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ISOTOPE EXCHANGE BEHAVIOUR OF NICKEL XANTHATE IN PRESENCE OF SUBSTITUTED ANILINES AND ISOMERIC PICOLINES

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Isotope exchange behaviour of nickel xanthate was investigated in the presence of aniline, *N*-methylaniline, *N*,*N*-dimethylaniline and three picoline isomers at 25 °C. The results showed that the labelled free nickel(II) replaces inactive nickel(II) in the complex. Hence the complex is labile in presence of all bases except β- and γ-picolines. The observed lability has been attributed to an adduct formation between the complex and the bases. The inert behaviour observed in the presence of β- and ν-picolines has been ascribed to the steric effect of the methyl groups on the adduct formation.

Introduction

It has been stated on the basis of isotope exchange studies that nickel xanthate is inert. However, it has been reported by LIM YAU YAN [1] that nickel xanthate forms adducts with bases such as anilines and pyridines and adduct formation leads to the transition from diamagnetic square planar tetracoordinated nickel complex to paramagnetic bis-adduct. This may be expected to change the isotope exchange behaviour of the complex. Isotope exchange study of nickel xanthate in the presence of aniline and pyridine has shown that the complex is labile [2]. However, one has to study the isotope exchange behaviour of the complex in the presence of a number of related bases before one could arrive at definite conclusions about inert or labile behaviour of the complex. Hence isotope exchange behaviour of nickel xanthate has been studied in the presence of aniline, *N*-methylaniline, *N*,*N*-dimethylaniline and the three picoline isomers. The bases chosen here help not only in establishing the behaviour of the complex but also in determining the effect of substituent on the rate of exchange.

*** In final form accepted May 26, 1980.**

Experimental

Materials

Nickel perchlorate (AnalaR), picolines (B. D. H. AnalaR) were used without further purification. Aniline, *N*-methylaniline and *N,N*-dimethylaniline were purified by the method described by SMITH and coworkers [3]. *N*-methylaniline and *N,N*-dimethylaniline were distilled under vacuum and dried over sodium hydroxide.

Preparation of the complex

Potassium ethyl xanthate was prepared by the method described by VOGEL [4]. The complex nickel xanthate was prepared using the method reported by DAKETERNEIKS and GRADDON [5] with a slight modification. The complex was prepared in aqueous medium. The pH of nickel solution (1 m*M*) was adjusted to the range 8.0 to 8.5. One per cent solution of potassium ethyl xanthate was added under constant stirring until the precipitation was complete. The resulting precipitate was filtered, washed with hot water and dried in vacuum. Estimation of nickel by conventional gravimetric method showed that the complex had a metal to ligand ratio of 1 : 2. This composition was also reported by DAKETERNEIKS and GRADDON [5].

Procedure

Solution of nickel perchlorate (0.875×10^{-2} *M*) nickel xanthate (0.825×10^{-2} *M*) *N*-methylaniline and *N,N*-dimethylaniline (2×10^{-1} *M*) and picolines (2×10^{-1} *M*) were prepared in acetone. Reaction mixture was made by mixing 10 cm^3 of nickel perchlorate 10 cm^3 of the complex and 5 cm^3 of each base. The reaction mixture was kept at 25 ± 1 °C in a thermostat. Sufficient amount of ^{63}Ni tracer (0.2 cm^3) was added in order to follow the reaction. The separation of free nickel was effected by adding 3 cm^3 of water to a 2 cm^3 aliquot of the reaction mixture at different time intervals. The activity of the separated free nickel in solution was measured with the aid of a liquid scintillation counter of type LSS 20 supplied by ECIL, Hyderabad, India. The course of the exchange was followed by measuring the activity as a function of time. The experiment was repeated with other bases also. The half time and the rate of exchange were calculated with the aid of McKAY's relations [6].

Results

The relation, $F = \dfrac{SA_t - SA_0}{SA_\infty - SA_0}$ was employed to calculate the fraction exchanged. In the relation SA_0, SA_t and SA_∞ denote the specific activity of *A*, nickel, separated at time o, *t* and ∞ minutes, respectively. Error in pipetting and counting contributes to an uncertainty of ±0.001 in *F* values [7]. Experimental data are given in Tables I and II. Semilog plots of $(1-F)$ *vs. t* are represented in Figs 1 to 4. The half time ($t_{1/2}$) of exchange was obtained both by graphical and least-square methods. The maximum difference between $t_{1/2}$ values obtained by the two methods was twice the experimental error. The $t_{1/2}$ values obtained by least-square method are presented in Tables I and II. Finally, the rate of exchange was calculated by the relations

$$\log(1-F) = -\frac{A\cdot B}{A+B}Rt$$

$R = \dfrac{0.693}{t_{1/2}}\,\dfrac{A\cdot B}{A+B}$ where *A* and *B* are the concentrations of nickel perchlorate and the complex (nickel xanthate).

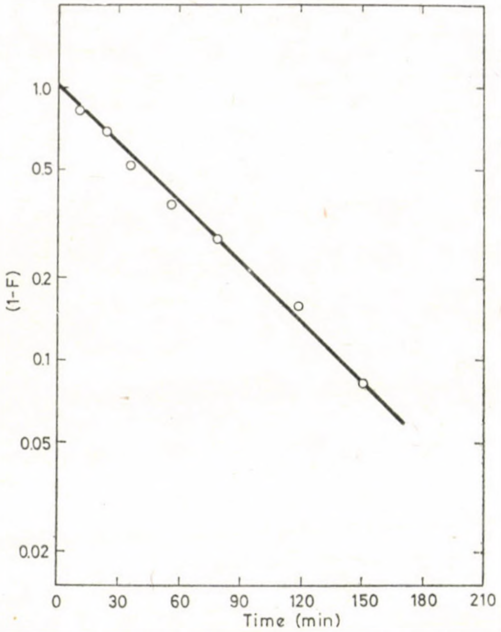

Fig. 1. Plot of $(1-F)$ *vs.* time for the system $Ni(xanthate)_2$—Ni(II) at 25 °C in presence of aniline. Complex $= 3.5 \times 10^{-3}$ *M*; Nickel(II) $= 3.3 \times 10^{-3}$ *M*; Aniline $= 4.0 \times 10^{-2}$ *M*

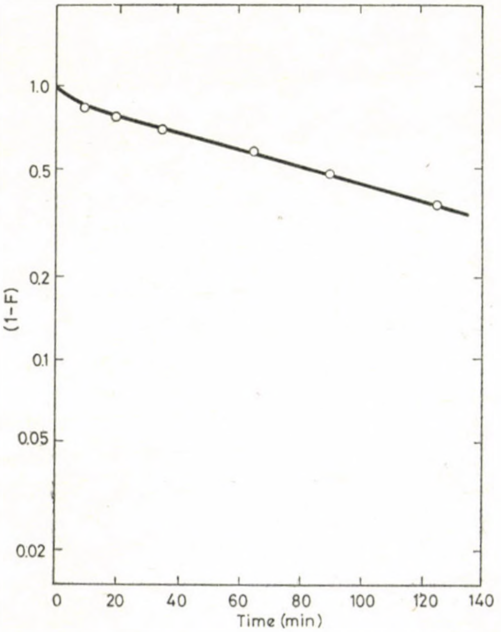

Fig. 2. Plot of $(1-F)$ *vs.* time for the system $Ni(xanthate)_2$-Ni(II) at 25 °C in presence of *N*-methylaniline. Complex $= 3.5 \times 10^{-3}$ *M*; Nickel(II) $= 3.3 \times 10^{-3}$ *M*; *N*-methylaniline $=$ $= 4.0 \times 10^{-2}$ *M*

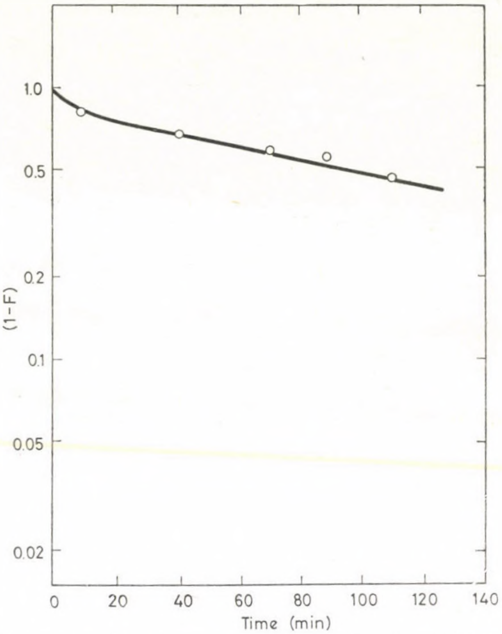

Fig. 3. Plot of $(1-F)$ *vs.* time for the system Ni(xanthate)$_2$—Ni(II) at 25 °C in presence of *N,N*-dimethylaniline. Complex = 3.5×10^{-3} *M*; Nickel(II)O = 3.3×10^{-3} *M*; *N,N*-dimethylaniline = 4.0×10^{-2} *M*

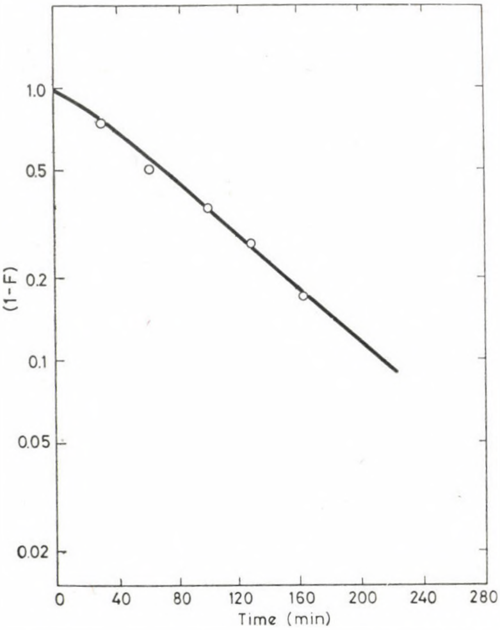

Fig. 4. Plot of $(1-F)$ *vs.* time for the system Ni(xanthate)$_2$—Ni(II) at 25 °C in presence of α-picoline. Complex = 3.5×10^{-3} *M*; Nickel(II) = 3.3×10^{-3} *M*; α-picoline = 4.0×10^{-2} *M*

Table I

Isotope exchange data of nickel xanthate in the presence of substituted anilines at 25 °C

Complex: 3.5×10^{-3} *M* Ni(II): 3.3×10^{-3} *M* Base: 4.0×10^{-2} *M*

S. No.	Time min	cpm	*F*	1—*F*
		Aniline		
1	0	25530	—	—
2	10	23862	0.18	0.82
3	25	22910	0.29	0.71
4	35	21000	0.50	0.50
5	55	19680	0.64	0.36
6	80	19001	0.72	0.28
7	120	17911	0.84	0.16
8	150	17168	0.92	0.08
9	∞	16444	—	—

$t_{1/2} = 43.3$ minutes, Rate $= 2.72\times10^{-5}$ moles/dm³/min

N-methylaniline

S. No.	Time min	cpm	*F*	1—*F*
1	0	27990	—	—
2	10	27120	0.15	0.85
3	20	26860	0.19	0.81
4	35	26257	0.30	0.70
5	65	25600	0.37	0.63
6	90	24950	0.52	0.48
7	125	24300	0.63	0.37
8	∞	22100	—	—

$t_{1/2} = 95.3$ minutes, Rate $= 1.24\times10^{-5}$ moles/dm³/min

N,N-dimethylaniline

S. No.	Time min	cpm	*F*	1—*F*
1	0	29600	—	—
2	10	28110	0.20	0.80
3	40	27112	0.33	0.67
4	70	26400	0.42	0.58
5	90	26210	0.45	0.55
6	110	25500	0.48	0.52
7	155	24650	0.66	0.34
8	∞	22060	—	—

$t_{1/2} = 125.6$ minutes, Rate $= 0.94\times10^{-5}$ moles/dm³/min

Table II

Isotope exchange data of nickel xanthate in the presence of three picoline isomers at 25 °C

Complex: 3.5×10^{-3} *M* Ni(II): 3.3×10^{-3} *M* Base: 4.0×10^{-2} *M*

S. No.	Time min	cpm	*F*	1—*F*
		α-picoline		
1	0	23797	—	—
2	30	21623	0.25	0.75
3	60	19527	0.50	0.50
4	100	18320	0.64	0.36
5	130	17520	0.73	0.27
6	165	16700	0.83	0.17
7	195	15502	0.97	0.03
8	280	15296	0.99	0.01
9	∞	15243	—	—

$t_{1/2} = 39$ minutes, Rate $= 3.00\times10^{-5}$ moles/dm³/min

Discussion

The data in Tables I and II show that nickel xanthate becomes labile in the presence of aniline, *N*-methylaniline and *N,N*-dimethylaniline, α-picoline. The observed lability may be attributed to an adduct formation between the complex and the four bases, consequently this leads to the transition from the diamagnetic square planar nickel complex to paramagnetic bis-adduct as reported by LIM YAU YAN. It became necessary to reinvestigate the exchange behaviour of nickel xanthate in the presence of aniline as the exchange data collected at 30 °C by RANGAMANNAR could not be used for the comparative study attempted here. However, the complex exhibits inert behaviour in the presence of β- and γ-picolines. This shows that the paramagnetic bis-adducts are not formed between the complex and these two bases. This may be attributed to the steric effects of methyl groups in the two picolines.

Finally, the rates of exchange observed in the presence of aniline, *N*-methylaniline and *N,N*-dimethylaniline decrease in the order aniline > methylaniline > dimethylaniline. This order shows that the aniline forms an adduct which destabilizes the metal ligand bonds to a greater extent.

*

The authors thank Prof. M. V. RAMANAIAH and Dr. S. K. PATIL, Radiochemistry Division, BARC, India, for the facilities provided and valuable discussion. One of the authors (GRKN) gratefully acknowledge the U.G.C. for the financial assistance given to this research programme.

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STUDY OF INTERACTIONS IN AQUEOUS SOLUTIONS CONTAINING CYCLODEXTRIN, GLUCOSE AND BORATE

EXCLUSION OF THE FORMATION OF STABLE D-GLUCOSE–CYCLODEXTRIN COMPLEXES ON THE BASIS OF POTENTIOMETRIC AND KINETIC MEASUREMENTS

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The interaction of α-, or β- or γ-cyclodextrin and D-glucose in aqueous solutions has been studied by the potentiometric method, using borate as auxiliary complexing agent. It has been established on the basis of the mathematical analysis of pH versus time curves that the interaction between cyclodextrins and D-glucose, strongly hydrated in aqueous solution, is wery weak, and can be neglected. Thus, there is no reason to assume that drugs introduced into the organism in the form of cyclodextrin inclusion complexes will be displaced from the complex by glucose or similar low-molecular hydrophilic substances present in the body fluids.

According to results obtained in recent years, cyclic α-, β- or γ-cyclodextrins consisting of 6, 7 or 8 anhydroglucose units, form inclusion complexes only with weakly hydrated organic molecules of appropriate size [1]. In contrast to this, HOFFMAN *et al.* reported the preparation of the β-cyclodextrin–glucose inclusion complex [2]. They isolated from the hot aqueous solution containing the two compounds a product with the composition of about 0.6 mol glucose/mol cyclodextrin. However, the rate of oxidation with periodate in aqueous solution was found to be identical for "free" glucose and glucose "bound in the complex". This fact contradicts complex formation. The authors did not investigate whether α- or β-D-glucose, rather different from the aspect of complex formation [3], enters into interaction with cyclodextrin.

It is not always easy to establish whether the solid products obtained in complexation experiments are inclusion complexes or physical mixtures, or whether the assumed guest molecule is incorporated only adsorptively or as a crystal inclusion in the cyclodextrin–water inclusion complex [4]. Anyway, if we wish to draw conclusions substantial also from the aspect of physiology, the results of solution equilibrium investigations will be decisive.

From the aspect of the application of cyclodextrins in the pharmaceutical and food industries [5], it is important to prove by direct investigations that there is not inclusion complex formation in aqueous solutions of cyclodextrins with glucose. Were cyclodextrin to form inclusion complexes also with well hydrated molecules of small size, this would make questionable the application of drugs and foodstuffs bound as guest molecule, because other substances present in large quantities in the organism (*e.g.* glucose) would displace them from the complex at the moment of introduction into the organism.

When the interaction between two compounds is difficult to study directly, a well known complex formation reaction of one reactant can be investigated in the presence of the other compound. In the given case we can conclude from the modification of glucose–borate complex formation in the presence of cyclodextrin, whether or not a cyclodextrin–glucose inclusion complex of appreciable stability is formed in aqueous solution.

We did not find data in the literature on the formation of cyclodextrin–borate complexes.

We found in the investigation of D-glucose–borate complex formation [6] that on adding an equilibrium mixture of α- and β-D-glucose to a solution containing borate ions the reaction proceeds according to the scheme:

$$\begin{tikzcd}
\beta\mathrm{Gp} \arrow[d, shift left, "k_{\mathrm{m}}"] & \\
\alpha\mathrm{Gp} + \mathrm{B}^- \arrow[u, shift left] \arrow[r, shift left, "\beta^{\mathrm{p}}_{011}"] & \alpha\mathrm{GpB}^- \arrow[l, shift left] \arrow[d, shift left, "k_{\mathrm{GB,OH^-}}"] \\
 & \alpha\mathrm{GfB}^- \arrow[u, shift left]
\end{tikzcd}$$

The complex [αGpB$^-$] of α-D-glucopyranose (αGp) formed with [tetrahydroxoborate](—) ion (B$^-$) is converted in a hydroxide ion catalyzed reaction, similarly as in the mutarotation of glucose, into the more stable D-glucofuranose–borate (αGfB$^-$), but in a considerably more rapid reaction. Thus, mutarotation and the pyranose–furanose complex conversion can be studied separately from one another on the basis of pH (or electromotive force) data, recorded as a function of time [6].

Consequently, the interactions observed in aqueous solutions containing cyclodextrin and borate, then cyclodextrin, borate and D-glucose, have been studied by potentiometric methods developed earlier [6, 7].

Experimental

Reagents, method

Three times recrystallized boric acid and D-glucose of analytical purity, dried at 105 °C to constant mass, were used. α- and β-cyclodextrin were products of Chinoin, γ-cyclodextrin was a Sigma product, while the other materials used were of analytical purity.

The ionic strength of the solutions tested was adjusted with sodium perchlorate to $1.5 \cdot 10^{-2}$.

Electromotive force (e.m.f.) and pH were measured at 25 ± 0.2 °C as described in our earlier communication [6].

Symbols

CD, αCD, βCD, γCD are the general symbol of cyclodextrin and the symbols of α-, β- and γ-cyclodextrin, respectively;
C_{CD}, C_G, C_A are the concentrations of total cyclodextrin, glucose, and of the boron containing anions [6] in the solution, respectively, mol/dm³;
$K_m = [\beta Gp]_\infty [\alpha Gp]_\infty^{-1}$ is the equilibrium constant of the mutarotation of D-glucose;
β'_{011} is the apparent stability constant of the D-glucose–borate complex ($\log \beta'_{011} = 2.74$ [6]);
$\beta_{CDG} = [\alpha GpCD] [\alpha Gp]^{-1} [CD]^{-1}$ is the stability constant of the cyclodextrin–α-D-glucose complex;
$\beta_{CDB} = [CDB^-] [CD]^{-1} [B^-]^{-1}$ is the stability constant of the cyclodextrin–borate complex;
x, e, i (subscripts) refer to the state before the mixing of the two stock solutions containing borate and cyclodextrin, to the establishment of equilibrium of glucose–borate complex formation and to an arbitrary time, respectively.

The other symbols are the same as used in our earlier communication [6].

Investigation of cyclodextrin-borate interaction

25.0 mL of a boric acid–sodium [tetrahydroxoborate] solution containing 24 mmol/dm³ total boron (pH = 9.00) was titrated with α-, β- or γ-cyclodextrin stock solution according to the "Δe.m.f." method [7]. The concentration of α-, β- and γ-cyclodextrin was increased during the experiments up to 10.0, 9.0 and 8.1 mmol/dm³, respectively. The change produced by this in the e.m.f. value measured with a glass electrode did not exceed 0.2 mV (Δe.m.f.), as compared to values measured in solutions in the absence of cyclodextrin. Owing to the poor solubility of cyclodextrins, their concentration cannot be further increased in experiments of this type.

Next, solutions containing both cyclodextrin and borate were prepared (total boron concentration 24 mmol/dm³, α-, β- or γ-cyclodextrin concentration 23.4, 25.9 and 17.0 mmol/dm³ respectively). The solutions were heated to 50 °C, and after standing for 16 hrs at room temperature, then for 1 hour at 25 °C, the Δe.m.f. values, relative to a boric acid–borate solution treated in an identical way, but containing no cyclodextrin, were measured with a glass electrode. Δe.m.f. values measured in this way in the case of α-, β- and γ-cyclodextrin were 0.6, 0.73 and 0.50 mV, respectively (corresponding to a decrease in pH of 0.01, 0.012 and 0.008).

Assuming cyclodextrin–borate complexes of 1 : 1 composition, the stability constants were calculated on the basis of the known Δe.m.f. values and the total concentrations in the way described earlier [7]. Since the standard deviation of e.m.f. measurements was found to be (on the basis of 18 data) ±0.3 mV, and the value measured in this way is of the same order of magnitude as the error of measurement, the one-sided confidence limit calculated from the standard deviation was added to the Δe.m.f. values obtained, and only the maximal stability constants calculated from these values are given (Table I).

Investigation of the glucose–cyclodextrin interaction

The pH of 25.00 mL boric acid–borate solution of pH = 9.00 (20.0 mmol/dm³) was precisely measured, then 10.00 mL of a stock solution containing, in nearly equimolar quantities, glucose and one of the cyclodextrins, prepared 48 hours before the experiment, was rapidly added. In the solution obtained, the total concentration of glucose and α-, or β- or γ-cyclodextrin was 5.70, 5.80, 5.57 and 3.57 mmol/dm³, respectively. The change in e.m.f., measured with the glass electrode, was recorded at a sensitivity of 0.2 mV/mm and at a rate of 80 mm/min as a function of time.

On the basis of 6 parallel experiments, the reproducibility of the Δe.m.f. versus time curves was better than ±0.2 mV.

It can be seen from Fig. 1 that after mixing the stock solutions, Δe.m.f. increases only along a section of about 160 s. During this period the equilibrium quantity of α-D-glucofuranose–borate, formed from the α-D-glucose present, is attained [6]. The Δe.m.f., measurable after termination of the reaction in the presence of cyclodextrin is somewhat higher than in the absence of the latter. This may be indicative of the formation of a cyclodextrin–α-D-glucose complex, because the formation of this complex increases the total α-D-glucose content of the initial solution, and accordingly, the addition of borate, forming a more stable complex, produces a greater change in pH after termination of the faster reaction.

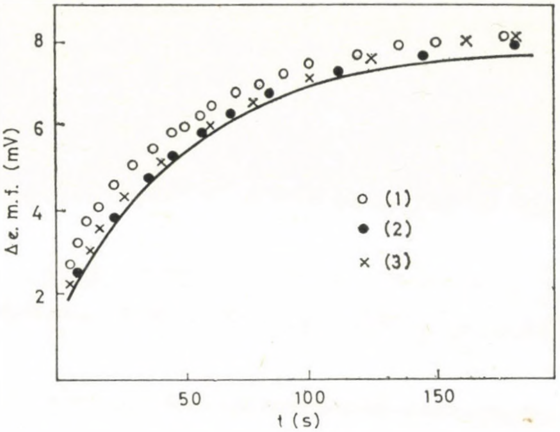

Fig. 1. Variation of e.m.f. with time, measured with a glass electrode in a solution containing borate (Total boron: 14.29 mmol/dm^3, pH = 9.0), D-glucose (C_G = 5.70 mmol/dm^3) and one of the cyclodextrins (time from mixing). (1) α-cyclodextrin, C_{CD} = 5.80 mmol/dm^3; (2) β-cyclodextrin, 5.57 mmol/dm^3; (3) γ-cyclodextrin, 3.57 mmol/dm^3. Continuous line: in the absence of cyclodextrin

Table I

Stability of cyclodextrin–borate and cyclodextrin–D-glucose complexes

On the basis of e.m.f. changes measured, the statement can be made at a significance level of $P = 0.95$ that the value of the stability constants does not exceed the values given in the table

Complex		Stability constant			
Symbol	Composition	Symbol	Possible maximum value		
			αCD	βCD	γCD
[CDB⁻]	Cyclodextrin–borate 1 : 1 complex	β_{CDB}	1.6	1.6	1.8
[αGpCD]	Cyclodextrin–α-D-glucose 1 : 1 complex*	β_{CDG}	16.1**	2.0	2.3

* The formation of a complex with β-D-glucose can be excluded
** Kinetic data prove that β_{CDG} in this case too is less than 10

In the calculation of the assumed 1 : 1 cyclodextrin–α-D-glucose complex the formation of the cyclodextrin–borate complex has been neglected, because its stability (Table I) is considerably lower than that of the glucose–borate species [6].

In the stock solution containing cyclodextrin and glucose, the concentration before mixing with borate were:

$$C_{CD} = [CD]_x + \beta_{CDG}[CD]_x[\alpha Gp]_x \tag{1}$$

$$C_G = [\alpha Gp]_x + [\beta Gp]_x + \beta_{CDG}[CD]_x[\alpha Gp]_x . \tag{2}$$

On attaining equilibrium after mixing, using the relationships deduced earlier for $[\alpha Gp]_e$ and $[B^-]_e$ [6], one obtains

$$C_{CD} = [CD]_e(1 + \beta_{CDG}[\alpha Gp]_e + \beta_{CDB}[B^-]_e)] \tag{3}$$

$$C_G = [\alpha Gp]_e(1 + \beta'_{011}[B^-]_e + \beta_{CDG}[CD]_e) + [\beta Gp]_x . \tag{4}$$

Express $[CD]_e$ from Eq. (3) and substitute it into Eq. (4), then rearrange after the substitution of K_m for $[\alpha Gp]_x$, we have:

$$[\alpha Gp]_x = \frac{1}{K_m}\left(C_G - C - \frac{\beta_{CDG}[\alpha Gp]_e C_{CD}}{1 + \beta_{CDG}[\alpha Gp]_e + \beta_{CDB}[B^-]_e}\right) \tag{5}$$

where

$$C = [\alpha Gp]_e(1 + \beta'_{011}[B^-]_e),$$

which can be calculated [6] from experimental data. By a similar reduction of equations 1) and (2):

$$C_G = [\alpha Gp]_x\left(1 + K_m + \frac{\beta_{CDG}C_{CD}}{1 + \beta_{CDG}[\alpha Gp]_x}\right). \tag{6}$$

If C_G, C_{CD} and C_A are known, the constants β_{CDG} belonging to the ΔpH_e values calculated from equilibrium Δe.m.f. can be numerically calculated from Eqs. (5) and (6) [6]. The one-sided confidence limit belonging to 95% significance level was added also in this case to the ΔpH_e values. Table I contains the maximal β_{CDG} constants calculated under the assumption of $\beta_{CDB} = 0$.

Conclusions drawn so far have been based only on the evaluation of the saturation section of the Δe.m.f. versus time curve. It has been investigated whether the full course of the curve supports our statement that the formation of stable cyclodextrin–glucose complexes

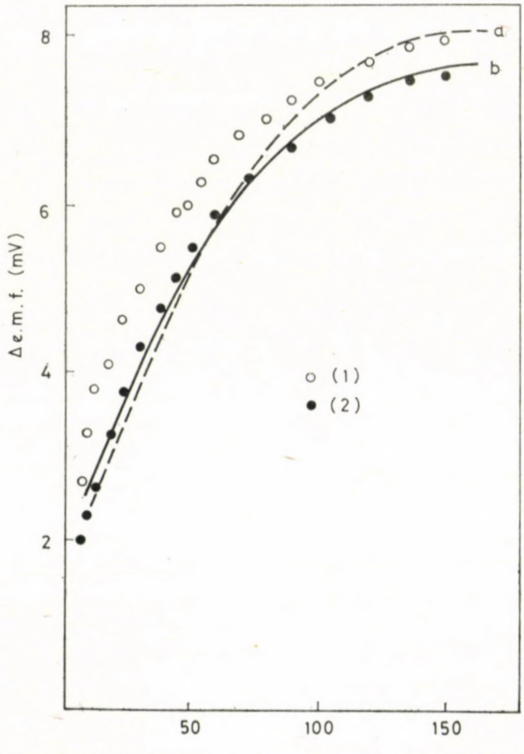

Fig. 2. Description of the Δe.m.f. versus *t* curve, measured with a glass electrode in a solution containing α-cyclodextrin, borate and D-glucose, assuming 1 : 1 cyclodextrin–α-D-glucose complexes of different stability (experimental conditions are the same as in *Fig. 1)*. Points (average of 6 measurements): (1) in the presence of cyclodextrin, (2) in the absence of cyclodextrin. Calculated curves: assuming stability constants of a) $\beta_{CDG} = 100$; b) $\beta_{CDG} = 10$

can be excluded. The rate equation of the formation of α-D-glucofuranose–borate, described earlier [6], has been used for the calculations with the following modifications.

Total α-D-glucose in the solution:

$$[\alpha\mathrm{Gp}]_x + [\alpha\mathrm{GpCD}]_x = [\alpha\mathrm{Gp}]_i + [\alpha\mathrm{GpCD}]_i + ([\alpha\mathrm{GpB}^-] + [\alpha\mathrm{GfB}^-])_i, \tag{7}$$

from this

$$[\alpha\mathrm{Gp}]_i = \frac{[\alpha\mathrm{Gp}]_x(1+\beta_{\mathrm{CDG}}[\mathrm{CD}]_x) - C_A\left(1 - \dfrac{1}{\mathrm{num\,log}\,\Delta\mathrm{pH}_i}\right)}{1+\beta_{\mathrm{CDG}}[\mathrm{CD}]_i}. \tag{8}$$

Assuming a given β_{CDG}, the concentrations $[\alpha\mathrm{Gp}]_x$ and $[\mathrm{CD}]_x$ can be calculated on the basis of Eqs (1) and (2). The value of β_{CDG} is low (Table I), and thus $[\mathrm{CD}]_i$ scarcely changes during the reaction, so that the following reduction was made in Eq. (8):

$$[\mathrm{CD}]_i = 0.5\,([\mathrm{CD}]_x + [\mathrm{CD}]_e)$$

(in the case of a given β_{CDG}, the value of $[\mathrm{CD}]_e$ can be obtained from Eq. (3) and from $[\alpha\mathrm{Gp}]_e$ calculated from experimental data [6]). On substituting Eq. (8) into the rate equation [6], Δe.m.f. *versus* time functions, corresponding to various β_{CDG} stability constants can be calculated using the other constants, determined earlier, as described in the communication [6], and these functions can be compared with the curves measured.

