predominant role of hydrogen in the development of catalytic effect has been confirmed, by many new particulars only some of these will be mentioned in the next section.

Irreversibly adsorbed hydrocarbons, methane, ethane can be comparatively easily removed from the surface of nickel and other metal catalysts with hydrogen at an elevated temperature.

However, only a part of it desorbes from the metal surface on the effect of heat treatment in vacuum. Complete desorption can never be achieved by subsequent heating in hydrogen atmosphere. It is because irreversibly adsorbed hydrocarbons underwent such extensive destruction upon heat treatment in vacuum that the carbon deposited can be removed only by oxidation. The presence of hydrogen prevents the "deep" decomposition of chemisorbed hydrocarbons.

The effect of hydrogen — inhibiting the decomposition and conserving the surface — can be revealed if hydrocarbon adsorption on nickel is investi-

* The author's inaugural lecture on becoming full member of the Hungarian Academy of Sciences presented on the 23rd November, 1979.

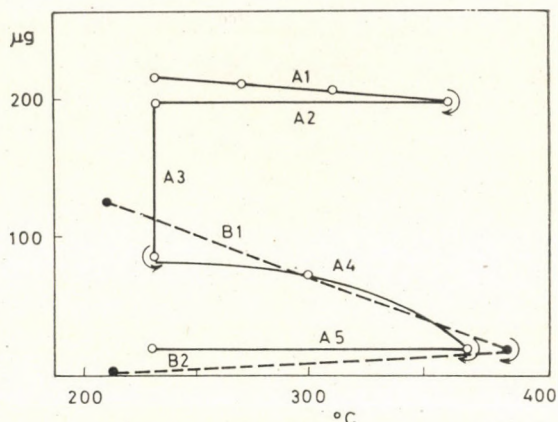


Fig. 1. Treatment of chemisorbed ethane: A₁ heating in vacuo, A₂ cooling in vacuo, A₃ treatment in H₂, A₄ heating in hydrogen, A₅ cooling in hydrogen, B₁ heating in hydrogen, B₂ cooling in hydrogen

gated [2]. In presence of hydrogen the chemisorption of butane is strongly suppressed: at 1 : 4 hydrogen-hydrocarbon mixture the quantity of chemisorbed hydrocarbon amounts to as less as 10% of that chemisorbed in absence of hydrogen. Under such circumstances only a few percents of the surface are occupied by chemisorbed butane at the temperature of hydrogenolysis. The chemisorbed butane is relatively easily removed with hydrogen [2] (activation energy is 50 kJ mol⁻¹). It should be mentioned that the amount of chemisorbed molecules cannot be diminished by increasing the partial pressure of hydrogen about ten times which shows that a part — about 10 percent — of the sites responsible for hydrocarbon chemisorption cannot be blocked by hydrogen.

The effect of metal, hydrocarbon and hydrogen being responsible together for the formation of active catalytic surface is further demonstrated by the selectivity values obtained in the hydrogenolysis of *n*-pentane on supported metal catalysts. On supported nickel and platinum catalysts the selectivity can be varied in a wide range with the change of dispersion and hydrogen pressure [3]. At small (40 mbar) hydrogen pressure the methane and butane ratio formed in *n*-pentane hydrogenolysis can be influenced to a significant extent by dispersion. On a highly dispersed system the methane to butane ratio amounts to about 30% of the value obtained on metallic powder. At high hydrogen pressure (300 mbar) the methane to butane ratio is practically the same measured on samples of different dispersions.

The isomerization to hydrogenolysis ratio on Pt/SiO₂ samples increases with hydrogen pressure but decreases with increasing dispersion.

The significant role of hydrogen can be considered as general characteristics of hydrocarbon reactions catalyzed by metals. This is obviously indicated by the data shown in Fig. 2 [1]. It is clearly seen that conversion depends on

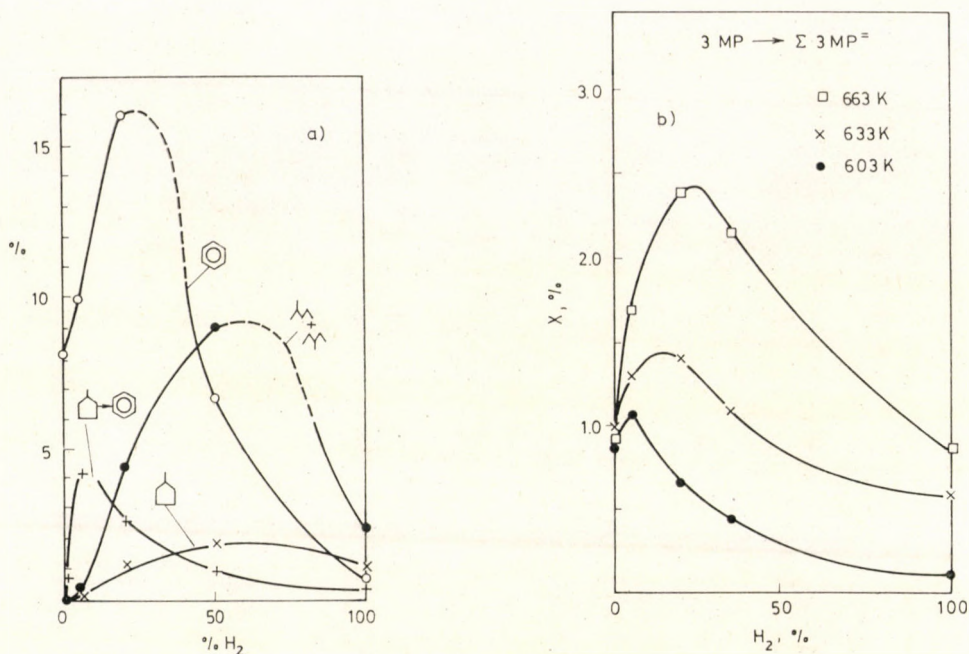


Fig. 2. Dependence of the formation of different products vs. hydrogen content of the carrier gas on platinum. a) reactant: *n*-hexane; b) reactant: 3-methyl-pentane, product: olefin with the same carbon number

hydrogen pressure by a maximum curve even in reactions in which hydrogen is a product or it is not a reaction partner.

The effect of hydrogen on the catalytic reactions is caused by several reasons. In particular, attention must be called to the influence of hydrogen treatment on the texture of a catalyst. It is obviously seen on platinum catalysts [5]. The freshly prepared platinum black possesses a fine grain size structure with an average 10 nm diameter as shown by electron micrograph (Fig. 3a). There is practically no change after 3 hours treatment in helium at 573–673 K. The average particle size is 11 nm and regular crystal shape can hardly be seen (Fig. 3b).

In presence of hydrogen at 473 K, a significant increase in crystallite size started. Crystallite size becomes very high (33 nm) in the case of heat treatment at 573 K and the appearance of the catalyst is completely different. The most of the crystallites are confined by regular crystal faces. The texture of hydrogen treated samples does not change afterwards.

Beside this texture effect, hydrogen also influences the adsorption-desorption equilibrium, the metal-substrate interaction thereby the catalytic reactions are shifted into different directions. Increase of reaction rates by hydrogen is revealed normally at low hydrogen pressures. In this range metallic surface

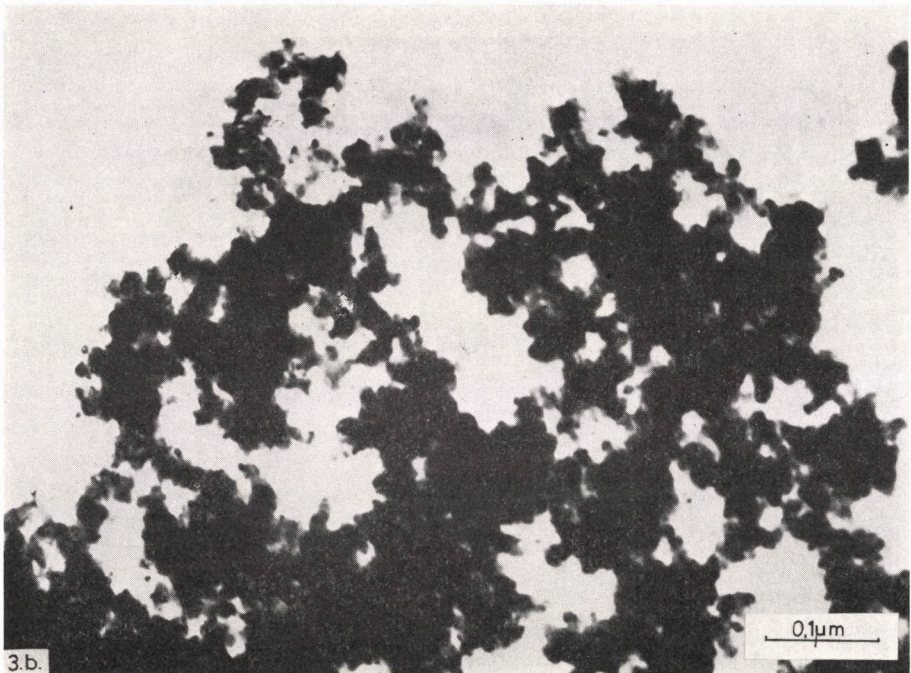
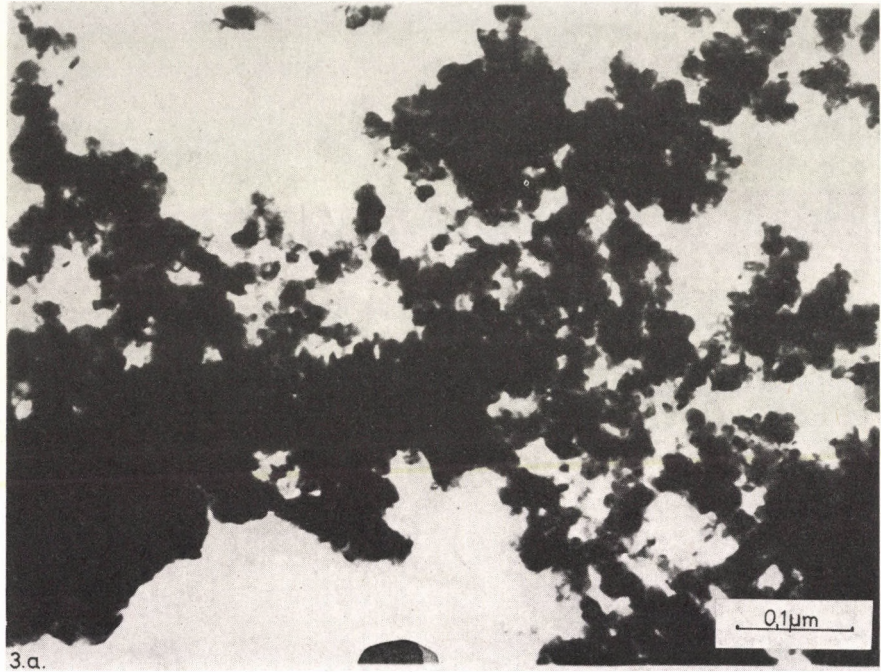


Fig. 3



Fig. 3. Electron micrograph of platinum black samples of different treatments. *a*) Fresh sample prepared from H_2PtCl_6 reduced by formaldehyde; *b*) After 3 hours treatment in He at 573–673 K; *c*) After 3 hours treatment in H_2 at 573 K

is protected by hydrogen from irreversibly bonded deposits, *i.e.* hydrogen occupies the most active sites thus chemisorption with C—H bond dissociation does not take place to a large extent. Product desorption is also increased in the presence of hydrogen. All these effects are due to fast hydrogen adsorption in comparison to the hydrocarbon chemisorption with C—H bond dissociation. This is confirmed by the large exothermic heat of adsorption as opposed to the endothermic heat of hydrocarbon chemisorption, as well as the higher rate and smaller activation energy of the H_2 — D_2 exchange compared to those in hydrocarbon and deuterium exchange on metals [4].

The following explanations can be suggested for the retarding and course shaping effect of hydrogen [1].

First, the adsorption of a substrate is generally diminished, in particular the adsorption by which the surface precursor of a given reaction is formed. On the 6th Congress on Catalysis [6] we have reported that in the case of Co, Ni and Pt — depending on the temperature and some other conditions — 3–4 different types of adsorbed species of methane and ethane can be distinguished on the same catalyst. The ratio of the different species is influenced also by hydrogen, as it was proved in connection with the adsorption of *n*-butane on nickel catalysts [2]. The formation of other adsorbed species has been indicated by

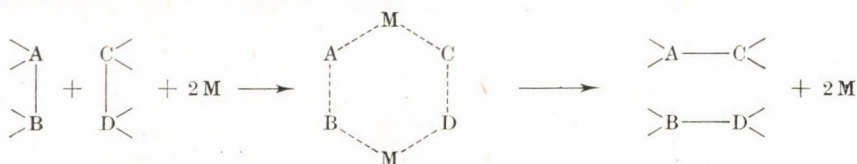
LEED and Auger spectroscopy and along with these studies now it is clear that the extent and direction of a catalytic reaction is predominantly influenced by the actual structure of a surface complex.

The second reason for the hydrogen retarding, and modifying effect is the hinderance of the system containing π -bonds. However, this leads to a further problem: what is the role of the structure of a reactant molecule in the catalytic effect?

2. The Role of Molecular Structure

It is generally accepted that the pathway of a heterogeneous catalytic reaction is basically controlled by an interaction between the catalytic surface and a part of the reactant molecule (one or two atoms, functional group). The remaining part of the molecule only slightly influences the reaction or its effect is of secondary importance. The energy barrier of a reaction is determined by the energy requirements of the formation and decomposition of a surface complex [4].

Schematically the energy barrier of a catalytic reaction



can be represented by equation (1)

$$\Delta U_1 = Q_{AB} + Q_{CD} - Q_{AM} - Q_{BM} - Q_{CM} - Q_{DM} \quad (1)$$

or

$$\Delta U_2 = -Q_{AC} - Q_{BD} + Q_{AM} + Q_{BM} + Q_{CM} + Q_{DM}$$

depending on whether the formation or the decomposition of the surface complex is the rate determining step.

Consequently, the energy barrier of a particular reaction is determined by the difference among the energies of forming and splitting bonds as well as that of catalyst-substrate bonds. This approach is true only if the part of the molecule not participating in the reacting group has a negligible influence on the bond energies, or if this influence is transferred to the same extent to the bonds between catalyst and substrate atom. If this is the case, the values of ΔU_1 and ΔU_2 do not change regardless of the whole molecules effect on the reacting bonds.

Many evidences are available that the extent of reaction, *e.g.* the decomposition of alcohols, is marginally influenced by the atom groups which are not

directly involved in the reaction. However, this simplified approach appears to be inadequate in the light of recent experiments.

Let us mention here some earlier results [2, 4, 6] in which it has been established that the extent of chemisorption of ethane (and butane) was considerably higher than that of methane. The reactivity of the former is also higher: the energy of activation of deuterium exchange in ethane is 15–50% smaller, than that in methane, the rate of exchange in ethane exceeds that of methane by one or two orders of magnitude depending on the metal catalysts used.

Now, the question arises: to what extent may the surface-substrate interaction be confined to the interaction between a few reacting atoms of the molecule and the surface? Based on the data concerning the hydrogenolysis this approach seems to be strongly opposed. This is caused partly by different reaction mechanism devoted to the different molecule structure; this will be discussed later. Before that it is worthwhile to consider some experimental facts in which the catalytic effect is strongly influenced by the molecule as a whole even at the same reaction mechanism.

First, let us consider the adsorption of hydrocarbons. According to the dependence of the hydrogenolysis rate on hydrogen partial pressure it is easy to deduce the following equation:

$$p_{w_{\max}} = \frac{b_{\text{CH}} p_{\text{CH}} + 1}{b_{\text{H}}} \quad (2)$$

where $p_{w_{\max}}$: the hydrogen partial pressure at maximum rate

p_{CH} : hydrocarbon pressure

b_{H} and b_{CH} : adsorption coefficient of hydrogen and hydrocarbon, resp.

The results calculated by equation (2) from earlier kinetic data [7] are presented in Table I.

Table I
Adsorption coefficient for some hydrocarbons
Catalyst: Pd, T (K): 558

CH	b_{CH}
C_2H_6	$2.5 b_{\text{H}} - 0.1$
$n\text{-C}_4\text{H}_{10}$	$19.6 b_{\text{H}} - 0.1$
$i\text{-C}_4\text{H}_{10}$	$15.8 b_{\text{H}} - 0.1$
$neo\text{-C}_5\text{H}_{12}$	$7.2 b_{\text{H}} - 0.1$

Although this method is inaccurate, it is obvious from the data, that the value of adsorption coefficient *i.e.* the adsorbability of hydrocarbon increases with increasing chain length. It is also seen that the adsorption coefficient of branched chain isomers is smaller than that of straight chain ones.




Further evidence can be obtained for the increasing reactivity of hydrocarbons of higher molecular weight from deuterium exchange measured on different metals [4]. The energy of activation from methane to ethane sharply decreases and from ethane it decreases monotonously.

The best indication for the influence of the not directly involved part of the molecule on the extent and direction of the catalytic effect is the accelerating effect of the appearance of π -bond.

It is well known that the rate of dehydrogenation of cyclohexene is generally 5–10 times higher than that of cyclohexane, while cyclohexadiene reacts even faster under the same condition (Table II) [8–10].

In order to explain the accelerating effect of π -bond it is straightforward to assume the easier adsorption of olefinic compounds. However, it has been established from the kinetic data that the adsorption of hydrocarbon molecules in the dehydrogenation of cyclohexane ring is not rate determining step [10],

Table II
Rate of dehydrogenation of cyclohexane, cyclohexene, cyclohexadiene on different metals
T: 575–625 K

Catalysts	W/molecule m ⁻² s ⁻¹		
			
Ni	3.2×10^{16}	4.1×10^{17}	8.5×10^{17}
Cu	1.1×10^{15}	1.8×10^{16}	—
Rh	5.8×10^{17}	4.1×10^{18}	5.9×10^{18}
Pd	8.1×10^{17}	5.4×10^{18}	2.0×10^{19}
Ag	5.4×10^{14}	1.3×10^{16}	2.6×10^{16}
Ir	4.5×10^{17}	3.0×10^{18}	3.4×10^{18}
Pt	8.1×10^{17}	3.0×10^{18}	5.2×10^{18}
Au	7.2×10^{15}	7.6×10^{15}	—
Fe	1.3×10^{15}	5.4×10^{15}	7.2×10^{16}
Mo	1.8×10^{15}	2.4×10^{16}	
V	2.7×10^{15}		
W	3.2×10^{14}		
Be	2.9×10^{13}	1.6×10^{15}	
Ti	3.4×10^{15}	1.0×10^{19}	
Co	1.1×10^{15}	6.3×10^{15}	1.3×10^{17}
Zn	6.7×10^{15}		
Zr	6.7×10^{14}		
Ru	2.5×10^{16}	3.3×10^{16}	
Re	1.6×10^{17}		

the higher rate of the dehydrogenation of the unsaturated ring cannot, therefore, be explained in this way. The higher reactivity of π -bonded reactant can also be demonstrated by the rate of cyclization which is considerably higher for olefins than for paraffins [11]. This effect can be interpreted by the formation of π - σ conjunction that results in the weakening the C—H bonds being in α -position to the π -bond, thus its bond energy is 85 kJ mol⁻¹ lower than that of the average C—H bond [12]. The accelerating effect of π - σ conjunction is also indicated by the faster hydrogen tritium exchange in propylene than that in ethylene on nickel and platinum catalysts [13].

The increased reactivity of molecules containing π -bond is also shown by the conversion of cyclohexanol, measured in our laboratory, on Co, Ni, Ru, Rh, Pd, Os, Ir and Pt catalysts [14—19]. The main products are summarized in Table III.

Table III
Main products of cyclohexanol conversion
(pulse system, hydrogen atmosphere)

Catalysts	t°C	C ₆ H ₁₁ OH	C ₆ H ₁₀ O	C ₆ H ₉ OH + C ₆ H ₈	<C ₆
Co	240	23	14.2	10.2	43
	360	1	10.4	9.7	68.2
Ni	270	66.1	29.3	4.6	2.4
	360	33.2	22.4	24.2	17.6
Cu	250	23.1	74.7	0.98	—
	300	6.2	80.0	5.97	—
Ru	240	71.5	21.1	2.3	4.4
	360	12.9	24.4	16.9	39.9
Rh	240	91.6	3.5	1.7	2.4
	360	34.5	1.3	5.5	58.3
Pd	240	62.4	2.0	35.4	0.3
	360	14.6	2.8	81.5	0.9
Os	300	54.4	19.0	—	26.6
	360	48.7	21.3	1.5	28.5
Ir	240	67.7	15.7	7.0	7.5
	360	18.9	15.2	8.5	57.1
Pt	240	11.9	8.4	79	—
	330	6.8	3.3	87.5	—

Tracer study on the mechanism revealed that the main pathway of cyclohexanol-benzene conversion is the reaction sequence



which occurs much faster than the cyclohexane-benzene conversion. This is indicated both by the direct comparison of reaction rates, and by the experiments carried out in presence of a mixture of ^{14}C -labelled cyclohexanol and unlabelled cyclohexane. By this experiment direct information can be obtained on the radioactivity of benzene, *i.e.*, to what proportion was benzene produced from cyclohexanol and from cyclohexane. From the radioactivity ratio the following conclusion can be drawn:

- i) benzene is formed exclusively from cyclohexanol on Pt and Co;
- ii) the rate of benzene formation from cyclohexanol is by 100%, 50% and 20% on Ni, Ru and Rh, respectively, higher than the corresponding rate from cyclohexane.

According to the data presented in Table III the six-membered ring underwent significant hydrogenolysis on most of the catalysts (except Pt, Pd and Cu). Under similar conditions the cyclohexane ring is hydrogenolysed at most by 1–2 percent [20]. Whilst in cyclohexanol, the extent of hydrogenolysis amounts to about 15–30% at 573 K.

The increased reactivity of the six-membered ring can be easily interpreted by the effect of carbonyl group formed *via* the dehydrogenation of alcohol. Infrared spectroscopy [21] was applied to study the chemisorption of cyclohexanol on platinum and rhodium catalyst. Indeed, at chemisorption a fast O–H dissociation takes place followed by the splitting off of a hydrogen atom from the vicinal carbon atom and with the simultaneous formation of carbonyl bond to the surface. Thereby, the mobility of hydrogen atoms in the neighbouring methylene group is enhanced. Thus, on platinum further dehydrogenation of the ring leads to the following surface species:



This can be considered to a precursor of phenol and benzene. On rhodium a different mechanism is operative. On the contrary to platinum, this catalyst possesses a high activity for hydrogenolysis (see later). Here the effect of carbonyl bonds is twofold: hydrogen atoms in α -position are weakened, on the other hand, the vicinal C–C bonds are also activated. (C–C bond energy in conjunction with double bond is by 90 kJ mol $^{-1}$ lower than the average value [12].)

All these data illustrated well not only the accelerating effect of the presence of an unsaturated system, but the location of the effect, too, *i.e.* it is obvious that the effect is not directly devoted to the position of double bond, but as a consequence, the reaction centre in the molecule is "transferred" to an other part of the molecule.

From this point of view it is interesting to compare the behaviour of cyclohexanol and phenol. Phenol-benzene conversion is significantly high as shown by the analysis and the experiments carried out in presence of labelled cyclohexanol. In this case the aromatic structure is accompanied with higher adsorbability and consequently higher reactivity. Here two pathways are competing: the adsorption of cyclohexanol takes place mostly via O—H bond dissociation, while π -complex formation is the main route for phenol.

It can be concluded that enhanced reactivity in catalytic processes is exhibited by unsaturated molecules. It is partly due to the increased adsorbability but — when the unsaturated character of the molecule is preserved by the formation of a surface π -complex its reactivity is still higher than that of the corresponding paraffinic systems.

Here we must emphasize that the substrate-catalyst interaction cannot be confined to the link between the reacting atoms and the catalytic surface, but the whole molecule should be considered in the elucidation of the mechanism. In this sense the difference between reactions catalyzed by heterogeneous, homogeneous catalysts or by enzymes can be largely diminished.

In the next part the effect of catalyst structure on the mechanism of heterogeneous catalytic reactions will be discussed.

3. The Role of the Structure of Catalyst Surface in the Mechanism of catalytic Reactions

The conceptualization of substrate-catalysts interaction modelling it by the structure of the surface and the reactant molecule is devoted to BALANDIN who discovered [22] and developed it for many decades [23, 24]. The theory could well explain the mechanism of different catalytic reactions based on the structural correspondence between the catalyst surface and the reactant molecule. Later, as the experimental technique was developed, an increasing amount of experimental data was found which somewhat contradicted the picture described by the above theory. In particular, it is referred to the mechanism of cyclohexane dehydrogenation [11]. The concept could not account for the atomic heterogeneity of the catalyst surface, *i.e.* for the different occupancy and orientation of the orbitals of the different crystal faces [25].

The principle of the structural accordance is emphasized by the recent LEED measurements: depending on the experimental condition the

substrate molecules form an ordered, epitaxial structure, or disordered deposits on stepped surface which may serve as a good model for the polycrystalline catalysts [26, 27]. The polycrystalline texture of metallic powder produced in hydrogen at high temperature has been proved in part I. The formation of "solid solution" on the substrate-surface interface can be indirectly confirmed by the fact that metals with the best catalytic activity (atomic diameter 0.22 — 0.3 nm) form solid solution with iron metal [28].

These led us to reconsider the role of geometrical factors in some catalytic reactions and to attempt to give an interpretation for it in the light of new informations about the π -structure and the atomic heterogeneity of the catalyst surface.

3.1. Dehydrogenation

Hydrogen-deuterium exchange in saturated hydrocarbons takes place with comparatively high rate at low temperature [4]. The threshold temperature for ethane is below 373 K. This shows that C—H bond rupture is a relatively easy process confirmed by bond energy calculation.

Dehydrogenation of straight chain hydrocarbon is strongly hindered thermodynamically [29]. The reaction therefore, takes place at high temperature (973—1023 K) with significant yield. At such a high temperature the hydrogenolysis becomes very remarkable.

Despite these facts, some olefin formation can be observed during the conversion of C_6 hydrocarbons carried out in pulse regime using hydrogen flow [4]. Metals with high activity for hydrogenolysis (Co, Ni, Ru, Rh) are exceptions. Olefin formation increases in certain concentration range of hydrogen as shown in Fig. 2b.

Dehydrogenation of cycloparaffines takes place to a much larger extent at lower temperatures.

Important role can be due to the crystal structure in this reaction. This is primarily shown by the dependence of the rate of dehydrogenation on the crystal lattice and on the atomic diameter of metal catalysts [10] (Fig. 4).

It is clear from the figure that the best catalysts for dehydrogenation belong to fcc structure.

The exceptionally great importance of crystal structure of the catalyst is further confirmed by cobalt sample containing fcc and hcp structure in different ratio, depending on the preparation. The dehydrogenation activity varies in the range of 4—5 orders of magnitude [30] and this difference is much larger than that for other, differently prepared samples [31].

It is seen in Fig. 4 that Pt, Pd, Ir, Rh and Re metals have the maximum activity. These metals are important from an other point of view [32]. In the product of the dehydrogenation of ^{14}C -labelled cyclohexane and nonradioactive

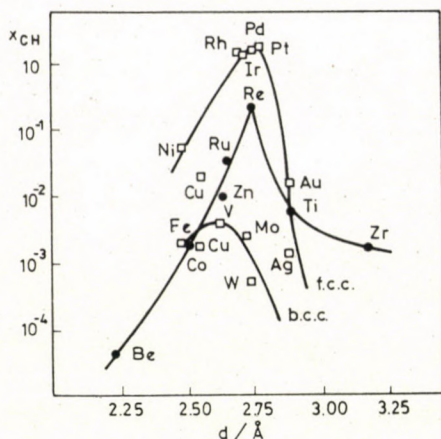


Fig. 4. The rate of cyclohexane dehydrogenation ($\times 10^{18}$ molecule/(s \times m 2)) vs. metal atom diameter

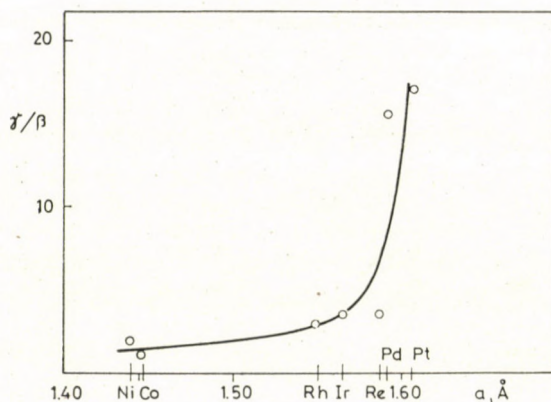


Fig. 5. Ratio of the radioactivity of benzene to cyclohexane vs. metal atom diameter

cyclohexene mixture the specific radioactivity of benzene (γ) considerably exceeds that of cyclohexene (β) especially in the case of Pd and Pt

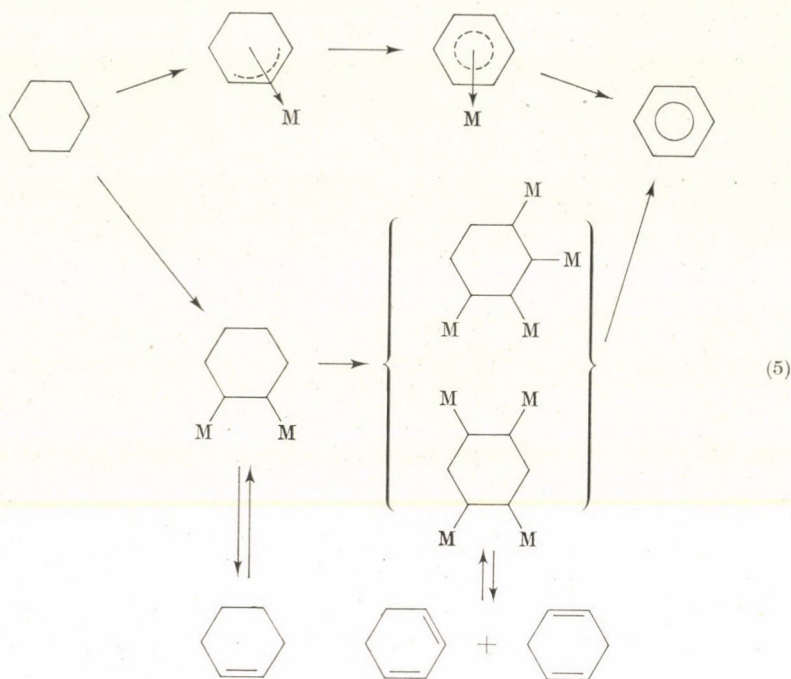
$$\gamma/\beta > 1$$

whereas on other catalysts (Ni, Co) this ratio is

$$\gamma/\beta \sim 1.$$

The γ/β ratio strongly depends on the atomic diameter as shown in Fig. 5.

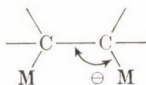
The above ratio gives information about the relative proportion of the two processes, *i.e.* the stepwise and direct dehydrogenation of the cyclohexane ring:



As shown in Figure 5 on Pt and Pd the direct dehydrogenation is the only route, on Re, Rh and Ir it is the predominant reaction pathway, whereas on Ni and Co the specific radioactivity of benzene and cyclohexene are equal showing the primary importance of the stepwise process.

What is the correlation between the occurrence of these reactions and the structure of the catalyst?

The stepwise dehydrogenation may take place on the atom doublets on which the valence angles in the surface intermediate formed do not considerably deviate from the ideal 109° .



For beryllium θ is 100.4° , for zirconium it is 112° , for metals with high dehydrogenation activity it is between 103 and 106° . The strain here is not too large, the steric energy for beryllium which is an inactive catalyst amounts to a value of about 100 kJ mol^{-1} . It can be, therefore, understood that the dehydrogenation of cyclohexane occurs on a large variety of metals as shown in Table II and Fig. 4. In stepwise dehydrogenation the presence of (100) and (110) crystal faces is a prerequisite for the formation of an adsorption doublet. This is because the e_g orbitals which point „outward” from the plane of the crystal face, are rather

unfilled for group VIII transition metals and thus σ -bond can be easily formed. This is the same for t_{2g} orbitals which are responsible for the backdonation of electrons being operative in the formation of π -complexes, especially, in the case of platinum [25].

On the contrary, the direct dehydrogenation requires different sites. With the progress of dehydrogenation the six-membered ring is linked to the surface by more and more metal atoms. From the symmetrical point of view (111) face corresponds to the six member ring. On a (100) crystal face some atoms of the ring is bonded to the top of the individual metal atoms, others are linked to the interatomic holes on the surface and thereby the possibility of the complete ring decomposition increases (see later) (Fig. 6).

Besides if the molecule occupied the position shown in Fig. 6 a large strain is developed in it which is geometrically rather unfavourable.

On crystal face (111) geometrically four possibilities can be considered (see Fig. 7).

Of these the first arrangement was favoured by BALANDIN. At the present knowledge, however, arrangement (4) is the most probable according to the structure of the surface electron orbitals *i.e.* on (111) face there is no orbitals which are perpendicular to the plane of the crystal face, their direction is only 36° for both e_g and t_{2g} (Fig. 8).

Thus, interaction between the substrate and the metal is operative primarily for the atoms which approaches the holes on the crystal face. (In the figure the orbitals responsible for the metal-metal cohesion is not seen.)

It is obvious from the figure that cyclohexane molecule can interact with the surface *via* the linkage of their atoms to the interatomic holes on the octa-

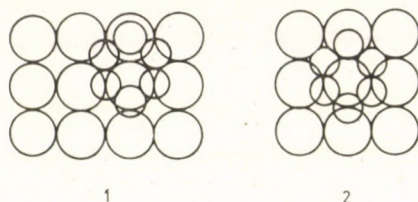


Fig. 6. The possible geometrical arrangement of cyclohexane ring on the (100) face

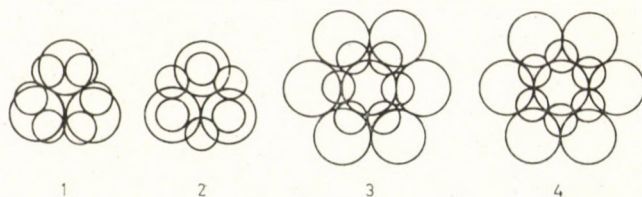


Fig. 7. Possible geometrical arrangement of cyclohexane ring on the (111) face

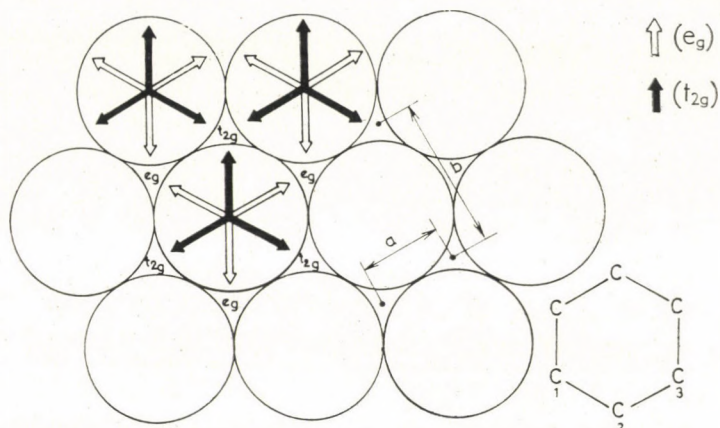


Fig. 8. Parameters of the (111) face and the possible geometrical arrangement of cyclohexane molecule distance in nm. Cyclohexane C_1-C_2 : 0.1526; C_1-C_3 : 0.506–0.632 (due to the molecular vibration).

Metals	a	b
Co	0.1445	0.2502
Ni	0.1440	0.2494
Rh	0.1550	0.2685
Pd	0.1590	0.2754
Ir	0.1565	0.2710
Pt	0.1605	0.2780
(0001) Re	0.1586	0.2747

(e_g) $36^\circ 12'$ angle above the plane (and t_{2g}) 30° angle above the plane orbitals are denoted by (1) and (2), respectively

hedral crystal face.* In this way the molecule can interact with both t_{2g} and e_g orbitals, being thus a possibility for the formation of σ -bond and π -complex leading to dehydrogenation and this corresponds to our idea about the dehydrogenation mechanism.

At the same time attention must be called to the fact that cyclohexane molecule can be arranged in the interatomic holes of an octahedral face *only* if the distance between vicinal holes is 0.152 nm or larger (C—C bond length) and that between each second hole is larger than 0.255 nm (bond length between 1—3 carbon atoms). According to the calculation, this condition is fulfilled for Rh, Ir, Pd and Pt (111) as well as for Re (0001). This is in accordance with the

* The molecules in these holes are bonded less strongly than in that of the (100) face. (In the latter case four t_{2g} orbitals and one e_g orbital from the one below the uppermost layer are directed to the interatomic hole.) Molecules on the (111) face are, therefore, less strongly bonded and the probability of C—C bond rupture is low (see later).

fact that the direct dehydrogenation on these metals, in particular on Pt and Pd is important. A π -complex can be formed on these metals which has been assumed by Rooney [33] and proved by Russian and Bulgarian scientists [34].



(7)

For the rest of the metals the interatomic holes are too close to be able to put cyclohexane molecule in an appropriate geometrical arrangement, thus here the stepwise dehydrogenation is operative.

This is supported by SOMORJAI and co-workers [26]. On stepped surface containing (111) terraces and (100) steps the cyclohexane \rightarrow benzene conversion does not increase with an increasing number of steps, but increases the hydrogenolysis and the formation of cyclohexene. This supports the idea that direct dehydrogenation occurs on (111) face while stepwise dehydrogenation as well as the ring hydrogenolysis takes place on the (100) face.

3.2. C—C bond splitting

3.2.1. Ethane hydrogenolysis

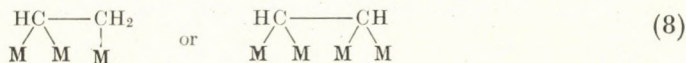
The energy barrier for ethane hydrogenolysis on metals is higher than that for reaction accompanied by C—H bond rupture such as dehydrogenation and hydrogen deuterium exchange [4]. This is well represented by the data concerning hydrogen deuterium exchange and hydrogenolysis of ethane summarized in Table IV. Hydrogenolysis requires higher temperature and energy of activation than those for the replacement of hydrogen by deuterium.

Table IV

Exchange and hydrogenolysis of ethane
E: energy of activation w_0 : initial rate, molecule $m^{-2} s^{-1}$

Catalysts	Exchange		Hydrogenolysis	
	<i>E</i>	$w_0^{(165^\circ\text{C})}$	<i>E</i>	$w_0^{(250^\circ\text{C})}$
Co	—	—	113	8.7×10^{12}
Ni	88	3.0×10^{15}	167	2.6×10^{13}
Rh	72	2.9×10^{16}	156	5.3×10^{17}
Pd	71	2.9×10^{16}	222	1.3×10^{12}
Re	63	6.8×10^{16}	130	6.9×10^{15}
Ir	82	7.6×10^{16}	163	3.9×10^{17}
Pt	79	5.0×10^{16}	222	1.9×10^{11}

Earlier works have established [35–39] that strong interaction between ethane molecule and metal is involved in hydrogenolysis which can be represented by scheme (8) and in which multiple bonded intermediates take part.



The correlation between the strength of hydrocarbon-metal interaction and the activity in hydrogenolysis was investigated in the following experiments [40]. Chemisorbed ethane was removed from the surface in a stream of hydrogen. The proportion (R) of the ethane chemisorbed at 493 K was determined by desorption at 523 K. The R values for different metals are presented in Fig. 9. From Pt and Pd ethane can be completely desorbed ($R \sim 1$). Small desorption can be experienced on Ni and Co ($R \sim 0.4$). The Rh and Ir, the most active catalysts in hydrogenolysis, have a medium R value ($R \sim 0.7-0.75$).

H/C ratio was also determined in ethane, chemisorbed on different metals at the same temperature. The data in Fig. 9 show that this ratio is the smallest with Ni and Co, *i.e.* most of the hydrogen atoms of ethane are lost at chemisorption. The highest value can be observed for Pt and Pd, thus the composition of the surface species is C_2H_4 . The most active catalyst in hydrogenolysis, the Rh, occupies a middle position (the H/C ratio is 1.3). From these experiments the conclusion can be drawn that the medium interaction between ethane and the metal corresponds to the highest activity in hydrogenolysis. Both at weak and strong interaction the catalytic activity becomes lower.