It can be seen from Fig. 2 that even the character of the curves calculated in this way is different from the data measured, and approaches the latter only in the last third of the 180 s measuring period. This difference becomes more and more pronounced on increasing the value of the β_{CDG} constant selected.

Discussion

Cyclodextrin–borate interaction

The minimal e.m.f. changes found in the experiments may have been due to the effect of the medium on the high-molecular organic compound or by the formation of acyclic associates containing H-bonds, or even by the modification of the cyclodextrin-perchlorate interaction [8]. If the data measured indicate the formation of a 1 : 1 borate complex, the stability of the complex approximates that of the cyclic ethylene glycol–borate complex [7] only in the case of α-cyclodextrin.

This result is consistent with knowledge on the structure of cyclodextrins [9] and borate complexes [7, 10]. The vicinal diol group of cyclodextrins is located namely at the border of the ring, in diequatorial position, unfavourable from the aspect of borate complex formation.

Cyclodextrin–glucose interaction

The e.m.f. versus time curve characteristic of D-glucose–borate complex formation [6] is slightly modified in the presence of cyclodextrin, and this may indicate the formation of a cyclodextrin–α-D-glucose complex. However, the stability constant of this complex is low and does not exceed the value shown in Table I, calculated under consideration of the measurement error.

According to the kinetic evaluation of the curve even these less stable complexes are not formed, and the experimental data can be interpreted also in this case by general medium effects.

Important from the physiological aspect is that practically the formation of cyclodextrin–glucose inclusion complexes in aqueous solution must not be taken into consideration even if the complexes of the stability given in Table I actually exist. Calculations on the basis of the mole fraction of the complexes and Eqs (1) and (2) under the assumption $\beta_{CDG} = 2.0$ show that in a nearly saturated aqueous solution of 15 mmol/dm^3 concentration of the β-cyclodextrin–glucose "inclusion complex" described by HOFFMAN *et al.* [2] only about 1% of the cyclodextrin would be bound to glucose. This is why the rate of oxidation of glucose "bound in the inclusion complex" was found by the above authors to be identical with the rate measured in the absence of cyclodextrin.

Our experiments supports earlier observations [1, 9], according to which, readily hydrated compounds do not form inclusion complexes as guest molecules. Thus, there is no reason to assume that drugs introduced in the form of cyclodextrin inclusion complexes into the organism will be displaced by glucose or similar substances at the very time of introduction into the body fluids.

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TRANSMISSION INFRARED SPECTROSCOPIC STUDIES OF STRUCTURE AND UV PHOTOCHEMISTRY OF URACIL THIN LAYERS

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Infrared transmission spectra of vapour-deposited uracil thin layers were recorded before and after irradiation. Using CsI substrates, uracil thin layers showed a great variety of crystalline structures differing in the range of ordering, orientation and morphology. Uniform layers were obtainable by covering the CsI substrates with a thin gold film. UV photoreactivity essentially did not depend on the structure of thin layers when well crystallized. UV photochemical reaction produced *cis*-syn dimers, but the formation of the *cis*-anti stereoisomer was not excluded either. Photodimers *in situ* occupied different isolated and distorted sites of very low or no symmetry. Very slow ordering over some weeks led to the crystallization of photodimers.

Introduction

The UV photochemical reactivity of pyrimidine bases in nucleic acids is a well known fact, and because of its biological importance it has been studied for a long time. It is also known that in the UV radiation injury of RNA, uracil plays the main role [1, 2, 3]. The UV photochemistry of uracil was studied through the investigations of model systems as well. Up to now, mostly solutions [4] or frozen aqueous solutions [5] were used, and the photoproducts were analyzed by different methods (column and this layer chromatography, UV and IR spectroscopy, *etc.*). However, these model systems have some disadvantages. In room temperature solutions the conformation of the reagent molecules is very different from that in RNA [6]. The high light scattering of the frozen systems makes it impossible to calculate the absorbed dose and they are not suitable for direct physical methods to follow the reactions. Dried layers of uracil were also studied [7]; but only isolated photoproducts were investigated and the systems were not applied for the investigation of the reactions inside the matrix *(in situ)*.

Using IR spectroscopy, we tried to find an appropriate method for the *in situ* study of the photochemical reaction in crystalline uracil thin layers. There are some papers referring to the structure of vapour-deposited thin layers [8, 9, 10], making use of the UV, IR spectroscopic or X-ray diffraction methods. In the case of IR spectroscopy, however, only some spectra were reported and their detailed study was not carried out [9, 11]. Besides, we have found some contradictions in the interpretation of the published data. The IR spectrum of irradiated lyophilized thin (15 μm) layers of uracil was studied by WAIT *et al.* in 1978. Despite the fact that their study was carried out using large doses of irradiation (1 hr of irradiation time, 100 W of mercury lamp) compared with those applied in the present work (see experimental), they observed alterations of the spectra only in the wavenumber range of 1550—1000 cm^{-1} and reported the appearance of not more than two bands (1152 and 1280 cm^{-1}) attributable to the photoproducts. No kinetic or structural considerations are presented for the photochemical process, only a weak suggestion can be read for the production of "loosely coupled" species. In the present paper we report on our investigations of uracil thin layers by transmission infrared spectroscopy. "Thin layers" should originally mean layers with a thickness of some tenths of a μm just as thin as layers used in UV spectroscopy. However, transmission infrared spectroscopy requires layers of the thickness of 5—50 μm. Thus the latter type of thin layers was investigated and the degree of crystallinity of the uracil, its photoreactivity and the kind and crystallinity of the *in situ* photoproducts was studied.

Experimental

Uracil was purchased from REANAL and was used without further purification.

Uracil thin layers were produced by evaporation and deposition of crystalline uracil in the way described before [8]. Evaporation conditions: temperature 135—140 °C; substrate at room temperature; pressure 0.1 Pa. As substrates, 5.5 mm thick CsI windows with a diameter of 25.2 mm were used. Infrared spectra were taken with a Perkin–Elmer Model 225 spectrophotometer in the 4000—200 cm^{-1} region.

In order to obtain the IR spectra of polycrystalline uracil, Nujol mulls were used for most of the spectral regions and halocarbon mulls for regions where Nujol absorbs. The irradiation of uracil thin layers was carried out by a Germicidal lamp (General Electric, 15 W) using argon gas protection. IR spectra were recorded before and after UV irradiation.

The covering of the substrates with gold layers was performed by a Jeol JEE type vacuum evaporator at 2.6×10^{-3} Pa, and thin layers of 20 nm were produced in each case.

Difference spectra characteristic for the uracil photoproduct were calculated from the spectra of unirradiated and irradiated layers. The transmission was checked from the spectrum in steps of 2 cm^{-1}. The incident intensity was determined by fitting base lines to the experimental transmission curve, and thus the extinction could be calculated point by point. In the case of spectra of irradiated state the extinctions at 1417 cm^{-1} and 1238 cm^{-1} were considered as characteristic for the amount of unaltered uracil molecules in the layers. It was supposed that these sharp bands attributed to uracil ring modes, were not overlapped by any photoproduct vibrational band. Thus a mean value of the fractional decrease of the amount of uracil molecules caused by irradiation could be determined from the change of these very extinctions. After this, the extinctions responsible for the spectrum of unaltered uracil were multiplied by this value and were substracted from those of irradiated uracil. The result was considered as the spectrum characteristic for the photoproduct. The calculation was performed on a Hewlett–Packard 9100 B type Computer and the spectrum was plotted by its X—Y recorder.

The X-ray diffractograms of the thin layers were obtained by a Philips PW 1051 X-ray diffractometer.

Infrared spectra and structure of uracil thin layers

The spectra of the thin layers Faces I—III shown in Figs 1a, b, c were registered on uracil thin layers obtained in different evaporation conditions (evaporation time and temperature were varied).

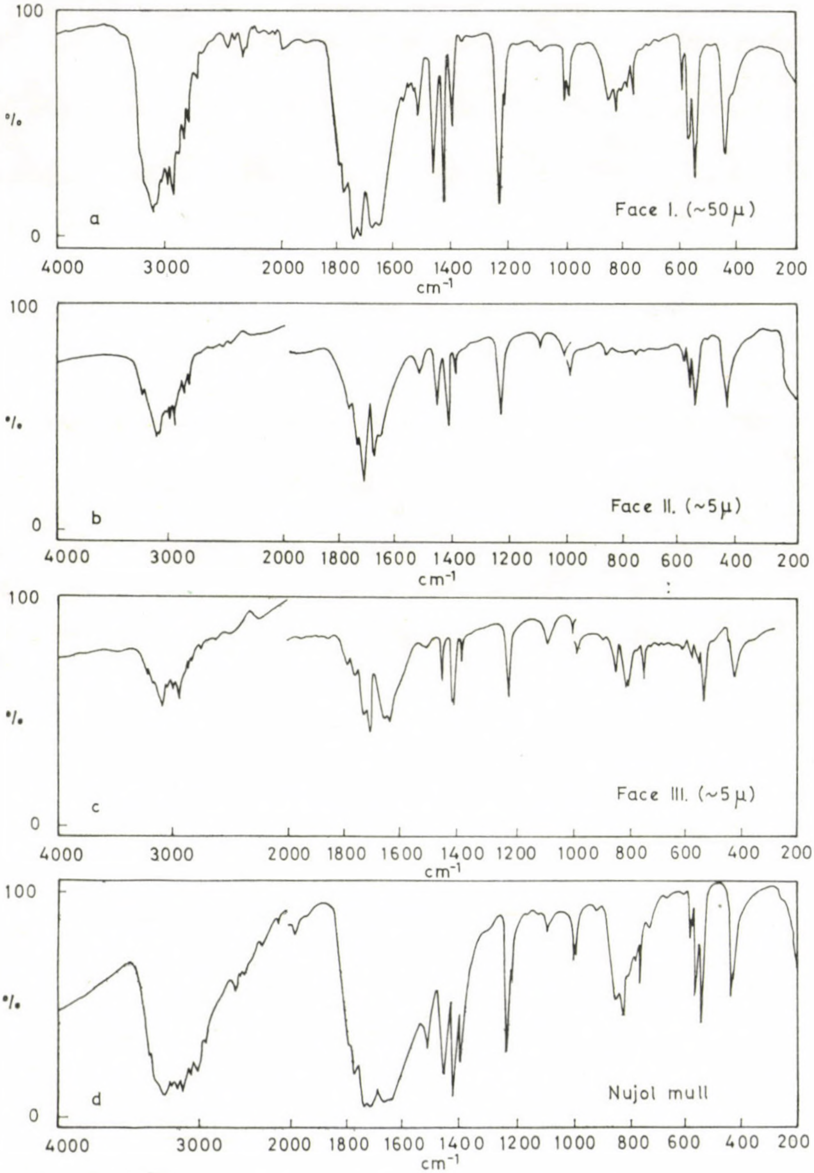


Fig. 1. Spectra of different uracil layers

The spectrum of polycrystalline uracil (Fig. 1d) is identical with the spectra reported earlier in the literature [12]. The spectra of Faces I—III obviously differ from that of the polycrystalline sample and they all differ from each other, too.

Table I shows the vibrational frequencies corresponding to the respective spectra in Fig. 1a, b, c, d. To check if any chemical reaction took place during evaporation, we analyzed the dissolved layers by gas chromatography. We found that the layers contained only uracil molecules. It follows that the differences between the layers must be related only to their physical structure. Although the spectra in Figs 1a—d seem to be quite different; Table I shows that all the frequencies of the corresponding spectral bands are equal and only their relative intensities and/or band shapes are different. The identity of the vibrational frequencies proves that only one allotropic modification appears in the layers. On the other hand, there may be rather great differences between the degrees of the crystallinity of the uracil layers. The more the bands split the more ordered uracil is.

X-ray measurements performed on the thin-layer samples have shown the relatively thick (~ 50 μm) layer to be long-range ordered. In general, well-defined X-ray reflections appear only if the range of the ordering (the size of the "crystallites") is greater than 10 nm. Two reflections from Face I have been found, those of the planes (001) and (230), respectively. This, means that

(i) Face I contains well developed microcrystallites

(ii) Face I contains crystallites of only two orientations.

The random polycrystalline sample shows reflections of high intensity from planes (120), (200) and (100), too. Infrared spectrum of Face I (Fig. 1a) is a typical crystal spectrum with well split bands. Although the IR spectra of Face II and Face III are also well or even better split, no X-ray reflection has been found from them.

The spectra of lyophilized uracil layers presented in the work of WAIT *et al.* [11] were not analyzed or discussed. GUMENIUK *et al.* [9] found that uracil thin layers evaporated at rather high temperatures (190—200 °C) showed a "laminated" amorphous structure, which easily transformed into a crystalline form, keeping the layers in an atmosphere of 100% water content. The crystalline form was characterized with the (320) and (310) crystallographic planes. We have to mention, however, that there are some doubts regarding the above interpretation of the X-ray diffractogram also published in the paper:

1. The reflection attributed to the (320) planes appeared in the diffractogram of GUMENIUK *et al.* at $2\Theta = 35.7°$. This angle, according to our calculation, based on the same crystallographic data [13] as used by GUMENIUK *et al.*, means a distance of 0.315 nm corresponding by no means to the distance

Table I

Vibrational frequencies of uracil layers

Nujol mull	Thin layers		
	Face I	Face II	Face III
3220 sh	3220 sh	3230 w	3225 w
3180 sh	3175 sh	3180 sh	3175 sh
3100 vs	3110 vs	3110 vs	3110 vs
3080 s	3088 s	3085 s	3080 s
3044 m	3042 sh	3044 w	3044 sh
2990 sh	2979 s	2995 m	2992 m
2940 s	2938 vs	2945 vs	2942 vs
2895 sh, b	2900 sh	2900 w	2900 w
	2890 m		
2860 m	2855 m	2863 m	2863 w
2820 m	2812 m	2928 m	2825 w
	2800 w		
2740 sh	2731 w	2745 w	2750 vw
1790 w	1788 sh	1795 vw	1790 vw
1767 m/w	1768 m	1766 w	1768 w
1736 sh	1736 vs	1740 m	1736 m
1718 vs	1718 vs	1717 vs	1717 vs
1673 vs	1676 s	1677 s	1675 s
1645 s	1643 s	1646 s	1645 s
1610 sh	1615 sh	1612 sh	1610 sh
1525 vw	1526 vw	1525 w	1525 w
1510 m	1515 m	1513 w	1513 m
	1456 s	1460 s	1458 s
1455 s	1447 sh	1447 sh	
		1424 s	1424 s
1417 sh	1422 s	1420 s	1420 s
1390 m/s	1394 m	1392 w/m	1395 m
1328 s	1233 s	1240 s	1237 s
1217 sh	1215 sh	1218 sh	1218 sh
1150 vw			
1099 w	1095 vw	1098 w/m	1099 w/m
1006 m/w	1005 m	1006 w	1006 m/w
994 m/w	982 m/w	995 m/w	995 m/w
920 vw			
853 m	850 m	857 w	858 m/s
822 s/m	822 m/s	823 w	823 m/s
810 sh		817 w	814 m
	805 sh	800 vw	802 sh
			799 sh
780 w	782 m/w	783 w	782 w
760 m	759 m	760 m	759 m
728 sh			734 sh
614 vw		615 w	612 w
584 m	584 m	586 w	586 m
578 vw			576 vw
564 m	565 m	566 m	565 m
560 sh	561 sh	561 sh	561 sh
		546 s	
545 s	543 s	542 s	543 s
531 sh	533 sh	532 sh	532 sh
434 m/s	438 m	436 m	436 m
425 sh	428 sh	427 sh	428 m

between the (320) planes (0.299 nm) but to that of the (001) planes (0.314 nm). The (320) planes should produce very weak reflection, thus the high intensity reflection at $2\Theta = 35.7°$ cannot belong to the (320) planes because of its intensity, either.

2. The assignment of the reflection at $2\Theta = 30.6°$ to the planes (310) must be wrong, too. The plane distance calculated with $2\Theta = 30.6°$ is 0.367 nm, which is very close to the distance between the planes (201) ($d = 0.363$ nm), while the distance between the planes (320) should be 0.329 nm.

The infrared spectra are influenced mainly by short-range order and are rather insensitive to long-range order. Long-range order is regarded as the perfect replication of unit cells by translation and it is therefore concerned mainly with translational symmetry, while short-range order is regarded as arrangements within the unit cell associated with point group symmetry.

According to the above facts, we conclude that all the samples are well ordered, but the range of their ordering must be quite different. While Face I is long-range ordered, Faces II and III are short-range ordered.

The samples may be different not only in their range of ordering but in their orientation as well. The orientation effect manifests itself in the relative intensities of the bands. The uracil ring forms a dihedral angle of 6° 6′ with crystallographic *ab* plane, (010), *i.e.* it is almost parallel to it. Therefore, in the case of perfect (001) orientation to the substrate, the out-of-plane vibrations of the molecules should not appear in the i.r. spectrum, while orientations like (hkO) should allow to appear maximal intensities of the out-of plane vibrational bands. Planes (230), (120), (200), (100) or combinations of all the above orientations or (hkl) orientations may produce a great variety of relative intensities.

Considering the spectra, Face II must be mostly of the orientation (001) due to the relatively weak intensity of the 700–900 cm^{-1} NH out-of-plane bending region (Fig. 1b). In Face III, some simultaneous orientation with uracil ring planes parallel and perpendicular to the substrate plane or orientation of (hkl) type (Fig. 1c) seems to occur. Face I contains orientations of (001) and (230), resulting in a spectrum (Fig. 1a) with relative intensities rather similar to that of the random polycrystalline mulled sample (Fig. 1d).

It is quite obvious that the high variety found in the structures of the vapour-deposited uracil layers may be influenced not only by the slightly varying parameters of the evaporation, but rather by the actual conditions of the substrate surfaces which the uracil has been deposited on. Since CsI is very sensitive to moisture, its surface is never reproducible. The standardization of the surface could be achieved by covering CsI with a thin gold layer of 20 nm before depositing uracil. In this way, we managed to get thin layers with a well reproducible structure of Face II.

Spectra of photoproducts

Figure 2 illustrates the expanded spectra of Face III before and after an UV irradiation for five minutes. The spectra of irradiated layers contain the bands of the photoproduct(s) and those of the remaining uracil monomers. We found the spectrum of irradiated Face III to be typical in its character for the other faces, too. In Table II we collected all the new bands that appeared after the layers had been irradiated. Table II includes the photoproduct bands of a sample (Face IV) of the same type as Face II; this type of layers was found to form in most cases. Data of Table II on Face I were collected

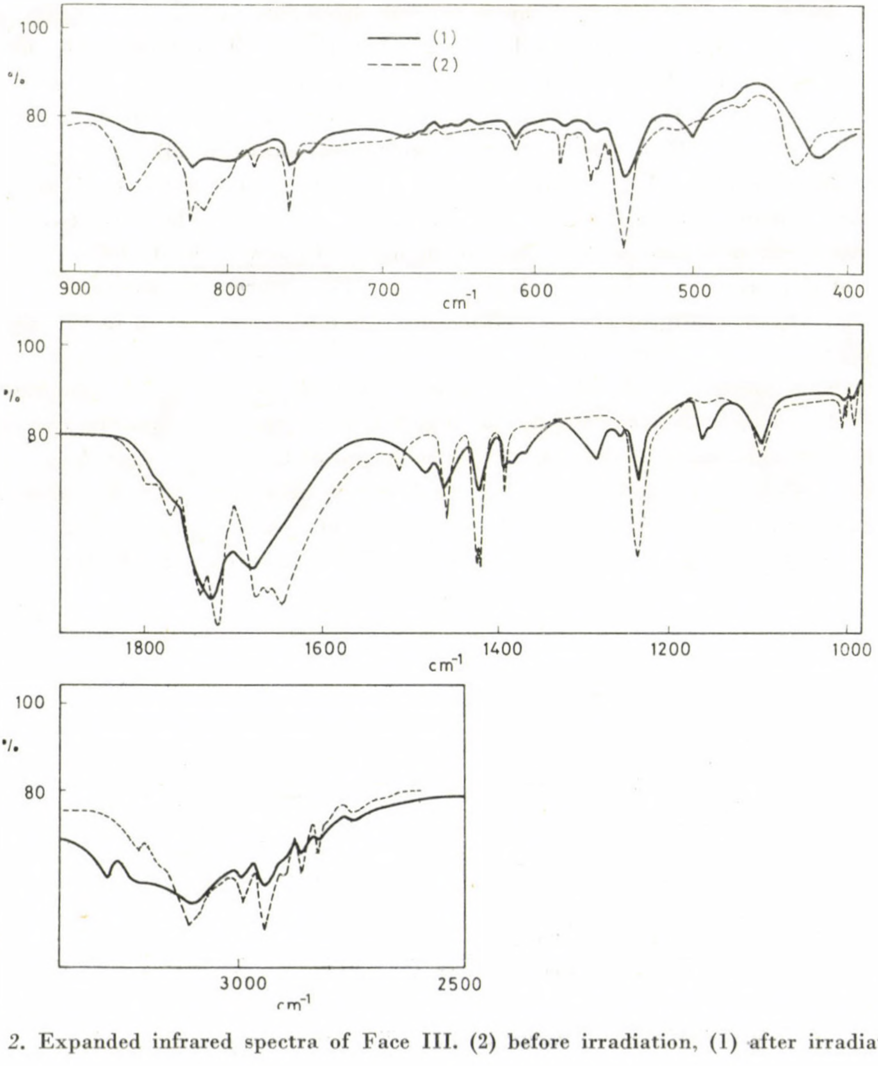


Fig. 2. Expanded infrared spectra of Face III. (2) before irradiation, (1) after irradiation

from spectra recorded after 10 and 130 min.; those of Face II after 3 min.; those of Face III after 5 min.; while those of Face IV after 3, 6 and 9 min. of irradiation. (From the point of view of photochemical changes, the absorbed energy is determinant. The absorbed dose depends on the time of irradiation, the light scattering and the thickness of the layer as well. Thus by applying different irradiation times we tried to compensate the differences in the layers studied.) Consulting Table II, we can say that the frequencies of the respective bands raised by irradiation agree rather well. However, in the range of the very strong and/or complex broad band systems, one can hardly identify the new bands. Therefore we tried to consider the difference spectra hoping that the difference spectrum would be identical or almost similar to that of the pure photoproduct(s). The difference spectrum was computed in each case, and a good agreement could be stated in the band positions. The difference spectrum for Face IV (irradiation time 6 min.) is shown in Fig. 3 and the frequencies of the peaks are collected in the fifth column of Table II.

We can see that the difference spectrum contains all the frequencies we could read from the original spectra obtained after irradiation. There are several additional bands, even in the frequency regions where we could not separate that new bands. We have to mention, however, that there are some risks of drawing far-going conclusions from the difference spectra.

(i) The drawing of the base lines is rather uncertain even in the case of complex band systems.

(ii) If the structure of the layer (crystallinity, morphology, orientation) is heterogeneous, the photochemical reaction may prefer the one or the other kind of these structures [8]. Thus, the spectrum of the sample may be a superposition of the spectra of the product and that of differently structured regions of uracil monomer, where the degree of ordering may depend on the course of the reaction. Therefore, we cannot be sure at all that the factor used in

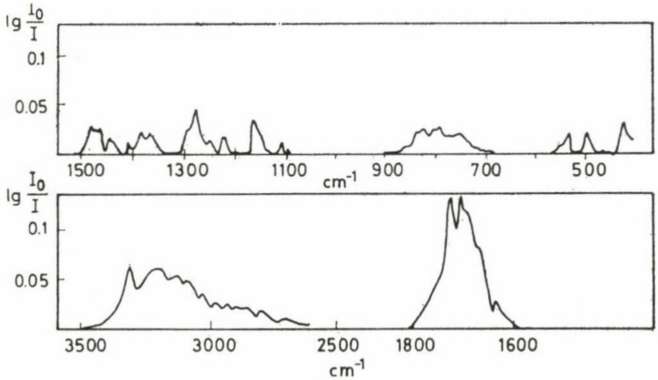


Fig. 3. Difference spectrum for Face IV (irradiation time = 6 min.)

substraction, which has been estimated for the 1417 or 1238 cm^{-1} bands, will be valid for all the other bands, too.

Taking the above considerations into account, some of the difference bands cannot be assigned with certainty to the photoproducts. Those frequencies which are marked by asterisks in the fifth column of Table II coincide

Table II

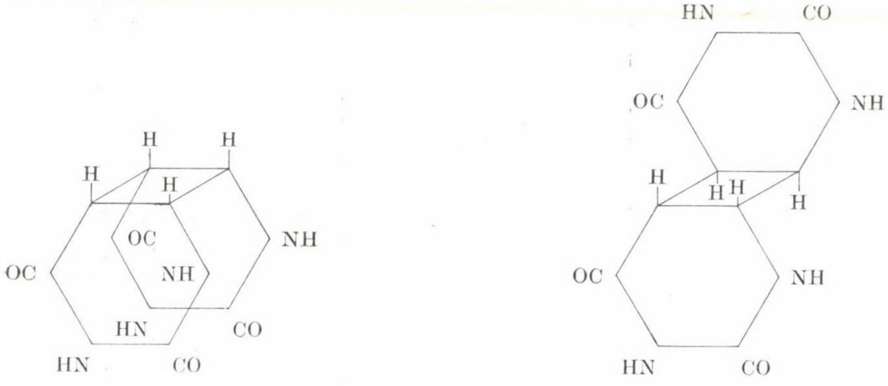
Vibrational frequencies of different irradiated layers and those of the difference spectrum

Face I	Face II	Face III	Face IV	Difference spectrum
				3350 sh
3300 sh	3300 sh	3300 m	3305 w	3300 m
				3220 m
				3195 m/w*
				3120 w
				3095 m/w
				2990 w*
				2930 w*
				2895 w*
				2855 w*
				1770 sh
				1719 sh*
1685 sh	1686 sh	1690 sh	1692 s	1690 m
				1663 sh*
				1635 vw
1530 – 1500 w, b				
1490 w	1485 vw	1485 w	1478 w	1480 m
	1462 w	1460 w	1460 w	1460 w
				1417 w*
				1400 sh*
1380 sh	1385 vw	1385 w	1385 vw	1383 w
		1368 sh	1365 vw	1368 w
1300 sh	1295 sh	1300 sh	1297 sh	1295 sh
1280 m	1282 m/w	1285 m/w	1282 m	1277 m
1260 sh	1267 sh	1260 vw	1256 vw	1250 w
				1243 sh*
				1230 vw
1170 m/w	1167 m/w	1168 m/w	1160 w	1163 m/w
1157 sh	1155 sh	1155 sh	1151 sh	1148 sh
				1140 sh
1116 sh		1115 sh	1115 w	1110 w
				860 vw*
				840 sh
				820 w*
				810 sh*
				795 w*
				772 sh
				755 w*
690 vw		680 vw, b	684 vw	
				605 sh
				535 w*
500 m	500 w	500 w	498 w	500 w
	427 sh	422 vw	425 vw	425 m/w

* Uracil band?

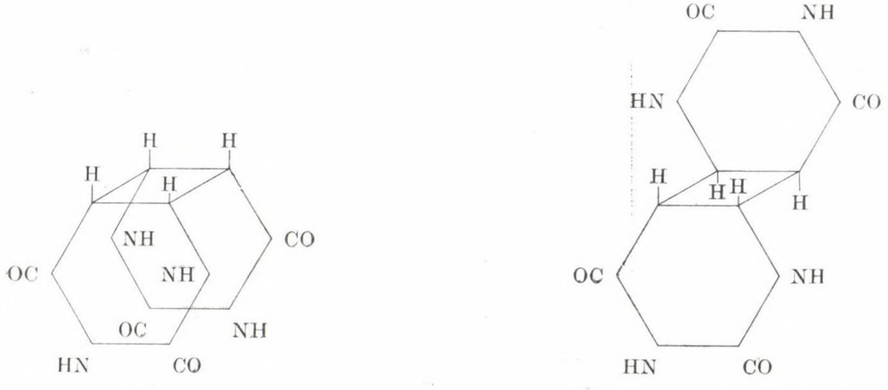
with frequencies that occur in the spectrum of pure uracil too. Thus they may arise from uracil in consequence of the error in the substraction procedure. The frequencies of the two product bands found by Wait *et al.* [11] approximately coincide with two of our product bands (Table II).

In order to identify the photoproducts, we considered the four possible stereoisomers of pyrimidine-cyclobutane dimers [15, 16] and compared our spectra of irradiated layers (Fig. 3, Table II) with infrared spectra of the pure crystalline photodimers recently published by Varghese [17] and Jennings [18] *et al.* Although our spectra show fewer bands than those of the crystalline dimers there are some characteristic bands that allow approximate assignments. The sharp band of the photoproduct at about 3300 cm^{-1} (Fig. 3, Table II) does not appear in the spectra of the different crystalline



cis-syn

trans-syn



cis-anti

trans-anti

Fig. 4. Structure of uracil dimers

isomers except in that of the *cis*-syn one (both α and β modifications). On the other hand, there is a sharp and strong band at about 500 cm^{-1}, which is characteristic for the spectrum of the *cis*-anti isomer (Fig. 4). In general, the other regions of our spectra sufficiently support this kind of product composition and there is no band contradicting it. Of course, we can exclude neither the occurrence of the other ismers *(trans*-syn and *trans*-anti) nor other types of photoaddition products in small quantities. Our results, however, are clearly contradicting the suggestion of WAIT *et al.* [11] that loosely coupled species of ill-defined geometry were produced in irradiated uracil layers.

The weak intensity is not the only property of the product spectra that gives rise to difficulties in identifying the photoproducts. The bands are rather broad and their distorted asymmetrical shape often indicates that they must contain more components not split. The broadness of the bands expected to be sharp according to the pure crystalline spectra of the photo-dimers, can be regarded as an evidence for the amorphous nature of the photodimers "*in situ*", *i.e.* there is no rotational symmetry relating two or more molecules to each other, either. In spite of the instability of their states, they do not become ordered in a few days. This probably means that the dimer molecules are isolated from each other or they are fixed by hydrogen bonding in a distorded structure. After keeping the samples at about 40—50 °C for some weeks, the broad bands of dimers show a quite remarkable sharpening or even splitting, indicating that the dimers have crystallized [8]. Thus the suggestion for isolated dimers can be neglected.