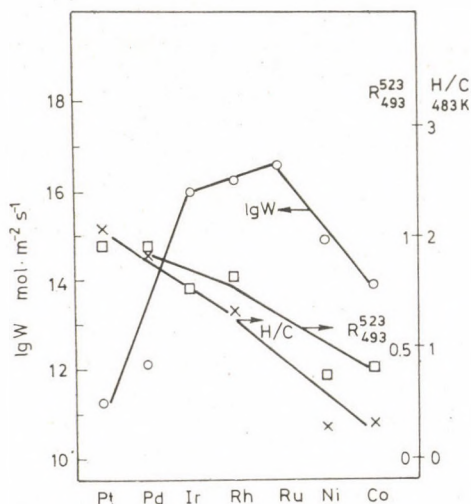


Fig. 9. Proportion of hydrocarbon desorbed in hydrogen at 493 K to the total amount of ethane chemisorbed (R_{493}^{523}); the H/C ratio in the substrate chemisorbed, w is the rate of ethane hydrogenolysis

According to the geometrical data, maximum activity is obtained on metals (Rh, Ir, Ru) with atomic diameter of 0.265–0.271 nm while neither smaller (0.249–0.250 nm for Ni and Co) nor higher atomic diameter (0.275–0.277 nm for Pt and Pd) gives the appropriate geometrical arrangement for C–C bond splitting.

If this geometrical correspondence is valid, the hydrogenolysis does not take place on the (111) face of fcc crystal structure and on the (0001) face of hcp metals. Since the hydrogenolysis requires the formation of multiple bonded intermediates thus structure of



is a prerequisite. On (111) and (0001) faces the probability of the existence of this structure is very low for two reasons: *i*) there is no orbital which is perpendicular to the plane of these faces, and *ii*) geometrical factors are not suitable. From the latter point of view it has to be mentioned that the strain in surface species (9) is very high due to the small valence angle (for Ni it is 76° for Pt 80° which corresponds to a steric energy barrier of 130 kJ mol⁻¹).

On face (100) and (1010) the e_g and t_{2g} orbitals are perpendicular to the plane of the crystal face. Here the MCM valence angle is 130–131° for Pt, and 121° for Ni the strain is, therefore, smaller. This is well illustrated by the difference between the energy of activation for the formation of CH₃D and CD₄ in methane-deuterium exchange since the CD₄ formation proceeds via surface species (9). The difference in activation energies for Pt is 30, for Ni 13 kJ mol⁻¹ [4].

Our theory that the probability of hydrogenolysis on the (111) face is low, well agrees with the observation of SOMORJAI and co-workers [26, 27]. On Pt (111) faces only dehydrogenation of cyclohexane took place, while hydrogenolysis only on stepped surface, especially on etched samples. The extent of hydrogenolysis increased with the number of steps and kinks. This is also a proof for the activity of (100) faces as well as for that of corners and edges. Simultaneously it also points to the lack of activity of (111) faces in C–C bond rupture of the cyclohexane ring.

From all these data it can be established that the activity revealed in ethane hydrogenolysis correlates to the strength of the metal-ethane interaction, the crystal structure, and the atomic heterogeneity.

3.2.2. Hydrogenolysis of C₃–C₆ hydrocarbons

The characteristic features obtained for ethane hydrogenolysis considerably deviates from that revealed in the C–C bond splitting of higher hydrocarbons. It is well represented on Fig. 10, in which the rates of hydrogenolysis

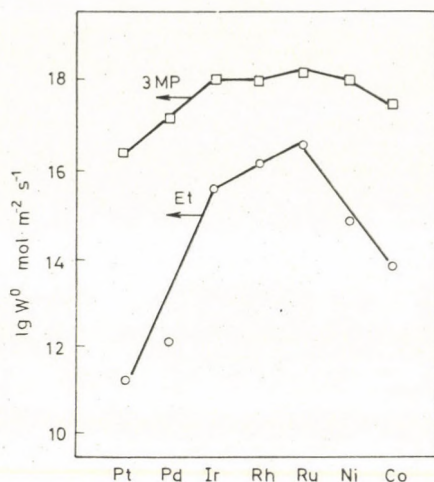


Fig. 10. Comparison of the rate of hydrogenolysis of ethane and 3-methylpentane

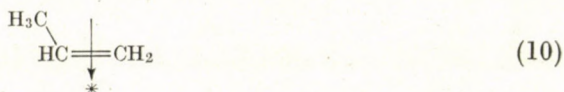
lysis of ethane and 3-methylpentane are compared. As shown in the figure the difference among the activities of the various metals in the hydrogenolysis of 3-methylpentane is much smaller than that of ethane. The rate of hydrogenolysis of hydrocarbons with more than two carbon atoms exceeds by several orders of magnitude (2–5) than that of ethane. The activation energy for ethane hydrogenolysis is higher than that for saturated hydrocarbons of higher molecular weight (Table V). *Neo*-pentane is an exception, its energy of activation is the same as for ethane. On the contrary, on platinum the activation energy of *neo*-pentane is small; its value is comparable to that of *iso*-butane. This is caused by the fast isomerization of neopentane on platinum, thus the product of isomerization is hydrogenolysed.

Table V

The apparent activation energy of hydrogenolysis of various hydrocarbons (in kJ mol⁻¹)

Catalysts	C ₂	C ₃	<i>n</i> -C ₄	<i>i</i> -C ₄	<i>n</i> -C ₅	<i>n</i> -C ₆	$\begin{array}{c} \text{C} \\ \\ \text{C}-\text{C}-\text{C} \\ \\ \text{C} \end{array}$
Co	113		88	88			
Ni	167	134	134	125	134	129	151
Rh	156		124				168
Pd	222		155	161	151		224
Ir	163		99				
Pt	222	100	96	109	180		113

The difference in activation energies between ethane and higher paraffins cannot be interpreted by the difference in bond strength. The bond strength in $C_2H_5-CH_3$ is smaller only by 12 kJ mol^{-1} than that in CH_3-CH_3 [12]. It must be, therefore, assumed that the significant differences in the kinetic parameters of the hydrogenolysis of ethane, *neo*-pentane and those of other hydrocarbons is correlated to the existence of $\alpha\beta\gamma$ -interaction between the reactant molecule and the surface which is more favourable than either the $\alpha\beta$, or the $\alpha\gamma$ species. In agreement with KEMBALL [41] it can be explained by the formation of π -complex preceded by the dissociation of two hydrogen atoms:



As we have mentioned, C—H bonds in α -position to the π -bond are weakened, thus the formation of multiple bonded intermediates is facilitated.

Now, the question arises: why can a particularly large difference be observed between ethane and the other hydrocarbons on Pt and Pd, while this difference is significantly smaller on Ni and Co? Spectroscopic data have provided evidences that π -complex is formed at the adsorption of heptene-1 and benzene on platinum surface, whereas on nickel no π -complex formation was observed. It is also supported by organometallic complexes.

As shown in Fig. 11a geometrical favourable adsorption of propane can take place on the (100) face of Pt and Pd: π -bonded complex is formed [25] by using the e_g or t_{2g} orbitals while the third carbon atom can be multiply linked to the neighboring platinum atoms. On Ni catalyst such an arrangement is not possible. Although the geometrical arrangement is appropriate for Ru and Rh, but the t_{2g} orbitals are filled to a lesser extent which, in turn, is not favourable for the formation of π -complex. In the case of iridium both the geometrical size

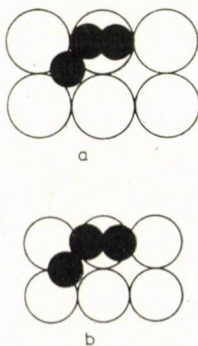


Fig. 11. Possible geometrical arrangement for π -olefin complex formed via propane adsorption; a: Pd, Pt; b: Ni

and the filling of the e_g and t_{2g} orbitals are the most favourable, therefore, the least difference can be observed between the activation energies of ethane and that of butane.

The selectivity differences observed in the hydrogenolysis on different metals can be interpreted by the effect of σ - π conjunction. It is well known, that on nickel terminal C—C bond splitting takes place while on Pt, Pd, Ir and Rh the C—C bond can also be cleaved [45] at the middle of the molecule.

As a result of the strong interaction between nickel and hydrocarbon, the hydrogenolysis commences at the end of the molecule, *i.e.* at the primary interaction. On Pt, Pd and Ir olefin can be formed at the same interaction [46]. This results in the weakening of C—H and C—C bonds in conjunction to the surface olefin group (*e.g.* in hexene-1), consequently C—C bond is splitted in the inner part of the molecule. We emphasize here that hydrogenolysis of C_3 — C_6 hydrocarbons may occur *via* two different mechanisms: the conventional, ethane type interaction (Fig. 12b, c) and an easier one *via* π -complexes on the (100) face.

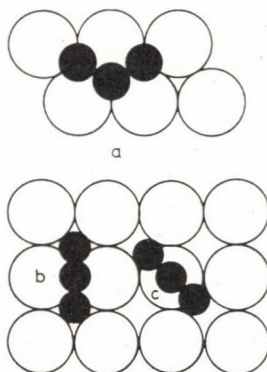


Fig. 12. "Three point" attachment. a, (111) face; b, c (100) face

We may not exclude hydrogenolysis on the (111) face either (see Fig. 2a) but its probability appears to be low in the light of the facts mentioned in connection with ethane. However, at longer chain, simultaneous interaction of more carbon atoms with metal atoms might facilitate hydrogenolysis without $\alpha\alpha$ interaction. Formation of π -allyl complex, similarly to the mechanism put forward for cyclohexane may also be operative in the hydrogenolysis on (111) face.

3.2.3. Hydrogenolysis of five-membered rings

C—C bond rupture of five-membered ring is an easier reaction than the catalytic hydrogenolysis of straight chain hydrocarbons. This is clearly indicated in Table VI [3].

Table VI

Reactivity of *n*-pentane and *c*-pentane on Ni and Pt

Catalyst	E, kJ mol ⁻¹		$\frac{w_{cP}}{w_{nP}}$
	<i>n</i> -pentane	<i>c</i> -pentane	
Ni	142	117	3.5
Pt	179	106	16

According to the Table under the same condition the five-membered ring is split faster than the C—C bond rupture of paraffins and the activation energy for the latter process is higher. There is a significant difference between Ni and Pt: the hydrogenolysis rate of cyclopentane and *n*-pentane differs much more on platinum than that on nickel.

The results obtained for methylcyclopentane agree well with this statement. In the conversion of methylcyclopentane always the ring is cleaved and cyclopentane practically cannot be observed [47]. Activation energy for 3-methylpentane hydrogenolysis is 167 kJ mol⁻¹ which is somewhat lower than that for ring opening (187 kJ mol⁻¹ [4]).

On platinum the plane of ring is parallel to the catalyst surface at adsorption while on nickel two-point attachment can be observed [3].

By comparing the hydrogen-deuterium exchange in cyclopentane and *n*-pentane it is shown that the exchange is faster in the ring than in *n*-pentane. The main deuterated products are d_1 , d_5 and d_2 , d_{10} on platinum and on nickel, respectively.

All these experimental facts give evidence that on nickel the ring opening occurs *via* 1,2-chemisorption followed by hydrogenolysis. This mechanism does not differ too much from that of straight chain hydrocarbon. On the contrary on platinum planar adsorption takes place, the carbon atoms of cyclopentane are attached to the interatomic holes similarly to the mechanism operative for cyclohexane. In this way one of the C—C bonds in the cyclopentane molecule is

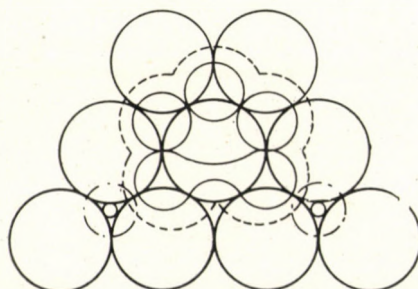


Fig. 13. Doublet-sextet mechanism of ring opening of a five-membered ring [51]

deformed thus bond rupture occurs (see Fig. 13). These data are in concordance with the conceptualization of KAZANSKY and his school [51].

The experimentation carried out on highly dispersed catalysts furnishes us with further evidences for the above idea [3]. On Pt/SiO₂ catalysts the rate of hydrogenolysis increases with dispersion to a greater extent than that of ring opening, that is, the difference between the two reactions becomes smaller. This can be explained by the lower probability of the planar attachment to the surface as the particle size of platinum decreases because the number of edges and corners increases on the expense of the planes.

The difference between platinum and nickel is caused by structural factors, *i.e.* the planar arrangement of the cyclopentane ring is possible because the distance between interatomic holes on platinum is larger than the C—C bond distance in cyclopentane (0.152 nm) while it is smaller on nickel.

3.3. Isomerization

The role of structural factors is well demonstrated also by isomerization. The isomerization of 3-methylpentane takes place only on metals which gives the possibility for the hydrocarbons to be accommodated, in the interatomic holes on the (111) face [48]. Thus, isomerization activity is revealed on specially prepared, hexagonal rhenium with high surface area [49], because the distance of the interatomic holes on the (0001) face is 0.1568 nm. Controversial data was obtained on ruthenium: in some cases isomerization was not found [38, 49] in other cases the formation of trace amount isomer could be observed [50]. It is understandable because the distance of the interatomic holes for octahedral crystal structure is 0.1533 nm while the C—C bond length in paraffins is 0.154 nm.

The importance of structural factors of metal is shown by the increased isomerization of hydrocarbons with decreased dispersion of Pt/SiO₂ catalysts [46]. Because the probability of planar attachment to the surface decreases with decreasing particle size. On highly dispersed catalysts the molecule is rather linked to the edges and corners which favours the hydrogenolysis.

*

Some concluding remarks concerning the hydrogen effect should be discussed further because as shown, hydrogen may accelerate or hinder the rate of reaction. This effect is different for various reactions, that is why the selectivity of hydrocarbon reaction is greatly influenced by the presence of hydrogen.

The accelerating effect can be observed at low hydrogen pressure, and this is in connection with alteration of dissociative chemisorption. Hydrogen may occupy interatomic holes to a large extent preventing thus the strong

hydrocarbon chemisorption on the (100) face. Hydrogen present in these holes facilitates the less strong links between the orbitals of carbon atoms and that of metal atoms.

The retarding effect of hydrogen is in connection with the surface occupied by hydrogen atoms therefore the shift of the dissociative chemisorption of hydrocarbons. By the increase of hydrogen concentration on the surface not only the formation of C—M σ -bonds is hindered, but also that of π -complexes. Hydrogen facilitates the hydrogenation of π -complexes or the formation of half hydrogenated species. Thus the accelerating effect which is due to the presence of π -complex, is diminished.

All these support our idea, *i.e.*, the catalytic effect is a cooperative action of all components of a catalytic system. The most important is the accordance between the structures of the reactant molecule and the catalytic surface, by which appropriate orientation is present on the surface.

*

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DEALKYLATION SIDE REACTION IN THE SYNTHESIS OF CHOLESTERYL CARBONATES AND CARBAMATES

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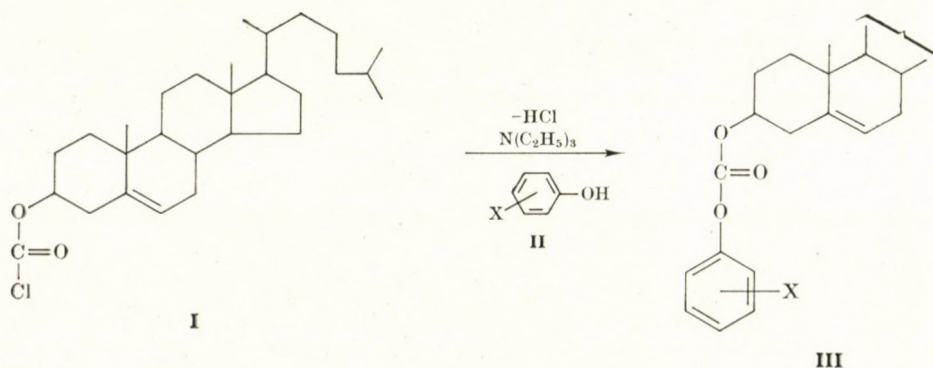
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Cholesteryl carbonates and carbamates were prepared by the reactions of cholesteryl chloroformate with the corresponding hydroxy- and aniline derivatives. In many cases the formation of a considerable quantity of a by-product was observed. It was found that cholesteryl chloroformate reacted with the triethylamine used as acid acceptor.

In the past ten years many homologous series with cholest-5-ene skeleton have been prepared [1–4]. The syntheses were carried out with a view to recognize the regularities within the homologous series and to obtain new compounds with favourable mesomorphic properties.

In the course of our work cholesteryl carbonates (III) and carbamates (VII) were synthesized with the aim of establishing the influence of various substituent groups on the formation of the mesomorphic phases [5, 6].

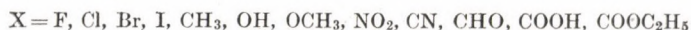
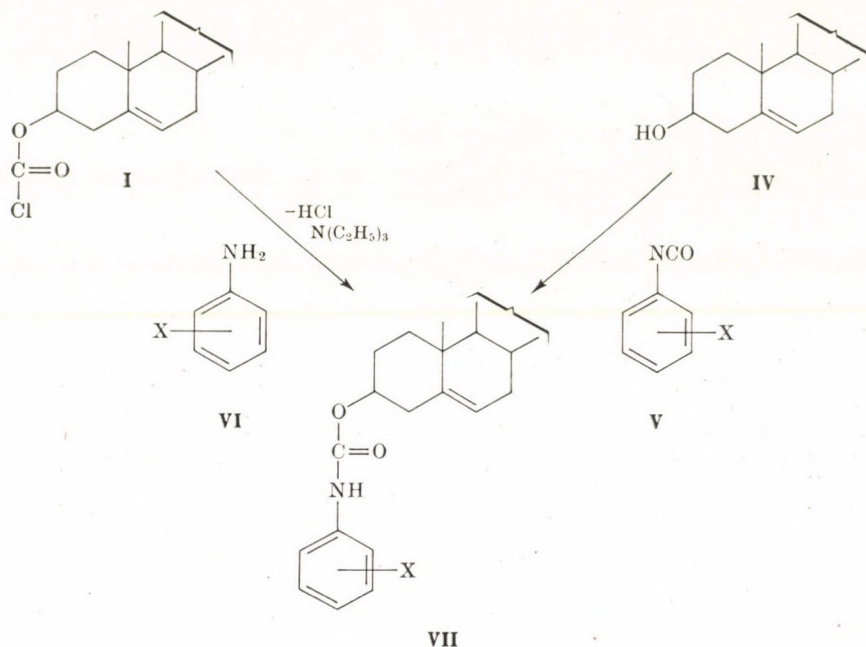
The cholesteryl carbonates (III) were prepared from cholesteryl chloroformate (I) with substituted phenols (II). As acid acceptor triethylamine was used.



X = F, Cl, Br, I, CH₃, OH, OCH₃, NO₂, CN, CHO, COOH, COOC₂H₅

Scheme 1

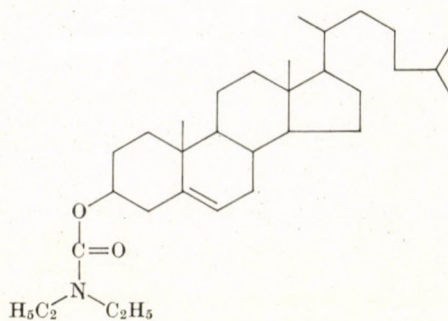
The *O*-cholesteryl carbamates (VII) were synthesized in two ways. Cholesterol (IV) was made to react with aryl isocyanates (V), or cholesteryl chloroformate (I) was combined with substituted anilines (VI). In the latter case, too, triethylamine was used as acid acceptor.



Scheme 2

During the synthetic processes it was found that (with the exception of the reactions with isocyanates) nearly all experiments gave rise to a by-product with steroid skeleton. In the course of the preparation of a considerable number (60) of the compounds, following the reactions with thin-layer chromatography, it was striking that this by-product was in each case the same, only its quantity being dependent on the reactants. In addition, it was found that long reaction periods and elevated reaction temperatures favoured the formation of the by-products. When pyridine was used as acid acceptor, the reactions took place more slowly, but no by-product was formed.

The by-product was isolated with the aid of column chromatography and, on the basis of IR and PMR spectra, combustion analysis data and the preparation of comparative compounds, it proved to be diethylaminocarbonyloxy- 3β -cholest-5-ene (VIII):

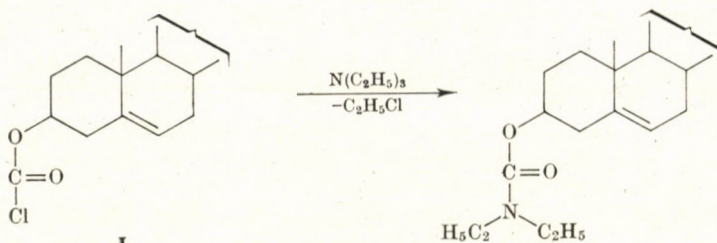


VIII

Scheme 3

The dealkylation reaction described by von BRAUN [7] was modified a few years later [8], ethyl chloroformate being used instead of cyanogen bromide.

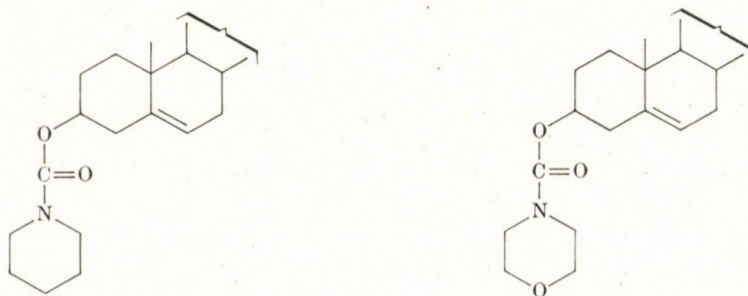
In our case the by-product resulted from a comparable process. Triethylamine reacted with cholesteryl chloroformate (I) to give, besides ethyl chloride, the by-product: diethylaminocarbonyloxy-3β-cholest-5-ene (VIII):



VIII

Scheme 4

In order to extend the scope of this dealkylation reaction, we attempted to dealkylate *N*-ethylpiperidine and *N*-methylmorpholine. The reactions were effected in benzene solution at 80 °C and the expected compounds (IX, X) were obtained. For the purpose of comparison, they were also prepared from piperi-



IX

X

Scheme 5

Table I
Physical properties of the compounds prepared

No.	Mol. formula	Mol. weight	Method	M.p., °C	Analysis %	
					Found	Calcd.
VIII	$C_{32}H_{55}NO_2$	485.77	isolated	151	C 78.95	C 79.12
					H 11.56	H 11.41
					N 2.97	N 2.88
			prepared	151	C 78.97	C 79.12
					H 11.20	H 11.41
					N 2.67	N 2.88
IX	$C_{33}H_{55}NO_2$	497.78	A	170	C 79.78	C 79.62
					H 11.10	H 11.14
					N 2.75	N 2.81
			B	170	C 79.96	C 79.62
					H 11.32	H 11.14
					N 2.69	N 2.81
X	$C_{32}H_{53}NO_3$	499.75	A	165	C 76.78	C 76.90
					H 10.90	H 10.69
					N 2.58	N 2.80
			B	165	C 76.52	C 76.90
					H 10.58	H 10.69
					N 2.74	N 2.80

dine and morpholine. The physical data of the compounds prepared are shown in Table I.

When mixtures of pyridine and cholesteryl chloroformate were subjected to the above conditions, no reaction occurred.

To sum up, it is concluded that cholesteryl chloroformate, similarly to ethyl chloroformate, can dealkylate tertiary amines. Therefore, when esters of chloroformic acid are allowed to react with compounds containing hydroxy or amino groups to obtain carbonates or carbamates, it is recommended to use pyridine as the acid acceptor, to avoid the formation of the by-product.

Experimental

M.p.'s were determined on a Boetius micro-hot-stage. The purities of all compounds were checked by TLC and their structures were confirmed by IR and PMR spectra. IR spectra were obtained in KBr pellets with a UNICAM SP 200 spectrometer; PMR spectra were recorded on a JEOL 60 HL spectrometer in $CDCl_3$, with TMS as internal standard.

Diethylaminocarbonyloxy-3 β -cholest-5-ene (VIII)

Cholesteryl chloroformate (I) (0.45 g; 0.001 mole) was dissolved in dry benzene (10 mL) with stirring, and 0.15 g (0.002 mole) of diethylamine in 10 mL of dry benzene was added during 10 min. Stirring was continued for 30 min, and the benzene solution was washed with cold dilute hydrochloric acid and water, and dried over anhydrous sodium sulfate. The benzene was evaporated and the product crystallized from a mixture of benzene-ethyl alcohol to yield 0.4 g of VIII, m.p. 151 °C.

1-Piperidinocarbonyloxy-3 β -cholest-5-ene (IX)

Method A: from piperidine, similarly as described for VIII. Yield: 0.4 g; m.p. 170 °C.

Method B: Cholesteryl chloroformate (0.45 g; 0.001 mole) was dissolved in 10 mL of *abs.* benzene, and 0.12 g (0.001 mole) of *N*-ethylpiperidine was added. The reaction mixture was refluxed for 5 h, the benzene solution was washed with cold dilute hydrochloric acid and water, and dried over anhydrous sodium sulfate. The benzene was removed and the product crystallized from benzene-ethyl alcohol to obtain 0.4 g of IX, m.p. 170 °C.

4-Morpholinocarbonyloxy-3 β -cholest-5-ene (X)

Method A: from morpholine, similarly as described for VIII. Yield: 0.4 g; m.p. 165 °C.

Method B: from *N*-methylmorpholine, similarly as given above for IX. Yield: 0.4 g; m.p. 165 °C.

*

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OXIDATION OF OXALIC ACID ON A PLATINUM ELECTRODE

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The oxidation of oxalic acid on a platinum electrode has been investigated as a function of potential, temperature, oxalic acid concentration and pH. It has been shown that earlier, apparently contradictory experimental results in conjunction with the dependence on pH can be made consistent, because the reaction rate changes at a given potential as a function of pH along a maximum curve. It has been established that there is a good agreement between experimental results and kinetic relationships, if the following scheme of mechanism is accepted. The reacting species is the undissociated oxalic acid, the actual concentration of which is determined by dissociation. Oxalic acid is reversibly adsorbed. Adsorption occurs under TEMKIN-conditions. There is an equilibrium between surface and solution with respect to the OH radical. The rate-determining step is the reaction of adsorbed oxalic acid with the adsorbed OH radical.

Owing to its practical importance and theoretical interest, several communications dealt in recent decades with the electro-oxidation of oxalic acid [1–15]. A survey of these works reveals that experimental results and consequently their interpretation differ considerably. The key to the solving of the problems is obviously the reacting species. The investigation of the effect of hydrogen ion concentration on the rate of electrochemical oxidation is of primary importance in achieving this aim. As shown by the data in Table I, the pH has not been changed within a wide interval in these works. The generalization of the partial results led to inconsistent conclusions.

It should be mentioned that the pH-dependence given by JOHNSON *et al.* [5] comprises self-contradiction when $\text{H}_2\text{C}_2\text{O}_4$ is assumed to be the reacting species.

The mechanism proposed by ATANASIU and GEANA [11] is unacceptable, because it reckons with the reversible reduction of CO_2 in the potential interval of oxidation, which can be excluded because of thermodynamical and empirical reasons.

Moreover, for the elucidation of the reaction mechanism the determination of the dependence of the reaction rate on concentration, potential and temperature is of basic importance. Relevant earlier results are summarized in Table II.

Table I

The reacting species and experimental proofs

The reacting species	Observation	pH-dependence $\left(\frac{\partial \lg i}{\partial \text{pH}}\right)_{c_i, T, \varphi}$	Ref.
$\text{H}_2\text{C}_2\text{O}_4$	Oxalic acid is oxidized only in acidic medium	0.55 (calculated)	[5]
HC_2O_4^-	The current diminishes with increasing sulfuric acid concentration	—	[9]
HC_2O_4^-	The increase in sulfuric acid concentration diminishes oxidation rate	—	[10]
HC_2O_4^-	No experimental data. On the basis of the assumed scheme of mechanism, pH dependence is obtained only in this case.	0.5 (calculated)	[11]
$\text{H}_2\text{C}_2\text{O}_4 + \text{OH}_{\text{ad}}$	At $\text{pH} > 3$ there is no oxidation at $\varphi \sim 1.5 \text{ V}$	—	[1]

Table II

Dependence of reaction rate on concentration and potential, and the activation energy of the process

Dependence on concentration $\left(\frac{\partial \lg i}{\partial \lg c_{\text{H}_2\text{C}_2\text{O}_4}}\right)_{\varphi, \text{pH}, T}$	Dependence on potential $\left(\frac{\partial \varphi}{\partial \lg i}\right)_{\text{pH}, c_i, T}$ (V/decade)	Activation energy (kJ/mol)	Ref.
0.35 ($\varphi = 0.53 \text{ V}$, $\text{pH} = 0.03$, $T = 353 \text{ K}$)	0.070 ($\text{pH} = 0.03$, $T = 353 \text{ K}$)	98.8 ($\varphi = 0.58 \text{ V}$) 91.7 ($\varphi = 0.63 \text{ V}$) ($T = 323-353 \text{ K}$) the rate-determining step is different, if $T < 303 \text{ K}$	[5]
1 (if $\lg i$ is plotted as a function of $c_{\text{HC}_2\text{O}_4^-}$ and $c_{\text{HC}_2\text{O}_4^-} < 10^{-1}$) < 1 (if $c_{\text{HC}_2\text{O}_4^-} > 10^{-1}$) ($\varphi = ?$, $\text{pH} \sim 0.05$, $T = 293 \text{ K}$)		64–25 ($\varphi = 1-1.3 \text{ V}$, $T = 280.5-323 \text{ K}$)	[9]
0.64–0.94 ($\varphi = 1.03-1.48 \text{ V}$, $\text{pH} = 0.03$, $T = 293 \text{ K}$)	0.076 ($\text{pH} = 0.03$, $T = 293 \text{ K}$ $\varphi < 1.1 \text{ V}$)		[10]
0.63–0.87 ($\varphi = 0.75-0.85 \text{ V}$, $\text{pH} = 0$, $T = 298 \text{ K}$)	0.103 ($\text{pH} = 0$, $T = 298 \text{ K}$, $\varphi = 0.85 \text{ V}$)		[11]

The main object of our present work is the elucidation of the dependence of the process on pH, under consideration of the aforesaid. At the same time, to resolve inconsistencies in the literature, the determination of the temperature-, potential- and concentration-dependence was also needed.

Experimental

The thermostable variant of the three-electrode cell, known from the literature, has been used. As measuring electrode platinum electrodes of 10 cm² geometrical surface, bright and platinized to various roughness factors, have been used. For the investigation of the different effects, from case to case electrodes of different true surface have been used, so that current can be measured with adequate accuracy, because the changing of potential, temperature or concentration in a relatively wide field brings about a change in current by several orders of magnitude. The reference electrode was a hydrogen electrode, immersed into the supporting electrolyte. Potential values marked with φ_r are referred to the potential of this electrode, while those marked with φ to the potential of the standard hydrogen electrode, taken as $E_h^0 = 0$ for the given temperature. The accuracy of thermostating was ± 0.05 K. HClO₄-NaClO₄ solutions of 1 mol/dm³ total concentration and phosphate buffer systems were used as base electrolyte. All the compounds (HClO₄, NaClO₄, NaOH, H₃PO₄, NaH₂PO₄, Na₂HPO₄, Na₃PO₄ and H₂C₂O₄) were of analytical purity, the solvent was bidistilled water. A Radelkis potentiostat type OH-405, a precision pH-meter type OH-205 and a digital voltmeter Model EMG 1363 were used.

Results and Discussion

Temperature- and potential-dependence of the reaction rate, activation energy of the process

It can be established from data in the literature [5, 9] that an increase in temperature results in a considerable increase of the reaction rate. However, it can be seen from data in Table II that various authors [5, 9] obtained different results with respect to activation energy and its change with the potential. Thus, it seemed expedient to investigate first the temperature-dependence of the process. Figure 1 shows potentiostatic polarization curves recorded at various temperatures. It becomes clear from the figure that an increase in temperature does not change the character of the polarization curve of oxalic acid, only a near parallel shift of the curves is to be observed. The slope of the polarization curve between the two sections of larger slope is at 353 K 113 ± 3 , at 293 K 94 ± 3 mV/decade. On the basis of this, the investigated section of the polarization curve can be described with a relationship of the following type:

$$i = k \exp \left(\frac{\beta F \varphi}{RT} \right), \quad (1)$$

where $\beta = 0.62 \pm 0.02$. The change of the slope with temperature is 0.31 mV/decade degree, corresponding to the temperature dependence $\frac{RT}{\beta F}$. The ap-

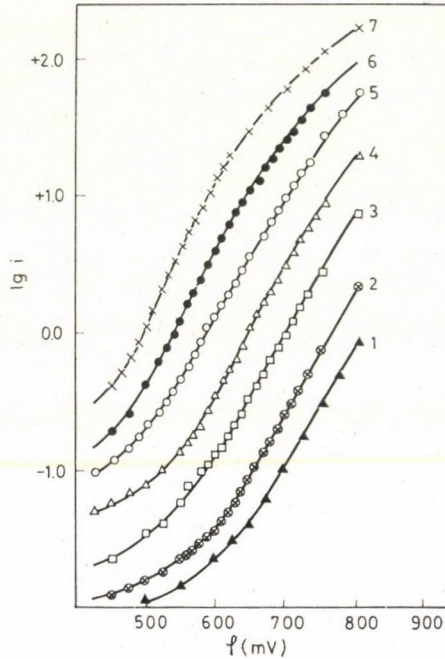


Fig. 1. The first section of the polarization curve of oxalic acid (0.2 mol/dm^3) at a platinum electrode at various temperatures. Base electrolyte: perchloric acid of 1 mol/dm^3 concentration. 1: 293, 2: 303, 3: 313, 4: 323, 5: 333, 6: 343, 7: 353 K

parent activation energy calculated from the relationship $\lg i - \frac{1}{T}$ was found to be $95 \pm 8 \text{ kJ/mol}$, when calculated on the basis of the polarization range from 550 to 850 mV (straight section) mentioned above. The dependence on the potential of values calculated in this way about -40 kJ/mol V . The contra-

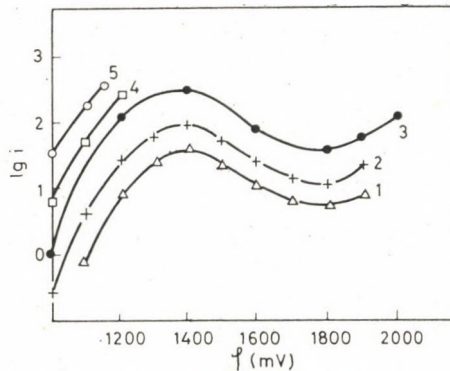


Fig. 2. Polarization curves of oxalic acid (0.2 mol/dm^3) at various temperatures in perchloric acid (1 mol/dm^3) base electrolyte at a bright platinum electrode. 1: 286.5, 2: 293, 3: 313, 4: 333, 5: 353 K

diction found in the literature [5, 9] can be explained under consideration of the fact that polarization curves are shifted with increasing temperature towards lower positive potentials. The comparison of curve sections of non-identical character led to the erroneous conclusion that the rate-determining step changes at 303 K [5]. For the same reason, neither can values determined in Ref. [9] be considered as characteristic of the process kinetics.

In the present communication only the potential range $\varphi_r < 1$ V is investigated, but Fig. 2 shows also the further section of the polarization curve pertinent to the oxidation of oxalic acid. It can be seen namely on the basis of Fig. 2 that the increase of the slope of the polarization curve is connected, at least in first approximation, with the fact that in the electro-oxidation of oxalic acid on platinum, similarly as in the case of several organic compounds [16], the inhibiting effect of the oxide layer must be reckoned with. The attention should be called to the fact that in the case of oxalic acid the diminishing of the reaction rate occurs only at considerably more positive potentials, than in the case of alcohols, aldehydes, formic acid, etc.

The concentration dependence of the reaction rate

The concentration dependence of the oxidation rate has been determined with the method described in Ref. [17]. In Fig. 3 the logarithm of the current is plotted as a function of the logarithm of total oxalic acid concentration ($\bar{c}_{\text{H}_2\text{A}}$)

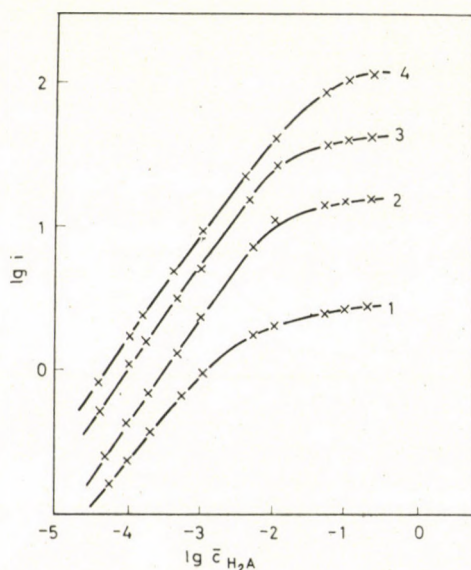


Fig. 3. Dependence of current on concentration in HClO_4 (1 mol/dm³) base electrolyte. $T = 353$ K. 1: 600, 2: 700, 3: 750, 4: 800 mV

in strongly acid ($\text{pH} = 0$) medium at 353 K. A similar set of curves has been obtained at higher pH values and at 293 K. It has to be mentioned, however, that in the case of $\text{pH} > 0$ the change of pH must also be taken into consideration in the concentration range of $\bar{c}_{\text{H}_2\text{A}} > 10^{-2} \text{ mol/dm}^3$. On increasing the capacity of the phosphate buffer, namely solubility limits are met, while on the other hand the increased phosphate concentration changes the adsorption of oxalic acid, *i.e.* the diminishing of the reaction rate to be expected.

Moreover, attention must be called to the fact that in systems containing phosphate the current values belonging to identical potentials are somewhat lower than in systems containing perchlorate. This can be attributed to the stronger adsorption ability of phosphoric acid. However, the character of the curves is not influenced by this effect. It can be seen from Fig. 3 that in the concentration range $\bar{c}_{\text{H}_2\text{A}} \leq 10^{-2} \text{ mol/dm}^3$ the dependence of the reaction rate on concentration can be given by an equation of type:

$$i = k c^\alpha \quad (0 < \alpha < 1). \quad (2)$$

The order of reaction determined on the basis of (2) is summarized in Table III.

To determine the type of adsorption, the plotting of $\frac{1}{i} - \frac{1}{c}$ has also been attempted (investigation of the applicability of Langmuir's isotherm), but this did not give either in the whole concentration range ($\bar{c}_{\text{H}_2\text{A}} = 5 \cdot 10^{-5}$ to $2 \cdot 10^{-1} \text{ mol/dm}^3$) a straight line, so that in the further work Eq. (2) will be used for the calculations. A relationship of this type has been found valid in a wide range for the electrocatalytic oxidation of organic compounds, and this has been attributed to the adsorption of the reacting particle at the inhomogenous platinum surface. It is assumed that the adsorbed form of the molecule is reacting,

Table III
Concentration dependence of the rate of oxidation at 353 K

$\varphi_r(\text{mV})$	$\alpha = \left(\frac{\partial \lg i}{\partial \lg c_{\text{H}_2\text{A}}} \right)_{\varphi, \text{pH}, T}$		
	pH = 0	pH = 0.55	pH = 2.25
600	0.63	0.6	0.68
700	0.72	0.75	—
750	0.72	0.75	—
800	0.72	—	0.85
900	—	—	0.87

Relative error of the order of reaction: $\pm 5\%$

and an adsorption equilibrium is established. This equilibrium is described by the FRUMKIN-TEMKIN logarithmic isotherm:

$$\Theta = \frac{1}{f} \ln a_{\varphi} c \quad \left(f = \frac{h}{\alpha} \right) \quad (3)$$

where Θ is the coverage, f , h , α are constants, and a_{φ} is a factor depending on the potential. At higher concentrations the current approaches a limit value. The usual explanation of this phenomenon is that the above isotherm describes only at medium coverage truly adsorption equilibrium.

The above dependence of current on concentration appropriately follows in first approximation, if we take into consideration that according to TEMKIN [18] the rate of the electrochemical reaction (i) changes exponentially with coverage (Θ) relevant to the reacting molecule, and thus

$$i = k \exp(h\Theta) \exp\left(\frac{\beta F \varphi_r}{RT}\right). \quad (4)$$

When (4) is combined with the logarithmic isotherm (3), the relationship

$$i = k c^{\alpha} \exp\left(\frac{\beta F \varphi_r}{RT}\right) \quad (5)$$

is obtained, and in the case of $\varphi_r = \text{constant}$ this agrees with experimental findings. It should be mentioned, however, that kinetic equation (5) can be considered only as an approximation, because a linear dependence of coverage has been neglected besides the exponential, and in the range investigated coverage has been considered as independent of the potential. Moreover, it has been taken into consideration that the product (CO_2) is not adsorbed, and besides the coverage relevant to the reacting molecule the coverage belonging to all the other species can be neglected. Though in the deduction of relationship (5) certain assumptions have been already made concerning the reaction mechanism, such as equilibrium and that the reaction proceeds through some kind of adsorbed state, the nature of the adsorbed species-still remained an unanswered question. Neither is it yet decided, whether the further conversion of the adsorbed species proceeds under participation of the adsorbed OH radical (OH_{ad}). The investigation of the pH dependence of the rate shows promise to answer these fundamental questions.

The pH dependence of the rate of oxidation

Figure 4 shows the polarization curves recorded in perchloric acid systems at various pH values, at 353 K in the case of $\bar{c}_{\text{H}_2\text{A}} = 0.1 \text{ mol/dm}^3$. It may seem remarkable that these systems can be easily measured even when $\text{pH} > 3$.

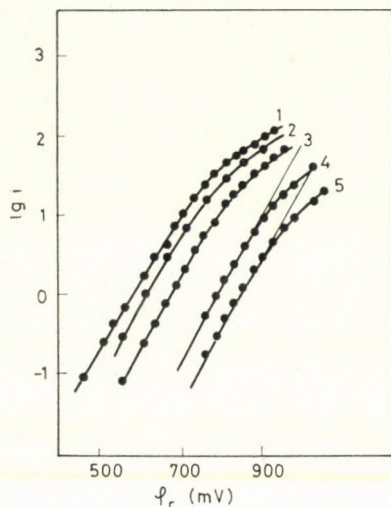


Fig. 4. Polarization curves at various pH values, 1 mol/dm³ total perchlorate concentration and $T = 353$ K. Oxalic acid concentration 0.1 mol/dm³. 1: 0, 2: 1.3, 3: 2.7, 4: 3.74, 5: 4.21 pH

However, it is easy to see that the buffer capacity of the system, containing in a concentration of 0.1 mol/dm³ oxalic acid, is sufficient to take up the H⁺ ions formed. The situation is naturally different, when $\bar{c}_{\text{H}_2\text{A}} \leq 10^{-2}$ mol/dm³, be-

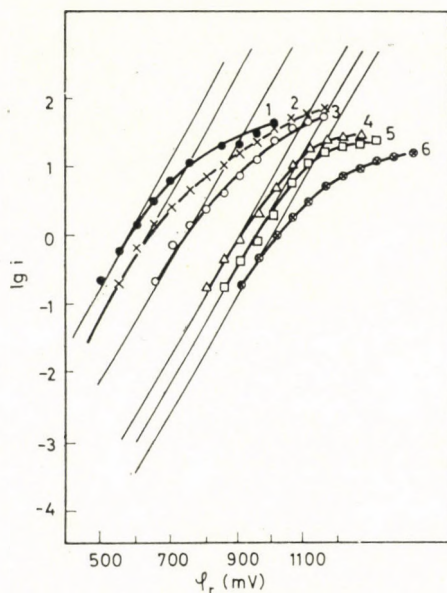


Fig. 5. Polarization curves in phosphate buffer solutions, $T = 353$ K. Oxalic acid concentration: 0.01 mol/dm³. Total phosphate concentration: 1 mol/dm³. 1: 0.55, 2: 2.4, 3: 3.55, 4: 4.8, 5: 5.27, 6: 6.28 pH

cause in this case the passage of a relatively small quantity of charge produces already a considerable change in the pH value. Therefore, in our further work, when a broader pH interval will be studied at $\bar{c}_{\text{H}_2\text{A}} = 10^{-2} \text{ mol/dm}^3$, phosphate buffer systems are used as base electrolyte. Polarization curves obtained in these investigations are shown in Fig. 5. (It should be noted that sets of curves of similar character were obtained for both systems at 293 K.) It can be readily seen from Figs 4 and 5 that polarization curves shift with increasing pH towards higher positive potentials. It follows from this that the reaction rate diminishes at a given φ_r , as shown by Fig. 6.

If φ is selected instead of φ_r as parameter, the reaction rate changes along a maximum curve as a function of pH, as shown by Fig. 7. It should be mentioned in conjunction with Figs 6 and 7 that corrected values were obtained

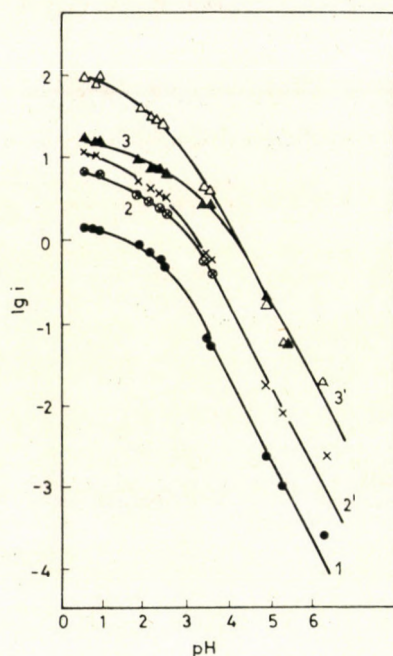


Fig. 6. Dependence of the reaction on pH at various φ_r potentials. $T = 353 \text{ K}$. 1: 600, 2: 700, 3: 800 mV. Corrected current values. 2': 700, 3': 800 mV. (For explanation see text.)

under utilization of the auxiliary lines in Fig. 5 (prolongations of the sections of a slope of about 110 mV/decade), and in our further work values determined in this way were used for the calculations. This offered a possibility to analyze the pH dependence of the process in a wide pH range at constant α and β values. An equivalent but more complicated solution is the consideration of the actual values, *i.e.* of the $\beta(\varphi)$ function.

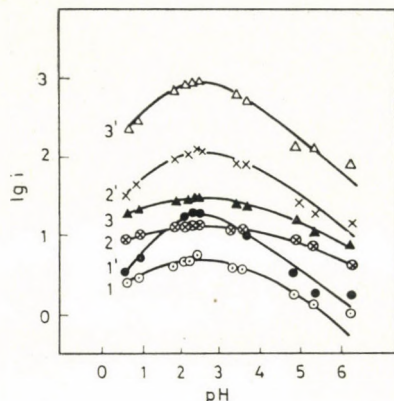


Fig. 7. Dependence of the reaction rate on pH at various φ values. 1: 600, 2: 700, 3: 800 mV. Corrected values. 1': 600, 2': 700, 3': 800 mV

It can be easily seen from the above said that the pH dependence of the reaction rate can not be described with a simple exponential function of type

$$i = K' c_{\text{H}}^x \quad (x \leq 0), \quad (6)$$

where c_{H} is the hydrogen ion concentration, K' a constant, at given φ or φ_{r} , and at constant temperature and $\bar{c}_{\text{H}_2\text{A}}$. Whether assuming a reaction mechanism based on direct charge transfer or under participation of OH_{ad} , this means that the consideration of another process depending on pH is needed. On the other hand, it becomes clear that the two apparently inconsistent experimental findings, namely that an increase in concentration of the acid used as base electrolyte diminishes the reaction rate [9, 10] and that oxalic acid is not oxidized in strongly alkaline medium [5], can be harmonized.

For the interpretation of the pH dependence observed, it seems obvious that first the fact should be taken into consideration that oxalic acid is a weak dibasic acid. Dissociation is described by the following well known relationships:

$$K_1 = \frac{c_{\text{HA}} \cdot c_{\text{H}}}{c_{\text{H}_2\text{A}}} = 6.5 \cdot 10^{-2} \quad (7)$$

$$K_2 = \frac{c_{\text{A}} \cdot c_{\text{H}}}{c_{\text{HA}}} = 6.1 \cdot 10^{-5} \quad (8)$$

where $c_{\text{H}_2\text{A}}$, c_{HA} , c_{A} and c_{H} is the concentration of $\text{H}_2\text{C}_2\text{O}_4$, H_2CO_4^- , $\text{C}_2\text{O}_4^{2-}$ and H^+ , respectively, in the solution. On the basis of the conservation of mass and charge the following relationship exists between the concentration of the

weighed oxalic acid ($\bar{c}_{\text{H}_2\text{A}}$) and the above concentrations:

$$c_{\text{HA}} = \frac{K_1 c_{\text{H}}}{c_{\text{H}}^2 + K_1 c_{\text{H}} + K_1 K_2} \cdot \bar{c}_{\text{H}_2\text{A}}, \quad \text{and} \quad (9)$$

$$c_{\text{H}_2\text{A}} = \frac{\bar{c}_{\text{H}}^2}{c_{\text{H}}^2 + K_1 c_{\text{H}} + K_1 K_2} \cdot \bar{c}_{\text{H}_2\text{A}}. \quad (10)$$

It should be mentioned that different data are published in the literature for the values of K_1 and K_2 , and their temperature dependence [19–20]. However, K_1 and K_2 values coming reasonably into consideration do not change considerably either the shape or the value of the function. Herewith, the task is evidently simplified to the incorporation of the change in concentration with pH of the presumable two reacting species ($\text{H}_2\text{C}_2\text{O}_4$ and HC_2O_4^-) into the appropriate kinetic equation.

Thus, let us substitute into equation (5) for the concentration c the actual c_{HA} and $c_{\text{H}_2\text{A}}$ values, respectively, obtained on the basis of (9) and (10).

The relationships

$$i = k \bar{c}_{\text{H}_2\text{A}}^\alpha \left(\frac{K_1 c_{\text{H}}}{c_{\text{H}}^2 + K_1 c_{\text{H}} + K_1 K_2} \right)^\alpha \exp \left(\frac{\beta F \varphi_r}{RT} \right) \quad (11)$$

and

$$i = k \bar{c}_{\text{H}_2\text{A}}^\alpha K_1^\alpha \frac{c_{\text{H}}^{\alpha-\beta}}{(c_{\text{H}}^2 + K_1 c_{\text{H}} + K_1 K_2)^\alpha} \exp \left(\frac{\beta F \varphi}{RT} \right) \quad (12)$$

and

$$i = k \bar{c}_{\text{H}_2\text{A}}^\alpha \left(\frac{c_{\text{H}}^2}{c_{\text{H}}^2 + K_1 c_{\text{H}} + K_1 K_2} \right)^\alpha \exp \left(\frac{\beta F \varphi_r}{RT} \right) \quad (13)$$

and

$$i = k \bar{c}_{\text{H}_2\text{A}}^\alpha \frac{c_{\text{H}}^{2\alpha-\beta}}{(c_{\text{H}}^2 + K_1 c_{\text{H}} + K_1 K_2)^\alpha} \exp \left(\frac{\beta F \varphi}{RT} \right) \quad (14)$$

are obtained, when taking into consideration that

$$\varphi_r = \varphi - \frac{RT}{F} \ln c_{\text{H}}. \quad (15)$$

The mathematical analysis of equations (11)–(14) clearly shows that relationships (11) and (12) are not consistent even with respect to their tendency with experimental results. On the other hand, if the experimentally determined values of α and β are substituted into relationships (13) and (14), resp., the curves shown in Fig. 8 are obtained, the good agreement of which with Figs 6 and 7 is evident. The comparison of the ratios of the measured currents with

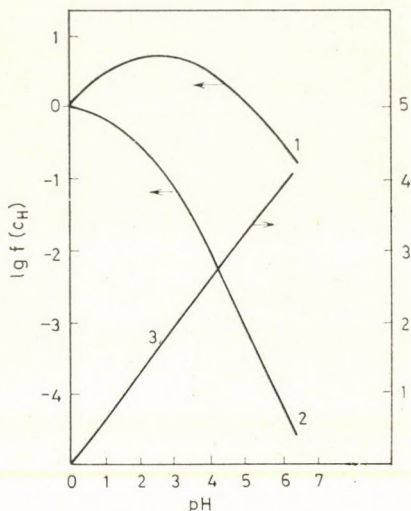


Fig. 8. Calculated values of various $f(c_H)$ functions at $\alpha = 0.65$, $\beta = 0.62$.

$$1: \frac{c_H^{2\alpha-\beta}}{c_H^2 + K_1 c_H + K_1 K_2}, \quad 2: \left(\frac{c_H^2}{c_H^2 + K_1 c_H + K_1 K_2} \right)^\alpha, \quad 3: c_H^{-\beta}$$

the calculated current ratios similarly reflects a good qualitative agreement. It should be noted that at $\text{pH} > 4.5$ values currents somewhat higher than calculated were observed. This can be attributed to the fact that a 5% difference in the α and β values results already a change of similar measure, but the phenomenon can be brought also in conjunction with the acidification of the solution in the immediate environment of the electrode, as assumed e.g. in the oxidation of formic acid [22].

Though used in equation (5), it has not been motivated that the dependence of the reaction on the potential can be described with the aid of φ_r , and not of φ . This means naturally no difference at constant hydrogen ion concentration, however, the system of equation (11)–(14) will be already fundamentally modified. Indeed, if φ stands in (5), the situation will be the very opposite, and the substitution of the concentration of the HC_2O_4^- ion into the kinetic equation will yield the favourable result, because now we have the relationships

$$i = k \bar{c}_{\text{H}_2\text{A}}^z \left(\frac{K_1 c_H}{c_H^2 + K_1 c_H + K_1 K_2} \right)^z \exp \left(\frac{\beta F \varphi}{RT} \right) \quad (16)$$

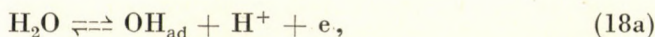
and

$$i = k \bar{c}_{\text{H}_2\text{A}}^z K_1 \frac{c_H^{\alpha+\beta}}{(c_H^2 + K_1 c_H + K_1 K_2)^z} \exp \left(\frac{\beta F \varphi_r}{RT} \right). \quad (17)$$

Equations (16) and (17) are not only with respect to their tendency, but virtually also numerically identical with relationships (13) and (14), if the experimentally

determined α and β values ($\alpha = 0.65$ and $\beta = 0.62$) are substituted. The apparent agreement that the pH value belonging to maximal HC_2O_4^- concentration, *i.e.* the location of the maximum of function (9) is at $c_{\text{H}} = \sqrt{K_1 K_2}$, which is in good approximation the same as the location of the extreme value of the function obtained experimentally, seems also to support the adsorption of the HC_2O_4^- ion.

Thus, let us investigate first the justification of the use of φ_r in the kinetic equation. Fundamentally, we can start here from the earlier observation, proved in a wide field, that in the oxidation of organic substances the dependence of current on potential can be described in an adequate way with the aid of φ_r [16, 23]. In this case, the $\lg i - \varphi_r$ polarization curves plotted at various pH values coincide. The situation is different in the case of oxalic acid, but the cause of this can be sought in first approximation in the dissociation of oxalic acid. Accepting thus the hypothesis [23], according to which in the rate-determining oxidation process proper the OH radical adsorbed at the surface (OH_{ad}) is the oxidizing agent in the steady state. This species may be formed in the following equilibrium processes:



Under consideration of the fact that the bonding energy of this adsorbed particle decreases with coverage, as follows from the theory of reactions [18] proceeding at inhomogenous surfaces, we can write:

$$i = k f(c) \exp\left(\frac{\beta\mu_{\text{OH}}}{RT}\right), \quad (19)$$

where $f(c)$ is some kind of concentration function relevant to the respective reacting molecule, and μ_{OH} is the chemical potential of the adsorbed OH radical. As the adsorbed OH radical is in equilibrium with the solution, it follows that

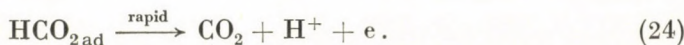
$$\mu_{\text{OH}} = \text{const.} + F\varphi_r. \quad (20)$$

Substituting (20) into (19), we have:

$$i = k f(c) \exp\left(\frac{\beta F\varphi_r}{RT}\right) \quad (21)$$

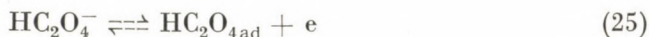
which is the same as equation (5), if the function established earlier is substituted for $f(c)$. However, since on the other hand, equation (5) agrees well with

the relationships found experimentally, in accordance with it the following scheme of mechanism can be accepted:



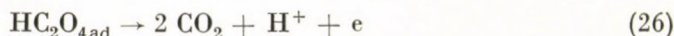
The reality of the adsorption equilibrium (22) is supported also by the fact that oxalic acid is adsorbed weakly and reversibly in the potential range investigated, as shown by HORÁNYI *et al.* [12–14] in tracer investigations. Naturally, the necessary but not sufficient condition of the acceptance of a scheme of mechanism is that kinetic equations following from it shall give a good description of experimental findings. However, it must be proved also that on the basis of another mechanism pattern no similar results are obtained. The analysis of JOHNSON and coworkers [5] can be taken as basis. They investigated a great number of possible mechanisms, and calculated under LANGMUIR's and TEMKIN's conditions the kinetic parameters. It can be established on the basis of this analysis on the one hand that there is no other pattern of mechanism which would yield adequate kinetic equations, and on the other hand that the introduction of φ_r in the way discussed above for the description of the potential dependence of the process is necessary, if undissociated oxalic acid is assumed to be the reacting species. (Negative results are obtained also, if further pre-equilibria or rate-determining processes, not investigated in Ref. [5], are taken into consideration.) However, JOHNSON *et al.* [5] did not take into consideration a mechanism, in which the HC_2O_4^- ion is the reacting species, having excluded its possibility on the basis of the pH-dependence. In this case it must be kept in view that the adsorption step is of necessity accompanied by charge transfer.

However, assuming in this case adsorption processes proceeding at an adequate rate, these should determine some kind of equilibrium potential. However, experimental experiences show that this is not the case. On the other hand, attention should be paid also to the results of adsorption investigations, according to which adsorption is weak and reversible, so that a radical conversion of the adsorbed molecule is improbable. Therefore, the existence of an adsorption equilibrium



is a priori questionable. However, on the basis of experimental findings Eq. (25) can not be the rate-determining step. For the further conversion of $\text{HC}_2\text{O}_{4\text{ad}}$

the following alternative possibilities can be taken into consideration:



and



If (26) is the rate-determining process, then the relationship

$$v_{26} = k c_{\text{HA}}^{\alpha} \exp \frac{(\alpha + \beta) F \varphi}{RT} \quad (28)$$

if (27), then the relationship

$$v_{27} = k c_{\text{HA}}^{2\alpha-1} c_{\text{H}}^{-1} \exp \frac{2\alpha F \varphi}{RT} \quad (29)$$

is obtained. It can be easily established that equations (28) and (29) are inconsistent with experimental results. It follows from the aforesaid that there is no scheme of mechanism, which would result relationships (16) and (17).

Taking all this into consideration, it is easy to see that the oxidation of oxalic acid on a platinum electrode is described by the same kinetical relationship, which was found valid in the case of numerous organic compounds, *i.e.* the dependence of current on the potential can be given with the aid of the relative potential. Contradictions in the literature in conjunction with the dependence of oxidation rate on pH can be resolved by taking into consideration the dissociation of oxalic acid. The essence of the scheme given for the mechanism of the process is the existence of an adsorption equilibrium with respect to the undissociated oxalic acid molecule, and the rate determining step is the reaction of the adsorbed oxalic acid molecule at the surface with the adsorbed OH radical.

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RECENSIONES

J. R. BLACKBOROW, D. YOUNG: *Metal Vapour Synthesis in Organometallic Chemistry*

Springer Verlag, Berlin—Heidelberg—New York, 1979, 202 pages

The book entitled "Metal Vapour Synthesis in Organometallic Chemistry", by J. R. BLACKBOROW and D. YOUNG, was published by Springer in 1979 as the ninth volume of the very valuable and up-to-date series "Reactivity, and Structure Concepts in Organic Chemistry". The work acquaints the reader with this new synthetic method; the description is made more comprehensible and vivid by 36 illustrations and 32 tables.

The aim of this book is to acquaint those interested in novel techniques of preparative chemistry with the fundamentals, technical particulars and fields of application of the new method of metal vapour synthesis, MVS.

The essence of MVS can be outlined as follows: "The use in synthesis of high temperature gaseous species such as metal atoms by their reaction with themselves or other materials in a condensed phase."

The literature on this subject, up to the first half of 1979, is systematically covered and listed at the end of the corresponding chapters. Examples chiefly from organic chemistry are quoted, i.e. reactions of metal atoms with various, principally organic substances are described in the course of the study of the syntheses and reactivity of organic and organometallic compounds.

According to the MVS method, atoms or molecules are excited to high reactivity in special ovens at temperatures above 1600 °C under highly reduced pressures (10^{-4} — 10^{-5} torr, i.e. $133 \cdot 10^{-4}$ or 10^{-5} Pa) and the highly reactive atoms or molecules are brought together with the chosen coreactants on a cold surface. The use of species such as atoms can provide synthetic advantage from both kinetic and thermodynamic considerations: in many cases syntheses become feasible which otherwise do not succeed, because of the relatively small reactive surface of the metal in the solid state, or an oxid layer covering the surface, or owing to a relatively high lattice energy, which prevents the reaction. It is supposed that the interaction between the high-energy particles and the reaction partner (substrate), always proceeds by several reaction steps *via* intermediary products, which cannot be isolated, to yield a final product that is stable and can be recovered under appropriate conditions. Where necessary, the book imparts some knowledge also about matrix-isolation-spectroscopy, MIS, used for the identification of special products.

After a short introduction which offers the fundamentals, and a brief criticism, of the preparative technique, the book is divided into three main parts dealing with the following subjects

- experimental techniques
- behaviour of metal atoms in matrices
- description of results of preparative experiments.

The last chapter summarizes recent results and progress in MVS; the latest commercially available MVS reactor is described and new results achieved in the field of transition metal compounds are presented.

This book is not encyclopaedical, yet briefly touches on every aspect of importance in the practical application of metal vapour techniques, thus experienced chemists and beginners may equally find useful information in the volume. It is of assistance for the practical work, the construction and operation of equipment, and for the production of new types and specimens of organometallic compounds.

The knowledge and application of MVS may become very important in the future, not only in research laboratories, but also in those where the industrial production of metal catalysts is studied.

J. NAGY

Recent Developments in the Chemistry of Natural Carbon Compounds, Vol. IX

Edited by R. BOGNÁR, V. BRUCKNER and Cs. SZÁNTAY

Akadémiai Kiadó, Budapest, Hungary, 1979, 420 pp.

The 9th volume of this renowned series contains three reviews in fields of current interest to natural products chemists; they are: "Synthetic Chemistry of Insect Pheromones and Juvenile Hormones" by K. MORI (Department of Agricultural Chemistry, University of Tokyo, Japan), consisting of 212 pages with 325 references; "Composition of Bulgarian Rose Flower Concrete. The Structure and Biogenesis of its Components" by B. STOIANOVA-IVANOVA (Department of Organic Chemistry, University of Sofia, Bulgaria), containing 82 pages with 141 references; "Chalcone Epoxides in Flavonoid Chemistry" by Gy. LITKEI (Institute of Organic Chemistry, Kossuth Lajos University, Debrecen, Hungary), comprising 114 pages with 346 references.

The report on the synthetic chemistry of insect pheromones and juvenile hormones is the most complete and useful of the recent reviews to organic chemists interested in this fascinating field. After a general introduction, Chapter II, entitled "Synthetic Methods Useful in Insect Chemistry", describes typical reactions and methods for the stereocontrolled synthesis of insect hormones and pheromones. The third chapter, "Synthesis of Insect Pheromones", provides a good review of the synthesis of each pheromone group. These groups are classified essentially by functional groups and are defined as follows:

- Pheromones with *E*-olefinic linkage,
- Pheromones with *Z*-olefinic linkage,
- Pheromones with conjugated diene system, *etc.*

Chapter IV, entitled "Synthesis of Insect Juvenile Hormones", describes the development of synthetic methods used in the synthesis of juvenile hormones and juvabione. This is followed by a brief summary of the practical use of insect pheromones and bioanalogs of juvenile hormone.

Reflecting Professor MORI's own interests, the topic most adequately treated in this book is the synthesis of juvenile hormones. Unfortunately, there is essentially no discussion of the mechanisms of even the most important reactions.

As a whole, the report provides an excellent overview of the structures and syntheses of these natural products. It will be of particular value to organic chemists, giving invaluable background material for all those interested in the isolation, structure determination, biological function, and practical use of insect pheromones and juvenile hormones.

The review on the composition of Bulgarian rose flower concrete gives a detailed account of the chemical components of Bulgarian rose flower and the biosynthesis of the long-chain compounds in the plant waxes. The chemical structures discussed include long-chain fatty acids, fatty alcohols, carbonyl compounds and diols, long-chain aliphatic lactones, and other cyclic compounds.

This part of the book is, to some extent, overextended and repetitive. However, it contains a mass of information often difficult to find in the chemical literature, which will be of great value to those specifically working in this field.

The third part of the book presents a comprehensive and up-to-date review on the role of chalcone epoxides in flavonoid chemistry. It is divided into three parts. The first is concerned with the oxidation of chalcones, rearrangement reactions of flavonoids and the structures of chalcone epoxides. The second is a short discussion of the chemistry of flavone- and aurone epoxides. In the last chapter the Algar—Flynn—Oyamada reaction is discussed and a new mechanism proposed.

This review is of great general interest to organic chemists, and particularly useful for researchers who are active in this branch of chemistry.

L. NOVÁK

INDEX

PHYSICAL AND INORGANIC CHEMISTRY

- The Role of Catalyst Surface and Structure of Molecules in Metal Catalysis, P. TÉTÉNYI. 237
Oxidation of Oxalic Acid on a Platinum Electrode, G. INZELT, É. SZETÉY 269

ORGANIC CHEMISTRY

- Cyclodextrin Complex of a Volatile Insecticide (DDVP), L. SZENTE, J. SZEJTLI 195
Carbohydrate Methyl Ethers, X. Hydrogenolysis of Benzylidene Acetals. Synthesis of mono- and di-*O*-Methyl Ethers of L-Arabinose, Z. SZURMAI, A. LIPTÁK, J. HARANGI, P. NÁNÁSI 213
Synthesis of Peptides Containing D-Glucosaminic Acid, II. Synthesis of some Tri- and Hexapeptides, K. GÁLL-ISTÓK, E. ZÁRA-KACZIÁN, L. KISFALUDY, GY. DEÁK .. 221
Cyclodextrin Inclusion Complexes of 2-Chloroethyl Phosphonic Acid, Zs. BUDAI, J. SZEJTLI 231
Dealkylation Side Reaction in the Synthesis of Cholesteryl Carbonates and Carbamates, P. M. ACÓCS 263

ANALYTICAL CHEMISTRY

- Thermochemical Aspects of Anion-Exchange Reactions, III. Calorimetric and Equilibrium Studies of Anion Exchange Reactions Involving Organic Ions, A. MARTON, T. PAP, J. INCZÉDY 203
RECENSIONES 285

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GYŐZŐ (VICTOR) BRUCKNER

(1900–1980)

On March 8, 1980, academician Győző (Victor) BRUCKNER, professor and former head of Department of Organic Chemistry of the Eötvös Loránd University, Budapest, the late leader of the Research Group for Peptide Chemistry of the Hungarian Academy of Sciences within this Department, died unexpectedly in the eightieth year of his life. By his death Hungarian natural science lost a most brilliant scientist and one of its greatest personalities in organic chemistry.

Győző BRUCKNER was born in Késmárk, on the first of November, 1900. He comes from a family of the teaching profession, his father was over a quarter of a century headmaster of the Lyceum of Késmárk, where BRUCKNER completed his secondary school studies with top marks. The 450 years old lyceum gave many renowned people to the country, and BRUCKNER always looked back with respect and fondness to the school, in the statutes of which, subsisting from 1703, the following paragraph can be read: "Students coming of various countries and families shall live in fraternal love, none of them shall scorn or revile the other, because he belongs to another nation." This spirit of humanity gave a life-long teaching and guidance also to BRUCKNER.

He pursued his studies at the Faculty of Chemical Engineering of the Technical University of Budapest and at the Faculty of Mathematics and Natural Sciences of the University of Szeged. In 1925 he was granted a chemical engineering diploma of eminent qualification, and in 1928 he obtained a "sub auspiciis Gubernatoris" degree of Ph. D. with chemistry as the major subject. The theme of his dissertation was from the field of inorganic or rather physical chemistry, concerning the neutral salt-effect in the reaction of potassium persulfate with potassium iodide [1, 2], and this remained his only scientific work whose subject was not in the field of organic chemistry.

Two factors had decisive role in the selection of his domain of science: in 1926 he joined the staff of the Institute of Organic and Pharmaceutical Chemistry of the University Szeged, working under Tibor SZÉKI, and in the academic year 1927–28 he worked as holder of a Hungarian state scholarship in the Institute of Organic Chemistry of the Technical University Berlin-

Charlottenburg under the leadership of Prof. A. SCHÖNBERG. The friendly atmosphere of cooperation in Szeged and the pulsating scientific life in Berlin committed him for good to organic chemical research and university teaching. With full devotion and great energy he set about the building of new university institutes in Szeged, started the equipping of the laboratories; the setting up of a creative workshop, the possible scene of the realization of his dreams, filled him with enthusiasm.

Important dates of his university career are the following. After his years as assistant, he was qualified in 1933 for honorary lecturer by the University of Szeged in the theme "Methodology of Organic Chemistry", and in 1938 he was appointed assistant professor to Albert SZENT-GYÖRGYI, in recognition of his scientific work and educational activity. In 1941 he was appointed university professor and at the same time Head of Department of the Institute of Organic Chemistry. In 1951 he was invited by the Eötvös Loránd University of Budapest as Head of Department for Organic Chemistry, and he remained the leader of this Department for twenty years. It is rather natural that during the decades of his teaching work he also plentifully did his share in the leading of the university. In Szeged, BRUCKNER was dean, and in Budapest he usefully functioned as member of the University Council and several boards. As a recognition of his teaching, educational and scientific work, the Eötvös Loránd University conferred on him a honorary doctor's degree, and on his retirement he received the Eötvös Loránd commemorative medal.

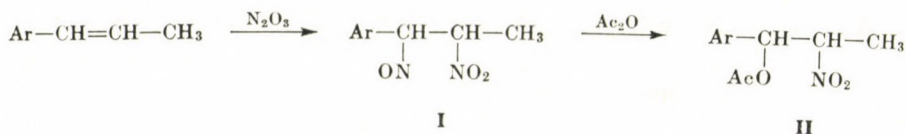
In 1946 Győző BRUCKNER was elected a corresponding member and three years later an ordinary member of the Hungarian Academy of Sciences. From 1950 on, up to his retirement, he was chairman of the Board of Organic Chemistry of the Academy, and he served on all the boards which played a part in the coordination, organization and guidance of organic and pharmaceutical chemistry. Until his death he was member of the Directorial Board of the Central Research Institute for Chemistry of the Hungarian Academy of Sciences and of the Directorial Board of the Pharmaceutical Research Institute. In recognition of his successful work in the development of pharmaceutical industry and pharmaceutical sciences, in December 1972 the Hungarian Pharmaceutical Society conferred on BRUCKNER the Gedeon Richter commemorative medal.

His scientific merits were held in high esteem both in foreign countries and by the Hungarian government, as testified by the Scheele medal of the Chemical Society of Stockholm (1947), two National (Kossuth) Prizes (1949 and 1955), the Order of Labour (1963) and the gold grade of the Order of Labour, awarded on his seventieth birthday (1970). In 1967 he was elected member of the Deutsche Akademie der Naturforscher Leopoldina (Halle).

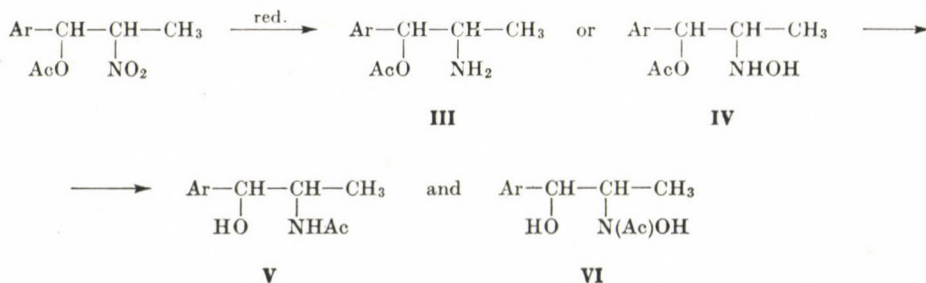
The year of scholarship in Berlin became one of the determinant stations of his scientific work. He published the results of his work in the journal

Berichte, and this paper, dealing with the conversions of thioethers on heating, became his first communication on an organic chemical subject [3]. The period in 1929 in the Institute of Medical Chemistry of the University of Graz, under the leadership of the Nobel Prize winner PREGL, was of similar importance. It was completely dedicated to the study and mastery of microanalysis, revolutionizing organic elementary analysis. The months in Graz resulted not only in a scientific contribution [5], but BRUCKNER also brought the methods back to Hungary and introduced them in our country, founding a microanalytical school in Szeged. Directly or indirectly, all Hungarian organic microanalysts acquired the knowledge of this modern technique, the principles of which did not change up to the present, on the basis of the laboratory experiences of the BRUCKNER school. The first microanalytical balance of the University of Budapest, the old "swinging" Kuhlmann, which was still in use at the beginning of the fifties, is even today a treasured relic at the Department of Organic Chemistry of the Eötvös Loránd University of Budapest.

The first truly important independent research result of Győző BRUCKNER was the recognition of the reversible *N-O* acyl migration in α -aryl- β -amino- and β -hydroxyamino-propanols. Similarly to every major work, this too had its antecedents. In the early thirties, in SZÉKI's institute in Szeged, BRUCKNER prepared the pseudonitrosites (I) of phenol ethers containing propenyl side-chain (asaron, methylisoeugenol, isosafrole) [6, 7, 8], which could be converted with acetic anhydride into the respective α -acetoxy- β -nitro derivatives (II):



Independently of the fact that asaron pseudonitrosite offered a possibility for the study of interesting isomeric conditions, the successful reduction of the acetoxy-nitro derivatives led to amino alcohols with potential biological action, similar to that of adrenaline. The reduction was performed by electrolysis [8, 14], during which it was found that, depending on the nature of the



cathode, amino or hydroxylamino derivatives may be formed [27, 38]. However, when the reaction mixture was made alkaline, not the amino or the hydroxylamino compound (**III** or **IV**) was isolated, but their acylated derivatives (**V** and **VI**); evidently an $O \rightarrow N$ acyl migration took place during the reaction in the presence of alkali.

The fact of acyl migration could be proved among others by the condensation of the *N*-acetyl compound with phosphorus oxychloride into a compound with isoquinoline skeleton (**VII**). This reaction is all the more worth mentioning as it became the starting point of the isoquinoline research of Győző BRUCKNER, to be discussed later in detail. The reaction proving the structure of the starting compound is shown in Fig. 1.

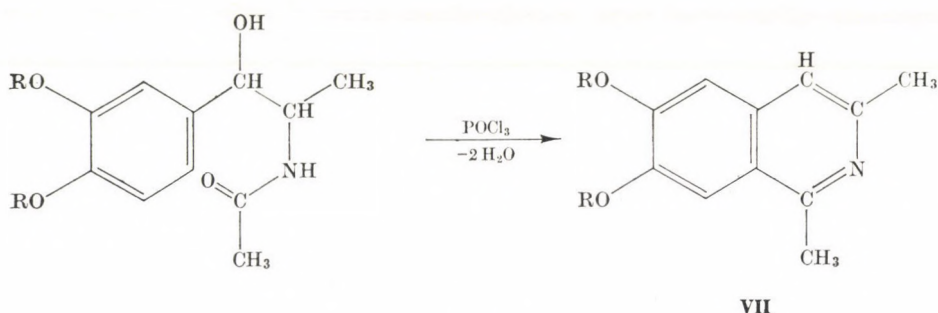
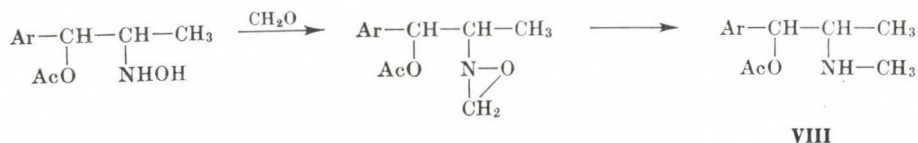


Fig. 1

The reversibility of acyl migration was equally readily proved. From a solution of the *N*-acetyl compound in hydrochloric acid a crystalline compound could be isolated, which gave the reactions of free amino groups, and could not be condensed into isoquinoline [8, 14]. It should be mentioned that this was the first time to observe acyl migration in the case of hydroxylamine derivatives.

Though the acyl migration reaction is a very rapid process, conditions could be found under which the *O*-acetyl group remained intact while the hydroxylamino group underwent a condensation reaction with an aldehyde. Reduction of the resulting product gave ephedrine derivatives (**VIII**) (the respective *N*-methyl compounds) [12, 13, 16].



BRUCKNER later proved that the migration in the $O \rightarrow N$ direction was always more rapid, than in the opposite direction and, though more slowly,

it also proceeded with acyl groups other than acetyl [29], offering thereby possibility for the preparation of other isoquinoline derivatives. Finally, not only acyloxy but alkoxy derivatives could be prepared from pseudonitrosites [9] for a study of their reactivity [10].

Investigations on the reversible *O-N* acyl migration were instrumental in the recognition of the very important fact that the process is strongly influenced by the steric structure of the molecule. BRUCKNER's pupils utilized this finding later in the solving of various problems, such as the elucidation of the steric structures of alkaloids with tropane skeleton or of chloramphenicol. It became evident during this work that stereochemical aspects have a far greater importance in organic chemical research than recognized previously.

The intramolecular condensation, proving the fact of *O* → *N* acyl migration, was an entirely new synthesis of isoquinoline, promising considerably better yields than the processes developed by SPÁTH *et al.*, or PICTET and GAMS. Since the pharmaceutical industry was keenly interested in isoquinolines with spasmolytic effect (*e.g.* papaverine), the subsequent experiments are now to be considered important from the practical point of view, in addition to their scientific interest.

The synthesis of 3-methylisoquinolines from isosafrole was developed in 1935–37 by BRUCKNER and KRÁMLI [15, 22]. The *N*-acetylamino compound (IX) obtained *via* the pseudonitrosite was converted in the way described into the *O*-acetyl compound, from which the acetyl group could be readily removed. The free amino group was then acylated with the optional acyl chloride *e.g.* with homoveratroyl chloride (X) and the product was condensed to an isoquinoline (XII) having spasmolytic effect. The final steps are shown in Fig. 2.

The advantages of the new synthesis, later further improved from the technical aspect, can be summarized as follows [25]. Ring closure yields in a single step directly the isoquinoline skeleton, so that palladium-catalyzed dehydrogenation, earlier unavoidable, is not necessary. The starting material of the synthesis of the acyl derivative, the arylpropanolamine (XI) need not be isolated; it can be prepared and used in the form of its stable *N*-acetyl derivative, which is directly made to react with the appropriate acid chloride. Finally, the starting phenol ethers containing propenyl side chain are relatively cheap and readily available compounds.

It should be mentioned that it has been proved later by BRUCKNER *et al.* by means of oxidative degradation that the ring closure with phosphorus oxychloride actually occurred in *m, p*-position with respect to the alkoxy group, thus, in the synthesis starting from methylisoeugenol the 6,7-dimethoxy derivative (XIII) is formed [37, 39, 44, 45]. This experimental series was needed, because synthetic work by PFEIFFER *et al.* during the structural analysis of brazilin erroneously indicated the other direction of ring closure, the formation of 7,8-dimethoxyisoquinoline (XIV) (Fig. 3).