Photoreactivity

The photoreactivity of the different layers was investigated in two ways.

1. We considered the decrease in the intensity of a uracil band (at 1238 cm^{-1}) normalized by its starting intensity as a function of the irradiation time. As we see in Fig. 5, Faces II, III and IV show similar photoreactivity. However, uracil of Face I decreases as little as 25% during irradiation for 130 min., *i.e.* its reactivity seems to be about one hundredth of that of Faces II—IV. Face I is a layer of long-range order, with well developed crystallites and thus it shows a very high light scattering, which may cause a loss of one or two orders of magnitude in the dose of irradiation. Taking also into account the high self-absorption of thick layers, the great difference in photoconversion cannot be attributed to the differences between short-range and long-range ordered structures alone.

2. We measured the increase of a product band as well (at 1160 cm^{-1}). We found the photoreactivity estimated in this way to be in accordance with the results described above.

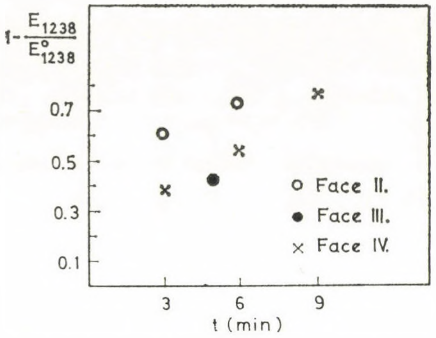


Fig. 5. **Relative increase of the number of converted uracil molecules as a function of irradiation time**

We examined the relation between the normalized intensity decrease of the 1238 cm^{-1} uracil band,

$$1 - \frac{E_{1238}}{E^{\circ}_{1238}}$$

and the normalized intensity of the 1260 cm^{-1} "product" band

$$\frac{E_{1160}}{E^{\circ}_{1238}}$$

The relation between these quantities, as can be seen in Fig. 6, is linear, however, what is quite surprising; the slope of the line is about 0.25, instead of 0.5 which was expected in a first approximation (the product is supposed to be formed by the addition of two uracils). This means that a 2-fold decrease of uracil produces only a 1/4 increase of the products assigned to the 1160 cm^{-1} band.

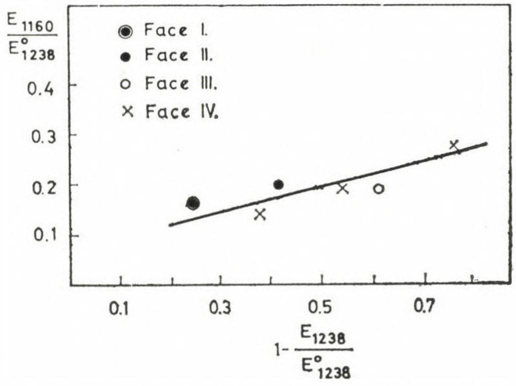


Fig. 6. **Increase of normalized intensity of the "product" band at 1160 cm^{-1} *versus* decay of the uracil molecules**

There are many possibilities to interpret the above phenomenon. To mention the most plausible one, various kinds of photoproducts may simultaneously be formed, but only one of them belongs to the vibrational band at 1160 cm^{-1}.

Another very reasonable explanation for the above phenomenon may be related to the amorphous state of dimers in situ, which results in very broad and diffuse spectral bands. Thus the estimation of the very increase of such bands would require the knowledge of the integrated intensities through the whole band instead of the height of the peak. Because of the low intensity of the photoproduct spectrum, the integrated intensities are unfortunately not available.

A similar phenomenon has been observed for the band system appearing between 1250—1300 cm^{-1} too.

Conclusions

For investigations of vapour-deposited uracil thin layers by transmission infrared spectroscopy, one needs layers of a thickness of 5—50 μm. Using CsI windows as substrates, uracil thin layers show a great variety of structures. The layers, first of all, differ from each other in their state of crystallinity. Although all are well crystallized, the range of ordering, the orientation and morphology of the microcrystals are rather different. Uniform layers are obtainable by covering the surface of the CsI substrate with a thin gold coating of about 20 nm.

The UV photoreaction does not essentially depend on the structure of the layer. Extensive losses in light due to light scattering and self-absorption occur in thicker ($\sim$50 μm) layers. The UV photochemical reaction mainly produces the *cis*-syn dimer, but the formation of the *cis*-anti stereoisomer is not excluded either. Photodimers *in situ* are occupying different and distorted sites of very low or no symmetry. Very slow ordering for some weeks leads to the crystallization of photodimers.

*

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SYNTHESIS OF PROTEIN MODEL COMPOUNDS BY SIDE GROUP MODIFICATION OF POLYAMINO ACID DERIVATIVES, III+

PREPARATION OF BIOLOGICALLY ACTIVE α-POLY-L-GLUTAMIC ACID DERIVATIVES WITH SYSTEMATICALLY ALTERNATE MACROMOLECULAR PROPERTIES

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Fractions with narrow molecular weight distribution range were prepared from originally polydisperse, side-group-modificated α-poly-L-glutamic acid derivatives by means of fractional precipitation. The molecular weight distribution and chemical composition of the fractions were investigated. The viscosities of the fractions were compared, and the average molecular weight of some fractions was determined by light scattering measurements.

Biological investigations showed that activity was greatly influenced by the macromolecular properties of the fractions.

Some years ago we reported the preparation of several types of side-group-modified α-poly-L-glutamic acid derivatives [1, 2]. These polymers had different biological avticities [3–6]; recently they were investigated as enhancers of poly I · poly C-induced viral resistance [7, 8]. It could be seen from the results of these investigations that the poly I · poly C potentiating activities of our polymeric compounds were highly influenced by their macromolecular parameters [9] *(e.g.* viscosity, the reaction conditions of their preparation, *etc.)*. Therefore, it seemed reasonable to prepare a group of compounds closely related in their chemical composition, and differing only in their macromolecular properties, such as the average molecular weight, molecular weight distribution, *etc.*

The starting material was α-poly-L-glutamic acid γ-(2-dimethylamino-ethyl) amide (**III**). It was prepared from α-poly-L-glutamic acid γ-alkyl-esters (**I**) by means of side group modification with 2-dimethylaminoethylamine (**II**) [1].

+ Part II: see Ref. [2]
Part I: see Ref. [1]

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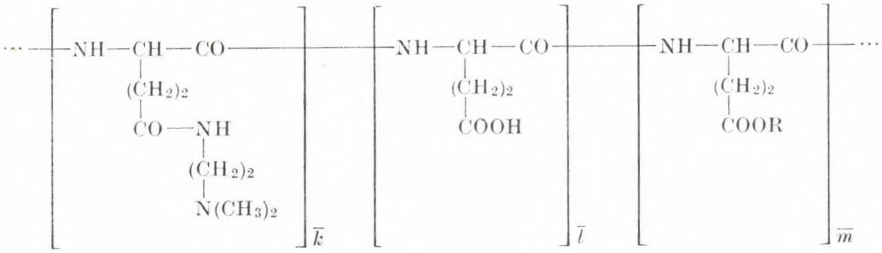
$$\cdots\left[\mathrm{NH{-}\underset{\begin{array}{c}|\\(CH_2)_2\\|\\COOR\end{array}}{CH}{-}CO}\right]_{\bar{n}}\cdots \xrightarrow{\mathrm{H_2N(CH_2)_2N(CH_3)_2}} \cdots\left[\mathrm{NH{-}\underset{\begin{array}{l}|\\(CH_2)_2\\|\\CO{-}NH\\ \qquad |\\ \qquad (CH_2)_2\\ \qquad |\\ \qquad N(CH_3)_2\end{array}}{CH}{-}CO}\right]_{\bar{n}}\cdots$$

I II III

R: CH_3 or $C_6H_5CH_2$

As we have shown earlier [1], the resulting compounds are in effect copolymers containing mainly cationic γ-(2-dimethylaminoethyl) side groups:



$$\cdots\left[\mathrm{NH{-}\underset{\begin{array}{l}|\\(CH_2)_2\\|\\CO{-}NH\\ \qquad |\\ \qquad (CH_2)_2\\ \qquad |\\ \qquad N(CH_3)_2\end{array}}{CH}{-}CO}\right]_{\bar{k}}\left[\mathrm{NH{-}\underset{\begin{array}{c}|\\(CH_2)_2\\|\\COOH\end{array}}{CH}{-}CO}\right]_{\bar{l}}\left[\mathrm{NH{-}\underset{\begin{array}{c}|\\(CH_2)_2\\|\\COOR\end{array}}{CH}{-}CO}\right]_{\bar{m}}\cdots$$

$\bar{k} + \bar{l} + \bar{m} = \bar{n}$

One of the most widespread methods of preparing fractions from a macromolecule with wide molecular weight distribution is fractional precipitation [10]. This method seemed suitable to obtain several series with systematically alternating macromolecular properties.

First we prepared two samples ("M" and "B") of the above compound, differing from each other in their average molecular weight and each having quite a wide molecular weight distribution (see Figs. 1 and 2, dotted lines). (The method of side group modification was described in our earlier papers [1, 2]. One of the starting polymers was poly-γ-methyl-L-glutamate with M 84500 and the other poly-γ-benzyl-L-glutamate with M 365000.)

For convenience, the hydrochloride salts were prepared from these polybasic materials. Preliminary analytical experiments showed that the so called "reverse method" (see Experimental) of fractional precipitation, using methanol as solvent and t-butanol as precipitant, was a promising procedure to obtain fractions with quite narrow molecular weight distribution. (*Cf.* Figs. 1 and 2.)

Using this method, we isolated five fractions (M_1—M_5) from the macromolecule "M" (having lower average M) and four fractions from that of "B" (having higher average M).

The best way of controlling the fractionation process and to check the result of fractionation is gel permeation chromatography (GPC). Thus a GPC method was developed for this purpose. (In view of the known difficulties in the GPC of polyelectrolytes, our method may also be of interest in a wider circle of application.)

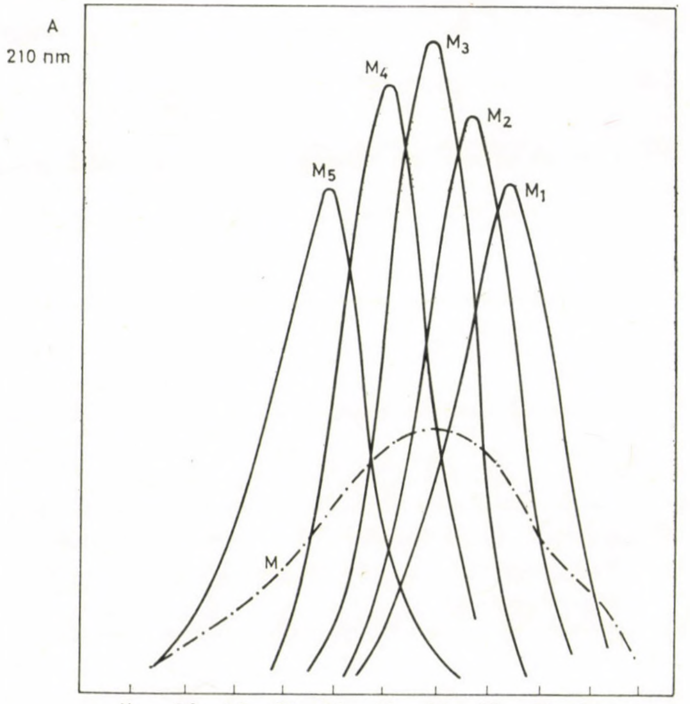


Fig. 1. GP chromatogram of "M" and the fractions isolated from it. The K_{av} values were calculated as follows: $K_{av} = \frac{V_E - V_0}{V_t - V_0}$, where V_E is the elution volume of the fraction; V_0 is the "outer volume" of the column (*i.e.* the volume among the gel grains); V_t is the total volume of the column including the pores of the gel; A absorbance at 210 nm

The chromatograms show that fractionation was successful; the obtained fractions had much narrower molecular weight distribution than the starting material.

The "volumetric divisional quotient" (K_{av}) was determined from the chromatograms (Table I). This value is characteristic of the volume occupied by the macromolecule in the GPC solvent. To study the relationship of the average molecular weights of the fractions related to each other, their reduced

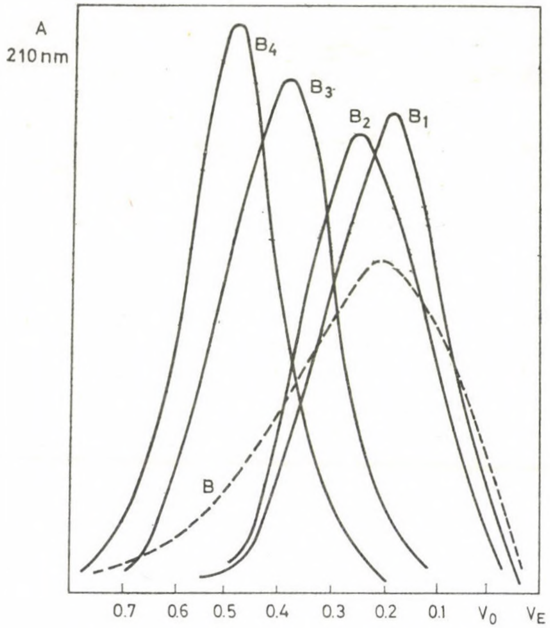


Fig. 2. GP chromatogram of "B" and the fractions isolated from it

specific viscosities were measured. As can be seen from the results summarized in Table I, in agreement with our expectations, the tendencies of the K_{av} and $\frac{\eta_{sp}}{c}$ values are similar.

Table I

Characteristics of the fractions determined in 0.1 *N* HCl *at a concentration of* 0.3%

	Chemical symbol	Weight, g	K_{av}	$\frac{\eta_{sp}}{c}$	$\overline{M}_{LS}$
Starting polymer M	poly-$DMAG^{94}$ Glu^{5} $Glu(5)OCH_3^1$	10.0	0.425	0.58	—
Fraction M_1	poly-$DMAG^{84}$ Glu^{6} $Glu(5)OCH_3^{10}$	1.9	0.263	0.89	200000
Fraction M_2	poly-$DMAG^{87}$ Glu^{10} MG^{3}	1.7	0.325	0.62	105000
Fraction M_3	poly-$DMAG^{82}$ Glu^{11} MG^{7}	1.3	0.415	0.43	—
Fraction M_4	poly-$DMAG^{86}$ Glu^{14}	1.4	0.500	0.30	23700
Fraction M_5	poly-$DMAG^{90}$ Glu^{4} MG^{6}	1.9	0.600	0.19	19500
Starting polymer B	poly-$DMAG^{97}$ Glu^{3}	2.7	0.200	1.76	—
Fraction B_1	poly-$DMAG^{94}$ Glu^{6}	0.8	0.175	2.29	218000
Fraction B_2	poly-$DMAG^{95}$ Glu^{5}	0.5	0.250	2.09	—
Fraction B_3	poly-$DMAG^{94}$ Glu^{6}	1.1	0.375	0.89	—
Fraction B_4	poly-$DMAG^{97}$ Glu^{3}	0.2	0.475	0.80	—

Our further aim was to obtain numerical data about the average molecular weights of the fractions. The weight-average molecular weight of five of them was determined using the light scattering method.

A computer program was constructed to evaluate the results, to draw the ZIMM diagrams and to calculate the $\overline{M}_w$ values. It is apparent from the data of Table I that their tendency is similar to that of the two other characteristics, $\frac{\eta_{sp}}{c}$ and K_{av}, of the macromolecules.

In the second column of Table I the symbols of the fractions indicating their chemical composition are shown. It can be seen from the data that there are no significant differences between the chemical compositions of the macromolecules, *i.e.* the fractionation took place solely according to their average molecular weights.

The biological activity of the fractions was assayed by I. MÉCS (Institute of Microbiology of the Medical School of Szeged). The results are summarized in Table II. Even these preliminary experiments have demonstrated that some of the fractions efficiently potentiate the interferon-inducing effect of poly I · poly C. All of them are more effective than the known DEAE-dextran. From the great differences between the activities of the several fractions it is evident that the macromolecular properties of the polycations profoundly influence their biological activity.

Table II

Minimal protective dose of poly I · poly C

	(μg/mL)
DEAE-dextran	4.50
M_1	1.12
M_2	0.06
M_3	toxic
M_4	0.28
B_1	toxic
B_2	toxic
B_3	1.12
B_4	0.56

Biological activity of the fractions. The minimal protective dose of poly I · poly C was determined in L 929 cells challenged by VSV (vesicular stomatitis virus). The polycations were used in 25 μg/mL concentration.

Experimental

Preparation of the fractions

10 g from the macromolecule "M" and 2.7 g from that of "B" were fractionated. The process was the same in both cases. A 7% aqueous solution was prepared from the polybasic material, and its pH was then adjusted to 6 with $6N$ HCl. The solution was liophylized and the obtained hydrochloride salt was used as the starting material of the fractionation.

A 2% methanolic solution was prepared from the polymer, followed by the dropwise addition of *t*-butanol until turbidity appeared. Some methanol was added to obtain a clear solution, and then dried air was pumped throught it until a milk-like opaque solution resulted. Two mL of this mixture was centrifuged at 6000 r.p.m. for 10—15 min and the optical activities of the supernatant and the methanolic solution of the precipitate were measured. From these measurements the ratio between the materials in the two phases was calculated. The whole solution was then warmed to 40 °C — at this temperature the solution cleared up — and cooled again to room temperature. The, now turbid, solution was centrifuged in a closed tube at 3500 r.p.m. for 1 h at 20 °C. The supernatant was decanted and this served as the starting solution of the preparation of the next fraction. The precipitate in the tube was dissolved in methanol, the solvent was evaporated and the polymer liophylized.

GPC of the fractions

A Sepharose 6B-packed 2.6×60 cm column prepared in $0.06M$ diethanolamine/$0.3M$ NaCl buffer solution (pH 8.9) was used for GPC of the fractions. A 0.2% solution of 2—3 mg polymer was prepared with the above eluent. The flow-rate was 8 mL/h. The absorbance of the post-column flow was measured at 210 nm, in 5-mL fractions.

Light-scattering measurements

Light-scattering measurements were performed in 0.1—1.0% methanolic solutions of the fractions. The solutions were filtered under pressure on an FHLP 047000 teflon filter. Light scattering was measured from 45° to 135° on 5° increments. The dn/dc quotient was determined by a differential refractometer. The measurements were evaluated according to ZIMM [11], by means of a computer programme constructed by Gy. PINTÉR. The linear iteration of the curves of the ZIMM diagram proved to be satisfactory with a significancy level of 0.987. The average standard deviation of the ZIMM plot was less than 1%.

*

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STUDIES RELATED TO THE SYNTHESIS OF MORPHINE, II*

CONVERSION OF O^6-DEMETHYLSALUTARIDINE INTO SALUTARIDINE

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In the biosynthesis and biomimetic total synthesis of morphine, salutaridine is one of the key compounds being convertible into the baine. A very simple, clearly arranged and efficient method has been developed for the preparation of salutaridine (**II**) starting from O^6-demethylsalutaridine (**I**): the reaction path consisting of steps 1 → 2 → 3 → 4 gives **II** from **I** in 65.5% yield.

In the biosynthesis of morphine alkaloids [1] an important intermediate is salutaridine (3,6-dimethoxy-4-hydroxy-7-oxo-17-methyl-5,6,8,14-tetrahydromorphinan; *R*-4-hydroxy-3,6-dimethoxymorphinan-dienone, **II**). It can be converted into the baine chemically, too [2, 3], hence it can be regarded as a key compound in biomimetic morphine syntheses.** Accordingly, several procedures have been developed for its preparation [2, 4, 5, 6, 7, 8, 9]. Some of these syntheses are less important from the preparative point of view, since the yields are low, as the methods were developed for structure confirmation [4], or for verification of the biochemical reaction path starting from reticuline, or for the simulation of this route *in vitro* and chemically [5, 6, 7].

For the preparation of considerable amounts of salutaridine (**II**) those procedures can be considered which start from compounds obtainable from thebaine [2, 8, 9]. The reaction path suggested by Rearick and Gates [9] is outstanding in simplicity:*** O^6-demethylsalutaridine (**I**), obtainable from thebaine directly [10] or in several steps [9, 11, 12], yields **II** in 27% yield when treated with about 8 moles of diazomethane in methanolic solution. The low yield is due to the facts that **I** remains partly unchanged during the reaction and a by-product, O^6-methylsalutaridine (**VIIIb**) is also formed.

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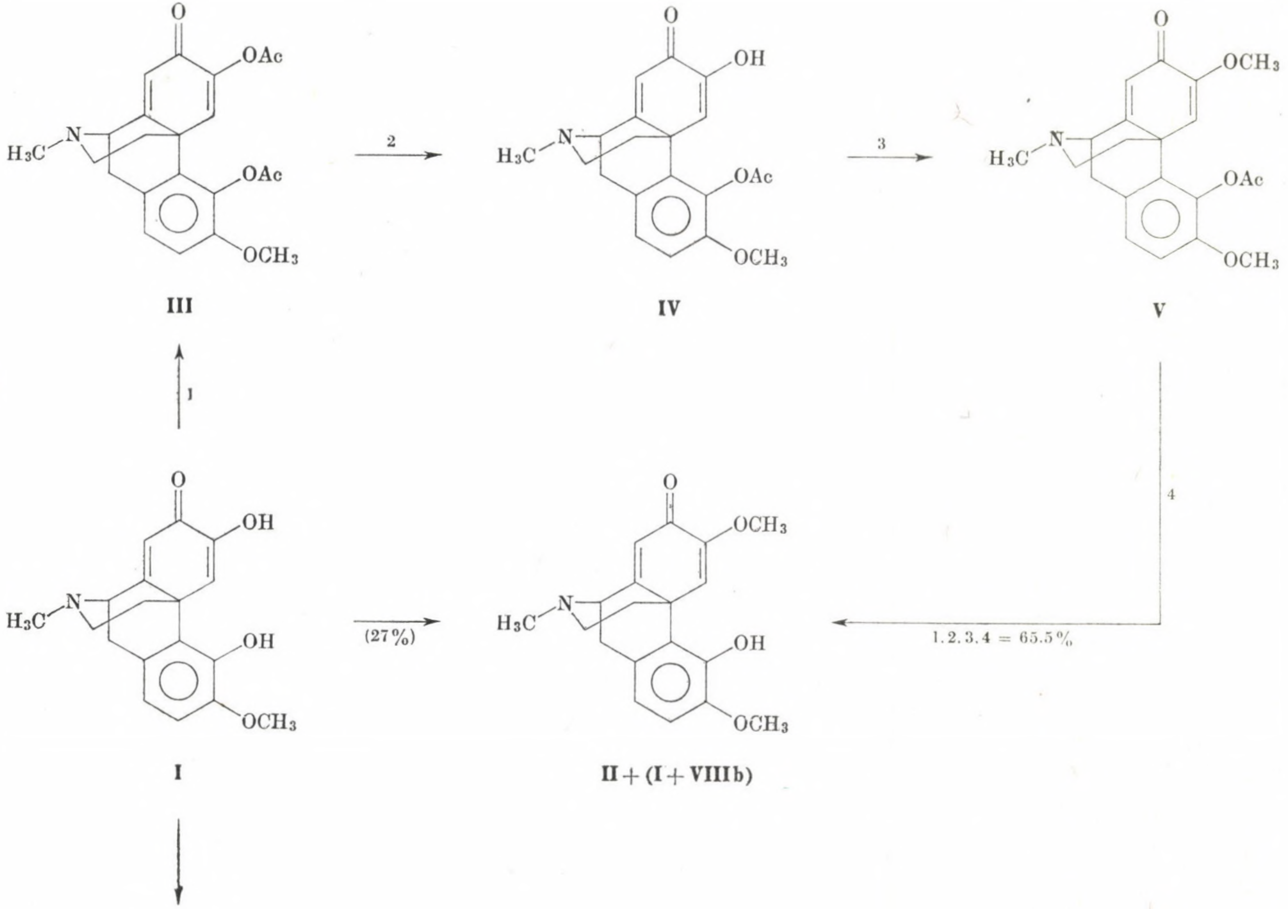
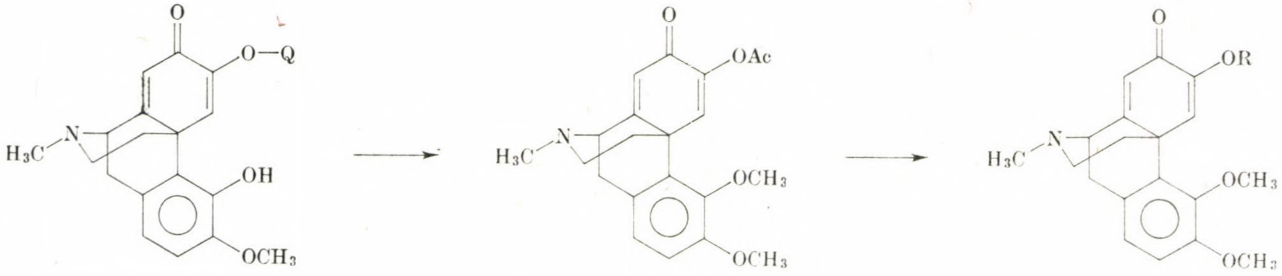
* We consider as Part I.: P. Kerekes, S. Makleit, R. Bognár: Acta Chim. Acad. Sci. Hung., **98**, 491 (1978).

** A process, well realizable also on industrial scale, was developed for the conversion of thebaine into codeine (S. Makleit, *et al.*: Hung. Pat., date of application April, 1978)

*** The authors' thanks are due to Prof. M. Gates for making available the experimental parameters


O
OAc
H₃C
N
OAc
OCH₃
III
2
O
OH
H₃C
N
OAc
OCH₃
IV
3
O
OCH₃
H₃C
N
OAc
OCH₃
V
1
4
O
OH
H₃C
N
OH
OCH₃
I
(27%)
O
OCH₃
H₃C
N
OH
OCH₃
II + (I + VIIIb)
1, 2, 3, 4 = 65.5%



VIa: Q = $COCH_3$
b: = COC_6H_5
c: = $SO_2—C_7H_7$

VII

VIII a: R = H
b: = CH_3

The aim of the present work was the development of a simple and efficient synthesis for salutaridine.

The elimination of the side reaction **I** → **VIIIb** seemed to be simple, by means of reversible blocking of the C-4 phenolic hydroxyl group, *e.g.*, by esterification.

However, according to our experiments, when the WELSH method [13], well applicable in the acetylation of morphine alkaloids carrying a C-3 phenolic hydroxyl group, that is, treatment with acetic anhydride in aqueous $NaHCO_3$ was employed, O^6-demethylsalutaridine(**I**) yielded O-^{4,6}-diacetyl-(**III**) and O^6-acetyl-O^6-demethylsalutaridine(**VIa**).

When **I** was treated with acetyl chloride in the presence of pyridine in dichloromethane, only the O^6-acetyl derivative (**VIa**) was obtained. Under the same reaction conditions, O^6-benzoyl-O^6-demethylsalutaridine (**VIb**) and O^6-tosyl-O^6-demethylsalutaridine (**VIc**) were also prepared.

The desired result was finally achieved, in a roundabout way: $O^{4,6}$-diacetyl-O^6-demethylsalutaridine (**III**) prepared with acetic anhydride in pyridine and isolated as a solvate in 75% yield can be partially deacetylated in 99% yield by treatment with ethanolic diethylamine to give O^4-acetyl-O^6-demethylsalutaridine (**IV**).

Saponification could also be carried out in dry methanol with diethylamine (yield 65.8%) and with sodium methoxide (57.2%).

Compound **IV** obtained in this way was alkylated with 3 moles of diazomethane in chloroform-methanol mixture to obtain O^4-acetylsalutaridine (**V**) [2]. This was then subjected to alkaline hydrolysis to give **II** in 65.5% yield calculated for **I**.

Methylation of **VIa** with diazomethane resulted in O^4-methyl-O^6-acetyl-O^6-demethylsalutaridine (**VII**) which on hydrolysis gave an isomer of **II**, O^4-methyl-O^6-demethylsalutaridine (**VIIIa**), a compound not reported in the literature heterofore.

Experimental

M.p.'s were determined on a Koffler hot stage and are uncorrected. Specific rotation values were measured with a Bendix NPL 143 D automatic polarimeter in chloroform (C) or ethanol (A) solutions ($c = 0.5$; $l = 0.2004$ dm). ^1H-NMR spectra were recorded with a JEOL Minimar 100 MHz instrument in $CDCl_3$ (TMS internal standard). The purity of the substances was checked by TLC on Merck Kieselgel 60 F_{254} layer (DC-Alufolien) using chloroform: acetone : diethylamine (5 : 4 : 1) developing mixture; the detecting agent was Dragendorff reagent.

O^6-Demethylsalutaridine (I)

This was prepared from thebaine, by the method described by BJELDANES and RAPOPORT [10], in 64% yield. M.p. 184—186 °C, $[\alpha]_D + 125°$ (C) (*lit.* [10] m.p. 184—186 °C; $[\alpha]_D + 130°$ ($c = 1.06$; C)).

NMR: δ 7.52 (1H, s, H_5); 6.14 (1H, s, H_8); 3.74 (3H, s, O^3-CH_3); 2.36 (3H, s, $N-CH_3$).

$O^{4,6}$-Diacetyl-O^6-demethylsalutaridine (III)

Compound **I** (6.267 g; 20 mmoles) was dissolved in a mixture of anhydrous pyridine (60 mL) and acetic anhydride (15 mL). The solution was allowed to stand at room temperature for 20 h then it was evaporated to dryness in vacuum. The syrupy residue was dissolved in ice-water (100 mL) and 10% $NaHCO_3$ solution was added to it until fizzing ended. After extraction with ethyl acetate (4×50 mL), the extract was washed with saturated NaCl solution, dried ($MgSO_4$) and evaporated to dryness. The residue was clarified in hot carbon tetrachloride filtered and crystallized to obtain 8.25 g; (74.83%) of **III**, m.p. 82–84 °C, $[\alpha]_D^{26}$ +118.8° (C).

$C_{22}H_{23}NO_6 \cdot CCl_4$ (551.234). Calcd. C 50.11; H 4.20; N 2.54; Ac 15.62. Found C 50.23; H 4.26; N 2.26; Ac 15.41%.

NMR: δ 7.56 (1H, s, H_5); 6.30 (1H, s, H_8); 3.76 (3H, s, O^3-CH_3); 2.41 (3H, s, $N-CH_3$); 2.36 (3H, s) and 2.26 (3H, s) (O^4- and $O^6-CO-CH_3$).

O^4-Acetyl-O^6-demethylsalutaridine (IV)

Compound **III**.CCl_4 (8.25 g; 14.97 mmoles) was dissolved in anhydrous ethanol (70 mL). Diethylamine (4 mL) was added to the solution and it was stirred at room temperature for 6 h. The reaction mixture containing crystals was evaporated to about 20 mL in vacuum. Filtration, washing with ether and hexane, and drying gave 5.57 g (99.67%) of the product, m.p. 180–182 °C, $[\alpha]_D^{24}$ +158.8° (C).

$C_{20}H_{21}NO_5 \cdot H_2O$ (373.392). Calcd. C 64.33; H 6.21; N 3.75; Ac 11.53. Found C 64.17; H 6.21; N 3.18; Ac 11.73%.

NMR: δ 7.13 (1H, s, H_5); 6.37 (1H, s, H_8); 3.78 (3H, s, O^3-CH_3); 2.43 (3H, s) and 2.41 (3H, s) ($N-CH_3$ and $O^4-CO-CH_3$).

O^4-Acetylsalutaridine (V)

Compound **IV** (5.57 g; 14.91 mmoles) was dissolved in a 1 : 1 $CHCl_3$: MeOH mixture (100 mL), the solution was cooled to 0 °C, stirred with a magnetic stirrer and about 3 equivalents of ethereal diazomethane solution was added to it in one portion. The solution was stirred at 0–5 °C for 35 min, and after the addition of acetic acid (0.5 mL) it was stirred at room temperature for further 30 min. The reaction mixture was filtered on silicagel (5 g), washed with chloroform (30 mL), and evaporated. The yellow, syrupy, slowly crystallizing residue was rubbed with hot ether (40 mL) and filtered off to obtain 5.02 g (91.1%) of **V**, m.p. 169–170 °C, $[\alpha]_D^{25}$ +150.3° (C); +124° (A). (*Lit.* [2] m.p. 171 °C; $[\alpha]_D$ +120° (c = 1.26, A)).

NMR: δ 6.91 (1H, s, H_5); 6.32 (1H, s, H_8); 3.79 (3H, s) and 3.76 (3H, s) (O^3- and O^6-CH_3); 2.42 (3H, s) and 2.40 (3H, s) ($N-CH_3$ and $O^4-CO-CH_3$).

Salutaridine (II) [2]

O^4-Acetylsalutaridine (V) (5.0 g; 13.5 mmoles) was dissolved in a mixture of ethanol (70 mL), and 10% NaOH (25 mL), and the reaction mixture was allowed to stand overnight at room temperature. After diluting with water (50 mL), the ethanol was evaporated in vacuum, the alkaline solution was extracted with ether (50 mL) and then saturated with CO_2 gas. The crystalline product was washed with water and dried. According to TLC it was chromatographically pure **II** (3.79 g), m.p. 192–194 °C.

The mother liquor was extracted with dichloromethane (3×30 mL) and dried (Na_2SO_4). Evaporation of the solvent and crystallization of the residue from ethyl acetate gave an additional 0.5 g of the product.

Yield: 4.29 g (96.2%), which is 65.5% referred to I. $[\alpha]_D^{25}$ +91.5° (C); +112° (A). (*Lit.* [2] m.p. 196–198 °C, $[\alpha]_D$ +111° (c = 1.69; A); *lit.* [9] m.p. 196–196.5 °C).

NMR: δ 7.27 (1H, s, H_5); 6.11 (1H, s, H_8); 3.80 (3H, s) and 3.66 (3H, s) (O^3- and O^6-CH_3); 2.38 (3H, s, $N-CH_3$).

[illegible]-Acetyl-O^6-demethylsalutaridine (VIa)

O^6-Demethylsalutaridine (I) (6.276 g; 20 mmoles) was dissolved in a mixture of anhydrous dichloromethane (60 mL) and anhydrous pyridine (2.1 mL; about 24 mmoles). The solution was cooled to 0 °C and acetyl chloride (1.85 mL, ~24 mmole) dissolved in CH_2Cl_2 (10 mL) was added to it dropwise, with stirring. The solution was allowed to stand at 0 °C for 1 h and at room temperature overnight, then it was washed with water (50 mL) containing $NaHCO_3$ (3.8 g) in a shaking funnel. After drying ($MgSO_4$), the solution was evaporated to dryness. The residue was crystallized from a mixture of dichloromethane and hexane to obtain 5.72 g (80.45%) of **VIa**, m.p.: prolonged melting from 172 °C; $[\alpha]^{26}_D$ $+112°$ (C).

$C_{20}H_{21}NO_5$ (355.376). Calcd. C 67.59; H 5.96; N 3.94; Ac 12.11. Found C 67.54; H 6.12; N 3.74; Ac 12.08%.

NMR: δ 8.24 (1H, s, H_5); 6.31 (1H, s, H_8); 3.78 (3H, s, O^3-OCH_3); 2.41 (3H, s, $N-CH_3$); 2.29 (3H, s, $O^6-CO-CH_3$).

Under the same reaction conditions, but when using benzoyl chloride as the acylating agent, **I** was converted into O^6-benzoyl-O^6-demethylsalutaridine (**VIb**) in 64.1% yield, m.p. 194—195 °C (from EtOAc hexane); $[\alpha]^{25}_D$ $+95°$ (C).

NMR δ 7.97 (1H, s, H_5).

O^6-Tosyl-O^6-demethylsalutaridine (**VIc**) was obtained similarly in 77.07% yield when the acylating agent was *p*-toluenesulfonyl chloride; m.p. 154—156 °C (EtOAc).

NMR: δ 7.98 (1H, s, H_5).

O^4-Methyl-O^6-acetyl-O^6-demethylsalutaridine (VII)

Compound **VIa** (1.066 g; 3 mmoles) was dissolved in methanol (75 mL), cooled to 0 °C, stirred with a magnetic stirrer, and about 5 equivalents of ethereal diazomethane solution was added to it. After 50 min acetic acid (0.1 mL) was added by drops and the mixture was then allowed to stand at room temperature for 30 min and evaporated to dryness in vacuum. The brown residue was dissolved in benzene (100 mL), washed with 10% $NaHCO_3$ solution and with water, dried over Na_2SO_4, evaporated to dryness, dissolved in hot ethyl acetate (40 mL) and clarified with carbon. Evaporation of the solvent gave non-crystallizing, chromatographically pure **VII** (0.913 g; 82.38%).

NMR: δ 7.87 (1H, s, H_5); 6.83 (2H, s, $H_{1,2}$); 6.31 (1H, s, H_8); 3.83 (3H, s) and 3.81 (3H, s) (O^3- and O^4-CH_3); 2.41 (3H, s, $N-CH_3$); 2.26 (3H, s, $O^6-CO-CH_3$).

O^4-Methyl-O^6-demethylsalutaridine (VIIIa)

A solution of the above product (**VII**) (2.47 mmoles) in ethanol (25 mL) was allowed to stand with 10% NaOH solution (5 mL) at room temperature overnight. After evaporation in vacuum, the residue was diluted with water (50 mL) and extracted with ether (30 mL). The aqueous solution was saturated with CO_2, extracted with chloroform (3×30 mL), filtered on Al_2O_3, dried ($MgSO_4$), then evaporated to dryness and crystallized from ethyl acetate to obtain 0.32 g (40%) of **VIIIa**, m.p. 198—201 °C, $[\alpha]^{25}_D$ $+108°$ (C). Mixed m.p. with **II**: 193 °C.

$C_{19}H_{21}NO_4$ (327.366). Calcd. C 69.7; H 6.5; N 4.3. Found C 69.65; H 6.45; N 4.08%.

NMR: δ 7.45 (1H, s, H_5); 6.83 (2H, s, $H_{1,2}$); 6.38 (1H, s, H_8); 3.88 (3H, s) and 3.84 (3H, s) (O^3- and O^4-CH_3); 2.43 (3H, s, $N-CH_3$).

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THERMOCHEMICAL ASPECTS OF ANION EXCHANGE REACTIONS, II

EXCHANGE REACTIONS INVOLVING POLYVALENT ORTHOPHOSPHATES

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HPO_4^{2-}/Cl^- and PO_4^{3-}/Cl^- exchange reactions were studied on Dowex 1×8 anion exchange resin at 25 °C at various total normalities. The thermodynamic equilibrium constants, calculated by the SALMON equation [3], decrease with increasing ionic charge indicating that in this case the Bjerrum-type electrostatic ion pairing with the resin cation cannot be a significant interaction from the selectivity point of view.

The standard enthalpies of ion exchange were obtained through calorimetric measurements and combined with the standard free energies to yield the standard entropies of exchange. These entropy values also show that electrostatic effects are less important than hydration processes.

Introduction

We have previously studied the $H_2PO_4^-/Cl^-$ and OH^-/Cl^- exchange reactions and have obtained the thermodynamic parameters, ΔG°, ΔH° and ΔS° for the two exchange processes [1]. We found that the Cl^--form Dowex 1×8 resin showed little affinity for either OH^- or $H_2PO_4^-$, and that in each case the unfavourable standard free energy change resulted from a very unfavourable enthalpy term; the entropy terms, although not very large, were favourable. Since the ionic charge of the phosphate anion can conveniently be changed by deprotonation, it is possible to study the effect of anionic charge on the thermodynamic parameters for ion exchange along the series $H_2PO_4^-/Cl^-$, HPO_4^{2-}/Cl^- and PO_4^{3-}/Cl^-, and in the present paper we report results of our equilibrium and calorimetric measurements that yield these thermodynamic parameters.

Experimental

The method of resin preparation and the details of the experimental procedure were basically the same as described previously [1]. Here only some additional details relevant to the present work are given. The HPO_4^{2-} form resin was prepared by washing the Cl^--form

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resin with 1 mol dm^{-3} Na_2HPO_4 solution until the acidified effluent was chloride free. The resin was then washed with slightly alkaline carbon dioxide free water.

The volume capacities of the swollen Cl^--form resins in 0.1, 0.01 and 0.005 mol dm^{-3} NaCl solutions were determined by the method described in ref [2], and the following values were obtained 2.19; 2.32 and 2.43 mequiv cm^{-3}, respectively. The mass capacity of the conditioned HPO_4^{2-}-form resin (water content 25 per cent) was 2.47 mequiv g^{-1} calculated either by the quantity of the desorbed HPO_4^{2-} or the quantity of the adsorbed Cl^- ions.

The 0.1 N stock solutions were prepared from reagent grade NaCl, $Na_2HPO_4 \cdot 12\,H_2O$ and $Na_3PO_4 \cdot 12\,H_2O$.

Results and Discussion

For the general ion exchange reaction (1),

$$n\mathrm{RCl}^- + \mathrm{Y}^{n-} \rightleftharpoons \mathrm{R}_n\mathrm{Y}^{n-} + n\mathrm{Cl}^- \tag{1}$$

where $Y^{n-} = H_2PO_4^-$, HPO_4^{2-} or PO_4^{3-}, the corrected rational selectivity coefficient is defined by eq. (2):

$$K'(\mathrm{Y}^{n-}/\mathrm{Cl}^-) = \frac{\bar{x}(\mathrm{Y}^{n-}) \cdot x(\mathrm{Cl}^-)^n}{\bar{x}(\mathrm{Cl}^-)^n \cdot x(\mathrm{Y}^{n-})} \cdot \frac{f(\mathrm{Cl}^-)^n}{f(\mathrm{Y}^{n-})} \tag{2}$$

where x and $\bar{x}$ are the equivalent fractions in solution and in the resin phase, respectively, and f is the activity coefficient in the solution phase. The ratio $f(\mathrm{Cl}^-)^n/f(\mathrm{Y}^{n-})$ was estimated through the DAVIES equation [2].

The thermodynamic equilibrium constant for the general exchange reaction of type (1) can be obtained [3] through eq. (3):

$$\ln K'(\mathrm{Y}^{n-}/\mathrm{Cl}^-) = \ln K^T(\mathrm{Y}^{n-}/\mathrm{Cl}^-) + \ln \left(\frac{\bar{C}}{TN}\right)^{n-1} - \frac{2}{n}\frac{\omega}{RT} \cdot \bar{x}(\mathrm{Y}^{n-}) \tag{3}$$

Here $K'(\mathrm{Y}^{n-}/\mathrm{Cl}^-)$ and $K^T(\mathrm{Y}^{n-}/\mathrm{Cl}^-)$ are the corrected selectivity coefficient and the thermodynamic equilibrium constant, respectively, $\bar{C}$ is the volume capacity of the swollen resin (mequiv cm^{-3}), TN is the total normality of the solution (mequiv cm^{-3}), $RT = 2479.2$ J equiv^{-1} at 298.2 K, n is the charge of the Y^{n-} ion, $\bar{x}(\mathrm{X}^{n-})$ is the equivalent fraction in the resin phase, and ω is the energy of interaction between two entering Y^{n-} ions in the resin phase (kJ equiv^{-1}). Eq. (3) is quite analogous to the SALAMON equation for uni-univalent exchange [1], and similarly predicts that a plot of $\ln K'(\mathrm{Y}^{n-}/\mathrm{Cl}^-)$ against $\bar{x}(\mathrm{Y}^{n-})$ should be a straight line.

In Fig. 1 are shown the ion exchange isotherms for the HPO_4^{2-}/Cl^- and PO_4^{3-}/Cl^- processes, and in Figs 2 and 3 are given the plots of $\ln K'(\mathrm{Y}^{n-}/\mathrm{Cl}^-)$ against $\bar{x}(\mathrm{Y}^{n-})$. As required by eq. (3), straight lines are obtained. From the intercept and slope of these plots, $K^T(\mathrm{Y}^{n-}/\mathrm{Cl}^-)$ and ω were calculated through the following equations:

$$\ln K^T(Y^{n-}/Cl^-) = \text{intercept} - \ln \left(\frac{\bar{C}}{TN}\right)^{n-1} \tag{4}$$

$$\omega = -\,\text{slope} \cdot \frac{nRT}{2}\,. \tag{5}$$

The standard free energy change was the calculated through eq. (6):

$$\Delta G^\circ = -\frac{1}{n} RT \ln K^T(Y^{n-}/Cl^-) \tag{6}$$

the obtained $K^T(Y^{n-}/Cl^-)$, ΔG° and ω values are summarized in Table I.

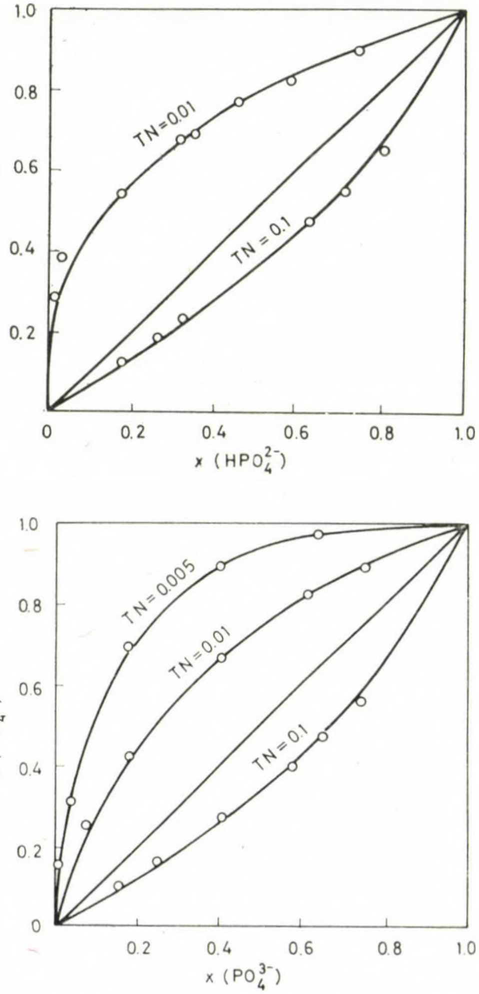

Fig. 1. Ion-exchange isotherms on Dowex 1×8 at 25 °C at various total normalities and pH values; a) $8.70 < pH < 9.00$, b) $11.00 < pH < 11.80$

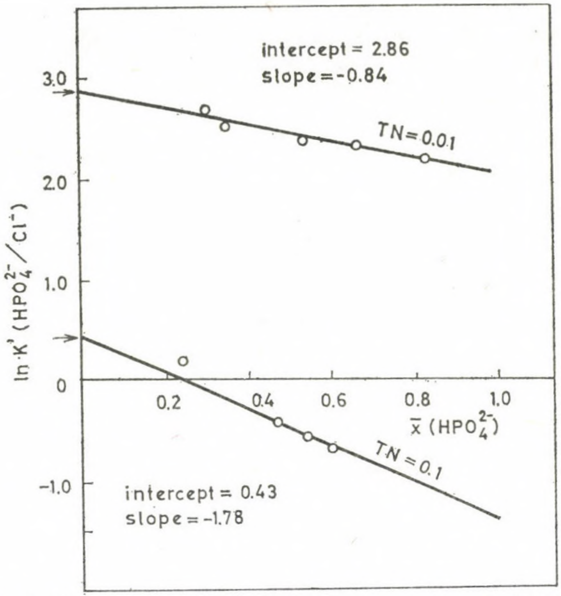

Fig. 2. Plot of ln $K'(HPO_4^{2-}/Cl^-)$ as a function of $\bar{x}(HPO_4^{2-})$

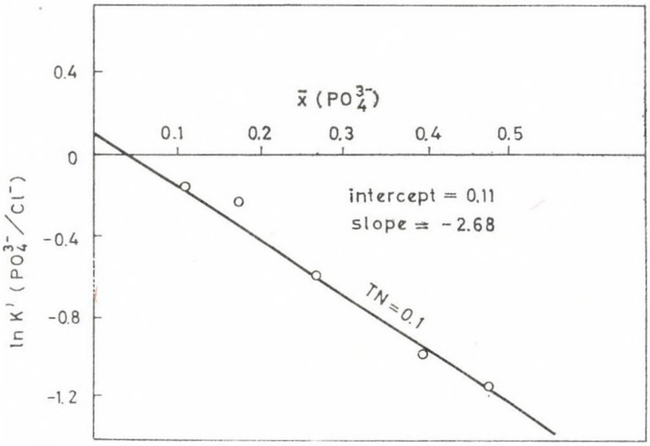

Fig. 3. Plot of ln $K'(PO_4^{3-}/Cl^-)$ as a function of $\bar{x}(PO_4^{3-})$

Table I

Thermodynamic data at 25 °C *for the phosphate/chloride exchange reactions on Dovex 1×8*

Ion exchanged against chloride, Y^{n-}	$K^T(Y^{n-}/Cl^-)$	ΔG°	ΔH°	ω	ΔS° J K^{-1} equiv^{-1}
		kJ equiv^{-1}			
$H_2PO_4^-$	$1.6 \cdot 10^{-1}$*	4.5	7.0	−1.36	8
HPO_4^{2-}	$7.0 \cdot 10^{-2}$	3.3	9.7	+4.41	21
PO_4^{3-}	$2.3 \cdot 10^{-3}$**	4.8	7.5	+9.96	9

* Taken from Reference [1]
** See also remarks in the text

The enthalpy change of the ion exchange reaction, ΔH_e, can be calculated from eq. (7), where Q_t is the measured total heat of exchange, C is the mass capacity of the resin, w the mass of the resin and $\overline{x}(X^{n-})$ is the mole fraction of ion Y^{n-} in the resin phase.

$$Q_t = \Delta H_e C w \overline{x}(X^{n-}) + \Delta H_i C w . \tag{7}$$

The heat of immersion, ΔH_i, of the HPO_4^{2-}-form resin in water and in 0.1 N Na_2HPO_4 solution was found to be -3.8 and -3.1 kJ equiv^{-1}, respectively.

Plots of ΔH_e against $\overline{x}(Y^{n-})$ are shown in Figs 4 and 5; the enthalpy change corresponding to the complete $\overline{x}(Y^{n-}) = 1$ conversion of the resin was obtained by extrapolation. The calculated standard enthalpy and entropy changes are given in Table I.

From the equilibrium constants in Table I, it can be seen that the resin shows an extremely low affinity for the bi- and tervalent orthophosphate ions as compared with the monovalent ion. Indeed, the affinity actually decreases with increasing ion charge. When the data are compared it must be born in mind that in the case of the PO_4^{3-}/Cl^- exchange the concentration of the OH^- ions in the solution is between 10^{-2} and 10^{-3} mol dm^{-3}. In addition,

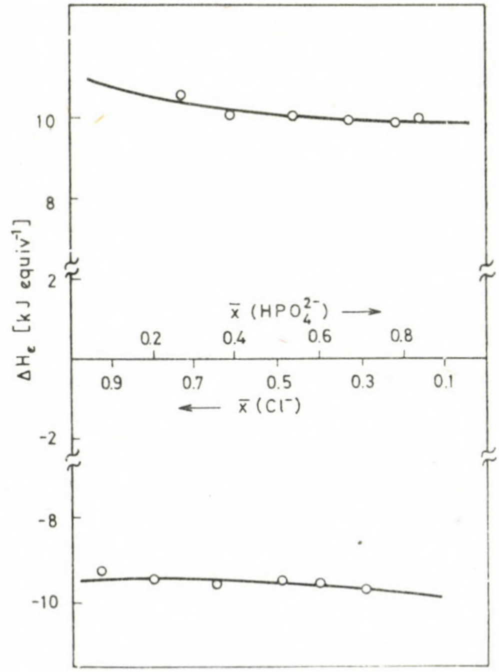

Fig. 4. Variation of ΔH_e as a function of the resin composition for the HPO_4^{2-}/Cl^- and Cl^-/HPO_4^{2-} exchange

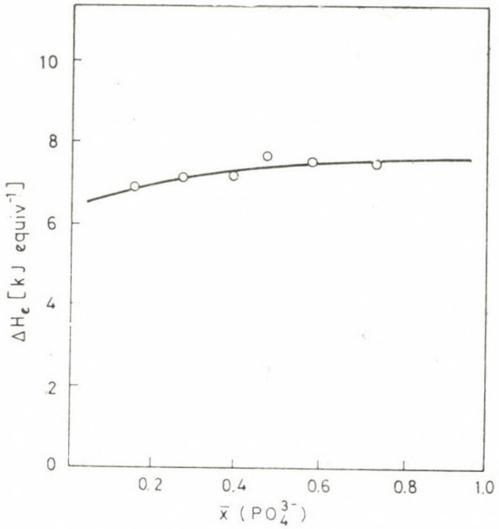

Fig. 5. Variation of ΔH_e as a function of the resin composition for the PO_4^{3-}/Cl^- exchange in the pH range from 11.00 to 11.80

the low value of $K^T(PO_4^{3-}/Cl^-)$ compared with the value [1] of $K^T(OH^-/Cl^-)$ indicates that the OH^-/Cl^- exchange could take place simultaneously with the main PO_4^{3-}/Cl^- reaction. Since no correction has been made for the OH^-/Cl^- side reaction the data for the PO_4^{3-}/Cl^- system must be regarded as less reliable than for the other systems. Any contribution by the OH^-/Cl^- exchange would result in the actual value for $K^T(PO_4^{3-}/Cl^-)$ being somewhat less than the quoted value in Table I.

Several models of the ion-exchange selectivity emphasize the importance of the Coulomb forces that govern the ion pairing between the resin-fixed ion and the counter-ion. This Bjerrum-type interaction is the explanation of the general rule often quoted for cation exchangers [4—6] that the selectivity increases with increasing ion charge. It is known, however, that the above electrostatic model is inadequate for the interpretation of anion exchange selectivity, and recent works [7—8] have emphasized, instead, the strength of the anion-water interactions in the bulk solvent.

The higher charged ion is more hydrated and since the dilute external aqueous phase offers more possibility for hydration than the concentrated resin phase, consequently the higher charged ion will prefer the aqueous phase. The degree of protonation of the anion or the strength of the base is an indication of the strength of the ion-water interaction. The more strongly an anion takes up a proton, $PO_4^{3-} > HPO_4^{2-} > H_2PO_4^-$, the more strongly the anion bonds to the water molecule and the more strongly it prefers the aqueous phase, $K^T(PO_4^{3-}/Cl^-) < K^T(HPO_4^{2-}/Cl^-) < K^T(H_2PO_4^-/Cl^-)$, which is indeed the observed selectivity order.

The thermodynamic data in Table I show that the unfavourable standard free energy changes are all due to very unfavourable enthalpies of exchange; the corresponding entropy values are positive *i.e.* favour the exchange. From the standard entropies of ions in aqueous solution [9], it is evident that the entropy of hydration of the gaseous anions must be increasingly negative along the series $H_2PO_4^-$, HPO_4^{2-} and PO_4^{3-}. Thus if dehydration of the anion on transfer from the aqueous phase to the resin phase was the only factor involved, the corresponding entropies of exchange should be progressively more positive as the charge on the anion increases. That the entropy value for the phosphate anion is less positive than expected may be due to factors other than anion dehydration. It should be noted, however, that results for the phosphate anion may notably be affected by interference from OH^-, as mentioned above, and also by the so-called site sharing phenomenon [10].

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THE PROBABILITY DISTRIBUTION OF NATURAL PARAMETERS DESCRIBING MUTUAL ORIENTATION FOR INDEPENDENT MOLECULES

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For the description of the mutual orientation of molecules in the case of three orientation degrees of freedom, the angles between the corresponding principal polarizability axes have been suggested. It has been shown that for independent molecules the joint probability density of these angles is symmetrical, unlike the joint probability density of Euler angles, which can also be used to characterize mutual orientation. It has been shown on this basis that these angles can be regarded as the natural parameters for the description of mutual orientation and as a convenient tool in the investigations concerned with the mutual orientation of molecules.

In addition to the polarizability of a molecule, the anisotropic component of molecular light scattering depends on the time average of the mutual relative orientation of the principal polarizabilities of molecule pairs. In order to calculate the intensity contributions of these molecule pairs, the probability distribution of the angles between the principal polarizabilities must be known. This also allows the parameters characteristic of mutual orientation to be calculated from experimental data.

We pointed out [1] that in the analysis of light scattering results it is not absolutely necessary to assume molecular associates of definite shape when the intensity of scattered light cannot be described sufficiently by a model in which molecules are oriented independently in space. It may well occur that the only effect is a certain preference in the mutual orientations of the actual neighbour molecules, without these neighbours being associated more strongly with one another than with other molecules, and, of course, without staying together as an associate.

Such cases can be treated practically by regarding the parameters which describe mutual orientation as random variables, and by determining their density functions. This function will reflect the interactions which influence mutual orientation.

This paper deals with the probability treatment of the mutual orientation of molecules in liquids. In this treatment, in order to describe the interactions between the molecules orienting one another, a new set of parameters will be introduced which, unlike the usually applied Euler angles, is more convenient to use in the given physical problem.

It will be shown that in terms of these parameters, for independent spatial orientation, the probability density function characteristic of mutual orientation is symmetrical.

Description of mutual orientation by Euler angles

The mutual orientation of two molecules can be described by three data, and the various orientations can be represented by points in a three-dimensional parameter space.

A well known and convenient method for describing mutual orientation is to give the Euler angles (see Fig. 1, which shows the coordinate systems spanned by the principal polarizabilities of two molecules).

Let us assume that initially the two coordinate systems coincide, and move the molecule with the primed axes. In the first step it is rotated around axis z by angle α. Thereafter it is rotated by angle β about the OP line, *i.e.* around the actual position of axis x'. Finally it is rotated by angle γ around axis z' which is already in its final position. If α, β and γ are given in a Cartesian coordinate system, the rotation is unambiguous in the rectangular domain $D = [0, 2\pi] \times [0, \pi] \times [0, 2\pi]$.

Assume now that the two molecules are neighbours, and they are incidentally in a position shown in the figure. The interaction between them tends to change this orientation. Since mutual orientation is determined by three data, the actual values of all three parameters may change. Let us denote the effects tending to change these parameters by F_α, F_β and F_γ. These forces,

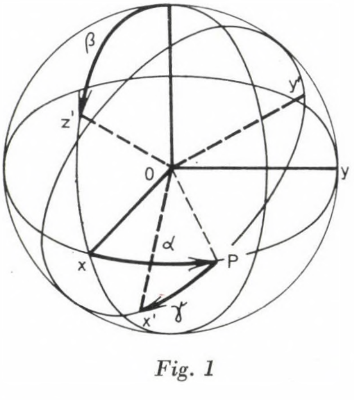

Fig. 1

as components form an orienting force field, $\mathbf{F}(\mathbf{r}^{\mathrm{E}})$, where $\mathbf{r}^{\mathrm{E}}$ is the position vector defined in the α, β, γ space of the Euler angles. By means of the identity $\mathbf{F}(\mathbf{r}^{\mathrm{E}}) = -\operatorname{grad} U(\mathbf{r}^{\mathrm{E}})$ an orienting potential field may also be defined.

If the forces tending to change angles α, β and γ *i.e.* the components of $-\operatorname{grad} U(\mathbf{r}^{\mathrm{E}})$ were known, one could give the orientation effect resulting from the interaction between the two molecules in the given position. Conversely, by taking into account the orientation effect of the other molecules too, from any experiment measuring the time average of mutual orientation (*e.g.* light scattering) one could obtain a parameter of the orientation potential acting between the molecules.

Neglecting specific parameters, what might be the shape of the potential of the forces which tend to change the mutual orientation of molecules? How can this force be decomposed into components?

Without being able to answer these questions, one fact seems to be evident: the α, β, γ space of Euler angles is inappropriate for the analysis of the mutual orientation effect of molecules. It is stressed that the above statement refers not to the way of describing mutual orientation, for which Euler angles are excellent, but to the description of the mutual orientation effect in a natural way. This will be discussed in detail, but first we return to the above questions. It may be added that even if it is possible to describe the mutual orientation effect of two molecules in a general form, instead of using the Euler angles, this can be done more conveniently in terms of another set of parameters which is closer to the physical essence of the problem.

Let us regard now the case of mutual orientation effect. The problem is whether the mutual orientation changes as a consequence of the interaction between two molecules, and if so in which way. In other terms the kind of interaction that may cause a given change in orientation must be understood.