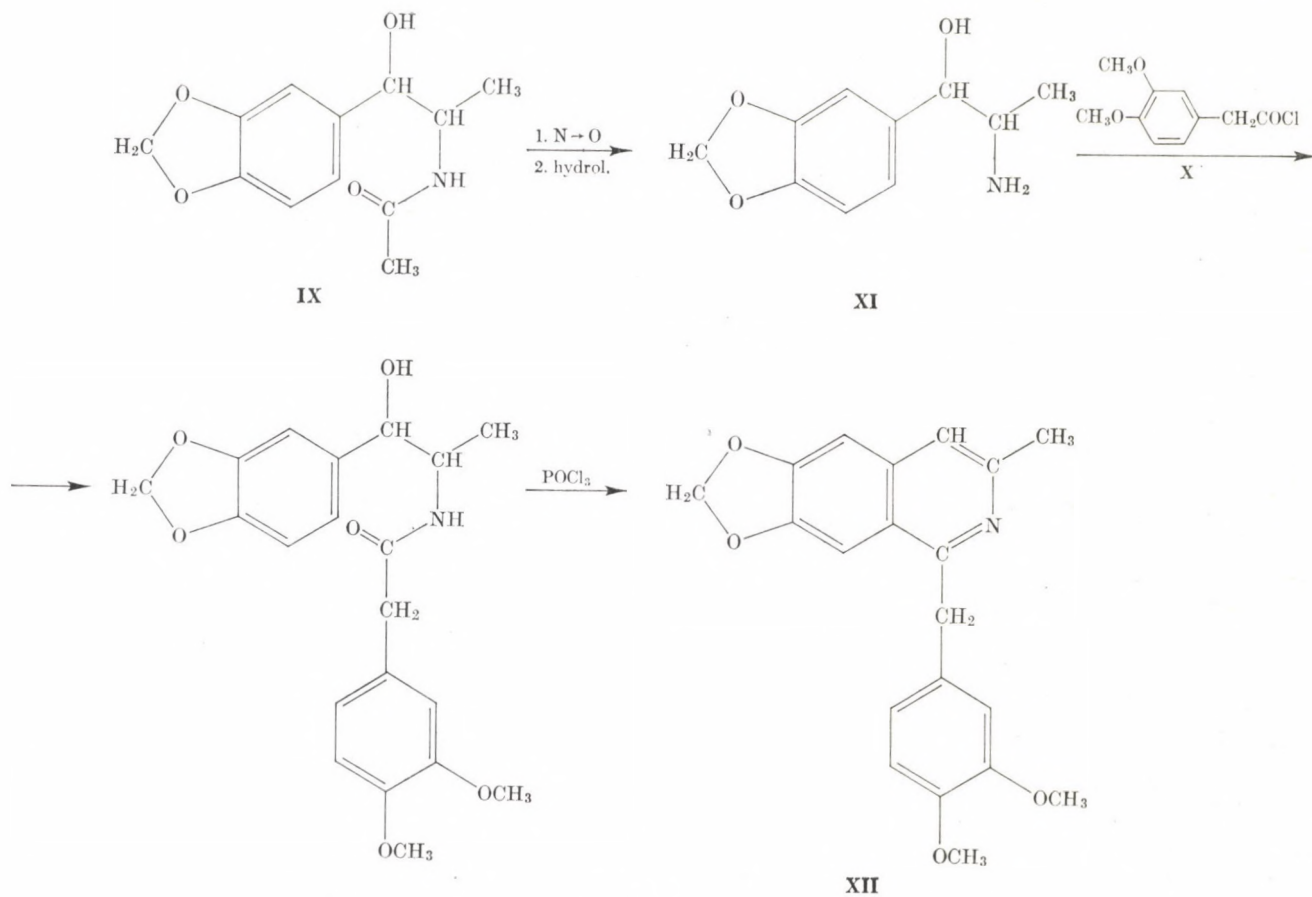


Fig. 2

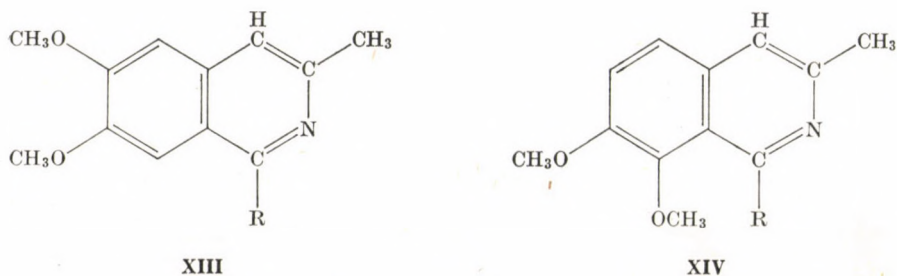


Fig. 3

It is worth mentioning that during the experiments conducted for years, several 3-methylisoquinolines were prepared which had higher activity than papaverine [41].

The chemistry of propenyl phenol ethers runs through the research years of Győző BRUCKNER during the war and the early postwar period. These reactive compounds made possible valuable observations of general validity in several interesting new fields of organic chemistry. Like in all topical fields, the researcher was also here in constant competition with foreign groups, and it happened time and again that a publication in a foreign journal gave new impetus to research. It is easy to understand that during the war-years the quantity of scientific information coming from foreign countries considerably decreased, and the researchers heard of foreign results often only from overdue numbers of *Chemisches Zentralblatt*, with a delay of years.

This applied also to the new research project of BRUCKNER, begun in 1941, concerning the possible adaptation of diene synthesis to aromatic systems. It was apparent that aromatic systems would reveal a reactive diene character only if this is ensured by a particular structure formed by linear anellation, an example being the characteristic addition reactions occurring at the carbon atoms in the μ -position of anthracene. Otherwise the double bonds of an aromatic system can only be induced to addition reaction with the philodiene maleic anhydride if only one of the double bonds of the diene is found in the aromatic system, while the other is located in a substituent of the ring, in conjugation with the aromatic system. An example for this is the addition reaction of 9-vinylphenanthrene and maleic anhydride, though it is known that the double bond in position 9,10 often behaves as a simple olefinic bond. Styrene itself reacts rather by heteropolymerization with maleic anhydride.

HUDSON and ROBINSON published in 1941, BRUCKNER in 1942 [33] their first work on the reactivity of propenylphenol ethers in diene synthesis. The proneness to polymerization of ω -alkyl styrenes is reduced, and alkoxy substituents increase the reactivity of the aromatic ring. Thus, methylisoeugenol (XV) (named in the paper isohomogenol) readily added to maleic anhydride, and the intermediate product achieved stabilization by rearomatization (Fig. 4).

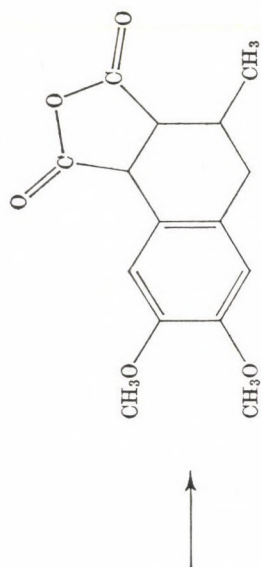
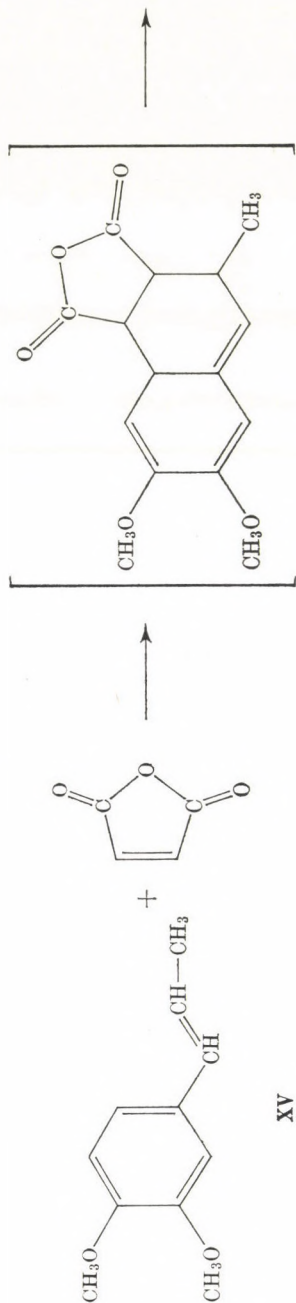
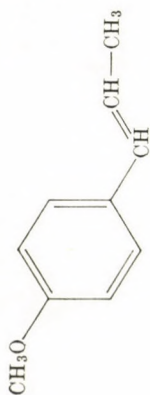
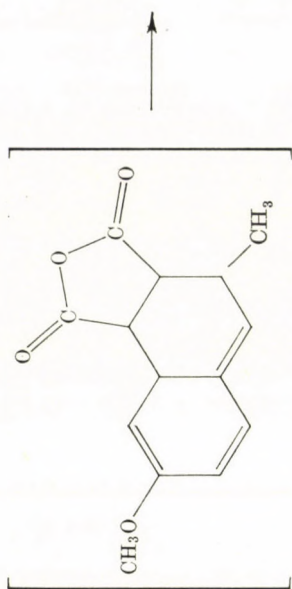


Fig. 4



XVI

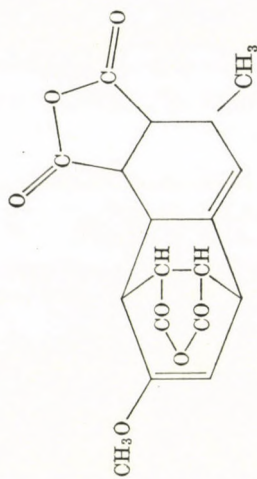


Fig. 5



It should be mentioned that during these experiments BRUCKNER succeeded in isolating also the dimer of isohomogol from the reaction mixture; elucidation of the structure of this compound by degradation, proving the tetraline basic skeleton of the dimer, was published by Sándor MÜLLER *et al.* in that very year.

While in the case of isohomogol (and isosafrole) the experiments yielded the same results as described by HUDSON and ROBINSON, Győző BRUCKNER, together with József KOVÁCS, effected also the addition reaction of anethole (XVI) elicitable with maleic anhydride, where the English authors did not succeed [40, 43, 47, 48, 52]. In this case the intermediate adduct formed was not stabilized by aromatization, but by the addition of a second molecule of maleic anhydride (Fig. 5).

By means of various chemical reactions, which cannot be discussed here in detail, the steric structure of the compound could also be proved; accordingly, the molecule can be pictured as shown in Fig. 6.

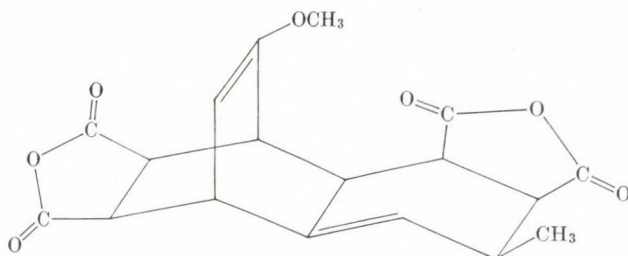


Fig. 6

The experiences gained in the diene syntheses with propenylphenol ethers could be utilized in further two cases for the explanation of reaction mechanisms misinterpreted in the literature; one of them was the reaction of 1,2-diarylethylenes [54], the other that of benzalazine [51] with maleic anhydride.

Undoubtedly, the scientific career of Győző BRUCKNER was highlighted by his researches on native polyglutamic acids. It falls to the share of few chemists to recognize a unique group of compounds, to isolate its individual members in the pure state, to elucidate their structure and to prove the structures by total synthesis. Concurrently with this series of experiments, BRUCKNER could also manage to confront views of foreign researchers who disputed the correctness of the structure elucidation and to prevail in the dispute. The synthesis of native polyglutamic acids is of far greater importance than just another scientific achievement: this work laid the foundations of Hungarian peptide chemical research, continuously developing from the beginning of the fifties, primarily under the leadership of Győző BRUCKNER, soon to gain international renown.

The isolation of native polyglutamic acid was undertaken still in the Institute of Organic and Pharmaceutical Chemistry of the University of Sze-

ged, in collaboration with microbiologist Prof. György IVÁNOVICS. IVÁNOVICS and BRUCKNER [21, 23, 23a, 32] were the first to recover pure polyglutamic acid from the capsular substance of virulent *Bacillus anthracis* and from the culture medium of the serologically related *Bacillus subtilis* (earlier *Bac. mesentericus*), and it did not take long to discover that this was a substance of partial antigenic (hapten) character, responsible for the serological relationship. The compound possessed unique properties unknown up to then; it was found to be a polypeptide, though it did not give the biuret reaction characteristic of polypeptides; it yielded a single amino acid, glutamic acid, on hydrolysis with hydrochloric acid, showing that the compound was a 'monotone polypeptide'. Even more interesting was the fact that the peptide isolated from the capsular substance (anthrax polypeptide) consisted exclusively of D(-)-glutamic acid, *i.e.* the configuration was opposite to that of amino acids present in proteins. Such an occurrence was unknown in nature up to that time. The polymer isolated from the culture medium (*subtilis* polypeptide) contained, besides D(-)-glutamic acid, more or less of the L-modification. The molecular weights of the products were found, by the van SLYKE amino-terminal determination, to be 6400—7100. Later it became evident that a substantially higher molecular weight was also possible, because under the conditions of the determination a time-dependent degradation, and hence a decrease in molecular weight could occur. It is remarkable that in their first communication

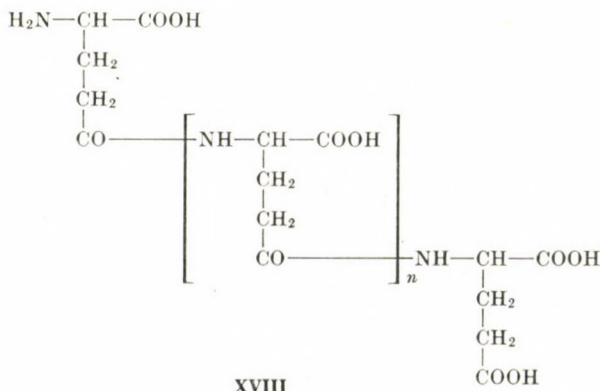
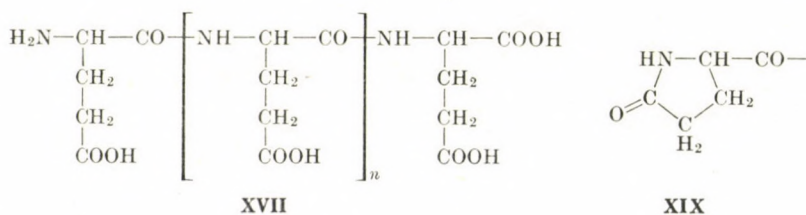


Fig. 7

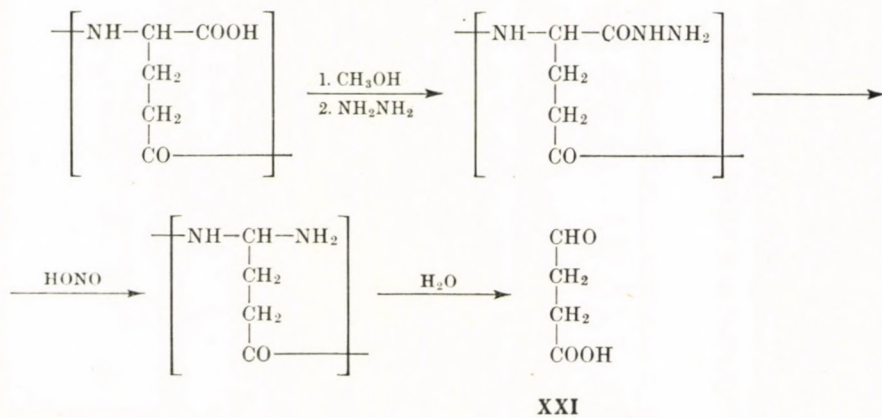
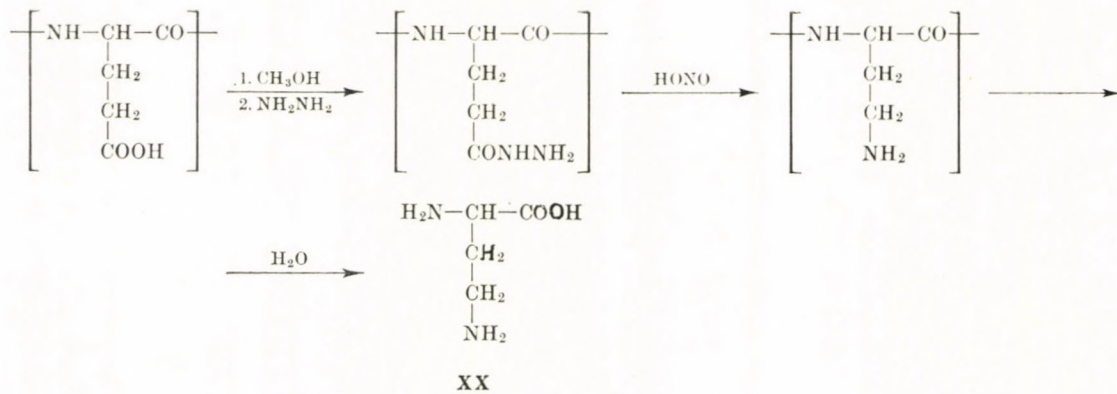
the authors mention among the possible structural elements, besides the α -bonding systems (XVII), the unusual γ -glutamyl bond (XVIII) and, on the basis of equilibrium weight measurements, even a possible pyrrolidone ring (XIX) closure.

The linkage through both carboxyl groups, and thereby the formation of branchings was excluded by the measurement of the flow birefringence of the polyglutamic acid solution [35].

During the war-years research work in conjunction with the structural analysis of native polyglutamic acids was suspended. However, in 1950 BRUCKNER, together with József KOVÁCS, started intensive research at the Institute of Organic Chemistry of the University of Budapest, motivated by views published in foreign countries between 1946 and 1950, according to which native polyglutamic acids are basically built up with α -glutamyl bonds. Since this improperly founded view was inconsistent with several observations (serological behaviour, negative biuret reaction), instead of speculation KOVÁCS and BRUCKNER took recourse to the methods of classical structural analysis, and effected the chemical degradation of polyglutamic acid [55, 56]. Starting with polyglutamic acid obtained from a *Bacillus subtilis* culture, they prepared the polymethyl ester, then the hydrazide; on subjecting this substance to Curtius' degradation followed by total hydrolysis, only β -formylpropionic acid (XXI) could be isolated; α,γ -diaminobutyric acid (XX), resulting from any possible α -glutamyl bonds was not even detected. The formation of the characteristic degradation products from the two kinds of glutamyl bonds is illustrated by the scheme shown on the opposite page.

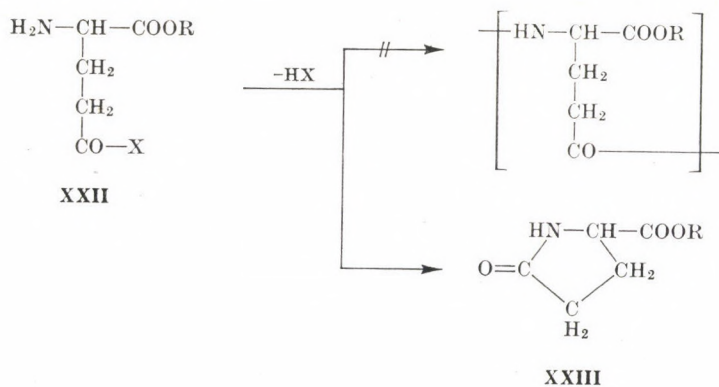
As a control experiment, α -polyglutamic acid was synthesized and its degradation performed. Here exclusively the expected α,γ -diaminobutyric acid was formed [57, 58, 66]. Repetition of the experiments by the Hofmann degradation of the respective amides [59, 61] supported the earlier finding, according to which *subtilis*-polypeptide is built up predominantly, but probably exclusively of γ -glutamyl parts. For the sake of completeness, degradation was performed also on anthrax-polypeptide, with similar results [65, 80].

Chemical synthesis is the most suitable way of proving the correctness of structural analysis. However, at the beginning of the fifties peptide chemistry was still in its infancy; for the preparation of γ -glutamyl peptides there was a sole example, the synthesis of glutathione. BRUCKNER and co-workers devised therefore a systematic series of experiments in which the preparation of α -polyglutamic acid was followed first by the synthesis of γ -polyglutamic acid of the L-series [71, 75, 79]; then, in succession the syntheses of γ -poly-D-glutamic acid [81, 87], of γ -polyglutamic acid containing alternately L- and D-glutamic acids [85] and of polyglutamic acid containing alternately α - and γ -bonds [74, 83, 84, 86] were achieved. The detailed summarizing communication on the total synthesis of the immunospecific haptens of the bacillus group anthrax-



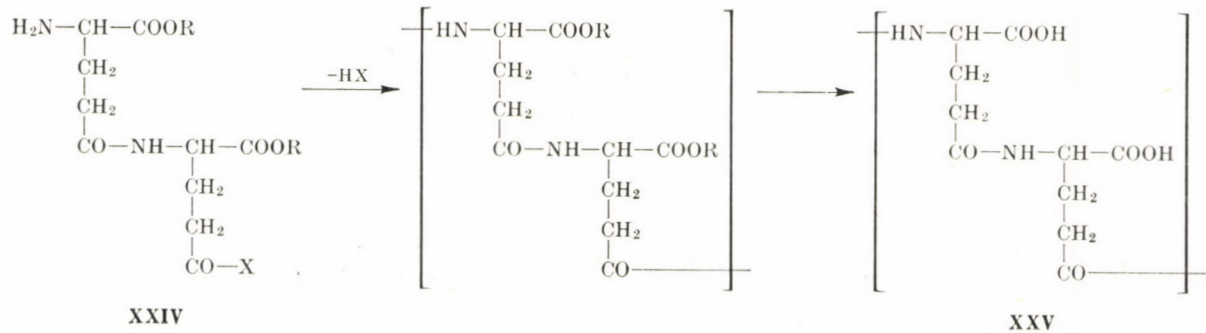
subtilis was published in 1958 [87]. Finally, much later, keeping abreast of the development of peptide-chemical methods, BRUCKNER and KAJTÁR published in 1968 an improved synthesis, which was suitable for the preparation of the polymer of high molecular weight also on the preparative scale [111]. A detailed analysis of these syntheses is not possible here; it is sufficient to describe the general principles and to mention the main methods used.

Evidently, a feasible way of building up the macromolecule is the polymerization of a suitably selected monomer. Regrettably, γ -polyglutamic acid can not be prepared from a glutamic acid derivative (XXII) containing an activated carboxyl group and a free amino group which can be acylated, because owing to the favourable steric conditions, in this case a pyrrolidone-carboxylic acid derivative (XXIII) is formed:



Thus, the molecule of minimal dimension suitable for polymerization, is a dipeptide with a free amino group, containing a γ -bond, adequately protected at the α -carboxyl groups and activated at the terminal γ -carboxyl group; this was called by BRUCKNER briefly the "startdipeptide". Under suitable conditions, a compound of this kind (XXIV) can be induced to polymerization to yield, after the removal of the protecting groups, γ -polyglutamic acid (XXV).

The methods of synthesis developed differed only with respect to the activation and the selection of the protective group R. Activation, and thus the polyacylation reaction, could be accomplished by the mixed anhydride, dicyclohexylcarbodiimide, thiophenyl activated ester methods, while methyl, benzyl and later *t*-butyl esters were selected for the protection of the carboxyl group. The serological identity of γ -poly-D-glutamic acid and the native polyglutamic acids was proved by IVÁNOVICS in [87]. Herewith, the successful Hungarian research work, followed all along with world-wide interest, was terminated. The results became examples in textbooks, and chapters in monographs [102].

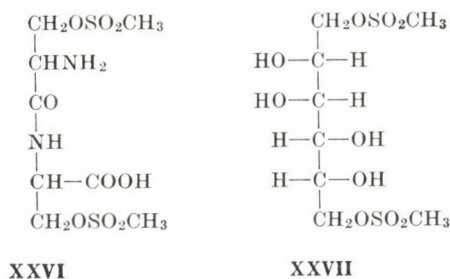


XXIV

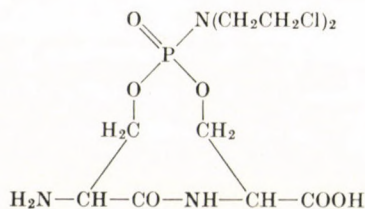
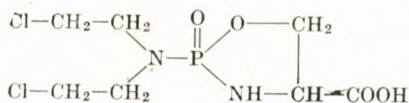
XXV

It is only natural that in the course of such a substantial work a whole generation of researchers grew up, and many scientific observations of major or minor importance were disclosed, so to say as by-products. Thus, BRUCKNER and co-workers were the first to describe the intramolecular transpeptidation of glutamic acid peptides [69, 73, 77, 93], a new method for the determination of the type of glutamyl bonds [90], the extension of experiences gained with polyglutamic acid to aspartic acid derivatives [70, 78, 88], and they studied the possible secondary structures of these compounds [109].

Research work carried out by BRUCKNER in collaboration with Maria SZEKERKE for the preparation of amino acid and peptide derivatives with cytoactive groups should be mentioned among the peptide chemical works. The control of cancer by chemotherapy belonged to the great possibilities of the fifties, and in that period the syntheses of several cytostatics were developed, many of which are efficiently used even today. However, all these compounds have the common disadvantage that they inhibit the growth of the healthy cells also. This toxic property can be mitigated to a certain extent, if the carrier of the reactive group (*e.g.* β -chloroethylamino-, bis- β -chloroethylamino, mesyl-, diazoacetyl-) is a compound, which is a component of the living organism, and thus not a completely extraneous substance. A few cytostatics containing amino acids were known already in 1960, and BRUCKNER and SZEKERKE [101] prepared the *O,O'*-dimesyl derivative of the dipeptide seryl-serine (XXVI), starting from the consideration that the relative position of the two mesyl groups in this compound is the same as in the cytostatic mannitol derivative (XXVII), already known at that time:



Though *O,O'*-dimesyl-seryl-serine did not prove to be an active substance, the introduction of other reactive groups resulted in efficient cytostatics. Thus, cyclic phosphoric acid ester derivatives, obtained from serine, seryl-serine and even polyserine with *N,N*-bis-(β -chloroethyl)phosphoric acid amide dichloride are all cytoactive substances with a high therapeutical index [103, 105]. Of these, the derivatives formed from the amino acid and the dipeptide are shown:



The experiments were extended also to other amino acids, thus the respective cyclic derivatives of β -phenylserine, β -hydroxyglutamic acid, cysteine and lysine have also been prepared. Biological tests were carried out in the Pathological and Experimental Cancer Research Institute of the Medical University, Budapest (Prof. J. BALÓ) and, in international cooperation, in the Chester Beatty Institute, London (Prof. A. HADDOW).

The top of peptide-chemical research, the last great work in research organization and experimental programme devised by the creator of Hungarian peptide chemistry, was undoubtedly the synthesis of the adrenocorticotrophic hormone. In this project BRUCKNER was no longer obliged to participate actively in the experiments, because by that time a generation of chemists had grown up under his tuition, who could be entrusted with the elaboration of the details of the immense synthetic work. His role was the coordination of the research groups performing the syntheses, the planning of the strategy how to build up this polypeptide consisting of 39 amino acids, and to keep constantly track of the progress of the synthesis. Work-meetings held periodically offered excellent occasions to discuss how to avoid numerous difficulties encountered in the course of this work, and to select the promising ways. His great experience in experimental work, his profound knowledge of theoretical organic chemistry and his stereochemical intuition became public property during these discussions, considerably facilitating the task of his co-workers doing the actual synthesis.

The project on the synthesis of the adrenocorticotrophic hormone was launched in 1959 as a coordinated joint work of the researchers of the Pharmaceutical Research Institute (Sándor BAJUSZ), the Chemical Works Gedeon Richter Ltd. (Lajos KISFALUDY) and of the Department of Organic Chemistry of the Eötvös Loránd University (Kálmán MEDZIHRADESKY). The aim set was the building up of the *N*-terminal fragment containing 28 amino acids of the hormone of porcine origin. At that time it was already known that this fragment was the carrier of the biological activity, so the synthesis of the complete hormone was not necessary.

The motivation of this synthesis was not purely theoretical; the pharmaceutical industry needed a corticotropin for the substitution of natural preparations, which are often contaminated by harmful proteins. The three research groups, dividing the sequence under the leadership of BRUCKNER completed

Ser-Tyr-Ser-Met-Glu-His-Phe-Arg-Trp-Gly-Lys-Pro-Val-
 -Gly-Lys-Lys-Arg-Arg-Pro-Val-Lys-Val-Tyr-Pro-Asp-Gly-
 -Ala-Glu-Asp-Gln-Leu-Ala-Glu-Ala-Phe-Pro-Leu-Glu-Phe

Fig. 8. The complete sequence of porcine ACTH (1959)

the synthesis of the fragments within two years, and reported the result in 1961 on the peptide symposium in Moscow. As it was important to elaborate a patentable process, these results were published [98, 99, 100] only after the filing of the applications. The three fragments suitable for further coupling were the following:

Z-Ser-Tyr-Ser-Met-Glu-His-Phe-Arg-Trp-N₂H₃;

Z-Gly-Lys(Tos)-Pro-Val-Gly-Lys(Tos)-Lys(Tos)-Arg-Arg-Pro-Val-Lys(Tos)-OH;

H-Val-Tyr-Pro-Asp-Gly-Ala-Glu-OH.

The research groups soon achieved the coupling reactions. Removal of the protecting groups gave the desired fragment consisting of 28 members. At that time this was the polypeptide with the largest number of members built up by synthesis, containing 14 different protein component amino acids. However, it soon became evident that in its original form the process was unsuitable for industrial production. Therefore, in 1962 the development of a new synthesis, using other protecting groups, was started. As the synthesis of the total molecule of porcine ACTH was described meanwhile by SCHWYZER, the new aim of the Hungarian researchers was the synthesis of the hormone of human origin. The prestige and mediation of Győző BRUCKNER were instrumental in completing this synthesis in 1966. In recognition of their accomplishment, the leaders of the research groups were awarded the National Prize in 1970.

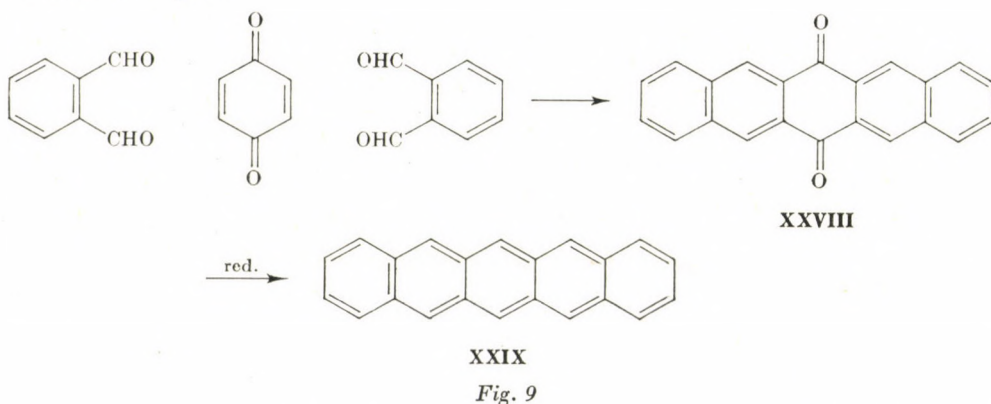
The selection of his research topics is characteristic of the wide scientific interest of Győző BRUCKNER. He virtually could not resist a scientific problem encountered, and attempted to answer any challenge with systematic experimental work of the greatest thoroughness. This is the reason why he has also a number of papers which are not related to one another; he dealt with several problems which turned out to offer no possibility of further development, hence he abandoned them after a brief investigation. As an illustration of BRUCKNER's versatility, it is worth to mention some of these research topics.

Investigations together with Tibor SZÉKI for the determination of the composition of the essential oil of *Asarum europaeum* [4] was actually an introduction to the later research work of great value on phenol ethers containing propenyl side chain. The arduous experimental work carried out at the beginning of the thirties might perhaps provoke a smile of a chemist in the age of gas chromatography and the mass spectrometer, yet the careful separation

and characterization of the products, the meticulous consideration of each established fact will ever remain an example to be followed by organic chemists and analysts.

The interest of BRUCKNER in natural products was revealed by his masterfully organized special courses, but he was also active researcher of the field; the identification of citrin, the crystalline flavone isolated from lemon juice [19] and of betulinic acid obtained from platan (*Platanus acerifolia*) bark [42] are gems of his scientific activity.

His thorough knowledge and excellent grasp of the literature helped him in several cases to achieve remarkable and surprising synthetic innovations. One of the best examples of this is the elaboration of a novel mode of preparation of pentacene [94, 95, 96]. Though the synthesis of the molecule, consisting of five linearly condensed benzene rings, had been described in 1953 by American authors, only about 50 mg of the hydrocarbon could be prepared in one batch. BRUCKNER and co-workers reduced the known compound pentacene-6,13-quinone (XXVIII) with aluminium cyclohexylate, to obtain 23 g of pentacene (XXIX) from the quinone, in a single step. The complete synthesis is shown in Fig. 9.



A series of experiments aimed at the stereoselective synthesis of quinic acid and its dehydrated derivative, shikimic acid, is also connected with the chemistry of natural organic compounds. According to assumptions, both acids are the products of carbohydrate metabolism, and are formed from sedoheptulose-7-phosphate. A synthesis starting from a sugar (the configuration of arabinose corresponds to that of these natural carboxylic acids) seemed to be a fine proof of the genetic derivation from sugars. According to the synthetic plan, the protected cyclohexane dicarboxylic acid derivative (XXXI) was to be prepared from D-arabitol (XXX) through the respective dihalogen or ditosyl compound, from which expectedly quinic acid (XXXII) and shikimic acid (XXXIII) can be easily prepared.

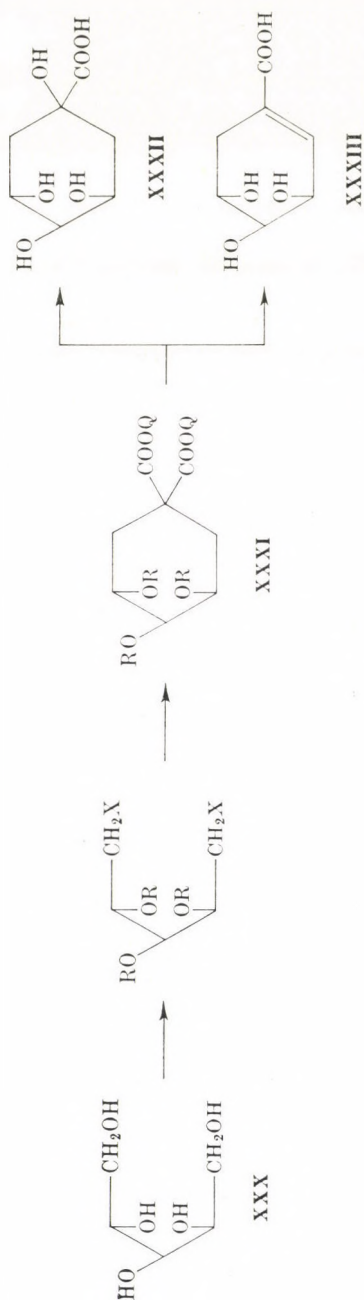


Fig. 10

The first derivatives were obtained in 1962 [104], then, after much difficulty, the dicarboxylic acid ester **XXXI**, the seminitrile [108], and a series of other arabitol derivatives were prepared [100, 116, 117]. Finally, the work in collaboration with János Császár was successful; 2,3,4-D-*arabo*-trimethoxy-5-tosyloxypentylcyanoacetic acid methyl ester (**XXXIV**), obtained from D-arabinose, could be converted into the respective cyclohexane derivative (**XXXV**), which yielded on saponification and partial decarboxylation a mixture of the trimethyl esters of dihydroshikimic acid and epi-dihydroshikimic acid (**XXXVI** and **XXXVII**) [118].

The diastereomers were separated by chromatography. Proving thus the genetic relationship, BRUCKNER and Császár omitted the synthesis of quinic acid, all the more so, as this was achieved in the meantime in a somewhat different way by foreign researchers.

In addition to Győző BRUCKNER the researcher, tribute should be paid to BRUCKNER the teacher, the pedagogue professor. Indeed, he himself declared that he appreciated his task of educating the youth even more than his research activity. Accordingly one of the important objects of his scientific research work was to contribute to the development of organic chemistry, and to impart this lively, fresh material of knowledge to the students. He told about his views of the relationship between research and teaching, about the importance of university education and lecturing, in his festal address on being conferred with the honorary doctors' title of the University, using the almost confession-like words:

"At university level only an active researcher of his branch of science can teach efficiently. Experiences gained during research, even if not in close contact with the selected thematics of his lecture course, have nevertheless a stimulating effect on teaching, because the researcher, learning from his own success or even failure, can better appreciate the research results of others, and estimate more reliably the intellectual activity leading to the solution of one of the secrets of nature. Living in this sphere of thought, his lectures become more vivid, arousing thereby the interest and the attention of the students. But lecturing also gives true pleasure and personal experience to the university lecturer, if, holding a close contact with his students, he can feel the reflection of the intellect and the thirst for knowledge of youth. This spurs him on to the continuous polishing of his lectures, and the train of thought he is following may become the source of new ideas, which can be utilized also in his research work. No doubt, I am under the influence of experiences gained in the course of long years of university teaching, when I think even today that though university textbooks or lecture notes edited by the departments are important and even indispensable, they can not replace the force of animated words, the direct and live contact between teacher and students".

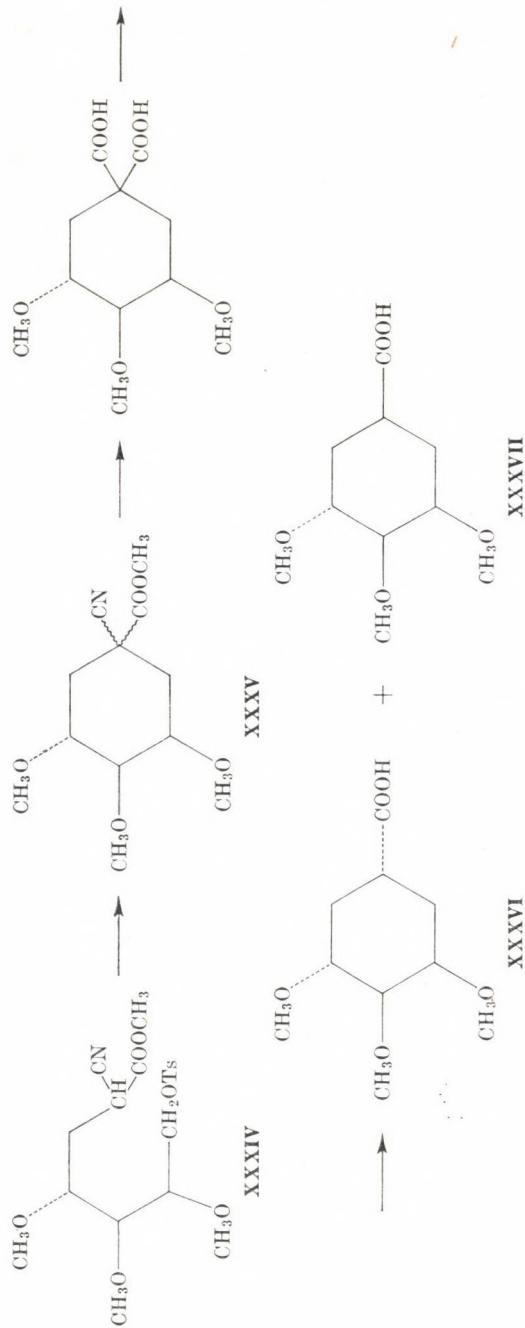


Fig. 11

Győző BRUCKNER remained always faithful to his principles, summarized by himself in the foregoing few sentences. For more than fifty years, even if with decreasing physical strength, but with unchanged, crystal clear intellect he remained lecturer of his beloved subject almost to his last hour. Thousands of students followed with eager attention his words, his masterly constructed lectures. One could not be bored at these lectures, the threads of chemical structural analysis were woven with the excitement of a novel, point and lesson were never absent, the seemingly dry subject-matter was made enjoyable by refined humor and witty turning points.

His immense handbook is the fruit of the fortunate combination of the mental frame of an experienced teacher and a research chemist. BRUCKNER begun the writing of this work thirty years ago, and after revised editions difficult to count, it has grown during the years to an extent of four thousand pages. The first volume of "Organic Chemistry" was published in 1952, and in later years, with the growing of the subject, even the volumes had to be divided. The work, unique in Hungarian textbook writing, consists today of six volumes, the last of which will leave the press in the near future.

BRUCKNER's "Organic Chemistry" is not only a handbook, its material being much more comprehensive than the knowledge required from the students but it is also a carefully organized monograph, a reliable work, based on the original data of the literature. Close collaborators participated in its compilation, edition, and later in the writing of some chapters, but the book in its entirety is the intellectual legacy of Győző BRUCKNER.

The scientist declaring humanity as the object of his life, remained true to the aim set, up to his death. Győző BRUCKNER had no enemies, only friends, and everybody could always surely rely upon his unselfish assistance, his readiness to help. He met the trials of life with a strong heart, and he was sympathetic to those who stood in need of solace. His personality radiated peace and harmony, and this was also a source of harmony for the whole community surrounding him. Fate took away from us besides a great chemist also a true man, and this is particularly distressing, because our loss is irreplaceable.

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THE PREPARATION OF ARYLGLYOXALS AND HETEROAROMATIC ALDEHYDES USING PYRIDONA

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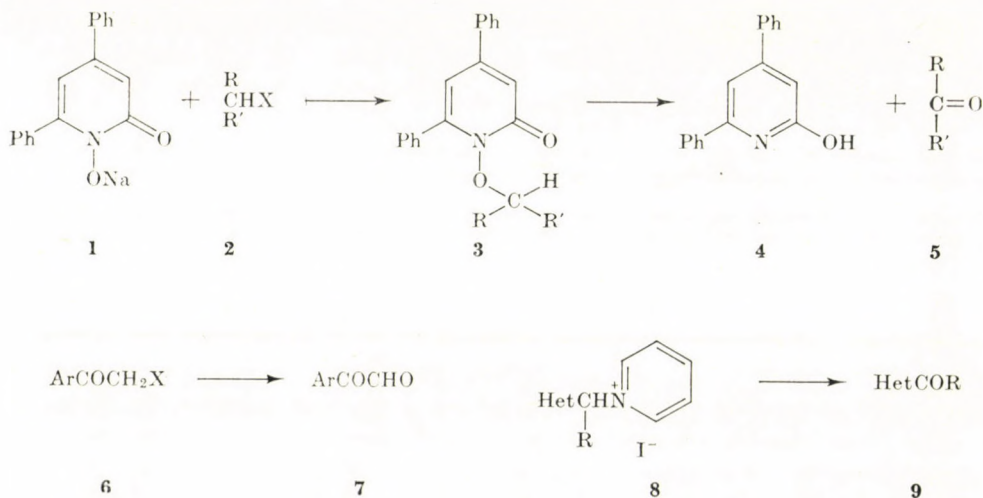
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Sodium 1-oxido-4,6-diphenyl-2-pyridone reacts with phenacyl halides to give arylglyoxals and with *N*-heteroarylmethylpyridinium⁺ cations to give heteroaromatic aldehydes and ketones.

PYRIDONA (1), the sodium salt of 1-hydroxy-4,6-diphenyl-2-pyridone, reacts with alkylating agents (**2**) to give intermediates (**3**) which decompose thermally or photochemically to yield 2-hydroxy-4,6-diphenylpyridine (**4**) (which tautomerises to the pyridone) and a carbonyl compound (**5**). This concept has been used in the conversion of alkyl and benzyl halides into ketones and aliphatic aldehydes in moderate yield and into aromatic aldehydes in good yield [1] and in the conversion of benzylamines *via* pyridinium salts into benzaldehydes [2].



* This paper is dedicated to the memory of my friend Professor Victor BRUCKNER, a fine chemist and a fine personality: Alan R. KATRITZKY.

Table I
Conversions of aroylmethyl

Aroylmethyl halide ArCOCH ₂ X					Arylglyoxal hydrate ^a			
Ar	X	M.p. (°C)	Lit. m.p.	Ref.	M.p. (°C)	Yield (%)	Lit. m.p.	Ref.
C ₆ H ₅	Br	—	—	—	70—73	70	72—74	<i>e</i>
4-BrC ₆ H ₄	Cl	118.5—119	116—117	<i>b</i>	109—112	55	132	<i>f</i>
4-ClC ₆ H ₄	Cl	101—101.5	101—102	<i>b</i>	105—108	27	120—121	<i>e</i>
4-CH ₃ C ₆ H ₄	Cl	56.5—57.5	55—56	<i>c</i>	84—87	45	105—106	<i>e</i>
4-CH ₃ OC ₆ H ₄	Cl	99.5—100.5	102	<i>d</i>	96—99	56	107—109	<i>g</i>

^a All crystallised as needles from water. ^b COLLET, A.: Compt. rend, **125C**, 717 (1897).
^c RYAN, H.: Chem. Ber., **31**, 2129 (1898). ^d TUTIN, F.: J. Chem. Soc., **97**, 2495 (1910). ^e MAURI, L., NARDI, D.: Farmaco Ed. Prat., **18**, 651 (1963); Chem. Abs., **64**, 1994d (1966). ^f ARNOLD,

Table II
N-[α -(Heteroaryl)alkyl]pyridinium

Het	R	Recrystn. solvent	Crystal form	M.p.(°C)	Yield (%)
2-Quinoly	H	80% aq. EtOH	yellow needles	227—228	90 ^b
4-Quinoly	H	aq. EtOH	yellow prisms	213—214.5	48 ^b
2-Benzothiazolyl ^a	H	EtOH	pale yellow plates	179—184	64
2-Benzoxazolyl	H	EtOH	pale yellow needles	193.5—194.5	26
2-Benzoselenazolyl	H	EtOH	brown prisms	171.5—172	46
2-Chromonyl	H	MeOH	brown needles	218—221	88
2,4-Dinitrophenyl	H	EtOH	brown plates	174—176	60
2-Pyridyl	Ph	EtOH	pink prisms	178—179	51

^a Found; S, 9.04%. Required; S, 9.05%. ^b Literature yield. ^c Literature yield of crude product. ^d Isolated as perchlorate. ^e KING, L. C., ABRAMO, S. V.: J. Org. Chem., **23**, 1609 (1958). ^f SCHULZE, W., WILLITZER, H.: J. prakt. Chem., **21**, 168 (1963). ^g RIED, W., GROSS,

We now describe extensions of this work in which one of the the R-groups of the intermediate (3) is electron-attracting. This should facilitate the step (3) \rightarrow (4) + (5): indeed, phenacyl halides (6) are converted into arylglyoxals (7) and the King reaction products (8) from alkylheteroaromatics into acyl heteroaromatics (9). In each case the intermediates of type (3) were not isolated but decomposed spontaneously.

halides into arylglyoxals

ArCOCH(OH) ₂						
% Found			Formula	% Required		
C	H	Cl/Br		C	H	Cl/Br
	—		—		—	
42.0	3.4	34.3	C ₈ H ₅ BrO ₂ ·H ₂ O	41.6	3.1	34.6
51.7	3.7	19.0	C ₈ H ₅ ClO ₂ ·H ₂ O	51.7	3.8	19.0
65.3	6.0	—	C ₉ H ₈ O ₂ ·H ₂ O	65.1	6.1	—
62.3	5.3	—	C ₉ H ₈ O ₃ · ¹ / ₂ H ₂ O	62.4	5.2	—

R. T., FUSON, R. C.: J. Amer. Chem. Soc., **58**, 1295 (1936). ² BECKER, H.-D., RUSSELL, G. A.: J. Org. Chem. **28**, 1895 (1963).

iodides (HetCHRPy⁺ I⁻)

Lit. m. p.	Ref.	% Found				Formula	% Required			
		C	H	N	I		C	H	N	I
238—239	<i>f</i>		—			—		—		
220—223	<i>f</i>		—			—		—		
180—182	<i>g</i>	44.2	3.1	7.8	35.6	C ₁₃ H ₁₁ IN ₂ S	44.1	3.1	7.9	35.8
190—191	<i>g</i>	46.2	3.3	8.2	37.8	C ₁₃ H ₁₁ IN ₂ O	46.2	3.3	8.3	37.5
178 ^d	<i>h</i>	38.7	2.7	6.6	—	C ₁₃ H ₁₁ IN ₂ Se	38.9	2.8	7.0	—
222—223	<i>i</i>		—			—		—		
169—171 ^e	<i>j</i>		—			C ₁₂ H ₁₀ IN ₃ O ₄	37.2	2.6	10.9	32.8
—	—	54.6	4.0	7.4	33.7	C ₁₇ H ₁₅ IN ₂	54.6	4.0	7.5	33.9

R. M.: Chem. Ber., **90**, 2646 (1957). ⁱ SCHMUTZ, J., HIRT, R., LAUENER, H.: Helv. Chim. Acta, **35**, 1168 (1952). ^j Ref. [7]. ^e KRÖHNKE, F.: Chem. Ber., **88**, 851 (1955).

Preparation of arylglyoxals

Phenacyl bromide and various substituted phenacyl chlorides (prepared by Friedel-Crafts acylation of the corresponding arene with chloroacetyl chloride) were converted by pyridone at 20 °C into the corresponding arylglyoxals, isolated as hydrates in 52% average yield (see Table I). The melting points of the hydrates depend on the rate of heating and those recorded in the literature show considerable variation for the same compound: hence the hydrates were analysed as well as characterised spectrally.

Table III
Heteroaryl aldehydes and ketones (HetCOR)

Het	R	Reaction temp (°C)	Reaction time (h)	Recrystn. solvent	Crystal form	M.p. (°C)	Yield (%)	Lit. m.p.	Ref.
2-Quinolyl ^a	H	160—170	3.5	light petroleum (40—60 °C), ethanol ^c	prisms yellow needles ^c	68—69 252.5—255 ^c	58 54 ^c	70—71 251—253 ^c	<i>e</i> <i>f</i> ^c
4-Quinolyl ^b	H	160	5	light petroleum (40—60 °C)	needles	50—51.5	82	52	<i>g</i>
2-Benzothiazolyl	H	145	5	light petroleum (40—60 °C)	prisms	73—74	20	73	<i>g</i>
2-Benzoxazolyl	H	160	4	ethanol ^c	orange needles ^c	229—231 ^c	5 ^c	230 ^c	<i>h</i> ^c
2-Benzoselenazolyl	H	160	5	ethanol ^c	yellow needles ^c	276—278 ^c	10 ^c	267—268 ^c	<i>i</i> ^c
2-Chromonyl	H	168	4	ethanol ^d	orange needles ^d	217—219 ^d	11 ^d	218—219 ^d	<i>i</i> ^d
2,4-Dinitrophenyl ^a	H	150	4.5	aq. EtOH	yellow plates	70—72	31	69—71	<i>j</i>
2-Pyridyl ^b	Ph	150	3.5	—	liquid	—	57	—	<i>b</i>

^a I. r. spectra identical to published spectra, POUCHERT, C. J.: The Aldrich Library of Infrared Spectra, 2nd edn Aldrich Chemical Co., 1975. ^b I.r. and ¹H n. m. r. spectra identical with those of authentic sample. ^c Data refer to 2,4-dinitrophenylhydrazone. ^d Data refer to phenylhydrazone. ^e HAMMICK, D. L. L., JOHNSTON, E., MORGAN, E. D.: J. Chem. Soc., **1957**, 5073. ^f KWARTLER, C. E., LINDWALL, H. G.: J. Amer. Chem. Soc., **59**, 524 (1937). ^g HAMER, F. M.: J. Chem. Soc., **1952**, 3197. ^h RIED, W., BENDER, H.: Chem. Ber., **89**, 1893 (1956). ⁱ SEYHAN, M.: Chem. Ber., **86**, 888 (1953). ^j BENNETT, G. M., BELL, E. V.: Org. Synth., Coll. Vol, **II**, 223 (1943).

Many methods are available for the preparation of arylglyoxals [3], including several from phenacyl halides or their equivalent phenacylpyridinium salts, especially (a) the KRÖHNKE reaction [4], (b) reaction with silver nitrates [5] and (c) reaction with dimethylsulphoxide [6]. Whereas our method avoids the acidic and basic conditions needed for (a), and AgNO₃ could be disadvantageous in (b), the high yields obtained with dimethylsulphoxide would appear to make this the method of choice.

Preparation of heteroaromatic aldehydes and ketones

Several active alkyl derivatives were converted by the King reaction (iodine and pyridine) into the pyridinium salts (8) (Table II) by literature methods except for the novel derivative of 2-benzylpyridine (2-methylpyridine is reported [7] to be unreactive in the King reaction). Reaction of these salts with pyridona was (after many trials) best conducted at 150–200 °C in triphenylpyridine as flux, the carbonyl compounds being distilled off *in vacuo* (Table III).

The present route represents an alternative to the KRÖHNKE reaction [8] in which the King reaction products are treated with *p*-dimethylaminonitrobenzene and the resulting nitrone hydrolysed. The present method avoids the use of base (in the first stage) and acid (in second stage of the KRÖHNKE reaction) and also is a single step.

There have been two previous approaches similar in concept to the present work: 2,4-dinitrobenzene with pyridine 1-oxide and iodine gave 2,4-dinitrobenzaldehyde *via* an intermediate salt [9], and (2 moles of) 2- and 4-picoline 1-oxide with iodine reportedly gave "pyridine aldehydes" [10].

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MECHANICAL-RHEOLOGICAL STUDIES ON POLYMER NETWORKS, I

EFFECT OF THE CONDITIONS OF CROSS-LINKING ON
THE MECHANICAL PROPERTIES

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Unidirectional compression measurements have been carried out on a series of chemically cross-linked poly(vinyl alcohol) gels. The influence of the initial polymer concentration, the degree of cross-linking, the chemical nature of the cross-linking agent, the medium of cross-linking and the chemical modification of the primary chains on the mechanical properties of the networks has been studied.

It has been established that the efficiency of the cross-linking process increases with increasing both the initial polymer concentration and (at the same initial concentration) the cross-linking density. The use of a thermodynamically better solvent, cross-linking agents with longer chains and — in the cases of vinyl alcohol-vinyl acetate copolymers — decreasing the acetate content are also favourable regarding the efficiency of the cross-linking process.

In contrast to existing theories, we have found that the value of $K_1 \nu_{e1}^* q_0^{-2/3}$ increases considerably with increasing the volume fraction of the polymer. On the basis of experimental data it has been concluded that the topological factor, $K_1 q_0^{-2/3}$, does not depend on the degree of cross-linking.

Introduction

In this series of papers we report on results concerning the mechanical and physico-chemical properties of chemically cross-linked polymer gels.

Though numerous papers have been published on this topic in the last few decades, the role of several parameters principally important from the point of view of the characterization of cross-linked polymers, has not been cleared yet. A few fundamental problems has not been solved so far, even theoretically. Such parameters as the concentration of the initial polymer solution (reference state), the molecular mass or molecular mass distribution of the primary polymer chains, the chemical nature of the cross-linking agent, the effect of the polymer analogous transformation of the network are contracted in one semi-empirical factor in the current theoretical equations.

It is also to be mentioned that the complex physico-chemical investigation of gels prepared from water-soluble polymers, which are more important for practical reasons, is very scarce.

In the first part of this series, the effect of some essentially important parameters is discussed, as *e.g.* the concentration of the polymer solution used for the preparation of the gel, the chemical nature of the cross-linking agent, the medium of cross-linking and the degree of cross-linking. Later on, the effect of the molecular mass and molecular mass distribution of the polymer on the mechanical properties of the gels will be studied on gel samples made from polymer fractions with different molecular masses. After that, an answer will be sought for the question how does the polymer-analogous transformation of cross-linked structures affect the most important structural features and physico-chemical properties of these systems.

Theoretical

In the case of the elastic deformation of homogeneous, isotropic and incompressible bodies, the change of the Helmholtz energy stored in system can be given by the so-called MOONEY—RIVLIN equation [1, 2, 15], as a function of the scalar invariants constructed from the main deformation ratios:

$$\Delta A_{el} = C'_1(I_1 - 3) + C'_2(I_2 I_3^{-1} - 3) \quad (1)$$

where

$$I_1 = A_x^2 + A_y^2 + A_z^2$$

$$I_2 = A_y^2 A_z^2 + A_x^2 A_z^2 + A_x^2 A_y^2$$

$$I_3 = A_x^2 A_y^2 A_z^2$$

and C'_1 and C'_2 are constants depending on the network and the temperature. A_x , A_y and A_z are the deformation ratios related to the isotropic, undeformed state ($A_x = A_y = A_z = 1$) (*e.g.* in the case of unidirectional elongation in the direction of the x -axis $A_x = L_x/L_{Vx}$, where L_x is the length of the deformed gel sample and L_{Vx} is that of the undeformed sample of volume V). If no change in the volume occurs in the course of deformation, $A_x A_y A_z = 1$.

In the case of unidirectional elongation or compression, the force can be expressed from Eq. (1) as follows:

$$f = \left(\frac{\partial \Delta A_{el}}{\partial L_x} \right)_{T, V} = 2C_1(A_x - A_x^{-2}) + 2C_2(A_x - A_x^{-2}) A_x^{-1} \quad (2)$$

where A_x is the deformation ratio measured in the direction of the force, $C_1 = C'_1/L_{Vx}$ and $C_2 = C'_2/L_{Vx}$.

A number of authors dealt with the connection between the change in the Helmholtz energy accompanying by the deformation and the molecular

parameters characteristic for the structure of the system. Expressions derived by different authors for ideal cross-linked systems (the distribution of the end-to-end distance of the network chains is Gaussian, the chains link junction points, *i.e.* there are no free chain-terminations, there are neither inter-, nor intramolecular interactions, there are no loops in chains, no cycles, *etc.*) can be given in the following general form [3, 4, 5]:

$$\Delta A_{el} = \frac{kTK_1\nu_{el}}{2}(\lambda_x^2 + \lambda_y^2 + \lambda_z^2 - 3) + kTK_2\nu_{el} \ln(\lambda_x \lambda_y \lambda_z) \quad (3)$$

where K_1 and K_2 are constants, ν_{el} is the number of the elastically active chains in the system, k is the Boltzmann constant and T is the temperature. Deformation ratios λ_x , λ_y and λ_z refer to the deformation of the cross-linked system related to the reference volume V_0 (unperturbed state) in which the chains do not exert any elastic force on the cross-links. This does not necessarily correspond either to the actual volume V of the gel being in swelling equilibrium with the solvent, or to the volume V_d of the dry network.

If in the course of deformation no change occurs in the volume, the second term in Eq. (3) can be neglected. For this case, the force can be given for unidirectional elongation or compression in the following form:

$$f = \left(\frac{\partial \Delta A_{el}}{\partial L_x} \right)_{T,V} = \frac{1}{L_{0x}} \left(\frac{\partial \Delta A_{el}}{\partial \lambda_x} \right)_{T,V} = \frac{kTK_1\nu_{el}}{L_{0x}} \left(\lambda_x - \frac{V}{V_0\lambda_x^2} \right). \quad (4)$$

L_{0x} is the length measured in reference state in the x direction.

Introducing the deformation ratio measurable macroscopically

$$f = \frac{kTK_1\nu_{el}}{L_{Vx}} \left(\frac{V}{V_0} \right)^{2/3} (A_x - A_x^{-2}) \quad (5)$$

where

$$A_x = \frac{L_x}{L_{Vx}} = \lambda_x \left(\frac{V}{V_0} \right)^{-1/3}$$

Upon using molar quantities instead of molecular ones in Eq. (5), the following expression can be obtained:

$$f = \frac{RTK_1\nu_{el}^*V_d}{L_{Vx}} \left(\frac{q_i}{q_0} \right)^{2/3} (A_x - A_x^{-2}). \quad (6)$$

In Eq. (6), ν_{el}^* is the concentration of elastically active chains in the dry network, q_i and q_0 are the volume degrees of swelling of the gel in swelling

equilibrium and in the reference state, respectively, and R is the universal gas constant.

Upon comparing Eqs (2) and (6), it can be established that if $C_2 = 0$, the term $2C_1$ can be identified with the term containing molecular parameters relevant to the network. The condition $C_2 \neq 0$, on the other hand, can yield information concerning deviation from the ideal behaviour.

Thus, on the basis of Eqs (5) and (6), from the force-deformation functions determined experimentally, information can be obtained on parameters characteristic for the network structure, as *e.g.* the concentration of the elastically active chains, the reference state q_0 , the factor K_1 connected with the spatial structure of the gel and the deviation of the real systems studied from the ideal model systems serving as basis for calculations.

Experimental

Materials and methods

Type Kuraray Poval 420 poly(vinyl alcohol) (PVA) was used for the experiments. The industrial product was hydrolyzed with alkali to remove its acetate content; after that, fractions with too high or too low relative molecular masses were removed by fractionation with *n*-propanol (*p.a.* Reanal product). The relative average molecular mass of the fraction used was found 100 000 by viscosimetry, and 110 000 by sedimentation method.

Experiments have been also carried out on gels containing 10 and 30 mol% of acetate groups, respectively. Preparation of copolymers occurred by equilibrium reacylation in the presence of sodium dodecylbenzenesulfonate as catalyst, in the solution of the fractionated PVA, at 333 K. The copolymer prepared in this way contains the acetate groups statistically distributed along the chains.

Experiments were carried out on gels cross-linked at different initial polymer concentrations (\bar{c}_{PVA} : 3.0, 6.0, 9.0 and 12.0 wt.%). Gels have been prepared by considering that their polymer content — after hydrolyzing the acetate groups — should be identical with that of gels prepared directly from PVA. Gels have been prepared either in water or in a mixture of 90 wt.% dimethyl sulfoxide (DMSO, *p.a.* Reanal product) and 10 wt.% of water. As cross-linking agents, glutaric aldehyde (GDA, Merck) and succinic aldehyde (SDA) were used. At every concentration, four series of samples were prepared with different degrees of cross-linking (*dc*: 50, 100, 200 and 400). The degree of cross-linking is defined as the molar ratio of the monomer and the cross-linking agent. Preparation of gels occurred in a dismountable gel pouring frame suitable for yielding cylindrical gel specimens. The cross-linking process was performed under isothermal conditions at 298 ± 0.1 K. Unidirectional compression measurements were carried out at 298 K in an apparatus constructed by us, which allowed to measure stress-strain relations with high accuracy. For evaluation the arithmetic mean of three measurements was used [6].

Results and Discussion

The force-deformation relationship was measured on all the samples at constant volume ($q_i = q_c$) after taking them out of the frame, and also at swelling equilibrium in water and in DMSO and at different water activities [7].

It follows from Eq. (2) that plotting the ratio of the forces exerted on the samples and the $A_x - A_x^{-2}$ values calculated from deformation ratios against A_x^{-1} , C_1 can be determined at the extrapolated $A_x^{-1} = 0$ value, while C_2 from the slope of the curve. For all the systems studied, straight lines were

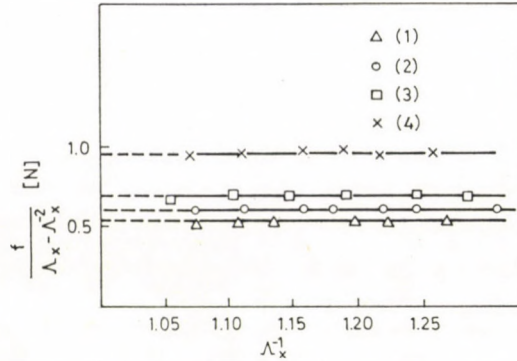


Fig. 1. Application of Eq. (2) to PVA gels at different swelling ratios (c_{PVA}^0 : 6 wt.%, degree of cross-linking: 100, cross-linking agent: GDA; v_2 : (1) 0.056, (2) 0.087, (3) 0.236, (4) 0.349)

found, and C_2 was always equal to zero within the limits of experimental error. This result is in accordance with literature data [8, 9], which say that in the course of unidirectional compression of swollen systems C_2 is generally 0. In Fig. 1 some examples are shown for functions obtained according to Eq. (2). Functions are seen for gels with different volume fractions ($v_2 = q_i^{-1}$) prepared with glutaric aldehyde in aqueous solution at a polymer concentration of 6 wt.% and with a degree of cross-linking of 100. It can be established that the change of the volume fraction influences C_1 significantly.

Information can be obtained regarding the cross-linking process, if the constant $2C_1$ determined at a swelling degree of $q_i = q_c$ is studied as a function

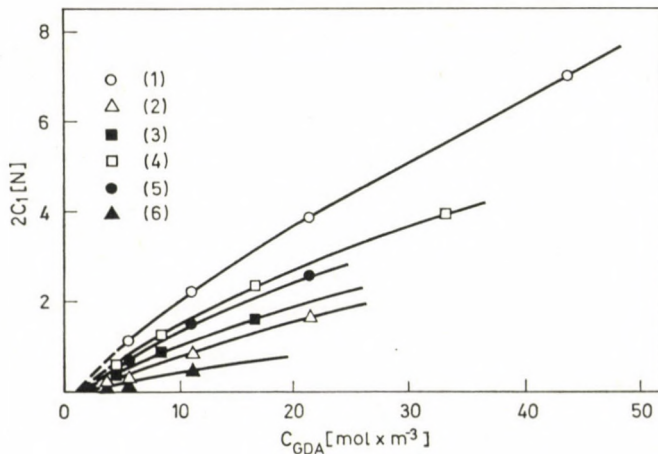


Fig. 2. Dependence of $2C_1$ on the amount of the cross-linking agent. (1) 12 wt.% GDA/DMSO, (2) 6 wt.% GDA/DMSO, (3) 9 wt.% GDA/water, (4) 9 wt.% GDA/DMSO, (5) 12 wt.% GDA/water, (6) 6 wt.% GDA/water

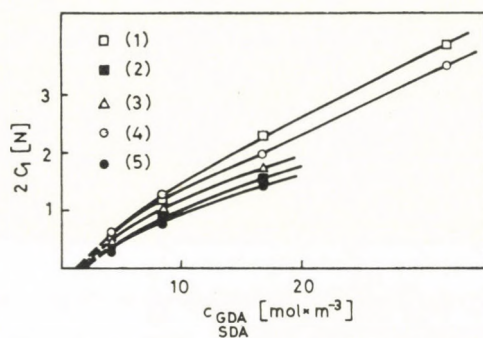


Fig. 3. Dependence of $2C_1$ on the amount of the cross-linking agent. (1) 9 wt.% GDA/DMSO, (2) 9 wt.% GDA/water, (3) 9 wt.% copolymer (30% hydr.) GDA/water, (4) 9 wt.% SDA/DMSO, (5) 9 wt.% SDA/water

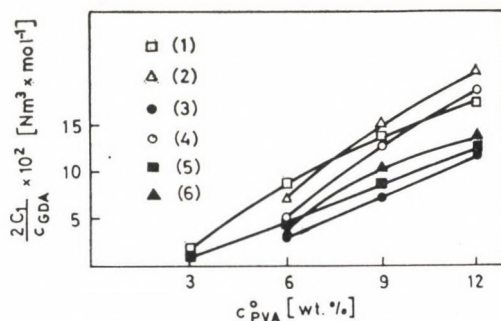


Fig. 4. Efficiency of cross-linking (dc = degree of cross-linking). (1) GDA/DMSO dc : 100, (2) GDA/DMSO dc : 400, (3) GDA/water dc : 200, (4) GDA/DMSO dc : 200, (5) GDA/water dc : 100, (6) GDA/water dc : 400

of the amount of the cross-linking agent added to the system (Figs 2 and 3), or if the changes in $2C_1$ caused by 1 mol of the cross-linking agent are plotted as a function of the initial concentration of the polymer solution (Fig. 4). From these representations it is seen that the increase of $2C_1$ with increasing amount of the cross-linking agent is controlled basically by the concentration of the polymer solution and its structure. For gels prepared at the same initial polymer concentration, $2C_1$ increases in parallel with the amount of the cross-linking agent and depends also on the medium of cross-linking and the chemical nature of the cross-linking agent. It is striking that cross-linking is more effective in DMSO–water mixtures than in pure water. The value of $2C_1$ is lower for gels cross-linked with SDA, and for those made from copolymers.

A mixture of 90 wt.% DMSO and 10 wt.% water is a better solvent for PVA than water [10]. In the former, chains are more elongated, and the segment density distribution is more homogeneous than in water. This is favourable

regarding the efficiency of the cross-linking process as both the probability of intramolecular cyclization and the possibility of the monofunctional reaction for the bifunctional molecules of the cross-linking agent decreases. In aqueous solutions, water being a poorer solvent of PVA ($\chi_{1,2} \approx 0.5$ [11]), polymer molecules are in a so-called supercoiled state, and due to the interaction between the strongly polar hydroxyl groups, the association of the molecules should be taken into account which leads to the formation of so-called microgel particles [12, 13, 14]. Therefore, when cross-linking occurs in water, a greater part of the cross-linking agent may be used for fixing the coiled state and the associates formed in the solution, than in DMSO-water mixtures. SDA is less ef-

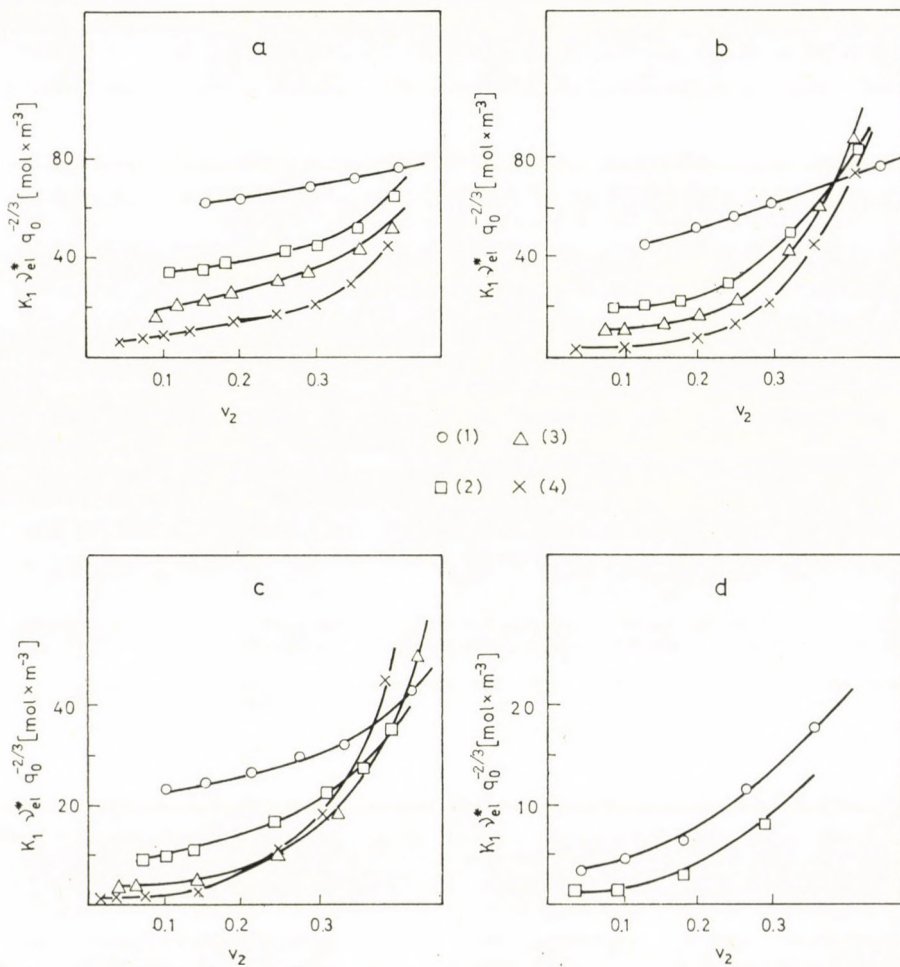


Fig. 5. $K_1 v_{e1}^* q_0^{-2/3} - v_2$ functions for PVA gels (cross-linking agent: GDA, medium of cross-linking: water, c_{PVA}^0 : a) 12 wt.%, b) 9 wt.%, c) 6 wt.%, d) 3 wt.%, degree of cross-linking: (1) 50, (2) 100, (3) 200, (4) 400)

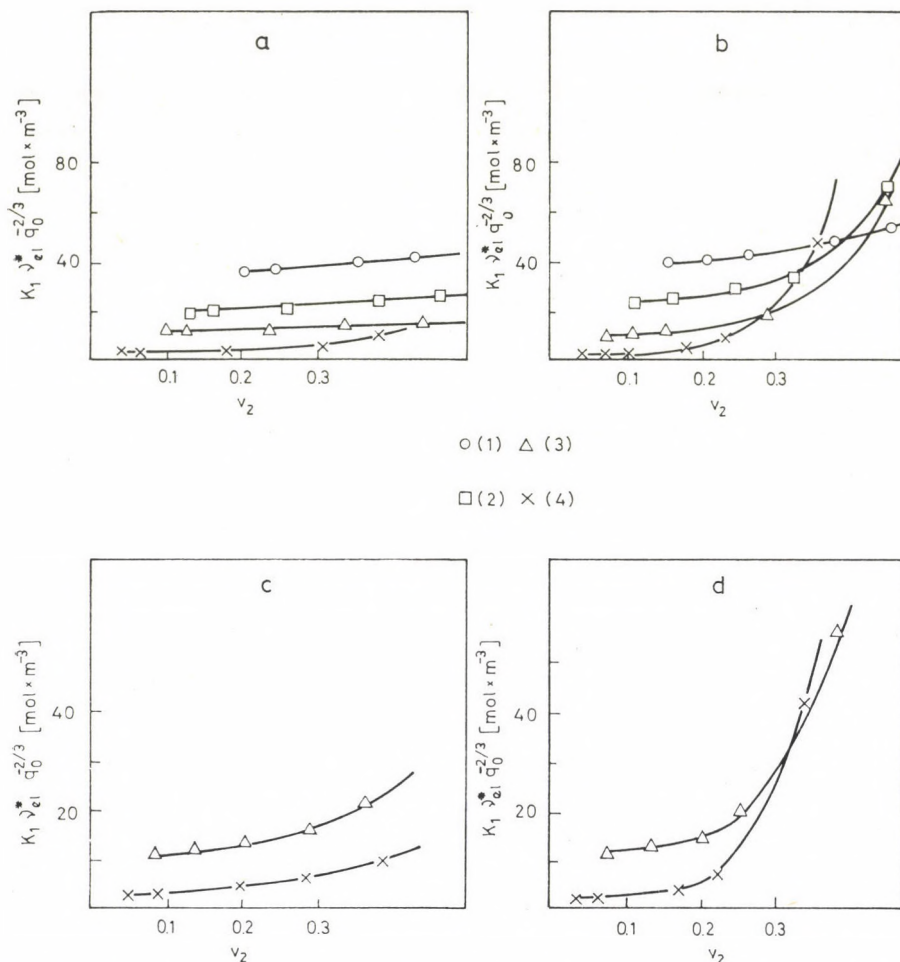


Fig. 6. $K_1 v_{e1}^* q_0^{-2/3} - v_2$ functions for vinyl alcohol-vinyl acetate copolymer gels and PVA gels. a) 9 wt.% copolymer (30 mol%), b) 9 wt.% copolymer (30 mol%, hydrolyzed), c) 9 wt.% copolymer (10 mol%), d) 9 wt.% copolymer (10 mol%, hydrolyzed); degree of cross-linking: (1) 50, (2) 100, (3) 200, (4) 400

fective than GDA (Fig. 3), probably because its carbon chain is shorter by one methylene group, which may cause steric hindrance of the reaction of both of its functional groups. Upon using copolymers, steric factors can play a role as well, since the number of reactive functional groups diminishes due to the 30 or 10 mol% acetate content of the copolymer.

In Figs 2 and 3, it is apparent that by decreasing the amount of the cross-linking agent the curves intersect the abscissa before the origin. This can be explained by assuming that below the gel point the cross-linking agent added to the system is used up for linking chains originally present in the solution,

and the elastically active chains and the corresponding $2C_1$ values appear only above the gel point.

On the basis of the figure it can also be established that the amount of the cross-linking agent used up before the gel point does not significantly depend on the concentration of the polymer solution as there is no significant difference between the intercepts of the curves obtained for gels prepared at different initial polymer concentrations.

In Fig. 4 the mean values of the changes in $2C_1$ caused by one mol of the cross-linking agent are plotted against the initial concentration of the polymer solution. In addition to the facts already discussed, it can also be seen in this figure that with increasing polymer concentration, the mean values of $2C_1/c_{GDA}$ increase significantly. This can possibly be explained by the rising of the mean segment density with increasing the concentration, and thereby the probability

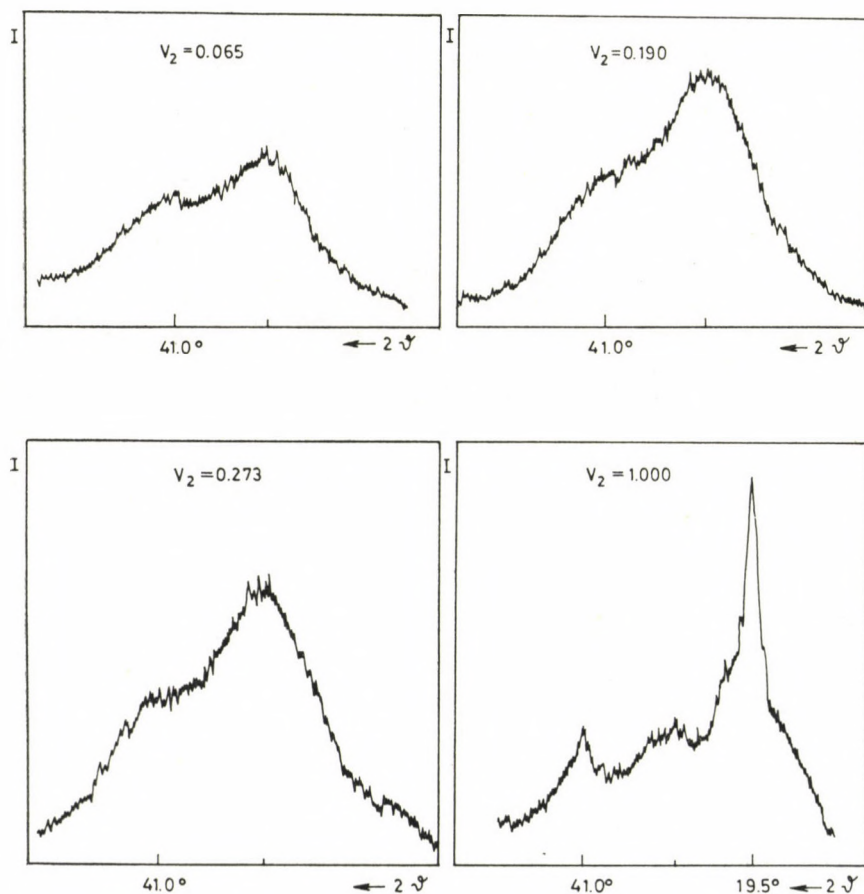


Fig. 7. X-ray diffractograms of PVA gels with different swelling degrees ($c_{PVA}^0 = 9$ wt.%, cross-linking agent: GDA, medium of cross-linking: water, $d_c: 200$)

of linking different molecules by the reactive functional groups of the cross-linking agent increases. At the same time, the probability of the monofunctional reaction of the cross-linking agent decreases.

From the $2C_1$ values obtained from Eq. (2), the product $K_1\nu_{el}^*q_0^{-2/3}$ in Eq. (6) can be calculated. According to the theory $K_1\nu_{el}^*q_0^{-2/3}$ is characteristic for a given system; it should be a constant containing the molecular parameters and is independent of the swelling ratio. In order to check its constancy, we determined the deformation *vs.* strain curves of gel samples being in swelling equilibrium with solutions having different water activities, and calculated the $K_1\nu_{el}^*q_0^{-2/3}$ terms from the known swelling degrees of the gels (Figs 5 and 6).

It is apparent that $K_1\nu_{el}^*q_0^{-2/3}$ initially increases weakly and linearly, but above $v_2 = 0.2-0.3$ strongly, with increasing the volume fraction of the polymer, and at about $v_2 = 0.4$, it exceeds the initial value by a factor of 30-40.

This phenomenon is connected with the ordering of chains and formation of crystallites with increasing polymer concentration. In order to prove this, X-ray diffraction measurements were performed. On the basis of the diffractograms (Fig. 7), it can be established that the height of the peaks at $2\theta = 41^\circ$, *i.e.* 0.2199 nm, and $2\theta = 19.5^\circ$, *i.e.* 0.4548 nm, significantly increases with increasing polymer concentration.

From Figs 5 and 6 it can be seen that for gels prepared at the same polymer concentrations, the slopes of the curves decrease with increasing cross-linking density. This can be explained by the lower mobility of net-points at higher degrees of cross-linking, when the interjacent cross-linking molecules prevent the chains from ordering. The changing of the term $K_1\nu_{el}^*q_0^{-2/3}$ with the volume fraction of the polymer is also smaller for the non-hydrolyzed gels prepared from copolymers. In these latter systems the acetate groups are

Table I

$K_1\nu_{el}^*q_0^{-2/3}$ values for gels prepared from copolymers ($v_2 \rightarrow 0$)
Medium of cross-linking: water
Cross-linking agent: GDA

Polymer concentration after hydrolysis (related to q_e) (wt.%)	Acetate content during cross-linking (mol%)	Degree of cross-linking	$K_1\nu_{el}^*q_0^{-2/3}$ (mol m ⁻³)	
			Hydrolyzed gels	Non-hydrolyzed gels
9	30	50	35.0	30.0
9	30	100	18.5	17.0
9	30	200	9.0	10.5
9	30	400	3.0	3.5
9	10	200	10.5	10.5
9	10	400	2.0	2.0

Table II

 $K_1 \nu_{el}^* q_0^{-2/3}$ values for PVA gels
 ($v_2 \rightarrow 0$)

\bullet CPVA (wt.%)	Cross- linking agent	Medium of cross-linking	$K_1 \nu_{el}^* q_0^{-2/3}$ (mol m ⁻³)			
			Degree of cross-linking			
			50	100	200	400
12	GDA	water	53.0	24.0	9.0	3.0
		DMSO-water	64.1	33.2	10.1	4.0
9	GDA	water	33.5	15.5	6.4	2.0
		DMSO-water	35.1	21.2	10.4	4.2
	SDA	water	27.5	14.0	8.1	3.5
		DMSO-water	30.0	16.5	6.0	2.1
6	GDA	water	18.5	6.0	2.2	0.7
		DMSO-water	26.0	9.1	2.5	1.0
3	GDA	water	3.5	1.4	—	—
		DMSO-water	9.0	2.0	—	—

distributed statistically along the chains and thereby sterically hinder the ordering.