Assume that a mutual orientation characterized by points $\mathbf{r}^{\mathrm{E}} \in D$ changes in a way that none of its parameters remain the same. It can be stated that the displacement of point $\mathbf{r}^{\mathrm{E}}$ is now not parallel with any of the coordinate axes. The displacement can be regarded as caused by a force acting in the appropriate direction, general in the α, β, γ space. The displacement as well as the force can be decomposed into components parallel with the axes. These force components, when investigated in different $\mathbf{r}^{\mathrm{E}}$ points, constitute the force field $\mathbf{F}(\mathbf{r}^{\mathrm{E}})$.

To what effect the changes in parameters can be attributed? Let us regard in this respect again the rotation in terms of Euler angles, and study the physical contents and reasons of the individual steps. It is evident at first that the role of the axes during rotation is not symmetrical. However, it is hardly probable that the real cause of rotation is also asymmetric, thereby matching the asymmetric description of rotation. The first and third steps are both rotations around the z' axis, the second is a rotation around x'. In this respect the role of axis labelled arbitrarily as y' appears to be irrelevant. In another notation this axis may receive the major role. The displacement described in terms of Euler angles contains, therefore, arbitrariness, which seems to be desirable to eliminate.

The natural parameters of mutual orientation

In order to solve the above problem, it appears convenient to define mutual orientation *e.g.* by the angles between the corresponding positive half-axes of the two molecules. In Fig. 2 the angle between x and x' is denoted by X, and Y and Z have similar meaning. The symmetric role of these angles as the parameters of mutual orientation follows from their definition. It can be expected therefore that these parameters allow the problem of mutual orientation effect to be treated symmetrically with regard to the three degrees of freedom.

Let us assume that the mutual effect of the two molecules manifests itself, in part, in a tendency of one of the molecules to move a given axis of the other (say x') away from its own (x) axis by a certain angle. This interaction, after the two molecules become neighbours, obviously causes a change in the value of X. With regard to this interaction the individual generatrices of the cone corresponding to the given X angle are indistinguishable. If the orientation effect is not exhausted in the above, and the y and y' axes also have an energetically more favourable position, the Y parameter of mutual orientation may also change after the encounter of the two molecules. Finally, it can also be conceived that the value of Z also changes in a direction approaching the position corresponding to a potential minimum.

Take now a Cartesian system with axes X, Y and Z. The mutual orientation is defined over a domain D of this system, symmetric in the variables.

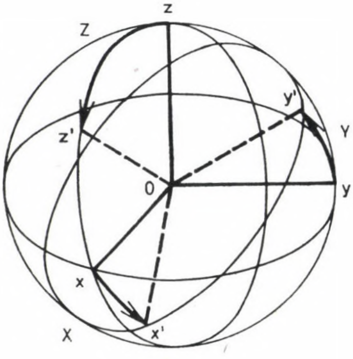

Fig. 2

Let us denote the individual points of this domain by $\mathbf{r} = (X, Y, Z)$. Owing to the interaction, the two molecules will depart from the given $\mathbf{r} \in D$ point. Let us characterize by F_x, F_y and F_z the force which tends to change the parameters X, Y and Z, actually giving the mutual orientation of the two molecules. Relation $\mathbf{F}(\mathbf{r}) = -\mathrm{grad}\, U(r)$ defines an orienting potential field $U(\mathbf{r})$ in the X, Y, Z space. One may well expect that the individual variables in the orientating potential field $(U(X, Y, Z)$ have such a role that the functions expressing the interactions between the various pairs of axes will have the same form in the actual variables (X, U or Z), apart from specific parameters (geometric, polarizability, *etc.)*. This is the feature we wanted to have, and will utilize in the further discussion of mutual orientation.

First we will take the case when the two molecules are oriented independently of one another with respect to an external coordinate system. In this case the neighbours have no orientation effect on one another. Interactions will be regarded as a perturbation on the probability disribution corresponding to the above case, *i.e.* the results obtained here will be used as a starting point in the discussion of various mutual orientation effects.

The rest of the paper deals with the mathematical description of the mutual orientation of independent molecules in terms of coordinates X, Y and Z.

The probability density of the natural parameters of mutual orientation

Take a rectangular spherical triangle x, y, z on a sphere of unit radius. Rotate this sphere around its centre randomly so as to produce an even distribution for the rotations in the following sense: if $x'y'z'$ denotes the rotated spherical triangle, ϑ is the zz' arc, φ is the $z'zy$ angle and ζ is the $zz'y$ angle, then

$$\frac{\partial^3}{\partial x_1 \partial x_2 \partial x_3} P(\vartheta < x_1, \varphi < x_2, \zeta < x_3) = \frac{\sin x_1}{8\pi^2}, \tag{1}$$

$$0 < x_1 < \pi; \quad 0 < x_2 < 2\pi; \quad 0 < x_3 < 2\pi.$$

(It can be seen from the density function that ϑ, φ and ζ are independent random variables.)

Let us denote the xx' arc by a, the yy' arc by b and the zz' arc by $c = \vartheta$, and regard them as random variables. The aim is to determine the joint probability density of random variables a, b and c. For this purpose some simple auxiliary theorems will be proved.

Auxiliary theorem 1

$$\cos a = -\cos\varphi\cos\zeta + \sin\varphi\sin\zeta\cos\vartheta \tag{2.1}$$

$$\cos b = \sin\varphi\sin\zeta - \cos\varphi\cos\zeta\cos\vartheta\,. \tag{2.2}$$

Proof: From the cosine theorem pertaining to the sides of spherical triangles and the sine theorem of spherical triangles one obtains, with the notation of Fig. 3:

$$\sin(y'z) = \frac{\sin\zeta}{\sin(\delta+\varphi)} \tag{3}$$

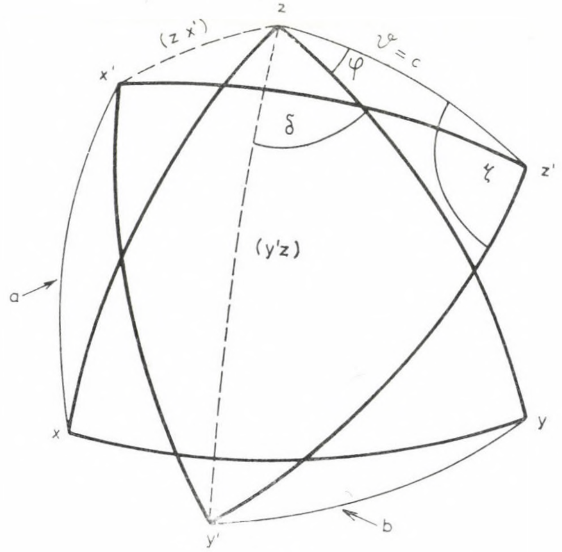

Fig. 3

$$0 = \cos(z'y') = \cos c\cdot\cos(y'z) + \sin c\sin(y'z)\cdot\cos(\delta+\varphi)\,, \tag{4}$$

$$\cos(y'z) = \sin c\cdot\cos\zeta \tag{5}$$

since

$$\cos b = \sin(y'z)\cos\delta = \sin(y'z)\cos([\delta+\varphi]-\varphi)\,, \tag{6}$$

by expanding $\cos([\delta+\varphi]-\varphi)$ and substituting (3), (4) and (5) into the resulting identity (2.1) can be obtained.

Equation (2.2) can be proved in a similar manner, only the role of $y'z$ is played by $x'z$.

Auxiliary theorem 2

The joint probability density of random variables

$$\begin{aligned} r &= \cos \vartheta \\ g &= \cos (\varphi + \zeta) \qquad (7) \\ h &= \cos (\varphi - \zeta) \end{aligned}$$

constructed from the random variables, ϑ, φ, ζ characterized by joint probability density (1) is

$$f(x_1, x_2, x_3) = \frac{\partial^3}{\partial x_1 \partial x_2 \partial x_3} P(g < x_1, h < x_2, r < x_3) =$$

$$= \frac{1}{2\pi^2([1 - x_1^2]\,[1 - x_2^2])^{1/2}}, \quad \text{if} \quad 0 < |x_1|, |x_2|, |x_3| < 1. \qquad (8)$$

Proof: Due to (1) r is independent of g and h, thus its probability density can be calculated separately and multiplied by the joint probability density of g and h to obtain the joint probability density of the three variables.

Therefore, from (1)

$$\frac{\partial}{\partial x_3} P(r < x_3) = \frac{\partial}{\partial x_3} P(\cos \vartheta < x_3) = \frac{\partial}{\partial x_3} P(\vartheta > \text{arc cos}\, x_3) =$$

$$= \frac{\partial}{\partial x_3} [1 - P(\vartheta < \text{arc cos}\, x_3)] = \frac{\partial}{\partial x_3} \left[1 - \frac{1 - x_3}{2}\right] = \qquad (9)$$

$$= \frac{\partial}{\partial x_3} \left[\frac{1 + x_3}{2}\right] = \frac{1}{2}.$$

In order to calculate the joint probability density of g and h, let us regard Fig. 4. *Inside* the tilted square with a diagonal of 4π the joint probability density of $\varphi + \zeta$ and $\varphi - \zeta$ is $\frac{1}{8\pi^2}$, whereas *outside* this square it is 0.

The value of $P(\cos [\varphi + \xi] < x_1, \cos [\varphi - \xi] < \beta_2)$ is given by the integral of the shaded areas according to the above density function, *i.e.*

$$P(\cos [\varphi + \zeta] < x_1, \cos [\varphi - \zeta] < x_2) =$$

$$= P(\varphi + \zeta \in [\text{arc cos}\, x_1, 2\pi - \text{arc cos}\, x]\ U$$

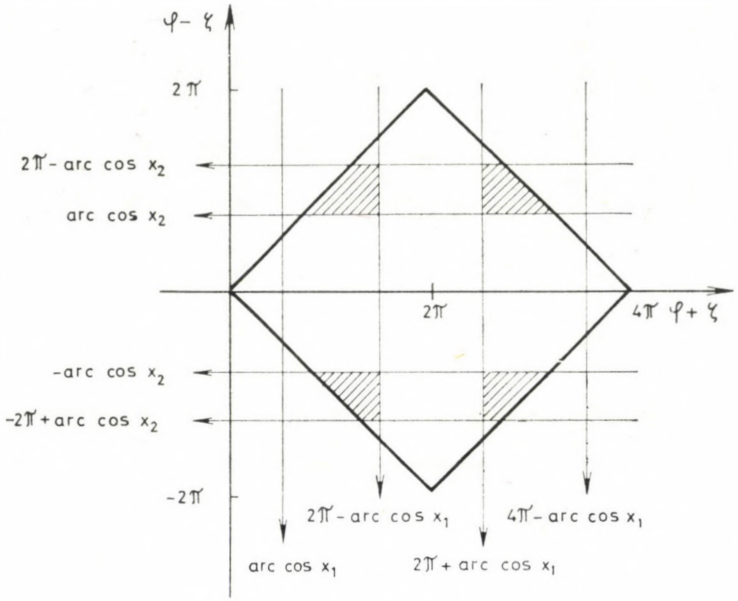

Fig. 4

$$U\,[2\pi + \text{arc cos } x_1, 4\pi - \text{arc cos } x_1];\ \varphi - \zeta \in$$

$$\in [+ \text{arc cos } x_2 - 2\pi - \text{arc cos } x_2]\ U$$

$$U\,[\text{arc cos } x_2, 2\pi - \text{arc cos } x_2]) =$$

$$= \frac{1}{4\pi^2}(2\pi - 2 \text{ arc cos } x_1) \cdot (2\pi - 2 \text{ arc cos } x_2),$$

utilizing the area halving property of straight lines passing the centres of rectangles. From this expression (8) can be derived by differentiation and the use of (9).

Auxiliary theorem 3

Let $p = \cos a$, $q = \cos b$, $r = \cos c$. Then

$$\frac{\partial_3}{\partial y_1 \partial y_2 \partial y_3} P(p < y_1, q < y_2, r < y_3) = \tag{10}$$

$$= \frac{1}{\pi^2[(1 + y_1 - y_2 - y_3)(1 - y_1 + y_2 - y_3)(1 - y_1 - y_2 + y_3)(1 + y_1 + y_2 + y_3)]^{1/2}},$$

where the expression under the square root is positive, and

$$0 \leqq |y_1|, |y_2|, |y_3| \leqq 1,$$

otherwise zero.

Proof: Following from (2.1) and (2.2),

$$g = -\frac{p+q}{1+r}$$
$$h = \frac{p-q}{r-1}\,. \tag{11}$$

The following theorem pertaining to the transformation of density functions is applied:

If $f(x_1, x_2, x_3)$ is the joint probability density of random variables X_1, X_2, X_3, and Y_1, Y_2, Y_3 are random variables for which

$$\begin{aligned} X_1 &= g(Y_1, Y_2, Y_3) \\ X_2 &= h(Y_1, Y_2, Y_3) \\ X_3 &= r(Y_1, Y_2, Y_3) \end{aligned} \tag{12}$$

and the functions g, r and h are differentiable throughout, then the joint probability density of random variables Y_1, Y_2, Y_3 is

$$h(y_1, y_2, y_3) = f[g(y_1, y_2, y_3),\ h(y_1, y_2, y_3),\ r(y_1, y_2, y_3)] \cdot \Delta\,,$$

where Δ is the absolute value of the Jacobian determinant. (The theorem is mentioned in Ref. [2] on p. 66 of Vol. **2**).

If in this theorem g, h and r play the role of X_1, X_2, X_3, and p, q and r the role of Y_1, Y_2, Y_3, we obtain from (8) and (11):

$$h(y_1, y_2, y_3) = \frac{\partial^3}{\partial y_1 \partial y_2 \partial y_3} P(p < y_1, q < y_2, r < y_3) =$$
$$= f\left(-\frac{y_1 + y_2}{1 + y_3},\ \frac{y_1 - y_2}{y_3 - 1},\ y_3\right) \cdot \tag{13}$$
$$\begin{Vmatrix} \frac{\partial g}{\partial y_1} & \frac{\partial g}{\partial y_2} & \frac{\partial g}{\partial y_3} \\ \frac{\partial h}{\partial y_1} & \frac{\partial h}{\partial y_2} & \frac{\partial h}{\partial y_3} \\ \frac{\partial r}{\partial y_1} & \frac{\partial r}{\partial y_2} & \frac{\partial r}{\partial y_3} \end{Vmatrix},$$

where, because of (11),

$$g = -\frac{y_1 + y_2}{1 + y_3},$$

$$h = \frac{y_1 - y_2}{y_3 - 1},$$

$$r = y_3$$

and f is the density function defined by (8).

Using the above auxiliary theorems, one can calculate the probability density function which characterizes the mutual orientation of independently oriented molecules in the X, Y, Z space.

Theorem: The joint probability density of a, b, c is

$$\frac{\partial^3}{\partial X, \partial Y, \partial Z} P(a < X, b < Y, c < Z) =$$

$$= \frac{\sin X \sin Y \sin Z}{\pi^2[(1 + \cos X + \cos Y + \cos Z)(1 + \cos X - \cos Y - \cos Z)]^{1/2}} \times$$

$$\times \frac{}{[(1 - \cos X + \cos Y + \cos Z)(1 - \cos X - \cos Y - \cos Z)]^{1/2}} \qquad (14)$$

if $0 < X,\ Y, Z < \pi$, and the expression under the square root is positive. Otherwise it is zero.

Proof: it follows from (10) and the transformation theorem.

It can be seen that the probability density $\frac{\partial^3}{\partial X \partial Y \partial Z} = f(X, Y, Z)$ is symmetrical as expected. This property can be utilized to advantage in studying the mutual orientation effect of molecules.

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C-NUCLEOSIDES, III*

SYNTHESIS OF *C*-(2-DEOXY-β-D-RIBOFURANOSYL) BENZOTHIAZOLE AND -TETRAZOLE AND 5-(β-D-ARABINOFURANOSYL) TETRAZOLE

TRANSFORMATION OF *C*-GLYCOSYL-TETRAZOLES INTO 1,3,4-OXADIAZOLE DERIVATIVES

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2-Deoxy-β-D-ribofuranosyl cyanide was converted into the corresponding 2-substituted benzothiazole derivative (**II**) with 2-aminothiophenol and into 5-[2-deoxy-3,5-di-*O*-(*p*-toluoyl)-β-D-ribofuranosyl] tetrazole (**III**) with sodium azide and ammonium chloride. 5-[2-Deoxy-3,5-di-*O*-(*p*-toluoyl)-β-D-ribofuranosyl]-2-methyl-1,3,4-oxadiazole (**IV**) was obtained from **III** with boiling acetic anhydride. **III** and the formerly synthesized *C*-glycosyl-tetrazoles were transformed into 5-glycosyl-2-trifluoromethyl-1,3,4-oxadiazole derivatives (**V**—**VIII**) with trifluoroacetic anhydride.

Crystalline 5-(2,3,5-tri-*O*-benzoyl-β-D-arabinofuranosyl)-2-methyl- (**XII**) and -2-trifluoromethyl-1,3,4-oxadiazole (**XIII**) were obtained from syrupy 2,3,5-tri-*O*-benzyl-β-D-arabinofuranosyl cyanide in several steps *via* the tetrazole derivative. The configurations of the compounds were established on the basis of their NMR spectra and by comparing them with the α-anomers (**XIV**, **XV**).

It has been shown that β-glycosyl cyanides react with azide ions in a cycloaddition reaction to give 5-β-glycosyl-tetrazoles, whereas with 2-aminothiophenol they undergo condensation to 2-β-glycosyl-benzothiazoles [1, 2]. Recently similar investigations [3, 4] have been reported by Yugoslav investigators. As expected [5], the *C*-glycosyl-tetrazoles are nitril-imine precursors; so they can be transformed into 5-glycosyl-2-substituted-1,3,4-oxadiazoles by acylation [1—3].

Our investigations have been extended to other glycosyl cyanides, and novel transformations of *C*-glycosyl-tetrazoles have been achieved. 2-Deoxy-3,5-di-*O*-(*p*-toluoyl)-β-D-ribofuranosyl cyanide [6] (**I**) could be converted in an excellent yield into **III**, and satisfactorily into the **II** benzothiazole derivative, using the earlier method [1, 2].

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* Part II, see Ref. [2]

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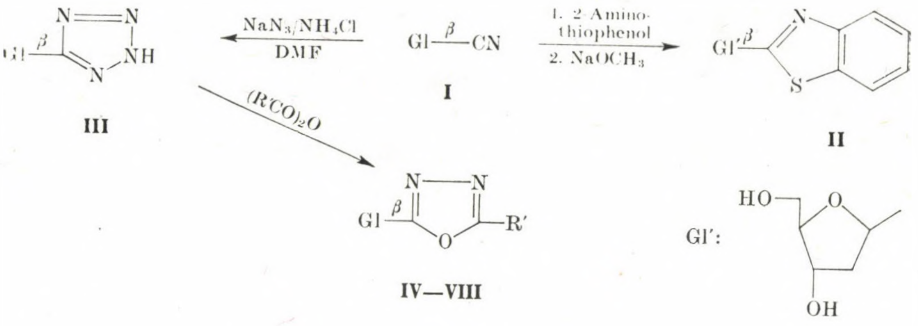
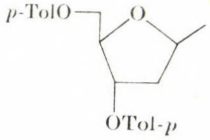
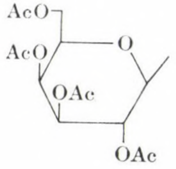
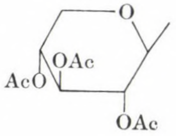
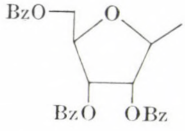
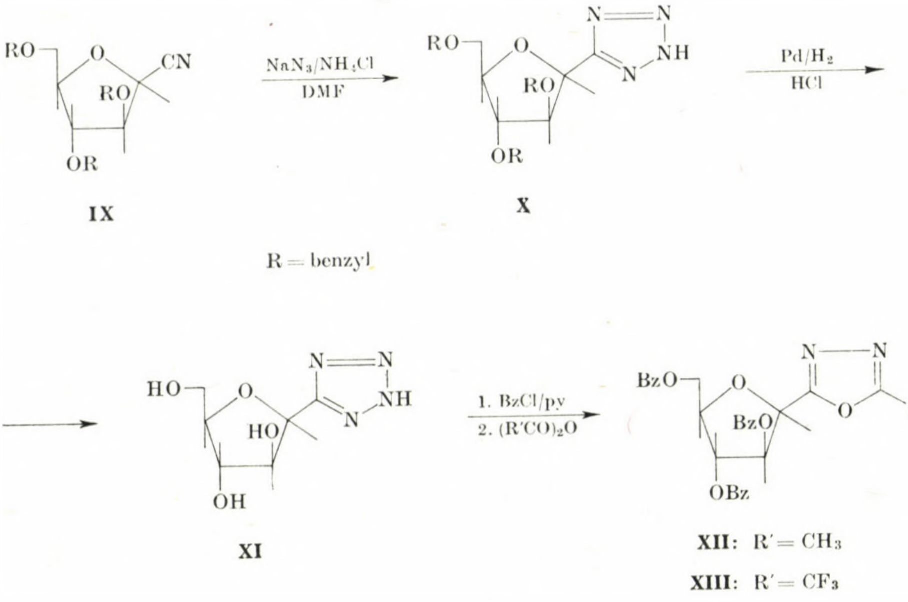


	Gl	R'
I, III—V		**IV** CH_3 **V** CF_3
VI		CF_3
VII		CF_3
VIII		CF_3

On the analogy of **III**, we synthesized 5-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-2-trifluoromethyl-1,3,4-oxadiazole (**VI**), 5-(2,3,4-tri-*O*-acetyl-β-D-xylopyranosyl)-2-trifluoromethyl-1,3,4-oxadiazole (**VII**), and 5-(2,3,5-tri-*O*-benzoyl-β-D-ribofuranosyl)-2-trifluoromethyl-1,3,4-oxadiazole (**VIII**) in excellent yields, starting from the formerly prepared 5(-per-*O*-acyl-β-glycosyl) tetrazoles [1, 2], by allowing them to react with trifluoroacetic anhydride.

It seemed interesting to synthesize the corresponding β-D-arabinofuranosyl derivatives, also in view of their potential biological effects. 2,3,5-

tri-*O*-benzyl-D-arabinofuranosyl cyanide [7] (**IX**), purified by column chromatography, was transformed into the corresponding tetrazole derivative (**X**) by means of an analogous reaction. We did not succeed in isolating either **X** or **XI** in the crystalline state. Therefore **XI** was *O*-acylated in the usual manner and then heated with the appropriate acid anhydride to give the corresponding 2-methyl-(**XII**) and 2-trifluoromethyl-1,3,4-oxadiazole derivative (**XIII**), respectively. These compounds were obtained as crystalline substances after purification by column chromatography.



IX

X

R = benzyl

XI

XII: $R' = CH_3$

XIII: $R' = CF_3$

By means of the above method, we also prepared 5-(2,3,5-tri-*O*-benzoyl-α-D-arabinofuranosyl)-2-methyl-(**XIV**) and -2-trifluoromethyl-1,3,4-oxadiazole (**XV**) from the known 5-(2,3,5-tri-*O*-benzoyl-α-D-arabinofuranosyl)tetrazole [4] (**XVI**). The characteristic data of the compounds are listed in Table I.

We deduced the configuration of the anomeric carbon atom from the NMR spectra of the compounds (Table II). It is known that the H-1 signal of the β-anomers of 2-deoxyribofuranosyl derivatives is of pseudotriplett character [8] and the sum of the coupling constants belonging to it (about 15 Hz) is larger than in the α-series [9, 10]. On this basis **II**, **IV** and **V** are regarded as compounds of β-configuration. This is also supported by our earlier observation that the C-1 configuration of glycosyl cyanides remains unchanged during identical transformations [1, 2].

The NMR spectrum gives no information on the anomeric configuration of **III**. However, its conversion into the oxadiazole derivatives **IV** and **V** of

Table I

Characteristic data of the compounds

Compound	Yield, %	M.p., °C	$[\alpha]_D$ (solvent)	Formula	Mol. weight	Analysis		^{1}H-NMR (δ[ppm]; J [Hz]) ^{a}CDCl$_3$; ^{b}pyridine-d_5; ^{c}acetone-d_6; ^{d}D$_2$O
						Calcd., %	Found, %	
II	48	130–131	+32.8° (pyridine)	$C_{12}H_{13}NO_3S$	251.3	N 5.57 S 12.76	5.60 12.68	^{b} 2.36–2.84 (m, 2H, H-2,2′) 4.03 (t, 2H, H-5,5′) 4.58 (m, 1H, H-4) 4.90 (m, 1H, H-3) 5.87 (dd, 1H, H-1, $J_{1,2} = 6$, $J_{1,2'} = 9$)
III	95	163–164	+1.4° ($CHCl_3$)	$C_{22}H_{22}N_4O_5$	422.4	N 13.26	13.28	^{c} 2.38 (2s, 6H, CH_3) 2.72–2.90 (m, 2H, H-2,2′) 4.48–4.72 (m, 3H, H-4,5,5′) 5.64–5.84 (m, 2H, H-3, H-1) 7.20–7.44 (m, 4H, aromatic) 7.80–8.12 (m, 4H, aromatic)
IV	92	102–103	–29.0° ($CHCl_3$)	$C_{24}H_{21}N_2O_6$	436.4	N 6.42	6.63	^{c} 2.36 (3s, 9H, CH_3) 2.52–3.00 (m, 2H, H-2,2′) 4.48–4.60 (m, 3H, H-4,5,5′) 5.46 (dd, 1H, H-1, $J_{1,2} = 6$, $J_{1,2'} = 9$) 5.84 (m, 1H, H-3) 7.24 (m, 4H, aromatic) 8.00 (m, 4H, aromatic)
V	91	106–107	–22.7° ($CHCl_3$)	$C_{24}H_{21}N_2O_6F_3$	490.4	N 5.71 F 11.62	5.95 11.27	^{c} 2.38 (2s, 6H, CH_3) 2.70–3.10 (m, 2H, H-2,2′) 4.52–4.70 (m, 3H, H-4,5,5′) 5,68 (dd, 1H, H-1, $J_{1,2} = 6.5$, $J_{1,2'} = 9$) 5.75 (m, 1H, H-3) 7.24–7.36 (m, 4H, aromatic) 7.92–8.08 (m, 4H, aromatic)

VI	84	125–126	+12.5° ($CHCl_3$)	$C_{17}H_{19}N_2O_{10}F_3$	468.3	N 5.98 F 12.17	5.78 12.14	[a] 1.93–2.19 (4s, 12H, CH_3) 4.19 (s, 3H, H-5,6,6′) 4.92 (d, 1H, H-1, $J_{1,2} = 9$) 5.18–5.64 (m, 3H, H-2,3,4)
VII	90	112–113	–32.9° ($CHCl_3$)	$C_{14}H_{15}N_2O_8F_3$	396.3	N 7.07 F 14.38	7.09 13.65	[a] 1.90–2.10 (3s, 9H, CH_3) 3.52 (dd, 1H, H-5*ax*) 4.32 (dd, 1H, H-5*eq*, $J_{5ax,5eq} = 11.5$) 4.84 (d, 1H, H-1, $J_{1,2} = 8.5$) 5.12 (o, 1H, H-4, $J_{4,5ax} = 10$, $J_{4,5eq} = 5.5$) 5.24 (t, 1H, H-3, $J_{3,4} = 8.5$) 5.42 (t, 1H, H-2, $J_{2,3} = 8.5$)
VIII	95	117–118	–67.6° ($CHCl_3$)	$C_{29}H_{21}N_2O_8F_3$	582.5	N 4.81 F 9.78	4.69 9.48	[a] 4.50–4.92 (m, 3H, H-4,5,5′) 5.60 (d, 1H, H-1, $J_{1,2} = 5.5$) 5.97 (dd, 1H, H-3, $J_{3,4} = 4.0$) 6.12 (t, 1H, H-2, $J_{2,3} = 5.7$) 7.20–7.70 (m, 10H, aromatic) 7.80–8.20 (m, 5H, aromatic)
XII	18	121–122	–60.1° ($CHCl_3$)	$C_{29}H_{24}N_2O_8$	528.5	N 5.30	5.70	[a] 2.30 (s, 3H, CH_3) 4.60–4.96 (m, 3H, H-4,5,5′) 5.78 (d, 1H, H-1, $J_{1,2} = 4.7$) 5.84 (dd, 1H, H-3, $J_{3,4} = 3$) 6.02 (dd, 1H, H-2, $J_{2,3} = 2$) 7.20–7.70 (m, 10H, aromatic) 7.88–8.20 (m, 5H, aromatic)
XIII	28	109–110	–41.5° ($CHCl_3$)	$C_{29}H_{21}N_2O_8F_3$	582.5	N 4.81 F 9.78	5.12 9.75	[a] 4.64 (m, 1H, H-4) 4.80–4.92 (m, 2H, H-5,5′) 5.82 (m, 1H, H-3) 5.90 (d, 1H, H-1, $J_{1,2} = 4.7$) 6.04 (dd, 1H, H-2, $J_{2,3} = 2$) 7.20–7.70 (m, 10H, aromatic) 8.04–8.20 (m, 5H, aromatic)

Table I (continued)

Compound	Yield, %	M.p., °C	$[\alpha]_D$ (solvent)	Formula	Mol. weight	Analysis		^{1}H-NMR (δ[ppm]; J [Hz]) ^{a}CDCl$_3$; ^{b}pyridine-d_5; ^{c}acetone-d_6; ^{d}D$_2$O
						Calcd., %	Found %	
XIV	72	syrup	+6.8° (CHCl$_3$)	$C_{28}H_{24}N_2O_8$	528.5	N 5.30	5.31	^{a} 2.50 (s, 3H, CH$_3$) 4.78 (s, broad, 3H, H-4,5,5′) 5.59 (d, 1H, H-1, $J_{1,2} = 2.5$) 5.86 (m, 1H, H-3) 6.14 (t, 1H, H-2, $J_{2,3} = 2.5$) 7.20–7.66 (m, 10H, aromatic) 8.04–8.24 (m, 5H, aromatic)
XVII	64	148–149	+48.6° (H$_2$O)	$C_8H_{12}N_2O_5$	216.2	N 12.96	12.62	^{d} 2.56 (s, 3H, CH$_3$) 3.80 (m, 2H, H-5,5′) 4.18 (m, 2H, H-3,4) 4.56 (t, 1H, H-2) 5.13 (d, 1H, H-1, $J_{1,2} = 5.1$)
XV	74	syrup	−1.2° (CHCl$_3$)	$C_{29}H_{21}N_2O_8F_3$	582.5	N 4.81 F 9.78	5.09 9.64	^{a} 4.79 (s, broad, 3H, H-4,5,5′) 5.67 (d, 1H, H-1, $J_{1,2} = 2.5$) 5.89 (m, 1H, H-3) 6.10 (t, 1H, H-2, $J_{2,3} = 2.5$)

Table II

Chemical shift (δ, ppm) and coupling constant (Hz) of the H-1 protons

Compound	H—1	$J_{1,2}$	$J_{1,2'}$	$J_{1,2}+J_{1,2'}$	Sugar
I[a]	4.90 (t)	7.7	7.7	15.4	2-deoxy-D-ribofuranose
II[b]	5.87 (dd)	6.0	9.0	15.0	
IV[c]	5.46 (dd)	6.0	9.0	15.0	
V[c]	5.68 (dd)	6.5	9.0	15.5	
XII[a]	5.78 (d)	4.7	—	—	D-arabinofuranose
XIII[a]	5.90 (d)	4.7	—	—	
XIV[a]	5.59 (d)	2.5	—	—	
XV[a]	5.67 (d)	2.5	—	—	
VIII[a]	5.60 (d)	5.5	—	—	D-ribofuranose
VI[a]	4.92 (d)	9.0	—	—	D-galactopyranose
VII[a]	4.82 (d)	8.5	—	—	D-xylopyranose

[a] $CDCl_3$; [b] pyridine-d_5; [c] acetone-d_6.