As the intermolecular interactions become more and more pronounced with increasing volume fraction of the polymer, the $K_1 \nu_{el}^* q_0^{-2/3}$ values characteristic for the gels were determined from the initial linear part of the appropriate functions by extrapolating to $v_2 = 0$, i.e. to infinite dilution. The rightfulness of this procedure is proven by the nearly identical values of $K_1 \nu_{el}^* q_0^{-2/3}$ obtained for the original copolymer and the hydrolyzed gels at $v_2 = 0$ (Table I).

The $K_1 \nu_{el}^* q_0^{-2/3}$ values thus determined for PVA gels are summarized in Table II.

Further information can be obtained for the gels by substituting certain factors of the $K_1 \nu_{el}^* q_0^{-2/3}$ term by values calculated for suitably chosen model systems.

On the basis of the statistical theory of cross-linking, the following relationship can be obtained for the concentration of the elastically active chains in unit volume of the dry network, if only chain terminations are considered:

$$\nu_{el}^* = \nu^* \left(1 - \frac{2d_2}{\nu^* \bar{M}_n} \right) \quad (7)$$

where ν^* is the concentration of network chains,
 d_2 is the density of the polymer, and

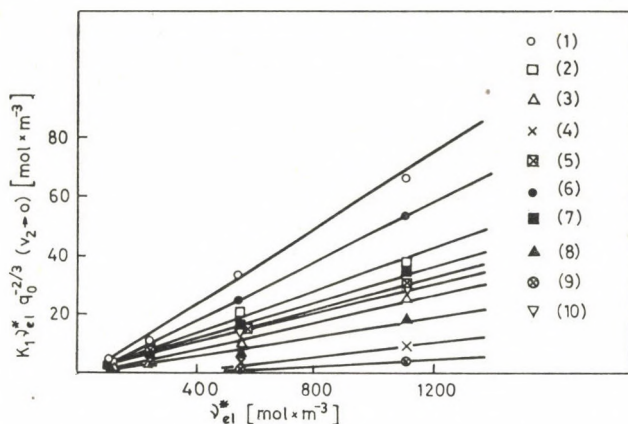


Fig. 8. Determination of the topological factor $K_1 q_0^{-2/3}$ (1) 12 wt.% GDA/DMSO, (2) 9 wt.% GDA/DMSO, (3) 6 wt.% GDA/DMSO, (4) 3 wt.% GDA/DMSO, (5) 9 wt.% SDA/DMSO, (6) 12 wt.% GDA/water, (7) 9 wt.% GDA/water, (8) 6 wt.% GDA/water, (9) 3 wt.% GDA/water, (10) 9 wt.% SDA/water

\bar{M}_n is the number average molecular mass of the polymer chains in the initial solution [15].

Plotting $K_1 v_{el}^* q_0^{-2/3}$ against the calculated values of v_{el}^* , information can be obtained for $K_1 q_0^{-2/3}$ (Fig. 8). From this representation it is seen that $K_1 q_0^{-2/3}$ is nearly independent of the degree of cross-linking *i.e.* v_{el}^* for gels prepared at the same initial polymer concentrations. This confirms the theoret-

Table III

$K_1 q_0^{-2/3}$ values for PVA gels

Polymer concentration (wt.%)	Cross-linking agent	Medium of cross-linking	$K_1 q_0^{-2/3}$	$K_1 (q_0 = q_c)$	$q_0 (K_1 = 1)$	$q_0 (K_1 = 0.5)$
12	GDA	water	0.050	0.237	89.4	31.6
		DMSO-water	0.058	0.293	71.5	25.3
9	GDA	water	0.032	0.184	174.7	61.8
		DMSO-water	0.038	0.219	134.9	47.7
	SDA	water	0.023	0.133	286.7	101.4
		DMSO-water	0.026	0.149	238.5	84.3
6	GDA	water	0.017	0.131	451.2	159.5
		DMSO-water	0.024	0.186	268.9	95.1
3	GDA	water	0.004	0.049	3952.9	1397.5
		DMSO-water	0.008	0.105	1397.5	494.1

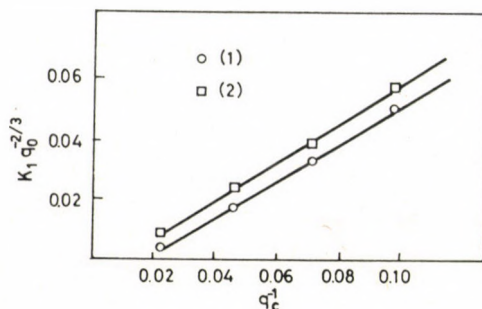


Fig. 9. Variation of the topological factor with the initial polymer concentration (cross-linking agent: GDA, medium: (1) water, (2) DMSO-water mixture)

ical standpoint that in this term the effect of the initial state of macromolecules on the gel formation is included. $K_1 q_0^{-2/3}$ values for gels cross-linked at different polymer concentrations are summarized in column 4 of Table III.

Assuming that the conformation of the chains in the initial polymer solution does not differ from that in the reference state, the parameter q_0 can be substituted by q_c . Factor K_1 is 1 or $1/2$, according to statistical thermodynamical calculations. In columns 5, 6 and 7 of Table III, the K_1 and q_0 values are contained for different conditions.

It is apparent that for the systems studied, $K_1 q_0^{-2/3}$ being very small, q_0 and K_1 considerably differ from the values calculated for ideal model systems, and that this difference increases with decreasing concentration of the initial polymer solution.

$K_1 q_0^{-2/3}$ can be regarded as a topological factor, as it yields information about the ability of the cross-linking agent to form elastically active chains. The experimental values found are similar to those determined by JACKSON and GILL [16] for PVA gels cross-linked with terephthalic aldehyde in aqueous solutions. The value of the topological factor rises with increasing concentration of the polymer solution, and depends on the medium of cross-linking (Fig. 9). These results, in accordance with our earlier conclusions, can be explained, as the increase of the average segment density of the system favours the formation of a homogeneous network and, on the other hand, in a better solvent at the same initial polymer concentration the conformation of the chains is more advantageous relating the cross-linking process.

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A STUDY OF THE CHEMICAL STATE OF TIN LAYERS DEPOSITED ON VARIOUS ALUMINIUM ALLOYS AND ELECTROPLATED WITH COPPER

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The interaction between several aluminium alloys and tin deposited onto them has been studied by means of Mössbauer spectroscopy. Contents of silicon in the aluminium helps most the intensive alloying at the interfaces. Copper electroplated onto the deposited tin layer also forms an alloy with the latter.

Introduction

Aluminium is decorative as well as resistant to corrosion. This resistance can be enhanced by means of relatively simple methods. There are, however, several fields of application where resistance to the wear (*e.g.* motorcar bumpers), electric conductivity (*e.g.* contact pieces) and solderability (*e.g.* electric fittings) are not satisfactory. This necessitates that aluminium should be plated with a continuous and well adhering layer of metal.

Direct electroplating of aluminium is not feasible because the cathodically deposited metal does not adhere to, and is easily detached from, the aluminium oxide layer formed upon exposure to air. Several methods are known for solving this problem: various interconnecting metal layers are deposited upon the aluminium surface. Lately one such method, *viz.* bronze-plating onto a tin film deposited from an alkaline solution of Na_2SnO_3 [1] begins to be used extensively also in industry. By means of this combination, corrosion resistances better than before can be achieved.

Many factors affect the adhesive power of the metal cladding, among others the composition, the structure, the affinity of the metal basis and the metal deposited.

In the course of these studies we attempted to collect information, by Mössbauer spectroscopy, concerning the chemical state of the tin layer that is deposited to aluminium variously alloyed and that enhances the adhesion of electrodeposited copper.

Experimental

Removal of fat and grease by alkali, removal of oxides by acid, deposition from an alkaline solution of tin were the preparative steps applied in the cases of variously alloyed aluminium samples. In some cases the layers of tin formed were studied as such, in others they were studied together with a *ca.* 2 μm thick copper deposit. Both sides of the aluminium samples were covered with tin or within tin and copper. A layer of tin thick enough for record-

Table I
Summary of experimental data

No. of sample	Main characteristics of the samples*	Temperature of recording of spectra**	Isomer shift, δ ($\frac{\text{mm}}{\text{s}}$)	Half width at half maximum Γ ($\frac{\text{mm}}{\text{s}}$)	Line intensity $\Gamma\eta$ ***
1	β -tin standard	r t	2.529 ± 0.003	0.99 ± 0.01	0.144
1	β -tin standard	N ₂ t	2.562 ± 0.003	1.84 ± 0.01	0.571
2	0.135 mm thick tin foil	N ₂ t	2.596 ± 0.005	2.29 ± 0.02	0.296
3	0.35 mol % Sn in Al 99.99 wt.% pure	N ₂ t	2.62 ± 0.02	1.03 ± 0.05	0.052
4	Sn deposited on to 0.015 mm Al foil 99.5 wt.% pure	N ₂ t	2.61 ± 0.03	1.08 ± 0.09	0.0069
5	Tin deposited onto 0.25 mm Al foil contg. 4 wt.% Cu and 2 wt.% Mg	N ₂ t	2.60 ± 0.03	1.2 ± 0.1	0.009
6	Tin deposited onto 0.35 mm Al foil contg. 17 wt.% Si, 1 wt.% Ni, 1 wt.% Cu	N ₂ h	2.595 ± 0.005	0.937 ± 0.015	0.0585
7	Same as sample 4, but the Sn deposited was covered by 2 μm galvanic Cu	N ₂ t	2.25 ± 0.15	1.4 ± 0.3	0.0028
8	Same as sample 6, with 2 μm galvanic Cu on the deposited Sn		1.89 ± 0.05	1.12 ± 0.09	0.0105
			2.60 ± 0.03	0.91 ± 0.08	0.0091

* Ten foils altogether were used in the cases of samples 4, 5 and 7, in order to obtain a layer of tin needed for the recording of the spectra; with samples 6 and 8, seven foils were used at a time, as the absorbent. In these two cases the thickness of the aluminium foils limited their number

** N₂t = temperature of liquid nitrogen, r t = room temperature

*** $\eta = \frac{N_{\infty} - N}{N_{\infty}}$, where N is the pulse count at the minimum point and N_{∞} is that for motion at infinite speed, i.e. the pulse count pertinent to the base line

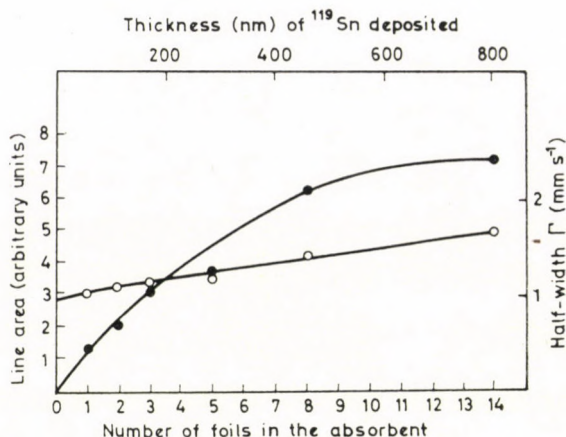


Fig. 1. Area and half-width of the Mössbauer line of β -tin as a function of the thickness of a layer of ^{119}Sn isotope enriched to 90%

ing a spectrum cannot be built up on a single foil of aluminium, therefore, from seven to ten foils were coated with tin or with tin and copper. These foils were stuck together: thus fourteen to twenty layers of tin were used as the absorber.

$\text{Ca}^{119\text{m}}\text{SnO}_3$, with an activity of 5 mCi (1.85×10^8 Bq) was used as the source of radiation. Data taken from the literature were also recalculated to refer to this source. The intensity of an X-ray radiation characterized by 24.74 keV was attenuated through a Pd-filter. The linear combination of Lorentzian curves was used for the computer evaluation of the Mössbauer spectra.

Mössbauer parameters of tin and of alloys of tin

The chemical position of tin deposited to the surface of aluminium and electroplated can be purely metallic or alloyed by the aluminium basis and by the copper layers galvanically deposited. In consequence, to be able to interpret Mössbauer spectra of tin coatings, the Mössbauer parameters of metallic tin, aluminium-tin and tin-copper alloys must be known.

In the literature, data for the isomer shift of metallic tin diverge. For β -tin at room temperature, values of 2.40–2.60 mm s^{-1} are quoted; data referring to the temperature of liquid nitrogen are between 2.50 and 2.65 mm s^{-1} [2, 3]. The divergence of the results noted by the various authors might be due to the inadequate purity, *i.e.* contamination or alloying, of the tin samples or to errors in the calibration of the instruments.

This suggested the expedience to have the Mössbauer parameters of β -Sn recorded by our instrument. In earlier work [4], we have found that electrodeposition produces β -Sn: thus the parameters of the α -modification need not be noted. For the checking operations two β -Sn absorber, sample 1, made by the New England Nuclear Corp., for Mössbauer spectroscopy and sample 2, of 99.9% pure tin foil (0.135 mm thick) available commercially were used. The relevant data are collected in Table I.

Only one piece of data for Al/Sn alloys was found in the literature [5]; according to this, the Sn-value is 2.245 mm s^{-1} for an aluminium which contains 0.05 to 0.1 mol % tin. The isomer shift we found for aluminium alloyed with 0.335 mol % tin, sample 3, is given in Table I. Mössbauer data for Cu–Sn alloys the entire range from zero to 100 mol % tin are to be found in the literature [6], thus no such testing was needed here.

We plotted, and used, a calibration diagram, Figure 1, for the estimation of the thickness of the layers of tin deposited. The thicknesses of the layers on the samples used for this purpose was determined by means of differential polarography [4].

Interpretation of data

The isomer shift of 0.335 mol % tin alloyed into 99.99% pure aluminium, sample 3, is in good agreement, within limits of error, with the δ -value of β -tin. This finding differs from that reported by DELYAGIN who noted an isomer shift lower by nearly 0.2 mm s^{-1} for aluminium alloyed with 0.05 to 0.1 mol % tin [5]. This difference may be due to the fact that tin is not in solid solution but in the form of small aggregates in the alloy used by us, while in the sample used by DELYAGIN there was less tin, and a greater part of it was in solution.

All this shows that the isomer shift in itself does not sufficiently characterize the alloying of the aluminium basis with tin deposited to it.

The half-width at half maximum for the Mössbauer lines vary within the interval of $0.9\text{--}1.8 \text{ mm s}^{-1}$ as a function of the thickness of tin layers; this is in agreement with data plotted in Figure 1. Also the half-width figures 0.99 and 1.84 mm s^{-1} found for a tin foil, sample 1, at various temperatures can be explained on the basis of some kind of thickness effect since the half-width of Mössbauer lines is a function of the effective thickness d_{eff} of a layer; this, in turn, is proportional not only to the thickness of the layer but also to the DEBYE—WALLER factor f [7]: $d_{\text{eff}} = d \cdot f$, where d is the thickness expressed as density on the surface mg cm^{-2} .

The figure for f is 0.05 in the case of β -Sn at room temperature, and 0.4 at the temperature of liquid nitrogen [4, 8]; thus, the decrease of temperature causes an increase, by nearly one order of magnitude, in the effective thickness of a layer and this causes a significant increase in the width of the Mössbauer lines.

With samples 4, 5 and 6 (without plated copper) the isomer shifts are in agreement, within limits of error, with the corresponding data for β -Sn; this does not preclude alloying the aluminium with the tin layer: the δ -value for the Al/Sn alloy, sample 3, metallurgically produced, agrees with the isomer shift of β -Sn.

Tin is deposited upon samples 4, 5 and 6 in the same way, thus we may suppose the thicknesses of the tin layers to be nearly the same. Therefore it is remarkable that $\Gamma \cdot \eta$ values, which are proportional to the effective layer thickness, scatter within a range of nearly one order of magnitude. This divergence can be explained on the basis of the divergence in the DEBYE—WALLER factors. Presumably the f value for sample 6 is prominently great. This effect is further enhanced by the circumstance that only seven aluminium foils were present in sample 6, while ten in the others. Thus in the former absorbent there is less tin present than in the latter ones. The Debye temperature of aluminium is significantly higher than that of tin: $\Theta_{\text{Al}} = 418 \text{ K}$, $\Theta_{\beta\text{-Sn}} = 189 \text{ K}$ [9], thus a more intensive connection of Sn atoms with the crystal lattice of

Al (diffusion into it, alloying, stronger adsorptive binding) explains the considerable increase of f for sample 6.*

The aluminium basis for sample 8 is the same as that for sample 6 but on the former the tin layer has been copper plated. The center of the spectrum in this case is shifted in the negative direction and the half-width increases to nearly twice the original value. By means of a computer fitting program, this spectrum can be resolved into two components. Table I contains the data of the components thus separated. The isomer shift of the one agrees with the

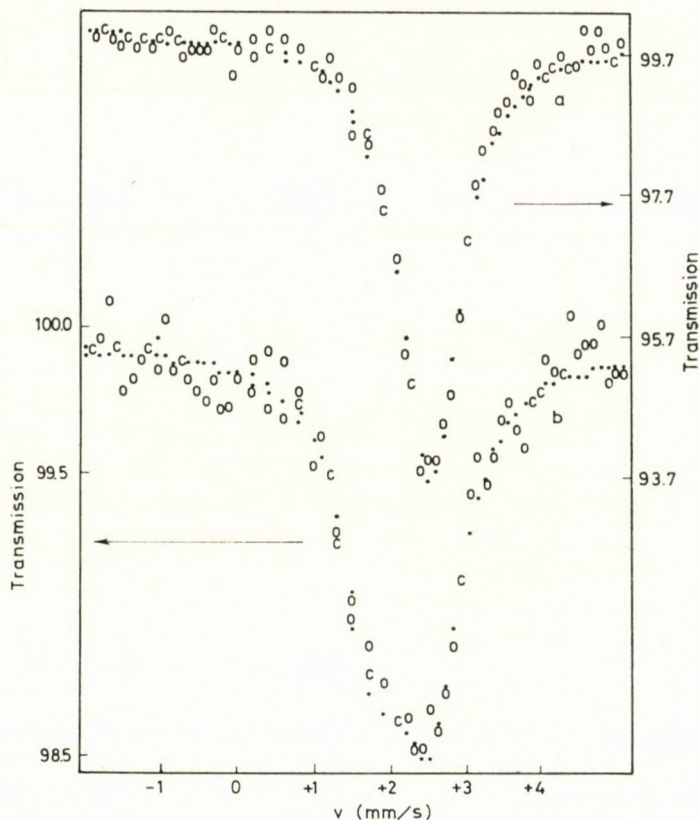


Fig. 2. Mössbauer spectra of samples 6 and 8, (a) and (b), recorded at the temperature of liquid nitrogen. (o stand for points as found · stand for points as fitted, C stand at coincided of points as found and fitted). Only every fourth channel is accounted for in this illustration. The source of radiation is BaSnO_3 with the activity of 1.5×10^8 Bq; spectra due to exposures for three days each

$$* f = \exp \left[- \frac{E_\gamma^2}{2Mk\Theta} \left(\frac{3}{2} + \frac{2T^2}{\Theta^2} \right) \right]$$

where E_γ = the energy of gamma photons; M = mass of a Mössbauer atom; k = Boltzmann's constant; T = temperature in K; and Θ = Debye temperature.

isomer shift of tin metal; for the other, δ is 1.89 mm s^{-1} and this agrees with the isomer shift of an alloy of about 30 mol % Sn and about 70 mol % Cu [6]. Also the comparatively great half-width of this line suggests that the Sn/Cu composition varies within a certain interval: this phase is not homogeneous. The line intensities pertinent to the two components are nearly the same; this suggests that the amount of tin in the two phases are nearly equal. Mössbauer spectra of samples 6 and 8 are shown in Fig. 2.

Consideration of the series of data shown in Fig. 1 permits to estimate the thickness of the layer of tin deposited on the aluminium surface, though uncertainties are greatly increased by the fact that the area of the Mössbauer lines is a function of layer thickness as well as of the DEBYE—WALLER factor and the latter — in the case of very thin layers [10] — also decreases with the layer thickness, thus line area does not decrease linearly but more intensively (exponentially) with the thickness of thinner layers. This effect does not operate, however, when the tin does not form a film on the aluminium surface but forms an alloy with it, as it most probably happens with sample 6. Taking into account all these factors, the thickness of the tin layer deposited on the surface of aluminium, can be estimated to be 1–3 nm.*

In a summary we may conclude that tin deposited on the surface of aluminium containing 17% silicon, sample 6, enters into a more intensive association, supposedly alloying, with the aluminium basis than do tin layers on the other aluminium alloys studied. In the course of the copper-plating process, part of the tin goes into solution and the part retained on the aluminium surface is intensively alloyed to copper.

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* The thickness of a tin layer deposited on 99.5 wt% pure Al and AlSi7Ni8Cu1 foil was determined also directly. Following the usual pre-treatment, a 1 dm^2 foil was kept immersed in 15 cm^3 10% H_2SO_4 . By means of atomic absorption spectra uniformly 10 to 20 ppm Sn was found in this solution made with the various alloys and in parallel tests. In good agreement with the result above, this corresponds to layers 2–4 nm in thickness.

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METAL CATALYZED DEHYDROGENATION OF CYCLOHEXANOL

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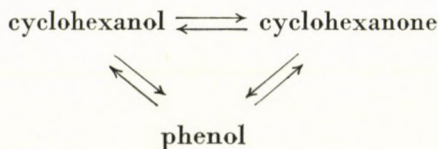
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Transformation of cyclohexanol has been investigated over metal catalysts of group VIIIb in the temperature range 453–633 K using hydrogen or nitrogen carrier gas. In the case of Co catalyst the effect of preparation upon the product distribution has been examined as well. The product distribution observed on various metals was compared on basis of ratios of various products. In terms of product selectivities the investigated metals can be divided into three groups: (1) dehydrogenating metals (Os, Co, Fe, Re, Ru); (2) aromatizing metals (Pd, Pt, Ni); (3) Ir and Rh occupying an intermediate position. The hydrogen response of these groups is also different: with Group 1 hydrogenolysis, with Group 2 aromatization and with Group 3 both reactions were accelerated in the presence of hydrogen.

Introduction

Cyclohexanol is one of the intermediates of polyamide manufacturing, therefore, its dehydrogenation to cyclohexanone has been the subject of several studies. Copper [1] and Ni [2] were among the useful and selective catalysts. The mechanism of this reaction represents considerable interest from the theoretical point of view, too, especially with respect to the possible surface intermediates of cyclohexanone formation and other reactions (aromatization and dehydration).

Earlier, we have reported detailed studies on the reactions of cyclohexanol in the presence of nickel [3] and platinum [4, 5] catalysts. A triangular reaction sequence



has been found to be valid. Radiotracer studies prove that only “direct” aromatization of cyclohexanol is detected over platinum [4, 6], whereas a “step-wise” reaction predominates over nickel and copper [6]. The detailed studies of various VIII B metals as well as rhenium in the reactions of 3-methylpentane,

methylcyclopentane [7, 8] and cyclohexane [9] stimulated us to extend these studies to cyclohexanol as reactant, too. Its main dehydrogenation product, cyclohexanone has been investigated as well, under identical conditions.

The present paper reports the temperature dependence and selectivity of the reaction over all VIII B metals. Results obtained with rhenium are to be reported separately [10]. Some data obtained with platinum have been taken from Ref. [5]; for comparison, however, measurements with nickel, and other data with platinum catalysts have been repeated in order to be able to ensure identical conditions. Metals will be compared on the basis of ratios of various products as suggested by YAMAMOTO and KWAN for phenol hydro- genation [11]. We used, however, several "ratios" of various classes of products to obtain as much information as possible.

Experimental

A pulse-microcatalytic apparatus was used as described by MANNINGER *et al.* [5]. The conditions of gas chromatographic analysis were identical to those described there. 1 μ L pulses of gas chromatographically pure cyclohexanol and cyclohexanone were introduced onto the catalyst, into purified nitrogen (or helium) or hydrogen carrier gas (30 cm³ min⁻¹).

Catalysts: Unsupported metals were used.

Iron was reduced from Fe(COO)₂ · 2H₂O in a flow of hydrogen, *in situ*, at 673 K for 1 h.

Cobalt: Co "powder" supplied by SCHÜCHARDT was pre-reduced at 573 K in hydrogen flow for 2 h. Co-"black" was prepared by reducing Co₂O₃ at 683 K for 1.5 h. The oxide was obtained from Co(NO₃)₃ by precipitating the hydroxide with ammonium hydroxide and subsequent drying.

Nickel was prepared in a way analogous to that described for Co-"black".

Ruthenium: Commercial Ru-powder (Degussa) was mixed with sodium chloride and digested by chlorine gas at 873 K. The soluble chloride obtained was reduced to metal black by HCHO in the presence of KOH [12].

Rhodium was reduced from RhCl₃ · 3H₂O by HCHO according to Ref. [12].

Palladium: Pd-powder was dissolved in aqua regia and reduced as above [12].

Rhenium: NH₄ReO₄ was reduced at 770 K by hydrogen in the presence of MgO, which was subsequently dissolved in HCl [10]. Pretreatment in hydrogen flow at 670 K for 24 h.

Osmium: Degussa metal powder was pretreated in hydrogen flow at 573 K for 1 h.

Iridium was prepared analogously to the procedure described for ruthenium. Another iridium sample was identical to Sample 2 in Ref. [13].

Platinum was reduced from H₂PtCl₆ by HCHO as described in Ref. [12].

Ruthenium, rhodium, palladium, iridium and platinum were pretreated according to Ref. [14].

Results

The products from cyclohexanol were cyclohexanone, phenol, C₆-cyclic hydrocarbons (benzene, cyclohexene and cyclohexane) as well as cracked products and oxygenated fragments. One of them corresponded to *n*-hexanol according to its retention time; C₆ aliphatic ketones seemed also to be present.

Primary dehydrogenation product is cyclohexanone. This is in several cases the main constituent of the effluent. In order to clarify its role in further reactions as well as to determine whether it is more or less reactive than cyclohexanone were also studied under identical conditions.

Hydrogen has been reported to have a very marked effect on catalyst activity and selectivity in hydrocarbon [15] and cyclohexanol [5] transformations over platinum. Therefore, hydrogen effects also were studied. This was done by introducing pulses into nitrogen or hydrogen carrier gas.

a) Temperature effects in nitrogen

Measurements were carried out in the temperature range between 453 and 633 K. The metals can be classified as follows.

Some metals (Co, Ru, Os, Ir and Rh) produce mainly cyclohexanone from cyclohexanol. The amount of aromatization is low but appreciable amounts of cyclohexene are detected. These metals can be called *dehydrogenating* metals.

The overall conversion degree is hardly dependent on the temperature. This is characteristic of Os, Co-powder, Rh; less valid for Co-black, Ru and Ir. Ru and Rh have been selected as typical metals; the yields as a function of temperature are shown in Figs 1 and 2. (A similar plot has been shown for Os and Ir in Ref. [16]).

With cyclohexanone feed, the overall conversion is, as a rule, lower than with cyclohexanol. Apart from phenol, some benzene, cyclohexene and lower amount of cyclohexanol are found (Figures 3 and 4).

Ni, Pd and Pt represent another group. Here the conversion depends on the temperature very strongly. The amount of cyclohexanone is, as a rule,

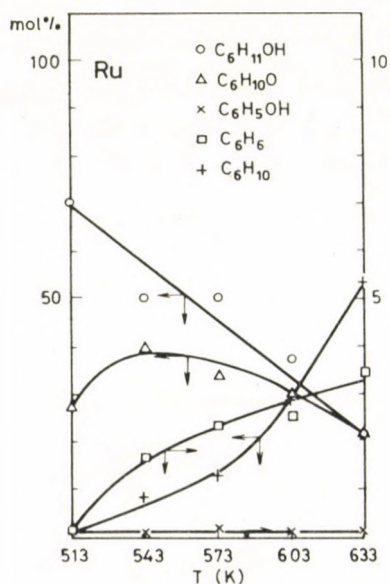


Fig. 1. Transformation of cyclohexanol on Ru, in N₂

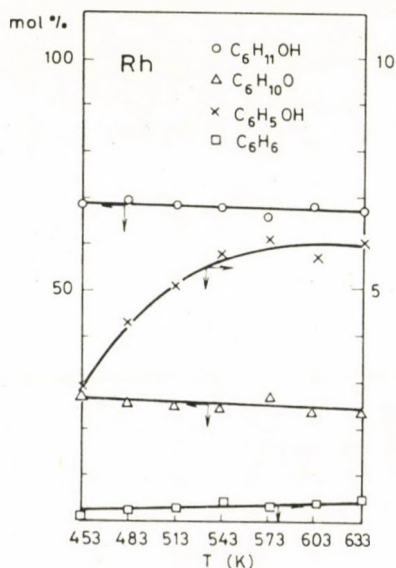


Fig. 2. Transformation of cyclohexanol on Rh, in N₂

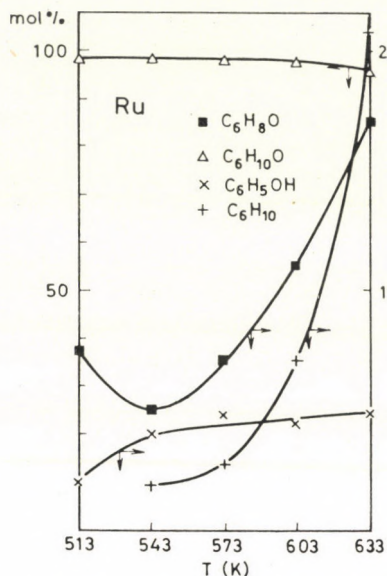


Fig. 3. Transformation of cyclohexanone on Ru, in N_2

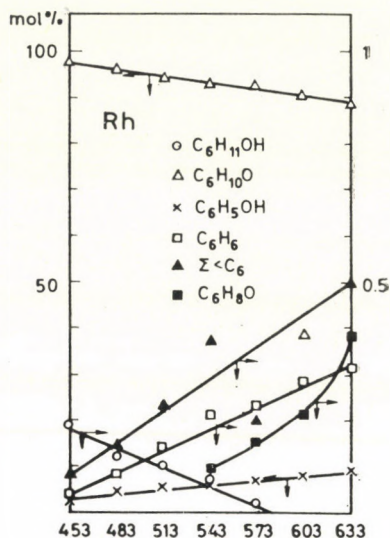


Fig. 4. Transformation of cyclohexanone on Rh, in N_2

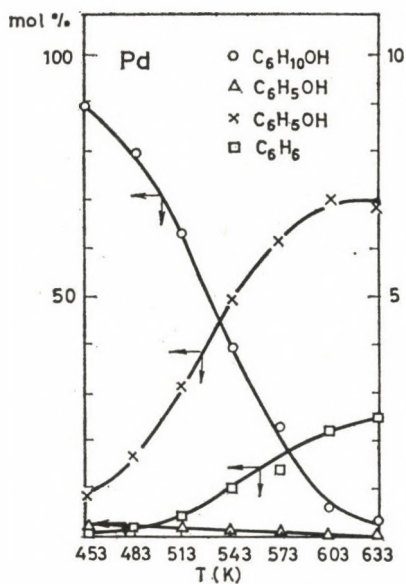


Fig. 5. Transformation of cyclohexanol on Pd, in N_2

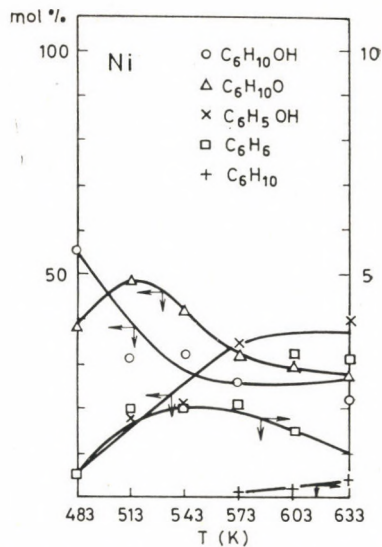


Fig. 6. Transformation of cyclohexanol on Ni, in N_2

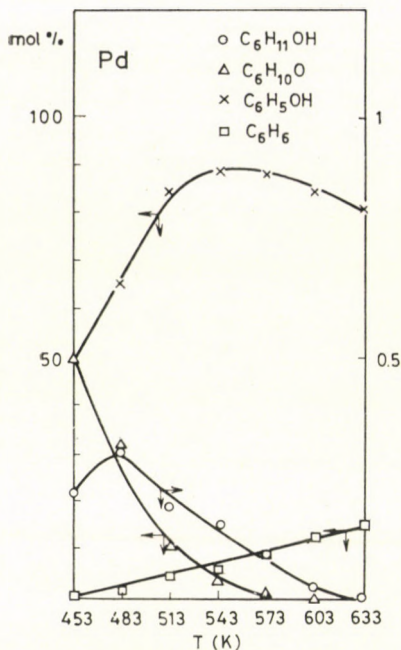


Fig. 7. Transformation of cyclohexanone on Pd, in N_2

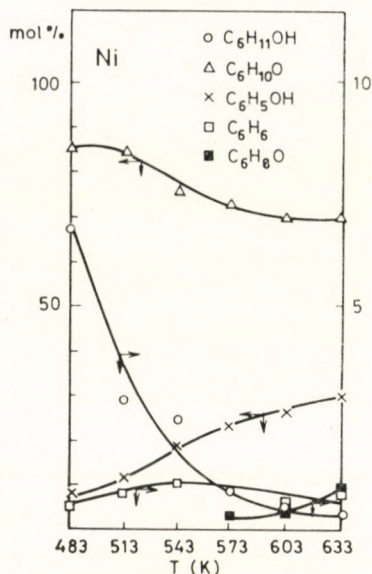


Fig. 8. Transformation of cyclohexanone on Ni, in N_2

low. Phenol and benzene are the main components of the end product. Results with Pd and Ni are shown in Figs 5 and 6.

Cyclohexanone is much more reactive over Pd. It forms mainly aromatics together with small amounts of cyclohexanol (Figs 7 and 8).

These metals can be called *aromatizing* ones.

b) Temperature effects in hydrogen

The application of hydrogen carrier gas may increase or decrease the overall conversion of cyclohexanol. No unambiguous correlation can be found here. There is a general trend, however, that hydrogen suppresses conversion at lower and enhances it at higher temperature (Table I).

A much stronger hydrogen effect is observed in the case of cyclohexanone feed. Its overall conversion is always higher in hydrogen than in nitrogen (Table II). The only exception is palladium. The temperature effect is the reverse here because the accelerating effect of hydrogen is generally much more marked at lower than that at higher temperatures.

The general term "hydrogen effects" include several particular features as far as selectivity changes are concerned. These are illustrated by yield plots analogous to Figs 1–8.

With ruthenium (*i.e.* a typical "dehydrogenating" metal) the overall conversion of cyclohexanol is hardly affected by hydrogen. The selectivity, however, is shifted very much towards cracking. Cyclohexanone formation is almost unchanged. Phenol formation is higher in hydrogen, although its

Table I
Conversion of cyclohexanol at low and elevated temperatures

Metal	Conversion (mol%)			
	in nitrogen		in hydrogen	
	453 K	633 K	453 K	633 K
Os	31	25	16	47
Co(p)	89**	92	22**	88
Co(b)	79**	89	77**	99
Re	47*	93	32*	90
Ru	30**	78	29**	87
Rh	31	33	2	65
Ir	48	45	28	81
Ni	45*	78	10*	67
Pd	20*	96	5*	85
Pt	25	92	8	96

* $T = 483$ K

** $T = 513$ K

Table II
Conversion of cyclohexanone at low and elevated temperature

Metal	Conversion (mol%)			
	in nitrogen		in hydrogen	
	453 K	633 K	453 K	633 K
Os	1	2	69	32
Co(p)	1*	7	29*	18
Co(b)	17*	10	84*	84
Re	3*	22	60*	58
Ru	1**	4	32**	34
Rh	3	10	8	68
Ir	5	7	82	68
Ni	15*	29	31*	46
Pd	68*	100	12*	93
Pt	24	80	70	89

* $T = 483$ K

** $T = 513$ K

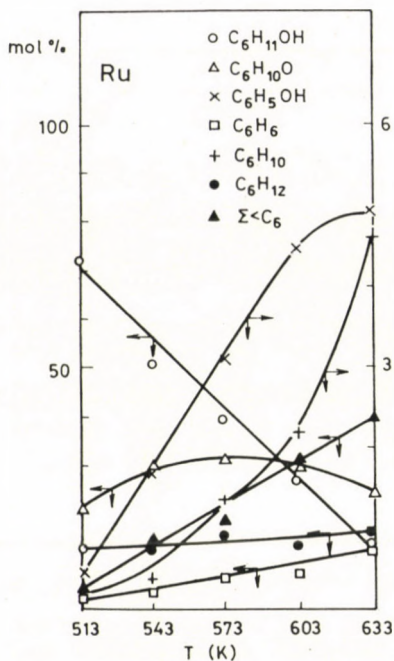


Fig. 9. Transformation of cyclohexanol on Ru, in H_2

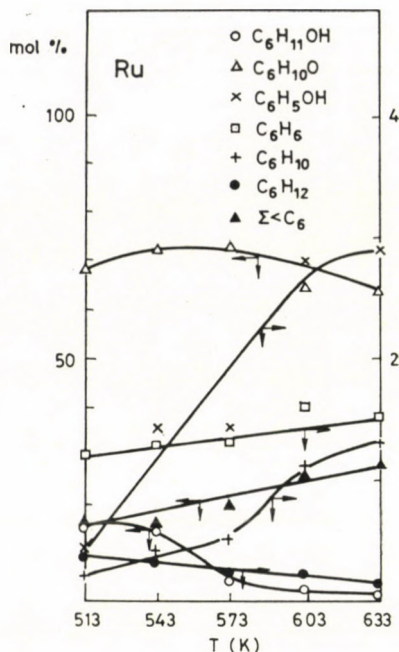


Fig. 10. Transformation of cyclohexanone on Ru, in H_2

absolute amount is still not too high. Cyclohexane formation is hardly influenced, cyclohexane formation being enhanced by hydrogen (*cf.* Figs 4, 1 and 9).

With cyclohexanone feed, hydrogen increases again the overall conversion over ruthenium. This, however, remains also almost temperature independent. This is mainly due to cracking and, to a lesser extent, hydrogenation to cyclohexanol. Hydrocarbon formation is lower than with cyclohexanol (*cf.* Figs 3 and 10).

With *rhodium*, hydrogen changes the composition more drastically. The plots for cyclohexanol and cyclohexanone are shown in Figs 11 and 12, respectively. A strong temperature dependence of the overall conversion is observed. The appearance of cracked products resembles the picture seen with ruthenium (Figs 9 and 10). At the same time, however, also considerable aromatization occurs. Hydrogenation of cyclohexanone to cyclohexanol at lower temperatures can also be pointed out.

Hydrogen exerts much weaker effects on the aromatizing metals. With palladium, similar results are obtained, therefore, its illustration is not necessary. Nickel has been selected as a typical metal (Figs 13 and 14). Hydrogen suppresses the overall conversion especially with cyclohexanol (Figs 6 and 13). It suppresses aromatization to some extent.

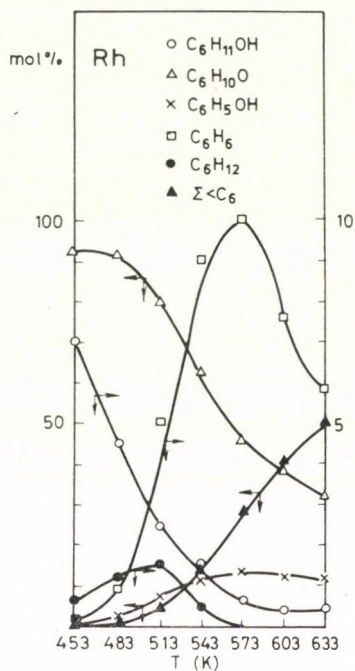
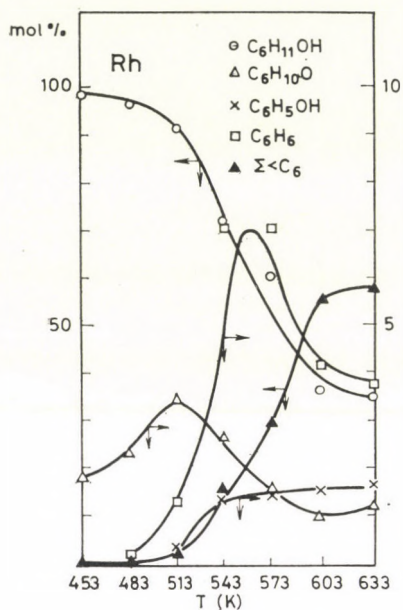


Fig. 11. Transformation of cyclohexanol on Rh, in H_2

Fig. 12. Transformation of cyclohexanone on Rh, in H_2

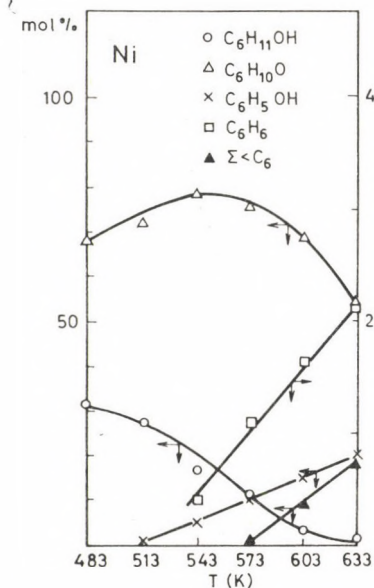
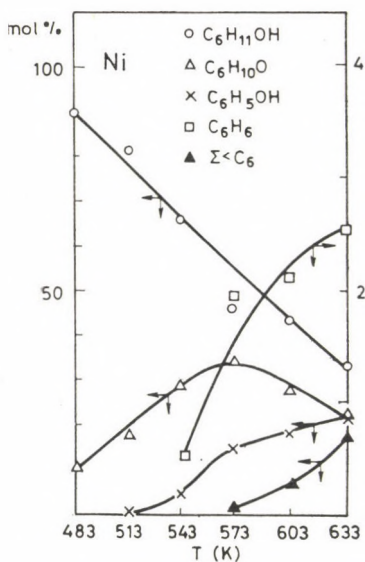


Fig. 13. Transformation of cyclohexanol on Ni, in H_2

Fig. 14. Transformation of cyclohexanone on Ni, in H_2

Table III
Transformation of cyclohexanol and cyclohexanone on iron in hydrogen

No.	Feed	Product composition (mol%)							
		<C ₄	C ₄ H ₁₂	C ₆ H ₁₀	C ₄ H ₆	C ₆ H ₁₀ O	C ₆ H ₁₁ OH	C ₆ H ₅ OH	Others*
1.	C ₆ H ₁₁ OH	2.29	11.35	22.95	0.64	43.58	15.55	2.37	1.26
2.	C ₆ H ₁₁ OH	2.39	8.51	16.42	0.44	50.15	19.44	1.87	0.78
3.	C ₆ H ₁₁ OH	2.19	10.98	20.64	0.28	46.03	16.75	2.00	1.12
4.	C ₆ H ₁₀ O	2.75	7.62	17.52	0.50	55.48	12.01	2.76	1.36

$T = 573 \text{ K}$

No. 1: measured immediately after pretreatment, 2: without regeneration, 3: catalyst was in a stream of H₂ at room temperature for overnight, then was heated up in H₂ to 573 K for 50 minutes prior to measurement, 4: without regeneration

* Unknown products (dimers and oxygenated products)

As far as other metals are concerned, Co and Os can be ranked together with Ru. Rhenium [10] also belongs to this group and so does iron. The activity of Fe was studied in hydrogen only (immediately after the thermal decomposition of iron oxalate). Typical results obtained with Fe are shown in Table III.

Iridium is similar to rhodium [16].

Aromatizing metals (Ni, Pd, Pt) keep their character in hydrogen, too.

c) *Effect of catalyst preparation*

This was studied with Co catalyst only. The commercial Co-powder proved to have large crystallites (60 nm) and was a rather stable f.c.c. metal. Co-black (prepared by reduction of Co₂O₃ obtained by precipitation of Co(OH)₃ from Co(NO₃)₃ and its subsequent dehydration) was much more disperse (22 nm) and was a 1 : 1 mixture of f.c.c. and c.p.h. metals.* Their catalytic behaviour was rather different.

Both cobalt catalysts acted like ruthenium-type metals in nitrogen, with almost temperature-independent overall conversion and predominant formation of cyclohexanone from cyclohexanol. Cyclohexanone feed gave an intermediate dehydrogenation product: cyclohexenone (C₆H₈)O (Table IV). It can be noted that of all the metals studied Co-black is the strongest dehydrogenating metal per unit surface in nitrogen [17].

A large difference appears in hydrogen. Whereas Co-powder exhibit strong dehydrogenating character in hydrogen, too, Co-black is a severely

* The authors are indebted to Drs. L. KERTÉSZ and I. MANNINGER for X-ray diffraction measurements.

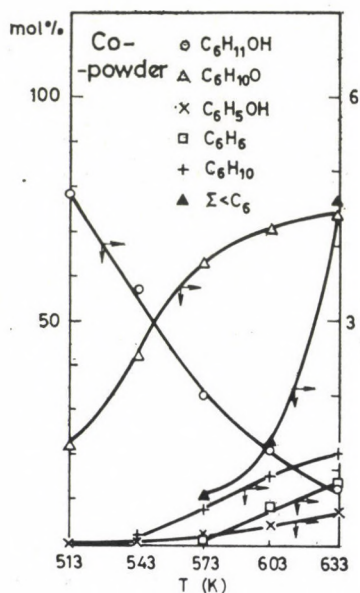


Fig. 15. Transformation of cyclohexanol on Co-powder, in H_2

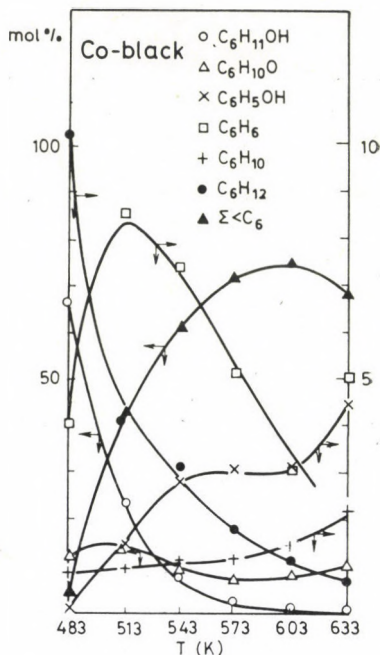


Fig. 16. Transformation of cyclohexanol on Co-black, in H_2

fragmenting metal (Figs 15 and 16). With cyclohexanone reactant, essentially the same difference is observed.

Both cobalts form detectable amounts of cyclohexene (except for Co-powder from cyclohexanone in nitrogen) (Table IV and Figs 15–16).

Table IV

Transformation of cyclohexanol and cyclohexanone on cobalt

Catalyst	Feed	Product composition (mol%)							
		<C ₆	C ₆ H ₁₂ +C ₆ H ₁₀	C ₆ H ₆	C ₆ H ₁₂ OH	C ₆ H ₁₀ O	C ₆ H ₅ OH	C ₄ H ₈ O	Others
Co(p)*	C ₆ H ₁₁ OH	0.21	0.27	0.17	10.94	85.11	3.04	—	0.26
	C ₆ H ₁₀ O	0.04	0.01	0.03	—	96.48	0.96	2.42	0.05
Co(b)	C ₆ H ₁₁ OH	3.32	3.01	1.74	8.67	72.21	8.31	—	2.74
	C ₆ H ₁₀ O	1.29	0.80	1.19	1.25	90.66	3.77	0.65	0.39

* p — powder, b — black

T = 573 K

Carrier gas: N₂

Discussion

The above treatment of metals already advances the possibility of some classification. After all, the distinction of three groups seems reasonable (including also Re to be discussed in Ref. [10]).

1. Group 1 includes dehydrogenating metals proper: Os, Ru, Co, Fe and Re. Copper [6] seems to be close to this group.

2. Group 2 consists of Ni, Pd and Pt; aromatization is characteristic of them.

It is justified to define a third, intermediate group for Rh and Ir. They are close to Group 1 in nitrogen, in hydrogen, however, they show enhanced cracking (like Group 1) and their aromatizing activity increases as well. This latter activity may reach that of metals in Group 2 [7].

Let us attempt to *quantify* the above classification. One of the possible methods to do so is to use the "ratios" of various products or classes of products as suggested by YAMAMOTO and KWAN [11]. The following "ratios" have been defined and used in this work.

Aromatic ratio: (Table V)

$$A = \frac{\text{phenol} + \text{benzene}}{\text{cyclohexanone}}$$

Aromatizing metals are those where this ratio is near to or higher than unity. It is seen that Rh and Ir are among the aromatizing metals in hydrogen. The behaviour of Co-black shows that it is, in some respects, close to Ni. It is, nevertheless, not an aromatizing metal (see later).

Benzene to phenol ratio: (Table V)

$$B = \frac{\text{benzene}}{\text{phenol}}$$

Table V shows that — in spite of very different overall yield values — various metals are surprisingly similar to each other inasmuch as the values of *B* from cyclohexanol and cyclohexanone are close to each other, except for Rh in H₂, where benzene formation is exceptionally high.

The next ratio (*C*) characterizes the adverse or favourable effect of hydrogen on the hydrogenolysis of the phenolic OH group (Table V):

$$C = \frac{(\text{benzene/phenol}) \text{ in hydrogen}}{(\text{benzene/phenol}) \text{ in nitrogen}}$$

Table V

Aromatic ratio from cyclohexanol (A), hydrogenolysis of phenolic OH group from cyclohexanol and cyclohexanone (B), and the effect of hydrogen on the hydrogenolysis of the phenolic OH group (C) in H₂ and N₂, respectively, at 573 K







Catalyst	Feed: C ₆ H ₁₁ OH					Feed: C ₆ H ₁₀ O		
	A		B		C	B		C
								
N ₂	H ₂	N ₂	H ₂	bz/ph in H ₂ bz/ph in N ₂	N ₂	H ₂	bz/ph in H ₂ bz/ph in N ₂	
Os	0.038	0.015	0.13	1.26	9.69	0.21	0.85	4.05
Co(p)	0.038	0.035	0.056	0.031	0.55	0.031	0.009	0.29
Co(k)	0.14	1.27	0.21	1.65	6.60	0.32	1.11	3.47
Fe	—	0.02	—	0.24	—	—	0.18	—
Re	0.038	0.069	1.40	1.31	0.94	1.07	1.57	1.47
Ru	0.10	0.29	1.92	1.86	0.97	—	0.89	—
Rh	0.23	5.61	0.051	4.87	95.49	0.032	0.80	25.00
Ir	0.21	1.29	0.39	0.50	1.28	0.16	0.56	3.50
Ni	1.15	0.50	0.061	0.13	2.13	0.037	0.10	2.70
Pd	71.39	2.35	0.23	0.15	0.65	0.10	0.10	1.00
Pt	8.05	2.68	0.69	0.51	0.74	0.54	0.40	0.80

Table VI

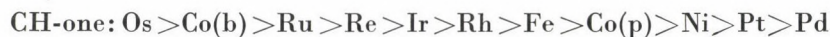
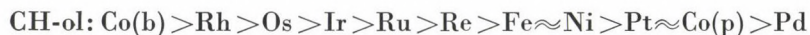
Comparison of dehydrogenation reactivity of cyclohexanone to cyclohexanol (*D*), ratio of phenol to and cyclohexanone (*E*),

Catalyst	<i>D</i>		H_2
	from $C_5H_{10}O$	from $C_6H_{11}OH$	
Os	0.24		0.028
Co(p)	0.28		0.16
Co(b)	0.53		0.56
Ee	—		0.11
Re	0.55		0.15
Ru	0.44		0.15
Rh	0.96		1.81
Ir	0.74		0.72
Ni	0.93		0.51
Pd	1.00		0.94
Pt	0.99		0.85

The ratio *E* (Table VI):

$$E = \frac{\text{< } C_6 \text{ fragments}}{C_6 \text{ dehydrogenation products}}$$

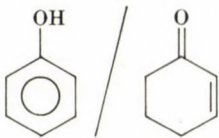
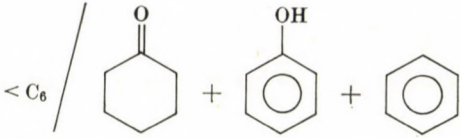
gives evidence for the enhanced cracking activity in hydrogen, especially with Group 1 and 3 metals. It is worth comparing the order obtained on the basis of the *E*-values in hydrogen at 573 K:



with those obtained for the activity of metals in 3-methylpentane hydrogenolysis [7]:



cyclohexenone (*D'*) and ratio of C—C bond hydrogenolysis and dehydrogenation from cyclohexanol at 573 K

Feed: C ₆ H ₁₀ O	Feed: C ₆ H ₁₁ OH	Feed: C ₆ H ₁₀ O
<i>D'</i>	<i>E</i>	
		
N ₂	H ₂	H ₂
0.29	0.92	53.8
0.51	0.01	0.44
1.52	4.81	8.8
—	0.05	0.84
3.70	0.36	4.8
0.29	0.47	7.4
23.76	2.94	1.15
7.51	0.87	1.6
26.00	0.05	0.14
> 8000	—	—
> 700	0.01	0.015

and ethane hydrogenolysis [18]:



The so-called "threshold temperature" (*i.e.* the *T*-value necessary to achieve a given low reaction rate) was used in the latter two cases for characterizing the activity of metals.

Cyclohexanone may either hydrogenate or dehydrogenate.

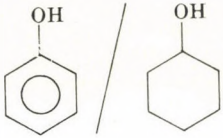
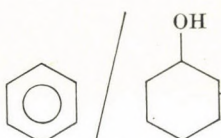
The ratio *F* (Table VII):

$$F = \frac{\text{phenol}}{\text{cyclohexanol}} \text{ (from cyclohexanone)}$$

evidences a predominant hydrogenation at lower and a predominant dehydrogenation at higher temperatures. Although this is in agreement with the general thermodynamics of the process [11], the various values obtained with

Table VII

Ratio of dehydrogenated products (*F*) and formation of products by utilizing hydrogen (*G*), at 573 K

Catalyst	Feed: C ₆ H ₁₀ O							
	<i>F</i>						<i>G</i>	
								
T (K)	N ₂			H ₂			N ₂	H ₂
	513	573	655	513	573	633		
equilibr.	0.25	63	5 × 10 ³	—	—	—		
Os	0.36	>2000	>1800	0.004	0.039	0.37	0.033	0.033
Co(p)	6.2	>2500	>3000	0.005	0.19	1.15	>800	0.017
Co(b)	0.78	3.02	>4000	0.05	1.00	4.13	0.95	1.11
Fe	—	—	—	—	0.23	—	0.041	0.041
Re	0.49	4.23	32.3	0.02	0.21	0.62	4.53	0.33
Ru	>2000	0.69	>1000	>120	0.35	>800	—	0.31
Rh	51.8	—	>8000	2.78	21.02	23.7	~300	16.72
Ir	7.3	—	>4000	0.15	2.71	11.1	~800	1.52
Ni	3.8	26.9	70	0.04	0.99	12.1	1.00	0.10
Pd	453	1127	8000	0.89	13.8	238	115	1.40
Pt	6.66	74.4	197	0.09	3.98	45.2	40	1.59

different catalysts as compared with the equilibrium value (Table VII) indicate without doubt that kinetic and not thermodynamic effects are important here. This is also shown by the very different hydrogen effects. This indicates that the "effective hydrogen concentration" [19] on the surface may differ very much from that in the gas phase and the nature of the metal plays a decisive role in determining this. Surface hydrogen originates from the carrier gas or — in nitrogen — from hydrogen producing reactions, *i.e.* dehydrogenation. It may either desorb or be utilized by hydrogen consuming reactions: cyclohexanone hydrogenation or hydrogenolytic splitting of the phenolic OH group.

Ratio G gives some approximate information about the direction of this utilization (Table VII):

$$G = \frac{\text{benzene}}{\text{cyclohexanol}} \text{ from cyclohexanone.}$$

Low *G*-values mean that aromatization is negligible as compared with hydrogen (Os, Fe). High *G*-values mean enhanced benzene formation, either *via* cyclo-

hexene (dehydration: Co, Re) or via phenol (aromatization: Rh, Ir, Pd, Pt). The similarity of Ni and Co (b) is noteworthy. Hydrogenation to cyclohexanol is accelerated by hydrogen atmosphere especially with Co(p), Pd, Re and Ni.

Conclusions

The above experimental data give a good qualitative and quantitative picture about the activity of various metals. It gives a profound basis to classify these catalysts into three groups. Group 1 and Group 2 differ from each other with respect to their inherent selectivities. These selectivities are influenced by the presence of hydrogen in a way characteristic of these different groups. The hydrogen response is the main factor serving as a basis for distinguishing Group 3 metals. Whereas they behave like Group 1 in nitrogen, a peculiar intermediate position combining the features of both groups is observed with them in hydrogen.

The general order of metal activity in hydrocarbon and cyclohexanol reactions shows many common features. The presence of an oxygen atom in the molecule enhances its reactivity. Aromatization of cyclohexanol takes place more rapidly than that of cyclohexane, whereas cyclohexene is more reactive than cyclohexanol. The primary interaction of the molecule with the metal must take place with the participation of the O-atom but it ensures a lower reactivity than a C=C double bond. Although the rapid formation of surface carbonyl from cyclohexanol has been shown unambiguously by IR studies [20, 21], cyclohexanone reacts more slowly, which may be due to its more stable bonding to the metal, partly blocking the active sites.

The presence of the OH group enhances not only dehydrogenation reactions: the yield of ring fragments is much higher than with cyclohexane [9].

It is true that fragmentation commences, as a rule, in the vicinity of the oxygen atom. The amount of such fragments as *n*-hexane is, however, generally low: strongly cracking metals (Table VI) give methane and other low molecular fragments. The comparison of the activity order according to the *E*-value (Table VI) with that found in the hydrogenolysis of hydrocarbons points to the relative reactivities of the oxygenated and the hydrocarbon parts of the molecule. Rh, Ir, Ru and also Ni are further back in the rank according to the *E*-value than in hydrocarbon hydrogenolysis. This means that they are more active in dehydrogenation than in C—C bond breaking, although their fragmentation activity (except for Ni) is not low. At the same time, the utilization of "retained" (or liberated during reaction) hydrogen for C—OH bond splitting (Ratio *G*) shows rather an opposite course: selectively fragmenting metals are inactive in the phenol→benzene reaction and vice versa.

All these data enumerated, together with radiotracer and infrared studies permitted us to put forward a generalized scheme for metal-cyclohexanol interactions; this will be discussed in a separate paper [17].

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OXAZEPINES AND THIAZEPINES, XI*

CONVERSION OF 1-THIOFLAVANONE DERIVATIVES INTO BENZOTHAZEPINONES

SHORT COMMUNICATION

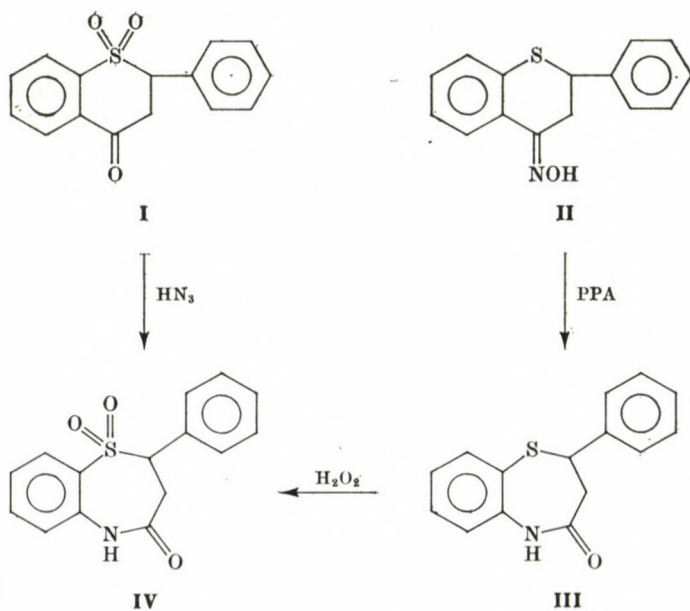
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In our previous paper [2] we reported that the Schmidt reaction of 1-thioflavanone gave 2,3-dihydro-2-phenyl-1,4-benzothiazepin-5(4*H*)-one and 2,3-dihydro-2-phenyl-1,5-benzothiazepin-4(5*H*)-one in 1 : 1 ratio. The same reaction has now been accomplished with 1-thioflavanone-1,1-dioxide (**I**) to obtain 2,3-dihydro-2-phenyl-1,5-benzothiazepin-4(5*H*)-one-1,1-dioxide (**IV**) as the single product. For a comparative structure elucidation compound **IV** was also prepared by the oxidation of 2,3-dihydro-2-phenyl-1,5-benzothiazepin-4(5*H*)-one (**III**).



* For Part X, see Ref. [1].

The Schmidt reaction of 1-thiochromanones and 1-thiochromanone-1,1-dioxides, variously substituted in the aromatic ring, was studied by WÜNSCH *et al.* [3] and it was found that 1-thiochromanones gave a mixture of 1,4- and 1,5-benzothiazepinones, while their sulfones yielded 1,5-benzothiazepinone-1,1-dioxides only. These results and our present findings show that the incorporation of the sulfur hetero atom into a sulfone group favours the formation of such intermediates, probably by modification of the electron distribution of the molecule, which then give 1,5-benzothiazepinones.

1-Thiochromanone could be converted into benzothiazepinone not only *via* the Schmidt reaction [3] but also by the Beckmann rearrangement of its oxime [4]. Now, we report on the Beckmann rearrangement of 1-thioflavanone oxime (II). The oxime was allowed to react with polyphosphoric acid (PPA), whereupon 2,3-dihydro-2-phenyl-1,5-benzothiazepin-4(5*H*)-one (III) was obtained. The presence of 2,3-dihydro-2-phenyl-1,4-benzothiazepin-5(4*H*)-one could not be detected in the reaction mixture. Hence it can be stated that the Beckmann rearrangements of 1-thiochromanone oxime and 1-thioflavanone oxime occur similarly, leading to the formation of 1,5-benzothiazepinones.

Experimental

M.p.'s are uncorrected.

The IR spectra were taken in KBr pellets on a UNICAM SP 200G instrument.

1-Thioflavanone-1,1-dioxide (I) [6], 1-thioflavanone oxime (II) [7], and 2,3-dihydro-2-phenyl-1,5-benzothiazepin-4(5*H*)-one (III) [5] used as starting materials were prepared by known procedures.

2,3-Dihydro-2-phenyl-1,5-benzothiazepin-4(5*H*)-one-1,1-dioxide (IV)

(a) Concentrated sulfuric acid (2.0 mL) was added, in portions, to a stirred and cooled mixture of 1-thioflavanone-1,1-dioxide (I) (2.0 g), sodium azide (2.0 g) and trifluoroacetic acid (20.0 mL). The mixture was stirred for further 2 h at 50 °C and then poured into water. The precipitated material was filtered off, washed free of acid, and crystallized from methanol to yield a white crystalline substance (1.7 g; 80.9%), m.p. 238–240 °C (decomp.).

(b) A mixture of 2,3-dihydro-2-phenyl-1,5-benzothiazepin-4(5*H*)-one (III) (1.0 g), 35% hydrogen peroxide (5.0 mL) and acetic acid (20.0 mL) was heated on a steam-bath for 3 h and then poured into water. The solidified substance was filtered off, washed free of acid, and crystallized from methanol to afford a white crystalline product (0.8 g; 72.7%), m.p. 239–240 °C (decomp.).

IR: $\nu_{\text{C=O}}$ 1680; ν_{SO_2} 1120, 1150 cm^{-1} .

$\text{C}_{15}\text{H}_{13}\text{NO}_3\text{S}$ (287.25). Calcd. N 4.87; S 11.15. Found N 4.90; S 11.26%.

Beckmann rearrangement of 1-thioflavanone oxime

A mixture of 1-thioflavanone oxime (II) (1.0 g) and polyphosphoric acid (10.0 g) was heated at 120 °C for 1 h, then diluted with cold water and neutralized with NaHCO_3 . The precipitated material was filtered off, washed with water and crystallized from methanol to yield 2,3-dihydro-2-phenyl-1,5-benzothiazepin-4(5*H*)-one (III) (0.65 g; 65.0%), m.p. 178–179 °C, *Lit.* [5] m.p. 176–177 °C.

IR: $\nu_{\text{C=O}}$ 1672 cm^{-1} .

$\text{C}_{15}\text{H}_{13}\text{NOS}$ (255.25). Calcd. N 5.49; S 12.54. Found N 5.34; S 12.55%.

*

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SYNTHESIS OF CHLORFLAVONIN

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The synthesis of chlorflavonin, a naturally occurring antifungal antibiotic, is reported.

The isolation and antifungal activity of chlorflavonin (**I**) were reported by RICHARDS *et al.* [1] in 1969. Detailed structure elucidation of the compound was then performed by BIRD and MARSHALL [2] who unequivocally proved that chlorflavonin was 3'-chloro-2',5-dihydroxy-3,7,8-trimethoxyflavone. The synthesis of this antibiotic has not yet been described in the literature.

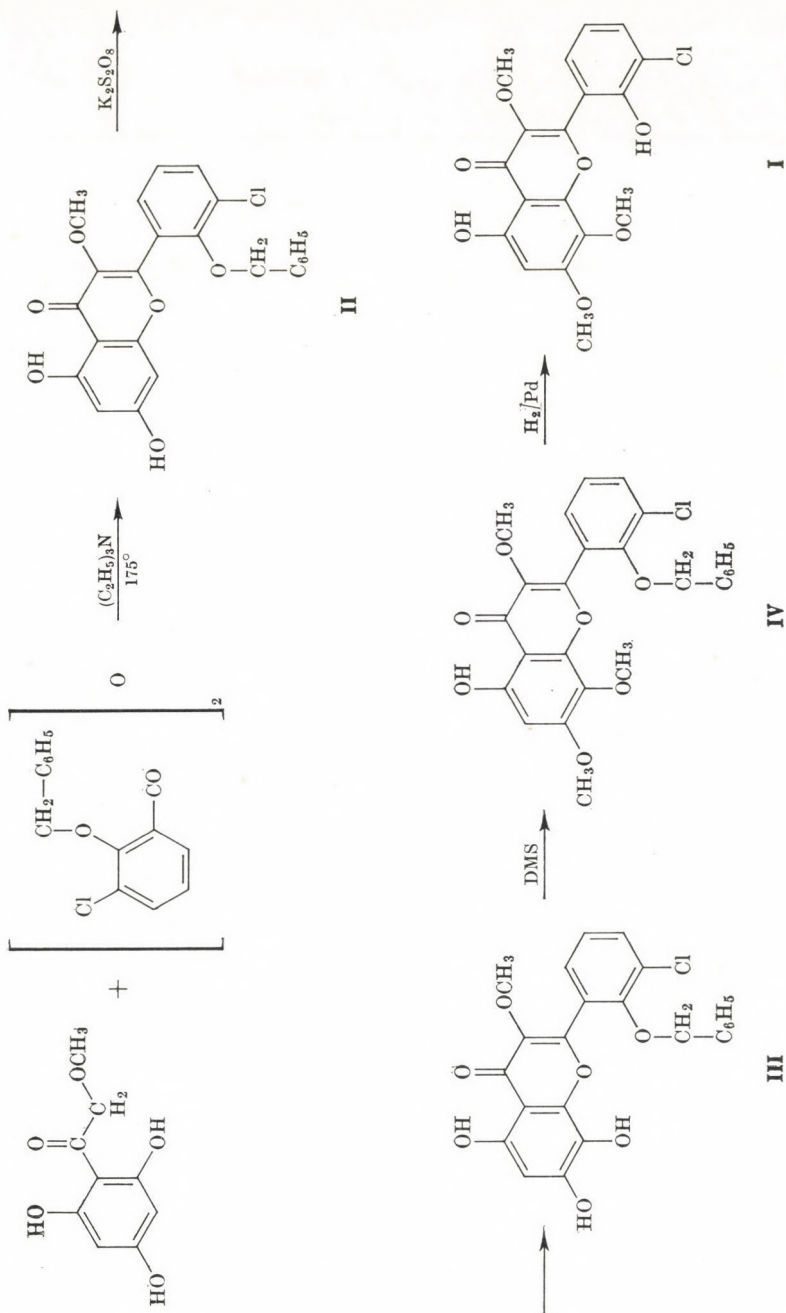
Of chlorflavonin derivatives, dimethylchlorflavonin (3'-chloro-2',3,5,7,8-pentamethoxyflavone) was prepared by AHMAD and RAZAQ [3] in 1977 and methylchlorflavonin (3'-chloro-5-hydroxy-2',3,7,8-tetramethoxyflavone) by us in 1979 [4]. In the present paper an unambiguous synthesis of chlorflavonin is reported. The major steps of this synthesis are shown by Scheme 1.

3'-Chloro-2'-benzyloxy-5,7-dihydroxy-3-methoxyflavone (**II**) was prepared from *o*-methoxyphloracetophenone and 2-benzyloxy-3-chlorobenzoic anhydride using the Allan–Robinson synthesis as modified by KUHN and Löw [5]. *Para*-oxidation [6] of compound **II** gave 3'-chloro-2'-benzyloxy-5,7,8-trihydroxy-3-methoxyflavone (**III**), which yielded 3'-chloro-2'-benzyloxy-5-hydroxy-3,7,8-trimethoxyflavone (**IV**) on methylation with dimethyl sulfate in acetone. Elimination of the benzyl group afforded then chlorflavonin (**I**), the physical constants and spectral properties of which were in full agreement with the published data [1, 2].

Experimental

M.p.'s are uncorrected.

The UV spectra were recorded with a UNICAM SP 800 instrument, and the IR spectra were obtained (in KBr pellets) with a UNICAM SP 200G apparatus. The NMR spectra were measured with a JEOL MH-100 spectrometer in deuteriochloroform (internal standard TMS, $\delta = 0$ ppm) at room temperature.



Scheme 1

2-Benzoyloxy-3-chlorobenzaldehyde

3-Chlorosalicylaldehyde [7] (2.24 g; 14 mmoles) was dissolved in dimethyl formamide (10 mL), and benzyl chloride (2.9 g; 23 mmoles) and dry potassium carbonate (4.5 g) were added. The mixture was refluxed for 1 h, cooled, diluted with water (10 mL) and acidified with a few drops of conc. hydrochloric acid, then extracted with chloroform. The solution was washed with water, dried over $MgSO_4$ and the solvent evaporated under reduced pressure to obtain a white crystalline product (2.3 g; 66.6%), m.p. 40 °C.

$C_{14}H_{11}ClO_2$ (246.7). Calcd. Cl 14.37. Found Cl 14.36%.

NMR: δ 5.18 (s, 2H, CH_2); 7.2–7.8 (m, 8H, aromatic protons); 10.16 (s, 1H, CHO).

2-Benzoyloxy-3-chlorobenzoic acid

(a) 2-Benzoyloxy-3-chlorobenzaldehyde (1.2 g; 5 mmoles) was dissolved in a hot mixture of ethanol (30 mL) and 10% $KHCO_3$ solution (12.5 mL). $KMnO_4$ (1.2 g) dissolved in hot water (15 mL) was added under reflux and with stirring; the reaction mixture was then refluxed for 2 h and filtered. The filtrate was acidified with conc. hydrochloric acid; the 2-benzoyloxy-3-chlorobenzoic acid precipitated on cooling. The crude product was crystallized from water to afford white needles (1.0 g; 76%), m.p. 95–96 °C.

(b) 2-Benzoyloxy-3-chlorobenzaldehyde (1.2 g; 5 mmoles) and silver nitrate (1.69 g; 10 mmoles) were dissolved in hot water (7.5 mL), then 40% sodium hydroxide (2.5 mL) was added, in portions, to the hot solution. The mixture was refluxed for 30 min, then filtered and the filtrate acidified with dilute (1 : 1) hydrochloric acid, with cooling. The precipitated material was filtered off and recrystallized from water to yield white needles (1.1 g; 84%), m.p. 95 °C.

$C_{14}H_{11}ClO_3$ (262.7). Calcd. Cl 13.49. Found Cl 13.91%.

NMR: δ 5.24 (s, 2H, CH_2); 7.3–8.0 (m, 8H, aromatic protons); 10.8 (s, 1H, COOH).

2-Benzoyloxy-3-chlorobenzoic anhydride

2-Benzoyloxy-3-chlorobenzoic acid (2.0 g; 7 mmoles) and dry pyridine (0.61 mL; 7 mmoles) were dissolved in dry benzene (12 mL), and thionyl chloride (0.27 mL; 3.5 mmoles) in dry benzene (14 mL) was added to the cooled solution. After 14 h stirring, the reaction mixture was poured onto crushed ice, the organic phase separated, washed with water, with $NaHCO_3$ solution, then with water again and dried over $MgSO_4$. The solvent was evaporated under reduced pressure, and the residue, which contained some starting material, was purified by column chromatography using Kieselgel 60 (Merck) and benzene-methanol 89 : 11 (v/v) eluent to obtain a syrupy substance (1.3 g; 73%).

$C_{28}H_{20}Cl_2O_5$ (507.3). Calcd. Cl 13.96. Found Cl 13.72%.

3'-Chloro-2'-benzyloxy-5,7-dihydroxy-3-methoxyflavone (II)

ω -Methoxyphloracetophenone (1.98 g; 10 mmoles) and 2-benzoyloxy-3-chlorobenzoic anhydride (20.29 g; 40 mmoles) were suspended in triethylamine (5 mL) and heated for 1 h at 175 °C. The cooled material was then refluxed in a mixture of methanol (100 mL) and 60% KOH solution (16 mL) for 30 min. The methanol was evaporated under reduced pressure and water (80 mL) was added to the residue. The aqueous solution was saturated with carbon dioxide to yield a yellow precipitate which was crystallized from aqueous ethanol to afford a crystalline product (1.0 g; 23%), m.p. 250 °C.

$C_{23}H_{17}ClO_6$ (424.8). Calcd. Cl 8.34. Found Cl. 8.20%.

IR: $\nu_{C=O}$ 1650 cm^{-1} .

3'-Chloro-2'-benzyloxy-5,7,8-trihydroxy-3-methoxyflavone (III)

3'-Choro-2'-benzyloxy-5,7-dihydroxy-3-methoxyflavone (II) (0.8 g; 1.8 mmole) and KOH (0.8 g) were dissolved in water, and $K_2S_2O_8$ (0.6 g) in water (20 mL) was added, in portions, to the cooled solution. After 12 h stirring and acidifying with hydrochloric acid, the unchanged starting material was filtered off $\cdot Na_2SO_3$ (1.5 g) and concentrated hydrochloric acid (15 mL) were added to the solution, then heated on a steam bath for 30 min to obtain a crystalline product (0.16 g; 20%), m. p. 175 °C, on cooling.

$C_{23}H_{17}ClO_7$ (440.8). Calcd. Cl 8.04. Found Cl 7.95%.

IR: $\nu_{C=O}$ 1650 cm^{-1} .

3'-Chloro-2'-benzyloxy-5-hydroxy-3,7,8-trimethoxyflavone (IV)

A mixture of compound **III** (0.16 g; 0.36 mmole), dimethyl sulfate (0.06 mL), K_2CO_3 (0.6 g) and acetone (5 mL) was refluxed on a steam bath for 1 h, then the solid material was filtered off. Hot water was added to the filtrate until turbidity, whereupon a yellow product precipitated which was recrystallized from aqueous acetone to yield a crystalline substance (0.10 g; 62%), m.p. 184 °C.

$C_{25}H_{21}ClO_7$ (468.8). Calcd. Cl 7.56. Found Cl 7.50%.

IR: $\nu_{C=O}$ 1650 cm^{-1} .

3'-Chloro-2',5-dihydroxy-3,7,8-trimethoxyflavone (I, Chlorflavonin)

Compound **IV** (0.10 g; 0.21 mmole) was dissolved in acetone (20 mL) and debenzylated with hydrogen (5 mL) in the presence of Pd/C catalyst (0.1 g). After removal of the catalyst by filtration, the solution was diluted with water to obtain a yellow solid (0.06 g; 75%), m.p. 210 °C, *lit.* [1] m.p. 212 °C. With ethanolic $FeCl_3$ it gave a deep green colour.

$C_{18}H_{15}ClO_7$ (378.75). Calcd. Cl 9.35; OCH_3 24.55. Found Cl 9.50; OCH_3 25.16%.

IR: $\nu_{C=O}$ 1660 cm^{-1} .

NMR: δ 3.78, 3.80, 3.86 (s, 9H, $30CH_3$); 6.32 (s, 1H, 6-H); 7.32–8.02 (m, 4H, 2'-OH and 4',5',6'-H aromatic protons); 13.15 (s, 1H, 5-OH). *Lit.* [2] δ 3.87, 3.92, 3.97 (s, 9H, $30CH_3$); 6.43 (s, 1H, 6-H); 6.9–7.8 (m, 4H, 2'-OH, 4'-H, 5'-H, 6'-H aromatic protons); 12.15 (s, 1H, 5-OH).

UV: λ_{max} (ethanol) 273, 320 (sh) nm; λ_{max} (ethanolic $AlCl_3$) 274, 325 (sh), 420 nm.

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Wir versuchten deshalb einen Zusammenhang zwischen den Substituenten R und der potentiellen Basizität des Gesamtsystems über eine direkte Basizitätsmessung zu finden.

Wenn die zu untersuchenden Basen einem einfachen Protonierungsgleichgewicht $B + H^+ \rightleftharpoons BH^+$ gehorchen, so ergibt sich der pk_s -Wert der korrespondierenden Säure nach der Henderson — Hasselbalch'schen Gleichung [3].

$$pH = pk_s + \log \frac{[B]}{[BH^+]} \quad (1)$$

Diese Gleichung gilt jedoch streng nur im Debye — Hückel-Gebiet. Wird die zur Protonierung erforderliche Säurekonzentration grösser als $10^{-2} M$, so ist eine Korrektur erforderlich. Ein adäquater Ausdruck für den thermodynamischen pk_s -Wert ist dann der H_0 -Wert bei Halbneutralisation ($H_0^{1/2}$). Trägt man $\log \frac{[B]}{[BH^+]} (\log I)$ gegen H_0 auf, so findet man in den meisten Fällen eine gute lineare Abhängigkeit. Der $\text{tg } \alpha(m)$ der resultierenden Geraden weicht jedoch sehr häufig von dem für Hammett — Basen idealen Wert 1 ab [4]. Für diesen Fall ergibt sich pk_s aus der Gleichung (2).

$$pk_s = mH_0^{1/2} [5,6] \quad (2)$$

Nach BUNNETT und OLSEN [7] berücksichtigt die Geradengleichung (3) die unterschiedlichen Wechselwirkungen der freien Basen und ihrer protonierten Formen mit dem Lösungsmittel besser. Der pk_s -Wert ergibt sich aus dem Schnittpunkt der Geraden mit der Ordinate.

$$\log \frac{[BH^+]}{[B]} + H_0 = \Phi (H_0 + \log [H^+] + pk_s) \quad (3)$$

Der Faktor Φ ist hierin eine Korrekturgrösse für den Solvationseffekt. Der Zusammenhang mit m ergibt sich aus der einfachen Beziehung $1 - \Phi \approx m$. (4)

Experimenteller Teil

Die Darstellung der vermessenen Verbindungen wurde von uns bereits früher beschrieben [8]. Die Reinheit ist durch mehrmaliges Umkristallisieren und durch die Elementaranalyse garantiert. Die Untersuchungen wurden mit einem UNICAM SP 800 der Firma Unicam in Quarzküvetten durchgeführt.

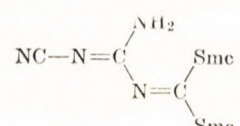
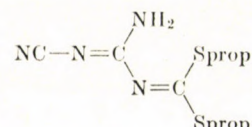
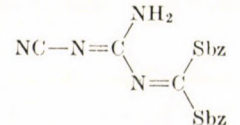
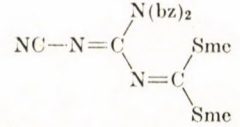
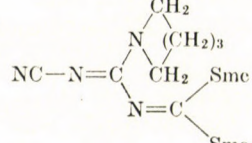
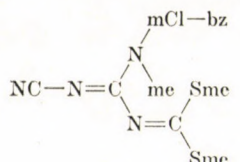
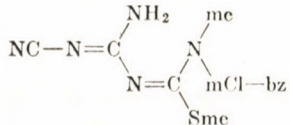
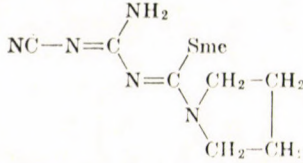
Bei verdünnten Schwefelsäuren bis zu 10 Gewichtsteilen H_2SO_4 verwendeten wir die H_0 -Werte von BASCOMB und BELL [9], bei höher konzentrierten die von PAUL und LONG [10].