β-configuration, being identical with the starting cyanide **I**, verifies the β-configuration. On the same basis also the **VIII** ribofuranosyl derivative can be regarded as a β-anomer.

The configuration of the arabinofuranosyl derivatives is verified by the known difference [10—12] in the chemical shifts and the coupling constants of the H-1 protons. It is to be noted that the coupling constant ($J_{1,2} = 5.1$ Hz) of the H-1 proton of **XVII**, obtained by deacylation of **XIV**, increased compared with the acylated compound. This effect is similar to the case of the tetrazole **XVI** where it was unambiguously verified that the anomeric configuration of **XVI** remained unchanged after deacylation [4].

The *C*-glycosides **VI** and **VII** having a pyranose ring unambiguously possess β-configuration, in accordance with the data in Table II.

Experimental

Optical rotations of the compounds were measured with a Perkin-Elmer 241 polarimeter; the NMR spectra were recorded with a JEOL Minimar MH-100 spectrometer. Melting points are uncorrected. The solutions were dried over anhydrous $MgSO_4$ and concentrated under diminished pressure on a water bath at 40–50 °C. TLC was performed on aluminium rolls pre-coated with silica gel 60 F_{254} (Merck). Chromatograms were developed with the same solvent systems as used for column chromatography. Detection was effected by iodine vapour at room temperature.

2-(2-Deoxy-β-D-ribofuranosyl) benzothiazole (II)

Compound **I** [6] (1 g) and 2-aminothiophenol (4 mL) were dissolved in 10 mL of *abs.* ethanol and boiled for 4 h under nitrogen. The solution was then evaporated to dryness and an ethanolic solution of the residue (10 mL) was allowed to stand with 0.4 mL of 1 *N* sodium methoxide solution for 24 h at 20 °C. After neutralization with cation exchange resin, the solution was concentrated and the residue recrystallized from chloroform-ligroin and then from ethanol-ether.

5-[2-Deoxy-3,5-di-*O*-(*p*-toluoyl)-β-D-ribofuranosyl]-tetrazole (III)

Compound **I** (3 g) was dissolved in *N,N*-dimethylformamide (15 mL). NH_4Cl (0.54 g) and NaN_3 (0.66 g) were added and the mixture was heated on a boiling water bath for 3 h. The solution was then evaporated to dryness, the residue shaken with water and extracted with ethyl acetate. After drying, the organic layer was concentrated and the residue recrystallized from ether-ligroin and then from aqueous alcohol.

Preparation of 5-(per-*O*-acyl-D-glycosyl)-2-methyl-1,3,4-oxadiazoles (IV, XIV)

The tetrazole (**III**, **XVI** [4]) (1 g) was allowed to react with acetic anhydride (2 ml) on a boiling water bath for 1 h.

In the case of **IV** the solution was evaporated, the residue taken up in methanol and the solvent evaporated. The resulting syrup was dissolved in chloroform, neutralized with saturated $NaHCO_3$ solution and, after drying, the solvent was evaporated. The residue was recrystallized from aqueous alcohol.

Isolation of **XIV**: the reaction mixture was treated with ice-water, then extracted with chloroform. The neutralized chloroform solution was dried, evaporated to dryness and the syrupy residue purified by column chromatography (Kieselgel 40, elution with $CHCl_3$: ether = 10 : 1, R_f: 0.43).

5-(α-D-Arabinofuranosyl)-2-methyl-1,3,4-oxadiazole (XVII)

Compound **XIV** (0.90 g) was dissolved in 10 mL of dry methanol. The solution was made slightly alkaline (pH ~ 8) with 1 *N* sodium methoxide and allowed to stand for 24 h at 20 °C. It was then neutralized with cation exchange resin, evaporated to dryness and the residue recrystallized from methanol.

Preparation of 5-(per-*O*-acyl-D-glycosyl)-2-trifluoromethyl-1,3,4-oxadiazoles (V—VIII, XV)

The tetrazole derivative [1, 2] (1 g) was dissolved in chloroform (1.5 mL). Trifluoroacetic anhydride (1–1.5 mL) was added and the mixture was warmed on a water bath (50 °C) until the evolution of gas had stopped (about 30 min). The solution was evaporated and the residue worked up as follows:

(i) The syrupy residue was recrystallized from ethanol to obtain **V**.

(ii) Methanol was added to and evaporated from the syrup several times; it was then dissolved in chloroform, neutralized with saturated $NaHCO_3$ solution, dried, and the solvent evaporated. The residue was recrystallized from aqueous alcohol (**VI**, **VIII**) or ethanol (**VII**). The syrupy **XV** was purified by column chromatography (Kieselgel 40, elution with benzene-ether (10 : 1), R_f: 0.52).

5-(2,3,5-Tri-*O*-benzoyl-β-D-arabinofuranosyl)-2-methyl-1,3,4-oxadiazole (XII)

2,3,5-Tri-*O*-benzyl-D-arabinofuranosyl cyanide [7] was purified by column chromatography on Kieselgel 40; the eluting solvent was benzene-ether (19 : 1); the fractions of R_f 0.60–0.65 gave a mixture containing mainly the β-anomer. The purified compound (1.85 g) was dissolved in *N,N*-dimethylformamide (10 mL). NH_4Cl (0.36 g) and NaN_3 (0.44 g) were added, and the mixture was heated for 5 h on a boiling water bath. After filtration, the solution was evaporated, the residue triturated with water, acidified with acetic acid, then extracted with chloroform. The syrupy tetrazole (**X**) obtained on evaporating the solvent was dissolved in methanol (25 mL) then hydrogenated at atmospheric pressure at 20 °C in the presence of palladium catalyst, prepared from 1.2 g of $PdCl_2$ by hydrogenation. The residue obtained on evaporating the filtrate was washed with ether and the syrup (**XI**; 1.1 g), which was insoluble in ether, was acetylated with a 1 : 1 mixture of acetic anhydride and pyridine (10 mL, 18 h, 20 °C). The mixture was poured into ice-water, the solution extracted with chloroform, then dried and the solvent evaporated. The syrupy residue was refluxed with 2 mL of acetic anhydride for 45 min and finally worked up as described in the case of **XIV**. The crude syrup was deacetylated with sodium methoxide as described above, then benzoylated with a mixture of 1 mL of pyridine and 1.5 mL of benzoyl chloride. The mixture was poured into ice-water, the product extracted with chloroform, dried, and the solution was evaporated to dryness. The syrup was crystallizable from ether-ligroin after purification by column chromatography (Kieselgel 40, elution with benzene-ether (9 : 1), R_f: 0.21).

5-(2,3,5-Tri-*O*-benzoyl-β-D-arabinofuranosyl)-2-trifluoromethyl-1,3,4-oxadiazole (XIII)

Crude, syrupy 5-β-D-arabinofuranosyl-tetrazole (see **XI**) (0.55 g) was treated with a mixture of 2 mL of pyridine and 0.94 mL of benzoyl chloride for 18 h at 0 °C. Work-up of the acylating mixture in the usual manner gave 0.8 g of tri-*O*-benzoate which was allowed to react with 0.8 mL of trifluoroacetic anhydride and then worked up according to method (ii) given above. The syrup was purified as described for **XII** (R_f: 0.78, in the same solvent) and crystallized from ether-ligroin.

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INVESTIGATION OF THE D-GLUCOSE-BORATE COMPLEXING REACTION

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The kinetics of the D-glucose–borate complexing reaction have been investigated at 25 °C, in solutions of $1.5 \cdot 10^{-2}$ ionic strength. Glucose solution, containing an equilibrium mixture of the α- and β-anomers, was added to dilute boric acid–borate solution, and the change in e.m.f. was measured by means of a glass electrode and recorded as a function of time. According to the mathematical evaluation of the data, the logarithm of the measured stability constant of the D-glucose–borate complex is 2.74 ± 0.05. The individual stabilities of the glucopyranose–borate and glucofuranose–borate complexes and the rate constants of their interconversion have been determined. The stability constant of the carbohydrate–borate complexes can be correctly obtained by pH-metry only when all the equilibria (mutarotational included) are taken into consideration, on the basis of a kinetical analysis of the data. The factors stabilizing D-glucose–borate complexes are discussed.

The D-glucose–borate complexing reaction has been known for a long time [1, 2] and used in the analysis of glucose [3]. The stability of the borate complex formed with the α-anomer is closer to the stability of *cis*-1,2-cyclopentanediol–borate, than to that of *cis*-1,2-cyclohexanediol–borate [4], therefore, some of the authors had assumed [1, 2, 4] that glucose, originally present in the pyranose form [3, 5], is converted into furanose in the course of the complexing reaction. On the other hand, other authors described glucopyranose–borate [6]. **MAZUREK** and **PERLIN** [7] attributed furanose structure to the complex on the basis of ^{1}H-NMR investigations, while **KENNEDY** and **HOW** [8], as a result of ^{11}B-NMR spectral studies, did not exclude the coexistence of both glucopyranose and glucofuranose complexes. The authors [7, 8] assumed linkage of the 1,2-, and **FOSTER** [9] that of the 2,4-diol group to borate, while others presumed the $O_3—O_5$- [10] or the $O_3—O_5—O_6$ borate complex [5].

Recently, on the basis of ^{1}H-NMR measurements, **ARONOFF** *et al.* [11] satisfactorily proved the α-D-glucofuranose–borate structure of the complex, where the 1,2-oxygens are involved in the linkage.

For the logarithm of the stability constant of the 1 : 1 complex, the values of 1.90 [12], 2.13 [4], 2.37 [13] and 2.376 [14] have been reported. It should be noted that **ARONOFF** *el al.* [11], on adding borate to D-glucose dissolved in deuterium oxide, observed the formation of a larger quantity of furanose than calculated on the basis of the stability constants with the assumption of furanose–borate. This indicates that the correct value is higher than those published.

No data seem to be available on the rate of the pyranose–furanose conversion caused by the attachment of the borate ion.

On evaluating the experimental methods published in the literature, it became evident that most of the authors used α-D-glucose stock solution, and did not take into consideration the modification of the mutarotational equilibrium of glucose during the period of time of determining the stability constant of the complex [4]. It can be seen, however, from the data in Table I that owing to hydroxide ion catalysis, the interconversion of the glucose anomers is fairly rapid reaction in the region of about pH 9, which is suitable for the investigation of the borate complexes, particularly if the initial solution contains only one of the anomers. Calculations made on the basis of the rate equation of mutarotation [17] and of the data in Table I, have shown that in a solution of about pH 9, half of the α-D-glucose originally present is converted into the β-modification in about 10 minutes. Hence the data in the literature on the glucose–borate system can only be considered as apparent complex stability constants.

In view of the aforesaid, we worked with solutions containing an equilibrium mixture of α- and β-D-glucose, the α-anomer content of which was calculated from the data in Table I. Since the rate of mutarotation is pH-dependent, we also used pH-metry for our investigations, making use of a variant of the difference-potentiometric method developed earlier [18]. In our present communication we report on the determination of the stability constant of the 1 : 1 D-glucose–borate complex and of the rate constant of the pyranose–furanose conversion of glucose when linked to borate.

Table I

Equilibrium and rate constants of the mutarotation of α-D-glucose
(literature data)

<table>
<tr><td colspan="4">$K_m = 1.762$</td><td>[3]</td></tr>
<tr><td colspan="5">$k_{-m} = k_{-m,0} + k_{-m,H^+} [H^+] + k_{-m,OH^-} [OH^-] s^{-1}$</td></tr>
<tr><td>$10^4 k_{-m,0}$</td><td>$10^3 k_{-m,H^+}$</td><td>k_{-m,OH^-}</td><td colspan="2">Temperature</td></tr>
<tr><td>0.638*</td><td>1.914*</td><td>170.1*</td><td>20 °C</td><td>[3]</td></tr>
<tr><td>1.60</td><td>4.30</td><td>162.5</td><td></td><td>[15]</td></tr>
<tr><td>2.72 ± 0.009</td><td>6.672 ± 0.192</td><td></td><td>25 °C</td><td>[16]</td></tr>
</table>

* Value calculated from the mutarotation coefficient with K_m.

Experimental

Materials

Boric acid was recrystallized three times from water. D-Glucose was of analytical purity, dried to constant mass at 105 °C; reagents of analytical purity were used.

The glucose stock solutions were allowed to stand at room temperature for 48 h before use. In this way the solutions contained an equilibrium mixture of the α- and β-anomers.

Measuring technique

Measurements were made at 25 $\pm$ 0.1 °C. The pH was measured with a Radiometer pHm4 instrument, by means of a Radiometer G200B glass electrode and an Ag/AgCl/15 mmol/dm^3 NaCl reference electrode, connected by a 15 mmol/dm^3 sodium perchlorate salt junction. The change with time of the electromotive force (e.m.f.) was recorded with a potentiograph Model Metrohm E536, to which a Metrohm EA109 glass electrode and the reference electrode described above were connected. During measurements a nitrogen stream, free of acid and base traces, was passed through the solution.

In the kinetic experiments the pH of a boric acid–borate solution of about pH 9, containing 20 mmol/dm^3 total boron, was accurately measured. Next, to 25.0 mL of this solution there was added 10.00 mL of glucose stock solution in one portion; in the resulting solution which contained 5.70 mmol/dm^3 of total glucose, the change in e.m.f. was recorded at a sensitivity of 0.2 mV/mm and a speed of 80 mm/min with the glass electrode.

During the parallel experiments the initial pH values varied between 9.21 and 8.15. Ionic strength was adjusted in each case with sodium perchlorate to $1.5 \cdot 10^{-2}$. The results of one of these experiments are shown in Fig. 1.

The response time of the measuring chain was checked by adding, under identical conditions, instead of the glucose solution, 10.00 mL of boric acid solution of 30 mmol/dm^3 concentration, or D-sorbitol solution of 6.2 mmol/dm^3 concentration (the borate complex of the latter is formed instantaneously) to the initial boric acid-borate solution. It can be seen from Fig. 1 that 2–3 s after the addition the measurable e.m.f. did not change anymore under such conditions.

In the case of higher e.m.f. changes, the settling time of the electrode potential rapidly increased even when boric acid was added. Moreover, the concentration of boric acid could not be increased in order to prevent the formation of polyborate ions [19]. Higher glucose

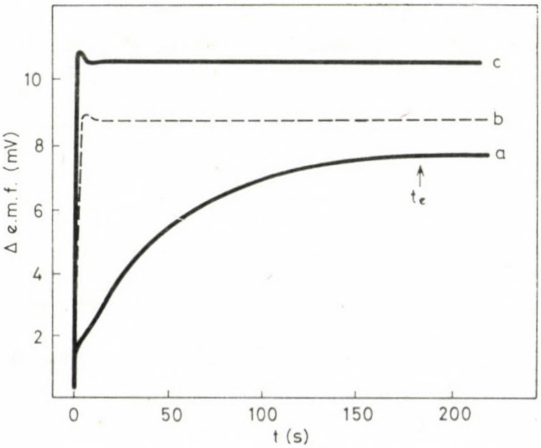

Fig. 1. Change of the electromotive force as a function of time measured with a glass electrode in 25 mL of boric acid-borate solution of pH 9, on the addition of 10 mL of one of the following reagents: (*a*) 20 mmol/dm^3 D-glucose solution; (*b*) 6.2 mmol/dm^3 D-sorbitol solution; (*c*) 30 mmol/dm^3 boric acid solution

concentrations could not be employed either, because we wished to work under conditions permitting only the formation of the 1 : 1 complex [11]. Thus all the experiments were carried out under the conditions described above.

Since small e.m.f. changes were measured, particular attention was paid to reproducibility. On the basis of six parallel experiments it was found that the deviation of the Δe.m.f. values belonging to the several points of time was at $t > 5$ s less than 0.2 mV.

The e.m.f. changes were converted by means of Nernst's equation to pH changes (ΔpH).

The pH of the starting boric acid–borate solution was measured with an accuracy of ± 0.01 pH unit (calculated from 9 measurements). It should be mentioned that the buffer solutions used for the calibration of the pH-meter were also stirred in the course of adjusting the instrument, because a difference of pH 0.01 was found between the stirred and unstirred boric acid–borate solution. A similar effect has been reported and explained in the literature [20].

For the determination of the protonation constant of boric acid in a solution of $1.5 \cdot 10^{-2}$ ionic strength, the solution containing 5.00 mmol dm^{-3} of boric acid and 15 mmol dm^{-3} of sodium perchlorate was titrated with 15.0 mmol/dm^3 sodium hydroxide solution, proceeding further as described in an earlier communication [21]. As a result a value of $\log \beta_{110} = 9.18 \pm 0.03$ was obtained.

The values of standard deviation given in the present work (with indication of the number of measuring data), and the reliability of the single numerical results refer to a significance level of $1 - p = 0.95$.

Symbols

HB, B^-	boric acid and the [tetrahydroxoborate]-ion;
αGp, βGp, αGf	α- and β-glucopyranose and α-glucofuranose;
$\beta_{110} =$	$[HB]\,[B^-]^{-1}\,[H^+]^{-1}$ protonation constant of boric acid;
β^{p}_{011}	stability constant of the α-D-glucopyranose–borate complex (Table II);
β'_{011}	apparent stability constant of the α-D-glucose–borate complex (Table II);
K_m	equilibrium constant of the mutarotation of glucose (Table I);
K_{GB}	equilibrium constant of the formation of the two kinds of α-D-glucose–borate complex (Table II);
k_m, k_{-m}	first order rate constant of the mutarotation of α- and β-D-glucose, respectively;
k_{GB}	rate constant of the conversion of α-D-glucopyranose–borate into α-D-glucofuranose–borate;
k^*	apparent rate constant of the preceding reaction (*cf.* Eq. (18));
t	reaction, time, s;
*, o, e, ∞	refer as subscripts to: the equilibrium state before the mixing of the glucose and borate solutions; the moment of mixing; the new equilibrium established on termination of mV-change; and finally, to the solution containing all the existing forms in equilibrium concentration, respectively;
i	subscript referring to an arbitrary moment of time ($t_0 < t_i < t_e$);
C_B, C_G, C_A	the total concentration of boron, glucose and sodium hydroxide, respectively, measured in the solution; (under the given pH conditions, the NaOH concentration is identical with the total concentration of the anions containing boron).

Table II

Constants describing the α-D-glucose–borate complexing reaction at 25 °C *and* $1.5 \cdot 10^{-2}$ *ionic strength, measured in solutions between pH* 8.0 *and* 9.2

Symbol and definition	Constant
$\beta^{p}_{011} = [\alpha GpB^-][\alpha Gp]^{-1}[B^-]^{-1}$	$\log \beta^{p}_{011} = 1.62 \pm 0.09$
$K_{GB} = [\alpha GfB^-]_\infty [\alpha GpB^-]^{-1}_\infty$	$\log K_{GB} = 1.09 \pm 0.15$
$\beta'_{011} = \beta^{p}_{011}(1 + K_{GB})$	$\log \beta'_{011} = 2.74 \pm 0.05$
$k_{GB} = k_{GB,OH^-}[OH^-]$	$k_{GB,OH^-} = 4190 \pm 410$ s^{-1}

Evaluation of the measured data

Fig. 2. shows the reaction equilibria which may afford an explanation of the experimental data in Fig. 1.

Depending on the way of interpreting the equilibria attained in about 180 s in a solution containing glucose and borate, various values of the stability constant of the complex can be derived from the equilibrium e.m.f. change belonging to time t_e.

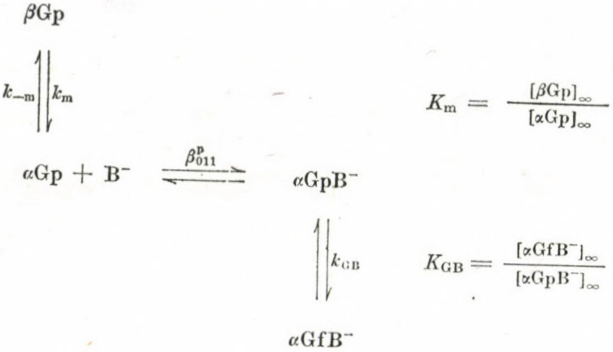

Fig. 2. Equilibria established in dilute solutions containing D-glucose and borate ion (B^-)

With the assumption that in 180 s all the reactions shown in Fig. 2 have attained equilibrium state (thus, according to the symbols used $t_e = t_\infty$):

$$C_B = [B^-]_e(1 + \beta_{110}[H^+]_e + \beta'_{011}[\alpha Gp]_e) \tag{1}$$

$$C_G = [\alpha Gp]_e(1 + K_m + \beta'_{011}[B^-]_e)\,, \tag{2}$$

according to the theorem of electroneutrality, in the pH range investigated we have:

$$C_A = [B^-]_e(1 + \beta'_{011}[\alpha Gp]_e)\,. \tag{3}$$

Since the change in pH is small,

$$C_B - C_A = [HB]_* = [HB]_e\,, \tag{4}$$

and dividing Eq. (3) by C_A we obtain [18]:

$$\text{num log}\ \Delta pH_e = 1 + \beta'_{011}[\alpha Gp]_e\,. \tag{5}$$

Solving of the relations (1)–(5) results in $\log \beta'_{011} = 2.38$, this value being in agreement with data cited in the literature [13, 14].

A different result is obtained if it is assumed that in the glucose solution containing an equilibrium mixture of the α- and β-anomeres, upon the addition of the borate ion the pyranose-furanose conversion of the complex proceeds at a considerably higher rate than mutarotation, which is slowed down under such conditions so that its change is negligible. Thus, the ceasing of the e.m.f. change shown in Fig. 1 has not been caused by the attainment of the final equilibrium state, but only by the termination of the more rapid reaction ($t_e < t_\infty$). Now

$$C_G - [\beta Gp]_* = [\alpha Gp]_* = [\alpha Gp]_e(1 + \beta'_{011}[B^-]_e)\,, \tag{6}$$

and using Eq. (6) instead of Eq. (2), the above calculation results in $\log \beta'_{011} = 2.74$.

This latter result is supported by the following consideration: if the total quantity of bound glucose is calculated for the point of time t_e:

$$[\alpha GpB^-]_e + [\alpha GfB^-]_e = \beta'_{011}[B^-]_e[\alpha Gp]_e \tag{7}$$

and we calculate as if the quantity of $[\alpha\mathrm{Gp}]_*$ at the point of time t_0 were to diminish by this quantity, the change of $[\beta\mathrm{Gp}]$ during 180 s in a solution of 9 pH would amount to a total of 14% on the basis of the rate equation [17] of the mutarotation of glucose. Since the increase in quantity of bound glucose is not instantaneous, but a time reaction taking place during the same 180 s period, mutarotation can actually be neglected under the given experimental conditions, as compared with the rate of the pyranose–furanose conversion in the complex.

This was further supported by a more detailed kinetical investigation of the reaction. Presuming that, notwithstanding the aforesaid, the rates of the two reactions shown in Fig. 2 are comparable, and of the two kinds of glucose–borate complexes that of the furanose type is considerably more stable then the other, the following scheme can be written:

$$\beta\mathrm{Gp} \underset{k'_{\mathrm{m}}}{\overset{k_{\mathrm{m}}}{\rightleftharpoons}} \alpha\mathrm{GpB}^- \xrightarrow{k_{\mathrm{GB}}} \alpha\mathrm{GfB}^- \tag{8}$$

$$k'_{-\mathrm{m}} = \frac{k_{-\mathrm{m}}}{\beta^{\mathrm{p}}_{011}[\mathrm{B}^-]} \,. \tag{9}$$

At constant borate concentration Eqs. (8) and (9) hold true. Though the borate concentration is changing with time under our experimental conditions, the curve can be partitioned into short sections, within which the concentration can be considered constant. Applying the Bodenstein principle separately to each of these sections, we have:

$$\frac{\mathrm{d}[\alpha\mathrm{GpB}^-]}{\mathrm{d}t} = k_{\mathrm{m}}[\beta\mathrm{Gp}] - k'_{-\mathrm{m}}[\alpha\mathrm{GpB}^-] - k_{\mathrm{GB}}[\alpha\mathrm{GfB}^-] \,. \tag{10}$$

The various momentary concentrations can be calculated by the repeated use of Bodenstein's principle; thus reducing Eq. (10) in the usual way [17] we obtain:

$$\frac{\mathrm{d}[\alpha\mathrm{GfB}^-]}{\mathrm{d}t} = \frac{k_{\mathrm{m}}}{1 + \dfrac{k'_{-\mathrm{m}}}{k_{\mathrm{GB}}}} [\beta\mathrm{Gp}] = k'[\beta\mathrm{Gp}] \,. \tag{11}$$

The numerical solution of Eq. (11) yields the individual k' constants, the values of which depend on the momentary borate concentration. In the pH range investigated $C_{\mathrm{A}} \approx [\mathrm{B}^-]_*$ and hence:

$$[\mathrm{B}^-]_i = \frac{C_{\mathrm{A}}}{\mathrm{num}\log \Delta\mathrm{pH}_i} \,. \tag{12}$$

Using Eqs (9), (11) and (12), k_{GB} can be calculated on the basis of the $k'_i - [\mathrm{B}^-]_i$ function, if the model used for the description of the reaction has been correct. However, a negative value was obtained for the rate constant calculated in this way, which is inconsistent with Eq. (10), and hence indicates that the reaction proceeds according to another scheme than the selected one.

Next, the model was investigated according to which only the pyranose–furanose conversion of the complex proceeds during the time t_{e} under the given reaction conditions, while the concentration of β-D-glucose practically remains unchanged.

In the case of a first order reaction leading to equilibrium, the conversion of any of the components (X) can be described by the relationship:

$$\ln \frac{\mathrm{X}_0 - \mathrm{X}_{\mathrm{e}}}{\mathrm{X}_i - \mathrm{X}_{\mathrm{e}}} = \frac{\mathrm{X}_0}{\mathrm{X}_0 - \mathrm{X}_{\mathrm{e}}} kt \,, \tag{13}$$

where X_0 is the total concentration of the substance, since it has been assumed in the deduction of Eq. (13) that the pure X modification is present in the solution at the moment t_0 [17]. The total concentration of the glucose–borate complexes changes from second to second, and the value given in Eq. (7) is only attained on termination of the reaction. Before this, on the basis of Eqs (3) and (12):

$$([\alpha\mathrm{GpB}^-] + [\alpha\mathrm{GfB}^-])_i = C_{\mathrm{A}}\left(1 - \frac{1}{\mathrm{num}\log \Delta\mathrm{pH}_i}\right) . \tag{14}$$

In Eq. (13) the momentaneous values of $[\alpha\mathrm{GpB}^-]$ are substituted for X_i. The $[\alpha\mathrm{Gp}]_i$ values needed for this are, from Eqs (6) and (14), the following:

$$[\alpha\mathrm{Gp}]_i = [\alpha\mathrm{Gp}]_* - C_\mathrm{A}\left(1 - \frac{1}{\mathrm{num}\log \Delta\mathrm{pH}_i}\right). \tag{15}$$

As the equilibrium concentration X_e can be expressed with the help of the total concentration and the equilibrium constant, in the case of glucose–borate complexes K_GB, it can be written on the analogy of Eq. (13):

$$\ln \frac{1 - \dfrac{1}{1+K_\mathrm{GB}}}{\dfrac{[\alpha\mathrm{GpB}^-]_i}{([\alpha\mathrm{GpB}^-] + [\alpha\mathrm{GfB}^-])_i}} = \frac{1}{1 - \dfrac{1}{1+K_\mathrm{GB}}}\, k_\mathrm{GB}\, t. \tag{16}$$

Since

$$1 + K_\mathrm{GB} = \frac{\beta'_{011}}{\beta^\mathrm{p}_{011}},$$

by substitution of Eqs (14) and (15) and by dividing by β^p_{011} Eq. (16) can be written in the following form:

$$\ln \frac{[\alpha\mathrm{Gp}]_* + C_\mathrm{A}\left(\dfrac{1}{\mathrm{num}\log \Delta\mathrm{pH}_i} - 1\right)}{\mathrm{num}\log \Delta\mathrm{pH}_i - 1} - \frac{1}{\beta'_{011}} = \ln\left(\frac{1}{\beta^\mathrm{p}_{011}} - \frac{1}{\beta'_{011}}\right) - k^* t, \tag{17}$$

where the term

$$k^* = k_\mathrm{GB}\,\frac{\beta'_{011}}{\beta'_{011} - \beta^\mathrm{p}_{011}} \tag{18}$$

is of constant value, determined by the rate and stability constants, and can be regarded as the apparent rate constant.

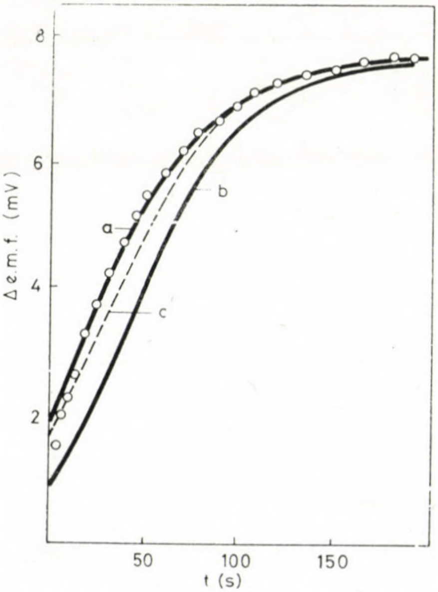

Fig. 3. Determination of the constants characterizing the D-glucose–borate reaction by changes in the e.m.f. data. ○ Measured data. Calculated curves: (*a*) $\log \beta^\mathrm{p}_{011} = 1.62$; $k^*_{\mathrm{OH}^-} = 4120\ \mathrm{s}^{-1}$; (*b*) $\log \beta^\mathrm{p}_{011} = 1.30$, $k^*_{\mathrm{OH}^-} = 5000\ \mathrm{s}^{-1}$; (*c*) $\log \beta^\mathrm{p}_{011} = 1.55$, $k_\mathrm{GB} = 3.18 \cdot 10^{-2}\ \mathrm{s}^{-1}$

On plotting the measured data according to Eq. (17), k^* and β^{p}_{011} can be calculated.

The k^* values obtained changed slightly as a function of the reaction time, and thus of the pH. We have assumed that this is caused by the pH-dependence of k_{GB}. The measured data could be well interpreted by hydroxide ion catalysis

$$k^* = k^*_{\mathrm{OH}^-}[\mathrm{OH}^-]$$

in the 8.0—9.2 pH range investigated.

Table II contains the constants determined, and Fig. 3 shows the agreement of functions calculated with the assumption of various constants.

Discussion

Our results highlight the fact that in the pH-metric determination of the stability constants of carbohydrate–borate complexes it is only the consideration of all the equilibria and the kinetical evaluation of the measured data that can yield unequivocal results. It can be seen from Fig. 1 that after the mixing the solutions of D-glucose and borate, the pH change, which is proportional to the e.m.f. change measured, is rapid in the beginning, and during about 180 s the reaction is apparently terminated. Actually, only the more rapid α-D-glucopyranose–borate → α-D-glucofuranose–borate conversion takes place during this time. After this, the reaction continues at the rate of the mutarotation of glucose, until the final equilibrium state has been attained. According to our calculations, in the system shown in Fig. 1 the e.m.f. continues to change by about 6 mV, but this reaction requires already more than 1 hour.

Our data support the assumption of KENNEDY and HOW, made on the basis of ^{11}B-NMR investigations [8], according to which the presence of a smaller quantity of glucopyranose–borate complex besides the complex of furanose conformation cannot be excluded; they also support the ^{1}H-NMR measurements of ARONOFF *et al.* [11], indicating that the stability of the D-glucose–borate complex is higher than the value published so far in the literature.

Fig. 4 shows the mechanism assumed by us for the pyranose–furanose conversion in the α-D-glucose–borate complex, where use was made, besides the kinetic data described above, also of the findings of DALE [22] concerning the stereochemistry of borate complexes and the results of ARONOFF *et al.* [11]. The driving force of the conversion is the considerably more favourable spatial arrangement of the furanose complex (in the pyranose form one B—OH and the C_3—H groups get very close to one another). The reaction cannot proceed through the open aldehyde form, as is the case in mutarotation (this is excluded also by the different values of the catalysis constants), because the C_1-anomeric oxygen of glucose is linked to boron. The occurrence of the heterolysis of the C_1—$O(C_5)$ bond in the moment of reaction is more likely; the positive charge remaining on carbon C_1 is compensated by the negative

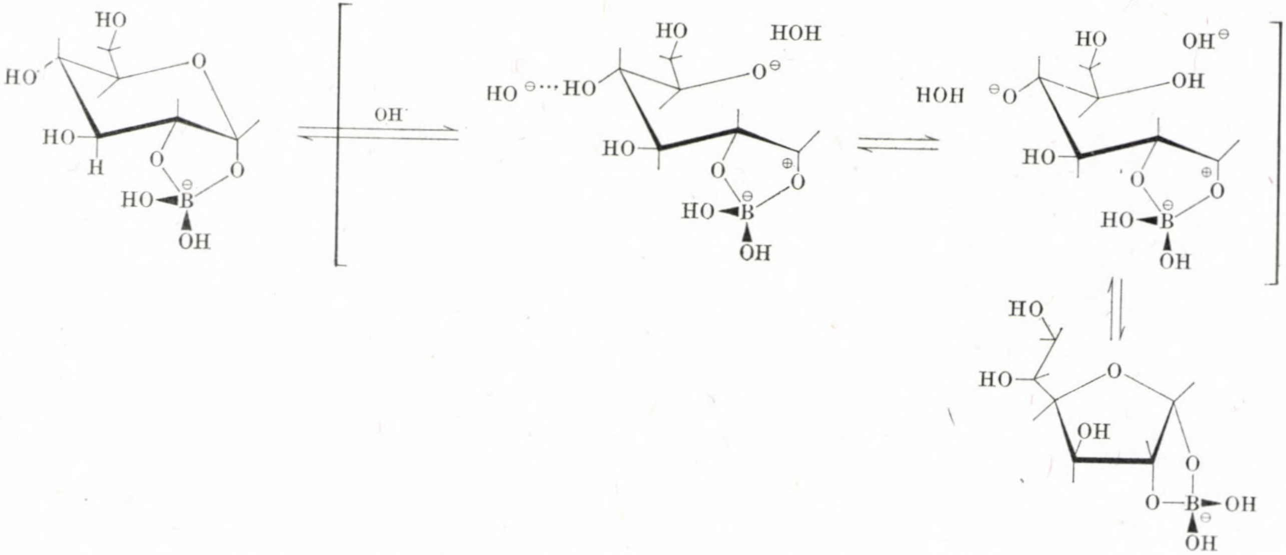

Fig. 4. Suggested mechanism of the pyranose-furanose conversion of the α-D-glucose–borate complex

charge of boron. It has been shown in our earlier work [23] that in polyalcohol-borate complexes the field effect of the negative charge of boron inhibits the hydroxide-catalysed reactions of alcoholic hydroxyl groups over a distance of about 0.4—0.5 nm. In the glucose complex the distance between boron and the C_4-oxygen is about 0.6 nm, however, this hydroxyl group is located in a shielded position, on the opposite side of the glucose ring, hence the form of hydroxide ion catalysis shown in Fig. 4 and made verisimilar by the kinetic data, may take place. After the dissotiation of the $C_4—OH$ proton the furanose form can be constructed by simple rotation also on a Stuart-Briegleb model.

It has been indicated in the introduction that earlier researchers [1, 2, 4] concluded the furanose conformation of the D-glucose–borate complex from the facts that its electrophoretic mobility and measurable stability constant were closer to the respective data of the borate complex of cyclopentane-1,2-diol ($\log \beta_{011} = 1.41$, 25 °C [4]), than to that of *cis*-1,2-cyclohexanediol ($\log \beta_{011} = 0.0$, 25 °C [4]; 0.28, 33 °C [24]). This conclusion on the structure of the complex proved to be correct. It is interesting that actually the stability constants of the α-D-glucopyranose–borate complex (β^{p}_{011}, Table II) lies closer to that of cyclopentanediol–borate.

Borate complexes of five-membered cyclic diols have higher stability, if there is an oxygen atom in the ring instead of carbon, adjacent to the diol group. This conclusion is evident from a comparison of the stability of pentose–borate complexes [12, 15] with that of *cis*-cyclohexane-1,2-diol. The stability of the α-D-glucopyranose–borate complex indicates that this rule is even more pronounced in the case of six-membered cyclic diols. In our opinion this phenomenon is partly caused by the anomeric dipole effect [3, 5], which stabilizes the *axial* position of the C_1 oxygen in D-glucose, as compared with cyclohexanediol. This effect is still more pronounced in the borate complex, because a negatively charged substituent is attached to the $C_1—O$ group. On the other hand, the oxygen heteroatom is more favourable also from the aspect of 1,3-interaction, as it hinders less the *axial* position of one of the non-bonding $B—OH$ groups with respect to the ring, than the methylene group of identical position in a cycloparaffin ring.

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SYNTHESIS OF 4-HYDROXYIMINO-1,4-DIHYDRO-3(2*H*)-ISOQUINOLINONES AND BENZOISOQUINOLINONES BY MEANS OF ISONITROSATION OF ISOQUINOLINONES

(PRELIMINARY COMMUNICATION)

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Earlier in the course of a study of the reactivity of the 4-methylene group of 1,4-dihydro-3(2*H*)-isoquinolinones we found [1] for the 1-aryl derivative that it reacted with aromatic aldehydes in the presence of sodium hydride or the likewise strongly alkaline Avramoff-reagent [2], to be converted, possibly by hydride ion migration and via the 4-benzylidene derivative, into 4-aryl-methyl-3-isoquinolinol. The 4-benzylidene derivative could be isolated under proper experimental conditions. Sodium ethoxide was found unsuitable for effecting this reaction. A role played by the hydrogen attached to the lactam-nitrogen was suggested by the fact that this reaction failed to occur with the *N*-methyl derivative of the parent compound.

A well known method of preparing α-dioxo compounds consists in converting the methylene adjacent to the keto group into oxime by means of introducing a hydroxyimino group, from the oxime the oxo group is then readily formed. This reaction was utilized by Decombe [3] for the transformation of the methylene group in position 4 of 1,3-dioxo-tetrahydroisoquinoline.

We studied whether the methylene at position 4 of 1-phenyl-1,4-dihydroxy-3(2*H*)-isoquinolinone can be made to react with butyl nitrite in the presenee of potassium *t*-butoxide, and found that the 4-hydroxyimino derivative could be isolated in good yields. This product was a mixture of the *Z* and *E* isomers, which could be separated by adsorption chromatography.

The question was raised whether the hydrogen attached to the lactam-nitrogen was indeed necessary for this reaction to occur. We found that the reaction also proceeded with the *N*-methyl derivative and in this instance, too, a mixture of the *Z* and *E* isomers was obtained. Such mixtures of the stereoisomers were also obtainable from derivatives that had a nitrogroup or a halo-

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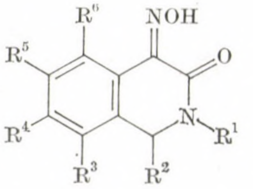
Table 1

4-Hydroxyimino-1,4-dihydro-

	R_1	R_2	R_3	R_4	R_5	R_6	Empirical[a] formula
1 **2**	H	C_6H_5	H	H	H	H	$C_{15}H_{12}N_2O_2$
3 **4**	CH_3	C_6H_5	H	H	H	H	$C_{16}H_{14}N_2O_2$
5	H	C_6H_5	H	H	H	CH_3	$C_{16}H_{14}N_2O$
6 **7**	CH_3	H	H	H	H	H	$C_{10}H_{10}N_2O_2$
8 **9**	CH_3	3'-NO_2-C_6H_4	H	H	H	H	$C_{16}H_{13}N_3O_4$
10	H	2', 6'-dichloro$-C_6H_3$	H	H	H	H	$C_{15}H_{10}N_2O_2Cl_2$
11 **12**	H	C_6H_5	$CH{=}CH{-}CH{=}CH$		H	H	$C_{19}H_{14}N_2O_2$
13	H	C_6H_5	H	H	$CH{=}CH{-}CH{=}CH$		$C_{19}H_{14}N_2O_2$

[a] All compounds were analyzed for C, H, N with results of at least 0.4% accuracy.



3(2H)-isoquinolinones

Isomer	M. p. (°C)^b	IR^c (KBr) cm^{-1}	^{1}H—NMR^d (ppm)
Z	167—168	OH chelat., 1660 —CO—NH—, 1058, 1028, 963 N—O(H)	C_1—H 5.91 (d); C_5—H 7.90 (m) N—H 9.75 (d); OH 15.65 (s)
E	194—195	OH: broad, 1620 —CO—NH—, 1595 aromat., 1028, 998 N—O(H)	C_1—H 5.80 (d); C_5—H 8.42 (m) N—H 9.00 (d); OH 12.47 (s)
Z	118—119	OH chelat., 1620 —CO—NH—, 1040, 972, 963 N—O(H)	C_1—H 5.50 (s); C_5—H 8.06 (m) N—Me 2.97 (s); OH 16.00 (s)
E	173—176	OH: broad, 1655 —CO—NH—, 1598 aromat., 1020 —N—O(H)	C_1—H 5.48 (s); C_5—H 8.95 (m) N—Me 3.06 (s)
E	214—215	OH: broad., 1670 —CO—NH—, 1600 aromat., 1030, 992 N—O(H)	C_1—H 6.57 (s); OH 9.05 Ar—Me 2.29 (s);
Z	148—151	OH chelat., 1642 —CO—NH—, 1055, 965 N—O(H)	C_1—H 3.63 (s); C_5—H 8.02 (m) N—Me 3.16 (s);
E	171—173	OH broad, 1670 —CO—NH—, 1592 aromat., 1022 N—O(H)	C_1—H 4.55 (s); C_5—H 8.65 (m) N—Me 3.16 (s)
Z	189—193	OH chelat., 1630 —CO—NH—, 1055, 960 N—O(H)	
E	221—222	OH broad., 1678 —CO—NH—, 1600 aromat., 1024 N—O(H)	
E	238—239	OH broad, 1690 —CO—NH—, 1595 aromat., 1028, 996 N—O(H)	
Z	238—239	OH chelat., 1650 —CO—NH—, 1047, 1040, 984 N—O(H)	C_1—H 6.50 (d); OH 15.79 (s) N—H 10.07 (d)
E	206—208	OH broad, 1660 —CO—NH—, 1070, 995 N—O(H)	
Z	196—198	OH chelat., 1662 —CO—NH—, 1100, 1025, 960, 930 N—O(H)	C_1—H 5.75 (s); OH 15.42 (s) N—H 9.55 (d)

[b] Uncorrected melting points, capillary-tube method.

[c] The IR spectra were recorded with a Perkin—Elmer 377 spectrometer; samples in KBr pellets.

[d] The NMR spectra were recorded with a Jeol FX-100 spectrometer.

gen atom on the 1-aryl group, and also when no substituent was present at position 1. Processing of the crude product obtained from the reaction with 1-(3'-nitrophenyl)-1,4-dihydro-3(2*H*)-isoquinolinone yielded both isomers as pure compounds. According to TLC, also the reaction of the 1-(2', 6'-dichlorophenyl) derivative gave two products, but here only the *E* isomer was isolated in pure state. The reaction of butyl nitrite with 1,4-dihydro-3(2*H*)-isoquinolinone not substituted at position 1 gave a product, the crystallization of which yielded the *E* isomer. Treatment of the crude product with diazomethane resulted in the methylation of this isomer and the *Z* isomer could then be separated by crystallization.

Molecular models clearly show that starting from a 5-substituted isoquinoline, steric hindrance should lead to the exclusive formation of only one, of the isomers (*Z*). In spite of this, in the reaction product of 1-phenyl-5-methyl-1,4-dihydro-3(2*H*)-isoquinolinone only the *E* isomer could be detected and was isolated in pure state. This suggests that the methyl group is not a significant obstacle. However, the expected steric hindrance was manifest in the case of the 1-phenyl-1,4-dihydro-3(2*H*)-benzo [*f*] isoquinolinone; in its reaction only one: the *Z* isomer was produced. When, in contrast, the isonitrosation reaction was performed with benzo [*h*] isoquinolinone, also the oxime isomer *E* was recoverable besides the *Z* isomer.

The structures given for these compounds are supported by results of elemental analysis, infrared and NMR spectra; several characteristic data are listed in Table I.

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RECENSIONES

Advances in Chemistry, Vol. 44

Editor: Béla Csákvári

Akadémiai Kiadó, Budapest 1979, 300 pages

Volume 44 of the series Advances in Chemistry contains two studies by József Dévay one of the most eminent scientists in the field of corrosion in Hungary, which are of great interest also from the practical point of view. The theme of these studies has been scarcely discussed in Hungarian technical literature, but even in foreign languages similar comprehensive monographic reviews are rather rare.

The first study of about 140 pages carries the title "Passivity, crevice corrosion, pitting". All three sections discuss both from the theoretical and practical aspect in a way and at a depth worthy of attention the chemistry of the relevant processes, causes and products, the mechanism of their formation, their kinds and the modes of influencing them. In this chapter, the interpretation of the concept and the phenomena of crevice corrosion, much discussed earlier, is of particular interest, as well as the theoretical and practical bases of protection against this kind of corrosion. Of similar interest is the investigation of pitting, a subject discussed more extensively. However, the author discusses very precisely, succinetly and very clearly the theory and practice of pitting, causing much damage. As a characterization of the extent of literature covered by the author, 437 references are cited for passivity, 248 for pitting, while 36 works are cited for crevice corrosion, which is a relatively high number, in view of the fact that crevice corrosion has been scarcely interpreted and investigated so far.

The title of the second part of about 160 pages of the volume is "Stress corrosion of metals". The investigation of this kind of corrosion becomes more and more important, and the study of its theory and practice comes into prominence. Such a modern and comprehensive review on the subject did not appear up to the present in Hungarian. The author discusses anodic and adsorptive stress corrosion mechanisms, problems of hydrogen embrittlement, compares and evaluates stress corrosion theories, discusses systems with a trend to stress corrosion, various types of stress corrosion tests and the possibilities of stress corrosion prevention. The extensive bibliography must also be pointed out in the case of this study: the bibliography at the end of the chapter contains 582 references.

In summary, the two comprehensive studies on corrosion, published in Vol. 44 of the series Advances in Chemistry can be considered as covering a gap both from theoretical and practical aspects, and not only for chemists, but also for researchers and practical experts working in other fields where corrosion must be prevented. In the reviewer's opinion, these studies merit publication in foreign languages, because both with respect to their high standard and good selection of theme, as well as the comprehensive covering of the subject, the book is thought to be of world-wide interest.

The book is a great asset to Hungarian corrosion literature.

E. Berecz

Francis A. Domino: *Plating of Plastics Recent Developments*

Noyer Data Corp., Park Ridge, N.J., USA, 1979, 385 pages

Already the predecessor of the book (Plating of Plastics with Metals, 1974) has been a surprise with respect to both its literary form and the rapidity of its appearance. The systematic review of the patent literature of a given theme is an immense help for engineers active in the field of applied research. This volume, following its predecessor after 5 years, characterizes well the acceleration of technical development, its extent exceeding by a third that of its forerunner.

The plating of plastics with metals has been used a few years before mainly for decorative purposes. Today its field of application is primarily electronics. Development is reflected by the increase in the number of platable plastics, by the automatability of the processes developed and by the search for more economic solutions, satisfying at the same time increasing technical demands. Thus, already the first chapter deals with a very important problem, with magnetic coatings. It discusses ferromagnetic coating alloys which can be used for metallization, and the key problem of the plating of plastics, the surface pretreatment. Of electroplatable plastics, it was ABS polymers that first wide-spread application, and these were followed by the polyolefins. The second chapter treats the problems of plating of these substances. Various pretreatment methods are discussed again, together with some modifications for the electroplating of these plastics.

The third chapter summarizes the methods of deposition of aluminium, nickel and cobalt, and of noble metals as an adhesion aid.

Important steps of surface pretreatment, sensibilization and activation, are discussed in this chapter.

The sensibilization and activation of plastics surfaces is the process producing metal crystal nuclei at the surface of the plastics as basis for the formation of further metal layers. This group of problems is treated in the fourth chapter. It is interesting to note that more and more processes based on non-noble metals are developed.

The fifth chapter discusses electroplatable plastics varieties. In addition to ABS polymers and polyclefins, polystyrene, polyamide and -imide, polyoxymethylene plastics and thermosetting resins appear. The electroplating of pretreated plastics surfaces raises several technical problems because of the low density, heat and solvent sensitivity *etc.*, of plastics. The sixth chapter deals with some, of these difficulties. Some special electroplating problems, as *e.g.* the coating of fibres, the formation of composite coatings and the production of printed circuits are covered in this chapter.

The seventh chapter summarizes the methods of electroless metal deposition as a pretreatment step. The chapter shows that even today processes based on noble metals and tin compounds are most often used. The practical application of the results of theoretical research, carried out in the last ten years in this field, can be readily followed.

The eight chapter, dealing with electroless copper baths, is of the greatest importance in the electroplating of plastics. The other electroless metallizing processes are summarized in the ninth chapter. The last chapter contains the patent of a few nonelectrochemical coating processes.

At the end of the book of 385 pages the companies that field the patents, the names of the inventors and patent numbers cited in the book are summarized.

The volume gives detailed abstracts of patent specifications with the intention of informing primarily researchers, and not patent attorneys, fluent in patent jargon. After giving the title of the patent, the names of the applicant and inventors, and the number of the patent, it summarizes the essence of the patent and gives examples on the mode of application.

In summary, "Plating of Plastics" will be of great help of researchers engaged in the development of new plastics plating processes.

F. HASKÓ

Benda W. HILL: *Chemindustry Experiments*

Franklin Institute Press, 1979

Vol. I; 213 pages, Vol. II: 144 pages

The book describes measurements and exercises for the laboratory practice of students in chemical engineering; Vol. I is intended for the students, while Vol. II is a manual for teachers.

A great merit of the compilation is the assembling of measuring tasks simple to realize, the attempt to link measurements to industrial problems, giving at the same time suitable practical background for general theoretical chemical knowledge. The first chapter describes laboratory devices and the most simple laboratory operations. The organization of the following 18 chapters is identical. Each chapter begins with a few exercises, which are to be solved by the students as preparatory work for the laboratory (simple calculations, the writing of formulas and chemical equations, *etc.*), this is followed by the statement of the object of the experiment, theoretical introduction, listing of the devices and materials needed for the measurement, labour safety prescriptions, the detailed description of the experiment, evaluation of results, description of the relevant calculations, instructions for the preparation of laboratory records, and finally, a list of literature.

A knowledge of industrial background is always an important aspect. Thus, the book gives information on chemicals prepared and used in the largest quantities in American chemical plants, on the industrial processes of the measurements, discusses associated industrial problems and their possible solution, and economical problems. The most important measuring tasks (forming each a chapter of the book) are the following: measurement of density; preparation and purification of important inorganic compounds; determination of the fluorine, chlorine, bromine, iodine, sulfur and nitrogen content of organic compounds by combustion method; exercise in gas laws and stoichiometry by the study of the reaction between calcium carbonate and nitric acid; acid — base titrations (citric acid, the acid component of hair spray and lithium carbonate serving as model compounds); redox titration for the analysis of drugs (according to monographs of the U.S. Pharmacopoeia); measurement of the heat of neutralization of ammonium hydroxide with various acids; determination of the order of reaction and reaction rate constant (for the dyeing process of cellulose fibres); determination of the equilibrium constant in esterification; measurement of solubility product; pH measurement (in conjunction with a process aimed at the more economical manufacture of citric acid); electrolysis of sodium chloride; preparation and analysis of synthesis detergents; decomposition of chalcopyrite ore (for the recovery of sulfur, copper and iron); identification of elements on the basis of their emission spectra; radiochemical experiments (application of a chemical dosimeter); removal of toxic trace elements from waste water.

In Vol. **II** the author gives for the teachers the solution of the exercises serving as preparation for the laboratory, calls the attention to the mistakes made mots often by the students, describes in detail typical laboratory records of the students to facilitate evaluation, discusses the preparation of chemicals, devices and instruments needed for the laboratory exercises.

Owing to the novel industrial concept, the book will be a useful aid for educational staff teaching chemistry at universities. Apparatuses intuitively assembled from simple devices are very instructive. The sole negative feature of the book published in 1979 is that it does not use the SI system of units.

J. NAGY

K. HÖLL: *Wasser*

Sechste, neubearbeitete Auflage

Walter der Gruyter Verlag, Berlin, 1979. 515 Seiten

Die Umweltverschmutzung birgt eine stets wachsende Gefahr für das gesamte System der Wasserversorgung in sich. Die Aufbereitung von Trinkwasser in befriedigender Qualität und ausreichender Menge sowie eine Abwasserreinigung, welche der immer strenger werdenden Anforderungen entspricht, stehen sowohl mit chemischen als auch mit biologischen und mikrobiologischen Problemen in engstem Zusammenhang. Diese Anschauung spiegelt sich im vorliegenden Buch in dem alle die Untersuchung und Charakterisierung des Wassers betreffenden, untrennbar zusammenhängenden Kenntnisse gemeinsam behandelt werden.

In *Teil 1* (363 Seiten, Verfasser K. HÖLL) des aus vier Teilen bestehenden Werkes wird die Chemie des Wassers in 10 Kapiteln behandelt. Nach der Beschreibung der verschiedenen Methoden der Wasserprüfung und Wasserbewertung sind je ein Kapitel den Wässern von Schwimmbädern und Baustellen sowie den Rezipienten für Oberflächenwässer und den Kesselwässern gewidmet. Ein weiteres Kapitel behandelt Mineral- und Thermalwässer. In den letzten Kapiteln werden 35 bei den Trinkwasserprüfungen übliche Reagenzien angegeben und die wichtigsten Fragen der Probeentnahme erörtert.

Teil 2 (44 Seiten, Verfasser H. RÜFFER) befaßt sich mit der Prüfung und Bewertung von Abwässern: Grundlagen der Abwasserprüfung, Probeentnahme, Sinkstoffgehalt, Schwebstoffgehalt, gelöste Stoffe (chemischer und biologischer Sauerstoffbedarf), Eutrophierung fördernde Stoffe (Phosphor- und Stickstoffverbindungen). Die Kriterien der Bewertung von Industrieabwässern werden gesondert behandelt.

Teil 3 (62 Seiten, Verfasser S. CARLSON) erörtert die bakteriologischen und virologischen Fragen des Wassers: allgemeine mikrobiologische Untersuchungen, einzelne Bestimmungsverfahren, virologische Prüfungen. Ein besonderes Kapitel ist den Virenproblemen von Schwimmbadwässern gewidmet.

Teil 4 (35 Seiten, Verfasser D. LÜDEMANN) behandelt das Thema »Biologie des Wassers«. Nach den allgemeinen Prüfmethoden werden die biologischen Trinkwasserprüfungen beschrieben, einige im Wasser lebende Mikroorganismen in Abbildungen gezeigt und die Möglichkeiten zur Bekämpfung der Mikroorganismen dargelegt.

Das Sachverzeichnis (17 Seiten) erleichtert die Handhabung des Buches.

Das vielseitige, unmittelbar nutzbare Kenntnisse vermittelnde Werk ist für Fachleute manningfaltiger Gebiete von Nutzen: für die Wasserforschung, für den Betrieb von Wasserwerken, für Probleme des Gesundheitswesens und der Biotechnik sowie für den Unterricht in den obigen Gebieten.

O. LIBOR

E. VÉRTES, L. KORECZ und K. BURGER: *Mößbauer Spectroscopy*

Akadémiai Kiadó Budapest — Elsevier Scientific Publishing Co. Amsterdam, 1979

Die verhältnismäßig junge, auf eine Vergangenheit von kaum 15 Jahren zurückblickende Mößbauer-Spektroskopie hat sich bereits in vielen Zweigen der Chemie als ein wirksames Mittel zur Bestimmung verschiedener Strukturparameter erwiesen.

γ-Strahlen werden durch ein oder mehrere Isotope von etwa 40 natürlichen Elementen emittiert. Die Kernniveaus, welche die Möglichkeit der Absorption bestimmen, hängen auf äußerst empfindliche Weise von den Eigenschaften der Elektronenumgebung des Kerns ab. Die Elektronendichte beeinflußt die Niveauabstände, die Asymmetrie der Elektronenverteilung wirkt auf die Quadrupolaufspaltung des angeregten Energieniveaus, die paramagnetische Elektronenumgebung spaltet die Niveaus auf. Die beiden grundlegenden kunstgriffe der Mößbauer-Spektroskopie bestehen darin, daß eine feste Phase mit niedriger Temperatur angewendet wird, wodurch der die Absorption hindernde Rückstoßeffekt äußerst gering gehalten wird, und daß die sehr feinen Änderungen der absorbierbaren γ-Energie mittels des durch Bewegen der Probe hervorgerufenen Doppler-Effekt verfolgt werden.

Der erste Teil des Buches behandelt die theoretische Deutung der Beziehungen zwischen Niveauentfernung, Quadrupolaufspaltung, magnetische Aufspaltung und der Elektronenstruktur sowie einen Überblick über den gegenwärtigen Stand der quantitativen Theorien. Ein besonderes Kapitel ist den Fragen der Meßtechnik gewidmet, worin auch die modernsten Methoden behandelt werden. In den weiteren Kapiteln werden die Anwendungsmöglichkeiten der Mößbauer-Spektroskopie angegeben.

Die Gesamtheit der Mößbauer-Parameter kann über folgende Fragen Aufschluß geben: Oxydationszustand des Atoms, wechselseitige Spin-Orientation der Elektronen, Ausmaß der Kovalenz in der Bindung des Atoms, Symmetrie der Elektronenwolke, Maß der Starrheit des Kristallgitters und Wechselwirkungen von Mößbauer-Kernen. Die nächstliegende und einfachste unter den Anwendungen der Mößbauer-Spektren ist die qualitative Analyse, d. h. die Identifizierung von Verbindungen. Der quantitativen Analyse kommt eine geringere Bedeutung zu, weil — obzwar die Methode empfindlich ist, wenn weitere Mößbauer-Kerne nicht im System vorliegen — in Gegenwart mehrerer Mößbauer-Kerne die Empfindlichkeit wesentlich abnimmt. Es ist nicht notwendig, daß die Untersuchung der Mößbauer-Spektren ermöglichende feste Phase niedriger Temperatur kristallin ist; sie kann auch glasigartig sein, wobei die Flüssigkeitsstruktur erhalten bleibt. Damit kommt der Mößbauer-Spektroskopie eine große Bedeutung bei der Untersuchung schnellgefrorener Lösungen zu. Mit dem Schnellfrier-Verfahren können die Hydratation, die kontinuierlich ineinander übergehende Solvatation und Komplexbildung sowie Elektronenaustausch-Reaktionen und Hydrolysevorgängen vorteilhaft untersucht werden.