Wegen der in allen untersuchten Fällen vorhandenen isobestischen Punkte können wir mit Sicherheit annehmen, dass die Basen mit ihren korrespondierenden Säuren im Gleichgewicht stehen.

Die ermittelten Messwerte sind in den Tabellen I und II aufgeführt.

Tabelle I

λ_{\max} der vermessenen Cyan-guanyl-imidio-dithiokohlensäurederivate I (B) und ihrer konjugierten Sauren (BH⁺) in Schwefelsäure

I Formel	B			BH ⁺		
	λ_{\max} [nm]	lg ϵ	[% H ₂ SO ₄]	λ_{\max} [nm]	lg ϵ	[% H ₂ SO ₄]
a 	242	4,1535	9,74	291	4,0897	60,72
b 	248	4,1046	9,74	293	4,0694	62,72
c 	250 s	4,1172	10 ⁻¹ m	300	4,0963	64,37
d 	244	4,3718	9,48	285	4,1075	83,00
e 	241	4,3854	2,11	275	4,2461	86,60
f 	242	4,3536	8,74	275	4,1154	83,00
g 	267 s 256	4,0763 4,1931	5·10 ⁻⁵ m 42,12	256 273	4,1931 4,0326	41,12 93,80
h 	227 255	4,0910 4,1140	5·10 ⁻³ m 43,41	255 275	4,1140 3,9395	43,41 95,34

Anmerkung: s = Schulter

me = CH₃; prop = C₃H₇; bz = CH₂-C₆H₅; m-Cl-bz = CH₂-m-Cl-C₆H₄

Tabelle II

Halbneutralisationspunkte und thermodynamische pK_s -Werte der Verbindungen I

I	λ [nm]	$H_0^{1/2}$	m	ϕ	pK_s
a	244	-2,310	1,343	0,411	-2,98
	290	-2,303	1,349		
b	230	-2,180	1,091	0,117	-2,35
	305	-2,691	0,763		
c	300	-2,676	0,688	0,361	-1,98
d	246	-4,133	0,994	0,006	-4,11
	285	-4,133	0,668		
e	240	-3,310	0,899	0,113	-3,02
f	242	-3,939	1,160	-0,179	-4,48
	285	-4,568	0,868		
g	256	0,412	0,860	0,828	0,57 ¹
	256	-5,786	0,643	0,386	-3,96 ²
h	255	0,873	0,825	-3,158	0,34 ¹
	255	-5,803	1,001	-0,001	-5,81 ²

¹ 1. Protonierungsstufe.² 2. Protonierungsstufe.

Diskussion

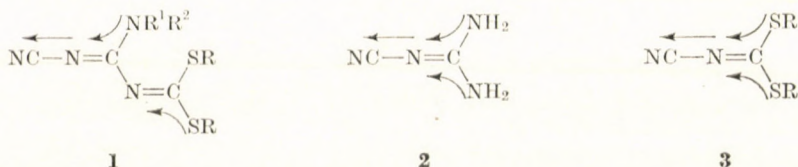
Zur Berechnung der pK_s -Werte nutzten wir sowohl Gleichung 2 als auch die Gleichung nach BUNNETT und OLSON [7].

Im Allgemeinen ergibt sich eine befriedigende Übereinstimmung in den Zahlenwerten. Grössere Unterschiede treten nur bei den substituierten Cyanuanyl-isothio-harnstoffen **lg** und **lh** auf, die als Vergleichssubstanzen von Interesse waren. Als Ursache für diese Unregelmässigkeiten sehen wir die beträchtlichen intramolekularen Wechselwirkungen. Wir geben hier den Werten nach Gleichung 3 den Vorzug.

Zur Kontrolle bestimmten wir die pK_s -Werte bei zwei verschiedenen Wellenlängen (s. Tabelle II), bei denen jeweils eine maximale Differenz der Extinktionen von Basen und Säuren zu beobachten war. Die teilweise beträchtlichen Unterschiede in den Ergebnissen erklären sich aus dem unterschiedlichen Lösungsverhalten der freien Basen und ihrer konjugierten Säuren. Die λ_{\max} Werte für beide Spezies sind in Tabelle I zusammengestellt. Da die Extinktions-

änderung der protonierten Form oft nur gering war, bzw. sehr starke Medium-effekte offensichtlich zu fehlerhaften Rechnungen führten, stützen wir uns ausschliesslich auf die pK_s -Werte, die sich aus der Absorption der freien Basen ergeben.

In allen Fällen handelt es sich um ausgesprochen schwache Basen. Dieses auf den ersten Blick etwas überraschende Ergebnis wird jedoch verständlich, vergleicht man die Cyanguanyl-imidio-dithiokohlensäurediester **1** mit dem Cyanguanidin **2**, was wegen der ähnlichen Strukturen durchaus zulässig ist. Der pK_s -Wert der korrespondierenden Säure des Cyanguanidins wurde von uns mit $-1,23$ bestimmt. Fasst man das Cyanguanidin als sogenanntes push-pul-System analog dem Cyanimido-dithiokohlensäurediester **3** auf, so wird deutlich, dass der Elektronensog der Nitrilgruppe durch die beiden Aminogruppen kompensiert wird.



Durch die sp^2 -Hybridisierung des einen Aminostickstoffs beim formalen Übergang von **2** zu den Verbindungen **1** verliert der Stickstoff nicht nur seine Donatorfunktion, sondern wird zu einem schwachen Elektronenacceptor. Gleichzeitig schirmt er den Elektronenschub der Alkylthiogruppen weitgehend ab, so dass ein Absinken der Basizität gegenüber **2** erwartet werden muss.

Durch die Protonierung wird dieser Schub bis zu einem gewissen Grade auch über den Stickstoff hinweg in dem Masse erzwungen, wie die Reste R eine partiell positive Ladung stabilisieren können, bzw. zur Erhöhung der Elektronendichte befähigt sind. In Übereinstimmung damit steigt die Basizität von **1a** zu **1c** wieder an. Im ungestörten, statischen Zustand ist der geringfügige elektronische Unterschied, wie bereits eingangs erwähnt wurde, nicht mehr oder nur noch andeutungsweise messbar.

Das weitere Absinken der Basizität bei den disubstituierten Verbindungen **1d** bis **1f** kann nur durch die nichtplanare Anordnung der Moleküle erklärt werden. Aus den Molekülmodellen ist ersichtlich, dass der Donator $-N=C(SCH_3)_2$ nicht mehr in einer Ebene mit dem Gesamtmolekül liegt. Der Elektronensog der Nitrilgruppe wird folglich nur noch durch die disubstituierte Aminogruppe kompensiert. Dies wird eindeutig durch die 1H -NMR-Messungen bestätigt. Die Energiebarriere für eine erzwungene Rotation um die $C-NR^1R^2$ -Bindung liegt bedeutend höher als bei den unsubstituierten Verbindungen.

Bringt man für eine Alkylthiogruppe einen besseren Donator ins Molekül, so sollte die Basizität ansteigen. In den Isothioharnstoffderivaten **1g** und **1f**

haben wir die Methylthiogruppe durch ein sekundäres Amin substituiert. Tatsächlich finden wir für **1g** einen pK_s -Wert von 0,57, für **1h** einen von 0,34. Beide Verbindungen sind also bedeutend basischer als das Cyanguanidin. Da es sich bei beiden um planare Verbindungen handelt, in denen eine ungestörte Konjugation möglich ist, ist die Frage nach dem Ort der Protonierung von sekundärer Bedeutung. In höher konzentrierten Säuren gelingt bei **1g** und **1h** eine Zweitprotonierung. Mit dem Ausfall der Aminogruppe als Donator nach der Erstprotonierung hat man einen Zustand, der dem der Verbindungen **1d** bis **1f** formal ähnlich ist. Tatsächlich liegen die pK_s -Werte in einer Grössenordnung.

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THE MECHANISM OF THE REACTION OF 2-BROMO-*N,N*-DIMETHYL-2,2-DIPHENYLACETAMIDE AND SODIUM METHOXIDE IN 2,2-DIMETHOXY- -PROPANE. A METHOD FOR ESTABLISHING THE RADICAL-ANION RADICAL CHAIN MECHANISM*

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Thermolysis of *N,N*-dimethyl-2,2-diphenyl-2-phenylazoacetamide (**1f**) in the presence of sodium methoxide in 2,2-dimethoxypropane furnishes *N,N*-dimethyl-2,2-diphenylacetamide (**1e**), the dimeric product **3** and 2-hydroxymethyl-2,2-diphenylacetamide (**1g**). An analysis of this result leads to the conclusion that the title reaction (which yields compounds **1e** and **3**) is a radical-anion radical chain process.

2-Bromo- (**1a**) and 2-chloro-*N,N*-dimethyl-2,2-diphenylacetamide (**1b**) have been found to furnish with sodium methoxide in methanol two *tele* substitution products (**2a**, **2b**) in addition to the normal product (**1c**) [1]** while in 2,2-dimethoxypropane (DMP) mixtures of the reduced (**1e**) and the dimeric product **3** were obtained [1, 2]. The formation of compound **3** suggested [1] that the reactions leading to the anomalous products possibly take place according to one or the other variant of the radical-anion radical (RAR) mechanism [3a—c], *i.e.* via $R^{\cdot}-Br^{\ominus}$ (see Scheme 2) and $R^{\cdot}-Cl^{\ominus}$, respectively, and the radical **4**. Independent generation of (*N,N*-dimethylcarbamoyl)diphenylmethyl (**4**)*** by thermolysis of *N,N*-dimethyl-2,2-diphenyl-2-phenylazoacetamide (**1f**) in the presence of sodium methoxide in methanol did not furnish even traces of compounds **2a** and **2b**; instead, substantial amounts of compound **1e** were obtained in addition to some **3**. This unambiguously rules out the RAR mechanism for the formation of compounds **2a** and **2b** from compounds **1a** and **1b** [4]. On the other hand, the results of crossing experiments carried out in the presence of sodium methoxide in DMP (which clearly demonstrated that under the conditions applied **3** is not formed by

* For a short communication, see SIMIG, Gy., LEMPERT, K.: Chem. Ber., **112**, 3520 (1979)

** Small amounts of the hydrolysis product **1d** were also isolated.

*** For the study of a related problem by a similar method, see Ref. [5].

Table I

Products and yields of the reactions of compound **1a** [2] and of **4** with sodium methoxide in DMP, and of compound **4** with DMP in the absence of sodium methoxide^a

Starting compound	NaOMe, equivalents	Products and yields, %		
		1e	3	1g
1a	4	40	30	—
4^b	4	22—25	15—17	21—22
4^b	—	18—23	—	14—22

^a) For the reaction conditions, see Table II and Ref. [2]

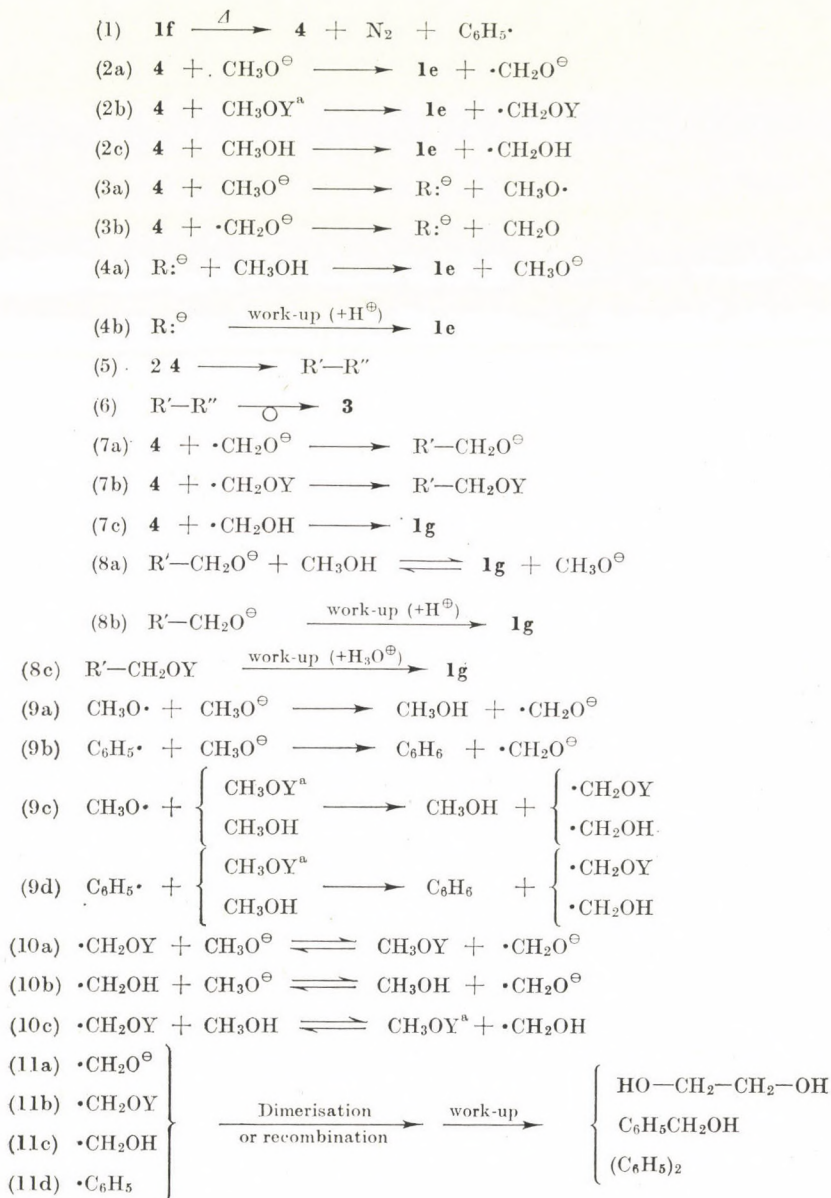
^b) Generated by thermolysis of compound **1f** [4]

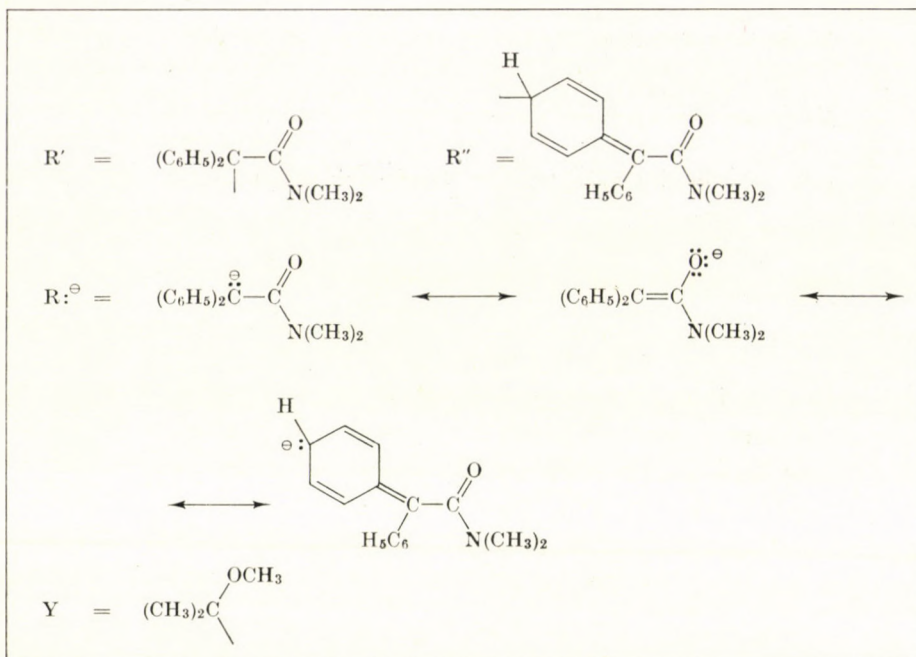
The complete sequence of events in the thermolyses is shown in Scheme 1. Formation of compound **1e** from radical **4** is assumed to take place both by hydrogen abstraction [Reactions (2)] and by one-electron reduction *via* the anion $R:\ominus$ [Reactions (3) and (4)]. The relative importance of these two pathways cannot be assessed on the basis of the available experimental results, *inter al.* because the final outcome of the sequence (3a), (9a) and (4a) is identical with the result of step (2a).^{*} Similarly, nothing is known about the relative importance of Reactions (2a)–(2c) because of the identity of the overall results of step (2a) and of the sequences (2b) + (10a) and (2c) + (10b). As shown by Equations (7) and (8), the formaldehyde radical anions, the α -radicals of the solvent and the α -radicals of methanol [formed according to Equations (9a), (9c) and (10b)] are assumed to be equivalent in their ability of inducing the formation of **1g**. As a consequence, the equilibria (10) are irrelevant in the present connection. The fate of the phenyl and methoxyl radicals, formed according to Equations (1) and (3), respectively, is shown in Equations (9); both radicals are capable of generating the formaldehyde radical-anion and its equivalents (in the above sense). The Reactions (11) are further possible pathways of stabilization of the formaldehyde radical-anion and its equivalents and of the phenyl radical; detection of the products of these reactions was not attempted.

In the reaction of compound **1a** with sodium methoxide in DMP the initiation step (1) of Scheme 1 is obviously replaced by steps (12) and (13) of Scheme 2. In connection with the interpretation of the results of the latter reaction it should be emphasised that, as shown by the thermolyses of compound **1f** in DMP, *whenever substantial amounts of the formaldehyde radical-anion or its equivalents* (in the sense used above) *are formed in the reaction mixture, part*

^{*} One-electron reductions are not feasible in the thermolyses performed in the absence of sodium methoxide. Under these conditions compound **1e** is therefore formed from radical **4** solely by hydrogen abstraction.

Mechanism of formation of **1e**, **3** and **1g** by thermolysis of **1f** in DMP
in the presence of sodium methoxide





* $\text{CH}_3\text{OY} = \text{DMP}$

Scheme 1

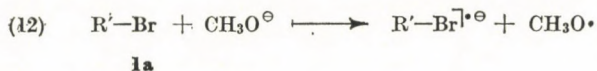
of the radicals **4** react with the latter to furnish compound **1g**. If, therefore, compound **1g** is not formed upon sodium methoxide treatment of compound **1a**, this must mean that — in contrast to the thermolyses — under these conditions *there is no accumulation of the formaldehyde radical-anion or of its equivalents in the reaction mixture, i.e.* that either no substantial amounts of these intermediates are formed according to Equations (9a) and (9c) of Scheme 1,* or that these intermediates are rapidly removed by some novel reaction which may not take place under thermolysis conditions. For the formaldehyde radical anion step (14) of Scheme 2 appears to be such a reaction [3c, 6, 7]; as a result, Reaction (7a) of Scheme 1 becomes completely suppressed.

No *similar* rapid scavenging reaction appears to exist for the α -radicals of the solvent DMP and of methanol. It has therefore to be assumed that either both the radicals **4** and the methoxy radicals react preferentially with methoxide anions [Reactions (2a) and (9a), respectively, of Scheme 1] rather than with the solvent DMP or methanol [Reactions (2b), (2c) and (9c), respectively];**

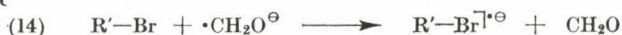
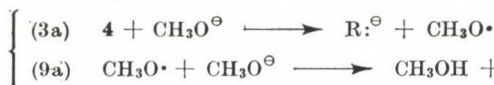
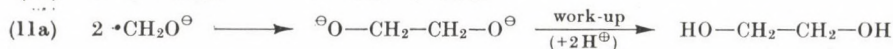
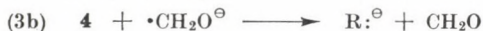
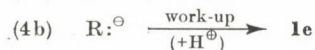
* Reactions (9b) and (9d) of Scheme 1 may not operate in the course of sodium methoxide induced decomposition of compound **1a**.

** Cf. with the observation that methoxide anions are much superior to methanol as hydrogen donors to *p*-nitrophenyl [8] and 4-isoquinoliny radical [7].***

*** Cf. with footnote 8 of Ref. [8].

Mechanism of formation of **1e** and **3** from **1a** and sodium methoxide in DMP*Initiation**Propagation*

or

**1a***Termination**Further reactions*

R', R'', R:\ominus, Y: see Scheme 1

Scheme 2

or that any α -radicals of DMP and methanol formed are rapidly consumed by reacting with methoxide anions [Reactions (10a) and (10b)].* Since the outcome of Reactions (2b) + (10a), and (2c) + (10b) of Scheme 1 is identical with that of Reaction (2a), the final conclusion emerging from the above

* For Reaction (10b) which, in contrast to Reactions (10a) and (10c), may take place not only by hydrogen abstraction but, predominantly, by proton exchange as well [6], this assumption is probably correct.

considerations is that among the Reactions (2) and (9) of Scheme 1 it is only (2a) and (9a) which may be considered efficient in the present case. As a consequence, Reactions (7b), (7c), (8), (10), (11b) and (11c) may be neglected — in addition to those already mentioned — when seeking the interpretation of the reaction of **1a** and sodium methoxide in DMP. This immediately leads to Scheme 2.

It should be pointed out once more that *non*-formation of compound **1g** in the reaction of **1a** and sodium methoxide in DMP is the result of the very rapid consumption, according to Equation (14), of the formaldehyde radical-anions formed *via* Reactions (2a) and (9a). In other words, conversion of **1a** into **1e** takes place predominantly by a *chain reaction*, one of the variations of the RAR reaction.

In the thermolyses performed in the absence of sodium methoxide none of the steps of Scheme 1 in which $\text{CH}_3\text{O}^\ominus$, and consequently $\cdot\text{CH}_2\text{O}^\ominus$, R^\ominus , $\text{R}^\ominus\text{—CH}_2\text{O}^\ominus$, $\text{CH}_3\text{O}\cdot$ and $\cdot\text{CH}_2\text{OH}$ would participate as reactants, may take place. Under these conditions therefore only steps (1), (2b), (7b), (8c), (11b), (11d) as well as that corresponding to the upper part of Equation (9d) and, for the moment, steps (5) and (6) may be considered to operate. As shown, however, by the *non*-formation of compound **3** in the absence of sodium methoxide, under these conditions steps (5) and/or (6) do not operate either. This may be explained by assuming step (6) to be a base-catalyzed prototropic rearrangement, and the dimerization step (5) to be reversible (similarly to the dimerization of the triphenylmethyl radicals).

Experimental

Thermolysis of compound **1f** in the presence or absence of sodium methoxide

Mixtures of compound **1f** [4], DMP and, in some cases, sodium methoxide (see Table II) were refluxed for 4–5 hrs. The resulting mixtures obtained in those experiments performed in the *presence* of sodium methoxide were acidified with *conc.* HCl and evaporated to dryness in vacuum. The residue was treated with water (40 mL), and the organic products were extracted with three portions (30 mL, each) of dichloromethane. The combined organic layers were

Table II

Thermolysis of compound **1f** in DMP in the presence or absence of sodium methoxide

Starting compounds					Reaction time, h	Products						Total yield, %
If		CH ₃ ONa		DMP cm ³		1e		3		1g		
g	mmole	g	mmole			g	%	g	%	g	%	
2.0	5.8	1.26	23.3	20	5	0.30	22	0.23	17	0.33	21	60
0.985	2.87	0.62	11.5	9.9	5	0.17	25	0.10	15	0.17	22	62
0.56	1.6	—	—	5.6	4	0.09	23	—	—	0.06	14	36
2.0	5.8	—	—	20	4	0.26	18	—	—	0.35	22	40

dried (MgSO_4), evaporated to dryness and worked up by column and TL chromatography (adsorbent: Kieselgel 60, 0.063–0.2, and Kieselgel $\text{PF}_{251+366}$, respectively; solvent: benzene–acetone, 7 : 3). The mixtures resulting from those experiments carried out in the *absence* of sodium methoxide were evaporated to dryness without previous acidification and the residues were directly worked up by chromatography. The products **1e** [1, 9], **3** [1] and **1g** [4] were identified by comparison (TLC, IR, m.p.; in the case of compound **3**, also $^1\text{H-NMR}$). For the yields see Table II.

In the thermolyses performed in the absence of sodium methoxide several non-identified products, as well as small amounts of 2-(4-biphenyl)-*N,N*-dimethyl-2-phenylacetamide [5] were also obtained.

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RECENSIONES

Structure and Bonding, Vol. 39.

Springer Verlag, Berlin, Heidelberg, New York, 1980

Vol. 39 of the successful series contains three reviews. The paper by D. W. CLACK and K. D. WARREN: *Metal-Ligand Bonding in 3d Sandwich Complexes* (pp. 2—31) deals with the bonding between the metal center and the ligand rings for different series of first row transition metal sandwich complexes containing three- to eight-membered rings. Stress is laid upon the complexes involving carbocyclic rings, but the effect of the introduction of boron and nitrogen into six-membered rings is also discussed. Besides symmetrical sandwich complexes, mixed sandwich systems involving two different ligands are also treated. The paper offers a clear and comprehensive review of the subject. 80 references.

The paper by S. F. MASON: *The Ligand Polarization Model for the Spectra of Metal Complexes: The Dynamic Coupling Transition Probabilities* (pp. 43—81) is a lucid and readable account of the model considering the perturbation of the ligand by the electrons of the metal. It is convincingly shown that this model is particularly useful in the explanation of the behaviour of chiral coordination compounds and the Faraday effect terms of achiral complexes. 82 references.

The third paper by L. R. BALSENC: *Sulfur Interactions with Metallic Surfaces and Interfaces Studied by Auger Electron Spectrometry* (pp. 83—114) points out the advantage of the application of Auger spectrometry in the study of various problems connected with the presence of sulfur at metallic surfaces and interfaces. First general information on Auger Spectrometry is given then various applications are treated. Unfortunately there are some ambiguous terms such as *oxidative sulfidation* and improper names like hydrocyanic acid. It is the impression of the reviewer that the long list of references (286 items) could have been shortened. For the statement "Catalytic activity is essentially a surface phenomenon . . ." — which on the one hand is not entirely true, on the other hand is trivial — three recent papers are referred to.

All in all Vol. 39 keeps the high level of the series. The typography is excellent.

M. T. BECK

M. W. RANNEY: *Heat Exchange Fluids and Techniques*

Energy Technology Review No. 50

Chemical Technology Review No. 143

Noyes Data Corp., Park Ridge, New Jersey, U.S.A., 1979, 392 pages

This is a well ordered review of patents, pertinent to heat-carrier media, heat exchangers, and heat exchange processes, granted in the U.S.A. between 1975 and 1979. This is also a long-needed book because nowhere else in the literature are we offered such a topically selected, detailed, and technologically inspired description of novel suggestions which, when realized, promise substantial savings of energy.

The several chapters abound in information. Construction and design of heat exchangers; heat-carriers; low-temperature processes; storage, transmission, and transport of heat, thermal insulation of, heat-conditioning and -regulation in buildings; utilization of the energy radiated by the sun, and that of geothermal energy; various industrial and specific applications are dealt with.

The usefulness of this book is enhanced by the feature that it is not restricted to the description of patented matter but gives pertinent comments and explanations as well.

Good guidance is given by the introductions to the several chapters.

Information here on novel liquid heat-carriers, azeotropes among them, and on techniques applicable by chemical industry and important also in the storage of foodstuffs is very useful for chemists and chemical engineers.

Applications proper to biological problems, e.g. deep-freeze storage of separate organs, treatment of living cells, might be mentioned as of specific interest.

Indexes, severally, of patent specifications, inventors, and patentees complete this volume.

Knowledge of basic thermodynamics and relevant physics and heat-engineering is needed for a useful perusal of this book.

Style of the text is clear and, in accord with its nature, concise: legal terminology not subservient to its aim is omitted. Understanding is facilitated by the reproduction of the drawings original in the patent specifications.

This book can be recommended for experts engaged in practical engineering or in research work, and will be a very useful source of information for those who professionally survey patent literature.

P. FÖLDES

L. BATA: *Liquid Crystals*

(Recent results of solid body research 7. Ed. T. SIKLÓS)
Akadémiai Kiadó, Budapest, 1980, 249 pages

The first two chapters of the book, illustrated with drawings and photos, deal with the structure of liquid crystals, their most important characteristics and the measurement of the same. The third chapter reports on the practical application of liquid crystals. This includes also liquid crystal displays, extensively used today by the manufacturers of modern watches and pocket computers. This chapter covers also the applicability of cholesteric liquid crystal films for diagnostic purposes, for the detection of changes of temperature caused by pathological condition on human and animal skin surfaces and in deeper tissue layers.

Though further chapters discuss mainly theoretical problems, these are also illustrated on hand of practical examples. As one of the examples, the investigations of HELFRICH are described, who applied the theory of elasticity to describe the deformation of red blood cells.

A survey is given on lipid-water interactions occurring in biological systems. Of similar importance is a knowledge of the liquid crystal properties of lipid-lipid systems, which nowadays is one of the main tasks of workers engaged in research on arteriosclerosis and steroid hormones. In a possible new edition of the book advances achieved in this field will be certainly included.

This study can be recommended to all those interested in liquid crystals in the field of physics, chemistry, biology and industry, who wish to keep abreast of advances in this subject.

D. SZABÓ

László KISS: *Kinetics of Electrochemical Metal Dissolution*

Akadémiai Kiadó, Budapest, 1980, 206 pages

The book deals with the essential problems of electrochemical metal dissolution, one of the most important groups of electrode processes both from the theoretical and practical aspects.

The book is divided into three main chapters.

In the first chapter the author briefly summarizes thermodynamical knowledge needed for the discussion of electrochemical metal dissolution, forming the main topic of the book.

With his object in view, the author discusses in the second chapter problems in conjunction with the dissolution of metals in the active state, with particular view to the kinetics

of electrode processes proceeding in several steps, but some problems of passivation and transpassive dissolution, as well as their practical applications, are also briefly mentioned.

The third chapter summarizes the fundamental laws of the basic processes of spontaneous metal dissolution and corrosion, of decisive importance from the point of view of practice.

A particular merit of the book is that the discussion of these themes is not restricted to the literature, but is based also on the results of the author and his coworkers, obtained in several decades of research work. References include several reviews, which help the reader to obtain an almost complete survey of the theme covered.

Owing to the large scope of the subject, problems of metal alloy dissolution, the kinetics of the formation of surface layers, problems of the dissolution in salt melts and non-aqueous solvents are not discussed, or mentioned only briefly.

The work is a worthy continuation of the traditions of Hungarian electrochemical sciences, and will be very useful for experts dealing with the kinetics of electrode processes and also in university teaching. The book will help also industrial chemists dealing with corrosion and other electrochemical processes in getting acquainted with electrochemical processes and in the interpretation of the same.

B. LENGYEL

Topics in Current Chemistry, Vol. 88

Organic Chemistry. Synthesis and Reactivity

Springer Verlag, Berlin, 1980, 170 pages

The new volume of the known series contains four surveys:

Steric Effects in Free Radical Chemistry, by Ch. RÜCHARDT.

The recognition that the α , p -dimer is formed in equilibrium with triphenylmethyl and not the α , α -dimer hexaphenylethane was interpreted as a result of the smaller steric strain in the α , p -dimer than in hexaphenylethane. Recently several new pieces of evidence have been found for the predominating influence of steric effects in free radical chemistry, which are discussed in four chapters (*Steric Effects in Homolytic Decomposition Reactions, in Aliphatic Substitution Reactions, in Free Radical Addition Reactions and in Dimerization and Disproportionation Reactions*) by the authors.

Silylated Synthons. Facile Organic Reagents of Great Applicability, by L. BIRKHOFFER and O. STUHL.

According to the words of the introduction "in the last two decades the importance of organosilicon chemistry has greatly increased. Especially, silylated synthons — synthesized by a great variety of silylation reactions — have won wide appreciation and became a highly valued and often used tool in every preparative chemist's hand". The authors then describe some of the main contemporary fields of use for silylated synthons and silylation techniques. First the reactions of organosilanes with unsaturated hydrocarbons, then with carbonyl compounds are discussed. The next chapter is devoted to silylated heterocycles, and the last chapter deals with the preparation and use of silylated reagents.

The 4a,4b-Dihydrophenanthrenes, by K. A. MUSZKAT.

4a,4b-Dihydrophenanthrenes are coloured unstable conjugated polyenes obtained photochemically by the irradiation of the corresponding *cis*-1,2-diaryl-ethylenes. During the past two decades the photocyclization of substituted diaryl ethylenes has assumed considerable synthetic importance. This compilation, however, is not concerned directly with purely synthetic aspects of the photocyclization. 4a,4b-Dihydrophenanthrenes offer a fascinating combination of unusual chemical and physical properties and the present review is intended to provide an up-to-date summary of the activity in this field.

Regio- and Stereo-Selectivities in Some Nucleophilic Reactions, by N. T. ANH.

This review deals with the stereochemistry of S_N2 reactions, 1,4 additions of organometallic reagents to conjugated carbonyls, additions to saturated ketones and 1,2 asymmetric induction, based on quantumchemical calculations, with the crucial role of non-perpendicular attack in asymmetric induction, and with the interpretation of FELKIN's model on T.S.

Gy. DEÁK

Jiro TSUJI: *Organic Synthesis with Palladium Compounds*

Volume 10 in the series *Reactivity and Structure Concepts in Organic Chemistry*
Springer-Verlag Berlin, Heidelberg, New York, 1980, 207 pp.

The use of organometallic compounds in organic chemistry — mainly in the form of homogeneous catalysts — has advanced enormously since 1938, when the first organic reaction catalysed by an organometallic complex the hydroformylation reaction was discovered. One of the highlights in this development was the invention of the Wacker process which uses PdCl_2 and CuCl_2 as catalysts for the oxidation of ethylene to acetaldehyde. Following this discovery many chemists have turned their attention to organopalladium chemistry and its applications to organic chemistry and accordingly this area of organometallic chemistry has contributed to its development personally.

Many unique and interesting organic reactions are possible using palladium compounds as stoichiometric reagents or as catalysts. Palladium compounds are usually convenient reagents being mostly stable and not seriously toxic. To become really useful for the organic chemist, however, the use of palladium in catalytic amounts is desirable because it is a rather expensive metal. As this book treats the chemistry of palladium compounds from the standpoint of organic synthesis emphasis is set on the following two main group of reactions:

1. oxidative reactions with Pd^{2+} compounds and
2. catalytic reactions.

The usefulness of the first type of reactions is ensured by the possibility to reoxidize the Pd^0 compounds (or in many cases the Pd metal) to the starting Pd^{2+} compounds and hence the whole oxidation process becomes catalytic with respect to palladium. Sometimes (like in the Wacker process) this is done *in situ*. Reactions of the second type proceed catalytically and do not need reoxidation.

Even within these limitations the author has selected information and preferentially treats organic reactions with high yields and selectivities. The usefulness of the book would be even more pronounced if it would contain somewhat more information on the reaction conditions used. Perhaps the most impressive for an organic chemist is chapter IV. 3. m. treating the application of palladium chemistry to natural product synthesis. The 993 references provide ample opportunity to acquire detailed information and prove the thorough knowledge of the author.

L. MARKÓ

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, Supplement and Extension to Volume 1, *Magnetic Properties of Free Radicals Part d2, Organic Cation Radicals and Polyradicals Index of Substances for Volumes II/1 and II/9*
R. A. FORRESTER, K. ISHIZU, G. KOTHE, S. F. NELSEN, H. OHYA-NISHIGUCHI, K. WATANABE, W. WILKER

Editors: H. FISCHER and K.-H. HELLWEGE

Springer-Verlag, Berlin—Heidelberg—New York, 1980, 369 pp

This book is the sixth part of and completes the supplement to the LANDOLT-BÖRNSTEIN New Series Volume II/1 entitled "Magnetic Properties of Free Radicals" published in 1965. The complete supplement, *i.e.* Volume II/9 consists of the following parts:

- Part a Atoms, Inorganic Radicals, and Radicals in Metal Complexes
- Part b Organic C-Centered Radicals
- Part c1 Organic N-Centered and NO Radicals
- Part c2 Organic O-, P-, S-, Se-, Si-, Ge-, Sn-, Pb-, As-, Sb-Centered Radicals
- Part d1 Organic Anion Radicals
- Part d2 Organic Cation Radicals and Polyradicals

The scope of the compilation and the organization of the Tables have been described in a previous review *Acta Chim. Acad. Sci. Hung.*, **98**, 497 (1978) referring to Parts *a* and *b*. Reviews on Parts *c1*, *c2*, and *d1* have also appeared.

As the chapters are numbered consecutively in Volume II/9, the present book contains the following ones:

- 18 Aromatic hydrocarbon cation radicals
- 19 Cation radicals from nitrogen-containing compounds
- 20 Aromatic cation radicals containing O and S atom
- 21 Organic C-, O-, and N-centered bi- and polyradicals
- 22 Organic bis- and polynitroxides

The aromatic hydrocarbon cations include cation radicals from benzene, polyphenyl, naphthalene, anthracenes, other condensed aromatics and from alkyl derivatives of the above mentioned compounds, further cation radicals from non-alternant hydrocarbons and miscellaneous compounds, from halogen derivatives of polyphenyls and from halogen derivatives of naphthalenes. ESR spectral data (or other relevant data) for a relatively large number of nitrogen-containing radical cations have been compiled and grouped into 16 subsections. The aromatic cation radicals containing oxygen or sulphur atom are divided into the following two groups: 1. those with functional groups containing O and/or S atoms substituted into the aryl groups; 2. heterocyclic compounds containing O and/or S atoms as ring members. A special chapter deals with organic polyradicals which are paramagnetic molecules having N number of unpaired electrons. It is assumed that a polyradical with N unpaired electrons can be divided into N segments and each segment can be assigned to have proper spatial and spin functions. The introduction to this chapter describes the scope of the Tables included here. The inherent stability of the nitroxide group and the relative ease of the preparation of organic bis-, tris-, and poly-nitroxides are pointed out to explain the relatively large number of substances covered in Chapter 22. The arrangement of compounds into sections follows that used in the Chapter on mononitroxides (Volume 9, Part *c1*).

The closing dates of the literature search for various chapters vary between 1976 and 1979.

The valuable Index of substances covering both Volumes II/1 and II/9 is worth of special mention.

Volume II/9 altogether contains data for about 8000 free radicals on about 3750 pages. Volume II/1 contained data for about 500 compounds on 154 pages. The Editors note in the Preface to Part *d2* that the large size of Volume II/9 shows the quick and unexpected development of the electron resonance spectroscopy for free radicals that corresponds to the importance of the measured data for further research and application. They also suppose that the field has approached a certain degree of saturation. It is expected that only supplements of relatively small size will be necessary to compile and publish in the future.

In conclusion I would like to note that to produce this compilation of the "Magnetic Properties of Free Radicals" was a great challenge and demanding undertaking, but it is no wonder that LANDOLT-BÖRNSTEIN and Spinger-Verlag solved it superbly.

I. HARGITAI

INDEX

GYÓZÓ (VICTOR) BRUCKNER (1900–1980), K. MEDZIHRADESKY..... 287

PHYSICAL AND INORGANIC CHEMISTRY

Mechanical-Rheological Studies on Polymer Networks, I. Effect of the Conditions of Cross-Linking on the Mechanical Properties, F. HORKAY, M. NAGY..... 321

A Study of the Chemical State of Tin Layers Deposited on Various Aluminium Alloys and Electroplated with Copper, A. VÉRTES, GY. VÉRTES, M. SUBA..... 335

Metal Catalyzed Dehydrogenation of Cyclohexanol, M. DOBROVOLSZKY, P. TÉTÉNYI, Z. PAÁL..... 343

ORGANIC CHEMISTRY

The Preparation of Arylglyoxals and Heteroaromatic Aldehydes Using Pyridone, A. R. KATRITZKY, A. V. CHAPMAN, H. M. DOWLATSHAHI..... 315

Oxazepines and Thiazepines, XI. Conversion of 1-Thioflavanone Derivatives into Benzothiazepinones (Short Communication), A. LÉVAI 361

Synthesis of Chlorflavonin, A. L. TŐKÉS, R. BOGNÁR..... 365

Structure and Reactivity of Activated C=N Double Bond, VI. Basicity Measurements on Cyanoguanyl-imido-dithiocarbonic Acid Diesters, E. R. DÁVID, R. EVERS (in German) 369

The Mechanism of the Reaction of 2-Bromo-*N,N*-dimethyl-2,2-diphenylacetamide and Sodium Methoxide in 2,2-Dimethoxypropane. A Method for Establishing the Radical-Anion Radical Chain Mechanism, GY. SIMIC, K. LEMPERT..... 375

RECENSIONES 383

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