Kurz nach ihrer Entdeckung kam die Mößbauer-Spektroskopie auch auf dem Gebiet der Biologie zum Einsatz. Die erste Möglichkeit dafür bot sich beim Eisenatom von Eiweißen auf Häminbasis. Eine außerordentliche Bedeutung erhielt die Methode für die Untersuchung von solchen Eisen-Schwefel-Eiweißen, die als solche allein, ohne den Eiweißanteil, nicht isolierbar sind, ferner für die Strukturuntersuchung von Eiweißen, die zur Speicherung von Eisenatomen fähig sind. Dazu kommt noch die Möglichkeit der Strukturuntersuchungen von Aminosäuren, Kohlehydraten, Fetten und Nukleinsäuren, die mit Eisenatomen Komplexe

zu bilden befähigt sind, sowie die Untersuchungen von biologischen Stoffen, die sonstige Mößbauer-Kerne enthalten, z. B. jodhaltige Eiweiße, kobalthaltige Vitamine usw.

Die Mößbauer-Spektroskopie spielt natürlich auch bei der Untersuchung der Struktur und der Phasenänderungen von Eisenlegierungen und intermediären Verbindungen eine wichtige Rolle.

Das Buch enthält 1400 Literaturhinweise, 130 Abbildungen und 100 Tabellen. Die Behandlungsweise des Stoffes macht es sowohl für Wissenschaftler als auch für Anwender der Mößbauer-Spektroskopie geeignet.

Das Manuskript des 1979 erschienenen Buches wurde von den Verfassern sicherlich viel früher dem Verlag übergeben. Damit könnte erklärt werden, daß einige Einheiten des außer Kraft gesetzten CGS-Systems hier und da noch vorkommen (Barn, Kilooersted, die dimensionlose dielektrische Konstante, Erg, Angström, sowie die unrichtige Schreibweise für mol · dm^{-3}).

Das Werk gibt ein genaues und umfassendes Bild über die Methode, die Möglichkeiten und die gegenwärtige Lage eines sich ständig weiter entwickelnden wissenschaftlichen Gebiets. Es wird den Forschern der interessierten Kreise viel Hilfe leisten können.

Gy. VARSÁNYI

LANDOLT-BÖRNSTEIN

Numerical Data and Functional Relationships in Science and Technology

New Series, Editor in Chief: K.-H. HELLWEGE
Group II: *Atomic and Molecular Physics*

Volume 9, *Magnetic Properties of Free Radicals*
Part c2, *Organic O-, P-, S-, Se-, Si-, Ge-, Sn-, Pb-, As-, Sb-Centered Radicals*

A. G. DAVIES, J. A. HOWARD, M. LEHNIG, B. P. ROBERTS, H. B. STEGMANN, W. UBER

Editors: H. FISCHER and K.-H. HELLWEGE

Springer-Verlag Berlin—Heidelberg—New York 1979, 320 pp

This book completes the third part, II/9*c* of Volume II/9 "Magnetic properties of free radicals". It deals with all organic radicals centered on heteroatoms except the nitrogen-centered radicals and the nitroxide radicals. Thus the organic O-, P-, S-, Se-, Si-, Ge-, Sn-, Pb-, As-, and Sb-centered radicals are covered here. The general introduction and the arrangement of the tables is the same as in the other parts of Volume II/9. [*cf.* Acta Chim. Acad. Sci. Hung., **98:** 497 (1978)]. The chapters are numbered consecutively in Vol. II/9 thus this book starts with Chapter 7 "Oxy- and peroxy-alkyl radicals". The next Chapter "Aroxyl radicals" completes the coverage of O-centered radicals. The vast majority of O-centered radicals are carbocycles. Among the O-centered radicals the hydroxyl and hydroperoxyl radicals are not included as they have been considered in the first part of Volume II/9 (*i.e.* in II/9*a*) among the inorganic radicals. There is a wealth of phosphorus-centered and sulphur-centered organic radicals, most notably phosphorane derivatives and sulphide derivatives. Compared with these, relatively few radicals with the other heteroatoms have been so far investigated.

The closing dates of the literature search for various Chapters vary between 1976 and 1978.

I. HARGITTAI

LANDOLT-BÖRNSTEIN

Numerical Data and Functional Relationships in Science and Technology

New Series, Editor in Chief: K.-H. HELLWEGE
Group II: *Atomic and Molecular Physics*

Volume 9, *Magnetic Properties of Free Radicals*
Part d1, *Organic Anion Radicals*

A. BERNDT, M. T. JONES, M. LEHNIG, L. LUNAZZI,
G. PLACUCCI, H. B. STEGMANN, K. B. ULMSCHNEIDER

Editors: H. FISCHER and K.-H. HELLWEGE
Springer-Verlag Berlin—Heidelberg—New York 1980, 904 pp

This book is the first part of Part d of Volume II/9 "Magnetic properties of free radicals". It covers the organic anion radicals. The second part of Part *d* expected also to appear soon will deal with the organic cation radicals and polyradicals. It will also contain an Index of substances for Volumes II/1 and II/9. This book is especially voluminous, well reflecting the ever-growing interest towards organic radicals and their magnetic properties. The general introduction and the arrangement of the tables is the same as in the other parts of Volume II/9. [*cf.* Acta Chim. Acad. Sci. Hung., **98,** 497 (1978)]. The chapters are numbered consecutively in Volume II/9 and this book contains the following ones:

12 Semidiones and related species
13 Semiquinones and related species
14 Anion radicals from nitro compounds
15 Anion radicals from nitroso compounds
15A Anion radicals from boron compounds
16 Hydrocarbon anion radicals
17 Anion radicals from heterocyclic compounds

Chapter 12 includes anion radicals with two or more conjugated carbonyl or thiocarbonyl groups, those from dionic systems as well as from trionic and tetronic systems, keto acids, polycarboxylic and thiocarboxylic acids, anhydrides, thioanhydrides, esters, thioesters, amides and imides. On the other hand, anion radicals from quinones and the protonated semidiones are found in Chapters 13 and 3, respectively. It is of special interest that data from *cis/trans* isomers are listed if available. Both the anion and cation radicals of semiquinone systems are covered in Chapter 13 the former vastly outnumbering the latter. The charge-transfer complexes of quinones are also dealt with here. The anion radicals from nitro groups of Chapter 14 are ordered primarily according to the number of double bonds conjugated with the nitro group. The coverage starts with systems without conjugated double bonds. Then follow the systems with conjugated double bonds. Finally the radicals with formal double bonds follow, *i.e.* the aromatic nitro compounds, an especially large group. Similar ordering principle has been observed in Chapters 15 and 15*A*. The vast majority of hydrocarbon anion radicals compiled in Chapter 16 are cyclic systems. The collection of the anion radicals from heterocyclic compounds (Chapter 17) does not contain the heterocycles with nitro and carbonyl groups as they have been dealt with elsewhere as ketyls, semidiones, semiquinones and nitroanions. The data are presented in the order of nitrogen-, oxygen-, sulfur-, selenium-, and phosphorous-containing heterocycles concluding with heterocycles containing two or more different heteroatoms.

The closing dates of the literature search for various Chapters vary between 1976 and 1978 with a few references even from 1979.

I. HARGITTAI

Liquid Crystals: The Fourth State of Matter

Ed. Franklin D. SAEVA.

Marcel Dekker Inc., New York – Basel

The book, consisting of 12 chapters, has been written by 15 leading specialists.

The first six chapters facilitate the comprehension of the basic concepts (*e.g.* nematic mesophases, cholesteric mesophases, smetic liquid crystals) with excellent illustrations and practical examples.

Information on thermotropic and lyotropic mesophases and on polarization optical and calorimetric measurements are pertinent also to liquid crystalline states occurring in biological systems. While a whole chapter is dedicated to biological membranes, data on the liquid crystal nature of plasma low density lipoproteins and of sterol derivatives are just indicated.

The chapter "Application of Liquid Crystals" gives a brief survey on the industrial and medical application of heat sensors and on the liquid crystal display of watches and pocket computers. This chapter tells us also that the introduction of liquid crystal flat television screens is to be expected in the next years.

This book will be of interest for persons unversed or well versed in the subject, working in the field of physics, chemistry, biology or industry.

D. SZABÓ

INDEX

PHYSICAL AND INORGANIC CHEMISTRY

ORGANIC CHEMISTRY

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ZOLTÁN CSÜRÖS

(1901—1979)

The death of Academician Zoltán CSÜRÖS is a loss deeply felt by Hungary's communities of higher education, science, and public life.

Born on the 6th February, 1901. Zoltán CSÜRÖS graduated in 1924 at the Department of Chemical Engineering of the Budapest University of Technical Sciences, and proceeded to work as demonstrator under Professor Géza ZEMPLÉN at the latter's reputable Chair of Organic Chemistry. In 1929 Zoltán CSÜRÖS received his Ph. D. degree and was offered a Rockefeller scholarship, which he could not accept, owing to family reasons.

In 1936 CSÜRÖS was named honorary lecturer, with plastics and lacquers as the special field of his studies; in 1938 he was advanced, as an associate professor, to the leadership of the Chair for Textile Chemistry, which he had founded. Full professorship was granted him in 1940. He was elected corresponding member of the Hungarian Academy of Sciences in 1946, and became Academician not much later. In 1947, Professor CSÜRÖS re-organized his department to cover the entire scope of organic chemical technology. Thousands of chemical engineering students made first acquaintance with organic chemical technology, textile- and plastics chemistry during the long era of Professor CSÜRÖS' pedagogical activity, obtaining inspiration and guidance for a lifetime to fulfil their duties in their profession and for the welfare of their nation.

CSÜRÖS began research work under the leadership of Professor ZEMPLÉN in the field of carbohydrate chemistry, and soon he became a co-worker of his master in important research projects, such as the elucidation of the structure of cellobiose. His Ph. D. thesis was concerned with the reactions of nitrosyl halides upon amino acids. In his further work CSÜRÖS remained faithful to the chemistry of carbonhydrates, glycosides, and natural macromolecules. He recognized the importance, when this was not yet obvious, of the chemistry and technology of synthetic and natural macromolecular substances, cellulose, leather, wool, paper and elevated the teaching of these subjects to university rank; in this he got a substantial start of a number of far-famed universities in industrially advanced countries. In his teaching and research work Professor CSÜRÖS was well aware of the needs of Hungarian industry, thus his research in textile chemistry significantly helped to raise the quality of Hungarian textile products; it is sufficient to refer to the method of crease-proofing by synthetic resins, a trail-blazing novelty at that time. He was early to realize that the Hungarian textile industry, a small one by international standards, cannot compete but by exceptionally fine qualities, attainable by sophisticated chemical finishing.

Well in advance of the factual emergence in Hungary of the relevant demands, Professor CSÜRÖS began to study, in the mid-forties, the topic of catalysis: the key problem of organic chemical industry. Thus he tackled the problems of selective hydrogenation and studies the rules which govern the catalytic oxidation of aromatic compounds. His ideas developed during these investigations served as the starting point in the work of an efficient school of Hungarian researchers of heterogeneous catalysis.

In the chemistry of synthetic polymers, his interest ranged from the rheology of plastified PVC systems, over the polymerization and co-polymerization of acrylonitrile and allyl compounds, to the study of the mechanism of the polymerization of caprolactam. It is impossible to miss the obvious that, besides contributing to the international development in this field of science by being the first to recognize several important correlations, Professor CSÜRÖS never lost Hungarian industrial production problems from sight. Production problems of intermediates of the organic chemical industry also belonged to his field of interest. In teaching as well as in research and laboratory exercises, he emphasized the importance of work on the chemistry of intermediary products, because he realized that the Hungarian petrochemical program, started at that time, will achieve full economic success if not only the main products (ethylene and propylene) find use, but also the other products and by-products are utilized. He also knew that the Hungarian pharmaceutical, agricultural-chemical, dye, and lacquer industries require the intermediates produced in this country, and the economical efficiency of these industries is greatly dependent on them.

Professor CSÜRÖS was also a brillant lecturer. Everything that has been just said shows that he anticipated by far, more correctly: that he precisely judged, the timeliness of his teaching work 10 to 15 years ahead; so that when expectable national demands became actual, well-prepared experts were there to cope with the tasks.

Professor CSÜRÖS was a public figure full of enthusiasm. He assumed responsible positions during the most difficult years of his University. Thus he served as Dean of the Faculty of Mechanical and Chemical Engineering in 1943—44, and as the Rector between 1946 and 1949, and again between 1957 and 1961. He prevented, as much as was possible, the removal by force of the equipment of the university at the end of World War II. The rebuilding of the devastated campus started when he was President of the University; after the counter-revolution he did his best to contribute to moral restoration.

Professor Csürös considered the popularization of scientific results a very important duty; he was member of the presidium of the Popular Science Association and chairman of the editorial committee of its Journal. He was also member of the presidium of the Hungarian Chemical Society; the president of the Teachers' Trade Union; a member of the presidium of the Hungarian Peace Council; the president of Section XI of the Patriotic Popular Front. Professor Csürös acted for long as the general editor of the journals ACTA CHIMICA ACAD. SCI. HUNG. and PERIODICA POLYTECHNICA.

His outstanding public work, the success of his scientific and educational endeavours were acknowledged by awards of high distinction. Thus he was recipient, in 1953, of a Kossuth Prize; four times, in 1956, 1958, 1961 and 1970, he was decorated with the Order of Labour, First Class; in 1970 he was honoured with the Liberation Jubilee Medal; and in 1973, on the occasion of his 70th birthday, he was awarded the Order, Second Class, of the Banner of the Hungarian People's Republic.

The Budapest University of Technical Sciences, and the Veszprém University of Chemical Technology, conferred upon Professor Csürös the rank of honorary doctor.

The death of Professor Csürös is a great loss for all of us who have been his students or collaborators. The memory of his colourful personality will be kept alive in the heart, and his many teachings will resound in the mind of thousands who have known him.

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THE BAEYER—VILLIGER OXIDATION OF 5α-CHOLESTANE-3,6-DIONE

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5α-Cholestane-3,6-dione (**1**) when treated with varying concentrations of perbenzoic acid (*p*-toluenesulfonic acid monohydrate as catalyst) invariably afforded 3-oxa-A-homo-5α-cholestane-3,6-dione (**2**). The product has been characterized on the basis of spectral properties and chemical transformations.

In continuation of our work on the Baeyer—Villiger oxidation of steroidal ketones [1, 2], we subjected **1** to perbenzoic acid oxidation.

Reaction of **1** with perbenzoic acid (different concentrations) in the presence of catalytic amounts of *p*-toluenesulfonic acid monohydrate furnished a single compound with m.p. 220 °C. This product analysed for $C_{27}H_{44}O_3$, which implied the insertion of only one oxygen atom into the substrate in the course of the reaction. Introduction of a single oxygen may lead to several possible isomeric monolactones such as **2**, **3**, **4** and **5**.

During our reinvestigation of the perbenzoic acid oxidation of 6-ketosteroids [2], we prepared the lactones **4** and **5**. The compound with m.p. 220 °C was different from these lactones, hence structures **4** and **5** could be eliminated. The IR spectrum had bands at 1735 (ε-lactone) and 1700 cm^{-1} (C=O). These IR values are in agreement with either of the structures **2** and **3**. Conclusive evidence in favour of **2** was obtained from the NMR spectrum. A broad multiplet for 2 protons at δ 4.27 is ascribable to methylene protons attached to ester oxygen, and its multiplicity can only result from its splitting by adjacent methylene protons. Thus the grouping $-O-CH_2-CH_2$ present only in **2** excluded the alternate structure **3** where the grouping $-O-CH_2-CH-$ would exhibit lesser multiplicity. In order to support the structure **2** chemically, the compound with m.p. 220 °C was subjected to alkaline hydrolysis which gave the hydroxy seco acid **6**, m.p. 188—190 °C. Furthermore, to substantiate the presence of a carboxylic function in **6**, it was treated with an excess of diazomethane which afforded the methyl ester **7**, m.p. 96 °C.

The noteworthy feature of this reaction is the formation of only the monolactone **2** and none of the conceivable alternative monolactones or dilactones.

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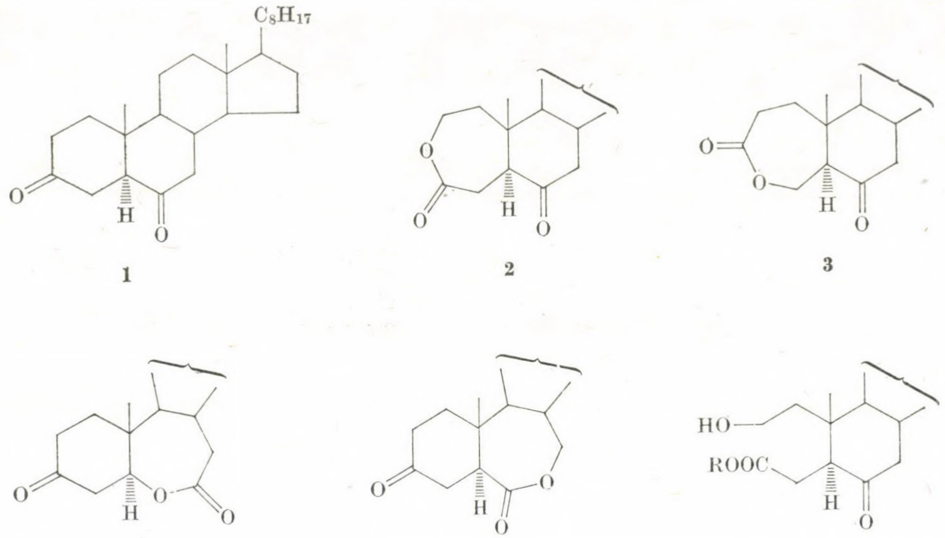

1 2 3

4 5

6 R = H

7 R = CH_3

Fig. 1.

It appears that steric features determine the course of reaction; the 3-oxo group being more exposed reacts predominantly instead of the relatively hindered 6-oxo group.

It is pertinent to mention here that at the beginning of the present century, WINDAUS [3] attempted to oxidize "Cholestandione" **1** by heating it at 70—75 °C for 3 hrs in acetic acid solution with an aqueous solution of ammonium persulfate. This was done long before the correct structure of cholesterol became established. With the nuclear location of the two oxo groups unknown, WINDAUS suggested the reaction product to be "Oxyketocarbonic acid" (m.p. 185—217 °C) which could be converted to its methyl ester (m.p. 105°). He expressed surprise at the response of only one oxo group towards the oxidizing agent, the other oxo group remaining intact. From our observations it seems likely that in the hands of Windaus the reaction followed a course analogous to ours, with the difference that under those reaction conditions, it went beyond the primary oxidation product **2** and yielded the hydroxy seco acid **6**.

Experimental

All m.p.'s are uncorrected. IR spectra were determined in Nujol with a Perkin—Elmer spectrophotometer. NMR spectra were run in $CDCl_3$ on a Varian A60 instrument with TMS as the internal standard. Thin-layer chromatographic plates were coated with silica gel. A 20% aqueous solution of perchloric acid was used as spraying agent.

Baeyer—Villiger oxidation of 1

To a solution of **1** [4] (2 g) in chloroform (35 mL) was added a chloroform solution of perbenzoic acid (1 mole-equivalent) along with a few crystals of *p*-toluenesulfonic acid monohydrate as catalyst. The reaction mixture was allowed to stand at room temperature for 48 hrs. The solvent was removed under reduced pressure and the residue extracted with an excess of ether. The ethereal solution was washed successively with water, $NaHCO_3$ solution (5%) and water, and dried over anhydrous Na_2SO_4 The removal of solvent gave a light brown residue which was chromatographed over silica gel (40 g) (fractions of 30 mL each were collected). Elution with benzene-ether (5 : 1) afforded **2**, which was crystallized from methanol to obtain 1.3 g of the pure product, m.p. 220 °C.

$C_{27}H_{44}O_3$. Calcd. C 77.88; H 10.57. Found C 77.90; H 10.52%.

ν_{max} 1735, 1700, 1050 cm^{-1}.

δ4.27 (m, 2H, C_2H_2), 3.15—2.3 (m, 5H, $C_{4a}-H_2$, C_5-H, C_7-H_2), 1.21, 0,92, 0.86 and 0.68 (5 methyl protons).

Treatment of **1** with 2 and 3 mole-equivalents of perbenzoic acid under similar reaction conditions invariably afforded **2**.

6-Oxo-2,3-seco-2-hydroxy-5α-cholestane-3-oic acid (6)

A solution of **2** (500 mg) in 5% methanolic NaOH (100 mL) was heated under reflux for 2 h. The solution was poured into water (500 mL), carefully acidified with dilute HCl and the precipitate thus obtained was extracted with an excess of ether. The usual work-up and removal of the solvent gave **6** which was crystallized from methanol to obtain 410 mg of the product, m.p. 188—190 °C.

$C_{27}H_{46}O_4$. Calcd. C 74.65; H 10.59. Found C 74.85; H 10.45%.

ν_{max} 3350—3200, 1710, 1700 cm^{-1}.

Methyl 6-oxa-2,3-seco-2-hydroxy-5α-cholestane-3-oate (7)

An ethereal solution of the seco acid **6** (200 mg) was treated with an excess of ethereal solution of diazomethane and the mixture was allowed to stand for 10 min. The excess of diazomethane was decomposed by the addition of a small amount of acetic acid. The usual work-up and removal of the solvent gave the methyl ester **7** (170 mg), m.p. 96 °C.

$C_{28}H_{48}O_4$. Calcd. C 75.0; H 10.71. Found C 75.20; H 10.63%.

ν_{max} 3500, 1720, 1710, 1190 cm^{-1}.

δ 3.63 ($COOCH_3$), 3.6 (m, 2H, C_2-H_2) 3.2—2.15 (m, 5H, C_4-H_2, C_5-H, C_7-H_2), 2.1 (m, 1H, O*H*, disappeared on shaking with D_2O), 1.23, 0,88, 0.8 and 0.6 (5 methyl protons).

*

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DYNAMISCHE ASPEKTE DES FESTEN ZUSTANDES

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Es wird die Funktion sogenannter Gitterdefekte im Hinblick auf die dynamischen Aspekte des festen Zustandes untersucht. Die statischen Aspekte werden unter Anwendung der Regeln für die Veränderungen der internuklearen Abstände des erweiterten Donator-Acceptor-Konzeptes illustriert. Punkt-Defekte werden als »Struktur-modifizierte und modifizierende Zentren« aufgefaßt. Betreffs ihrer Bildung wird auf Analogien bei der Eigenionisation in flüssigem Wasser verwiesen. Die Regelmäßigkeiten, durch welche im Gleichgewicht makroskopische Eigenschaften und Informationsgehalt erhalten werden, werden auf einen dynamischen Ordnungszustand zurückgeführt. Die Oberfläche enthält die Strukturinformation der eingehüllten Phase in integrierter Form und zeigt ein hochdifferenziertes, dynamisches Muster.

1. Einleitung

Die Strukturlehre von Kristallen wird von der Vorstellung des Idealkristalls beherrscht, obwohl er prinzipiell aus thermodynamischen Gründen nicht existieren kann: 1. müßte der Wert der Gleichgewichtskonstante für Platzwechselvorgänge null sein, was nur beim absoluten Nullpunkt möglich wäre [1], 2. dürfte er keine Verunreinigungen enthalten, 3. müßte seine Bildung im absolut leeren und feldfreien Raum erfolgen können und 4. müßte er unendlich groß sein, da jede Kristallgrenzfläche eine Unterbrechung des periodischen Aufbaues darstellt.

Die tatsächlich beobachteten Realkristalle welche eine fast unbegrenzte Vielfalt in Zusammensetzung und strukturellen Eigenheiten aufweisen, werden im bezug auf den fiktiven Idealkristall als »fehlgeordnet« beschrieben. Da diese Gesichtspunkte auf die Strukturen amorpher Phasen und von Gläsern überhaupt nicht anwendbar sind, ist eine einheitliche Beschreibung des festen Zustandes mit Hilfe der Idealvorstellung nicht möglich.

Ausgangspunkt naturwissenschaftlicher Erkenntnis kann nur die Beobachtung der Realität in ihrer Vielgestaltigkeit und Komplexität sein. Zur Beschreibung des festen Zustandes wollen wir daher von Realkristallen, amorphen Stoffen und Gläsern ausgehen und Überlegungen anstellen, welche dem Verstehen der Zusammenhänge dienen.

2. Das erweiterte Donor-Acceptor Modell

Zunächst wollen wir untersuchen, in welcher Weise das erweiterte Donor-Acceptor-Modell [2] herangezogen werden kann. Dieses hat sich vor allem zur Beschreibung des Verhaltens von Lösungen bewährt und ist grundsätzlich auf alle Arten molekularer Veränderungen anwendbar, da es nicht Zustände an sich sondern nur zwischen Molekülzuständen erfolgende Veränderungen erfaßt. In Übereinstimmung mit den Erfordernissen der Quantenmechanik werden die Veränderungen der Ladungsdichtemuster unter Berücksichtigung der zwischen den Molekülen erfolgenden Ladungsübertragungen und der Polarisationserscheinungen beschrieben. Bei der Wechselwirkung von zwei Molekülen wird das eine als Elektronendonator und das andere als Elektronenacceptor aufgefaßt. Der Elektronendonator greift mit dem Bereich hoher Elektronendichte am elektronenarmen Bereich des Elektronenacceptors an. Die Veränderungen der Elektronendichten setzen sich über den Gesamtbereich des betrachteten Systems fort [2].

In der Regel werden diejenigen internuklearen Abstände verlängert, an denen die Elektronenverschiebung vom elektropositivieren zum elektronegativeren Bindungspartner erfolgt und diejenigen verkürzt, an denen der Elektronenschub vom elektronegativeren zum elektropositiveren Bindungspartner eintritt. Erhöhung der Koordinationszahl bedingt Verlängerung und Erniedrigung der Koordinationszahl Verkürzung der am Koordinationszentrum vorhandenen Bindungen [2]. Je stärker eine zwischenmolekulare Wechselwirkung, desto größer sind die Verlängerungen der dem Angriff unmittelbar benachbarten internuklearen Abstände. Verlängerung einer Bindung führt zu Verkürzungen der diesen benachbarten Bindungen und umgekehrt. Als Regel gilt, daß sich alternierende Bindungsverlängerungen und Bindungsverkürzungen durch das gesamte molekulare System hindurch fortsetzen [2].

Zur Anwendung auf den festen Zustand wollen wir von den in Lösungen gewonnenen Erfahrungen ausgehen. Dazu ist es notwendig die gesamte feste Phase als ein einziges System aufzufassen [3].

3. Realkristalle

Realkristalle enthalten Fremdbausteine. Die Wirkungen der Fremdbausteine erstrecken sich im Prinzip über den ganzen Kristall und beeinflussen dessen makroskopische Eigenschaften [3]. So wird die Leitfähigkeit eines Germanium-Einkristalles nach Einbau eines Antimonatoms auf 100 Millionen Germaniumatome auf den hundertfachen Wert erhöht, oder Fluoreszenz in einem Zinksulfidkristall durch Einbau eines Kupferatoms auf 1 Million Zinkatome erzeugt. Selbst wenn es möglich wäre, einen Kristall herzustellen, der keine Verunreinigungen enthielte, so würde er trotzdem sogenannte Gitterbaufehler enthalten müssen, nämlich Leerstellen und Zwischengitterplätze (»Eigenfehlordnung«).

Wir wollen zunächst die Folgen der Besetzung eines Zwischengitterplatzes in einem aus gleichartigen Gitterbausteinen bestehenden Kristall aufgrund des erweiterten Donor-Acceptor-Modells erörtern: in einem kubisch-raumzentrierten Gitter verursacht die Besetzung eines oktaedrischen Lückenplatzes eine innere Verspannung, da die vom Zwischengitterplatz ausgehenden Abstände kürzer sein müssen, als diejenigen zwischen den benachbarten regulären Gitterbausteinen. Bei der Besetzung des Zwischengitterplatzes werden die Koordinationszahlen der dem Zwischengitterplatz benachbarten Gitterbausteine erhöht und daher alle von diesen ausgehenden Bindungen verlängert, was auch aufgrund der Pauling'schen elektrostatischen Valenztheorie [4] zu erwarten ist. Die Verlängerungen haben Verkürzungen der diesen benachbarten internuklearen Abstände zur Folge und diese wieder Verlängerungen in deren Nachbarschaft. Ein hiedurch entstehendes Strukturmuster ist in bildhafter vereinfachter zweidimensionaler Darstellung in Abb. 1 illustriert.

Die Koordinationszahlen der um eine Leerstelle angeordneten Gitterbausteine sind kleiner, als im Idealfall. Daher werden die internuklearen Abstände zwischen ihnen kürzer sein, als innerhalb der Elementarzelle [3]. Hiefür liegen experimentelle Befunde vor, nämlich an $TiC_{0,84}$, in welchem etwa jeder sechste oktaedrische Lückenplatz unbesetzt ist. In der Umgebung einer Lücke

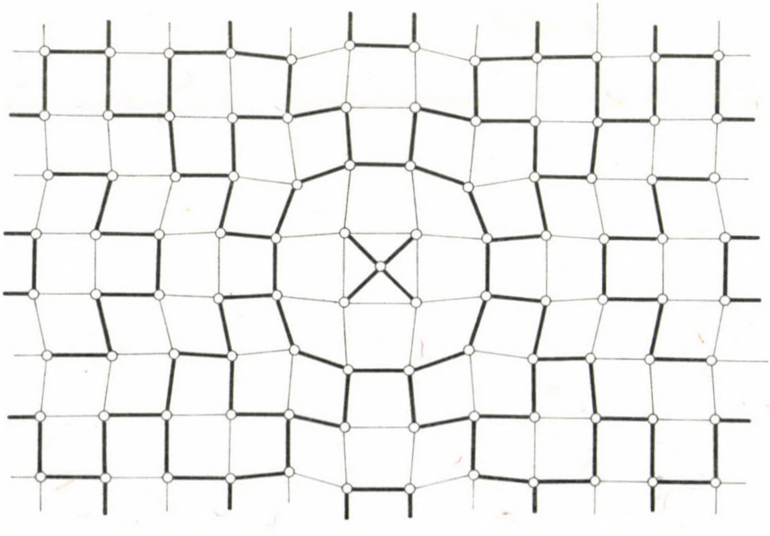


Abb. 1. Bildhafte, zweidimensionale Darstellung der inhomogenen Anordnung der Gitterbausteine um einen oktaedrischen Zwischengitterplatz welcher in ein kubisch raumzentriertes Idealgitter eingebaut wurde. Die dicken Striche bedeuten Verkürzungen und die dünneren Verlängerungen der internuklearen Abstände im Vergleich zu den idealen Gitterparametern

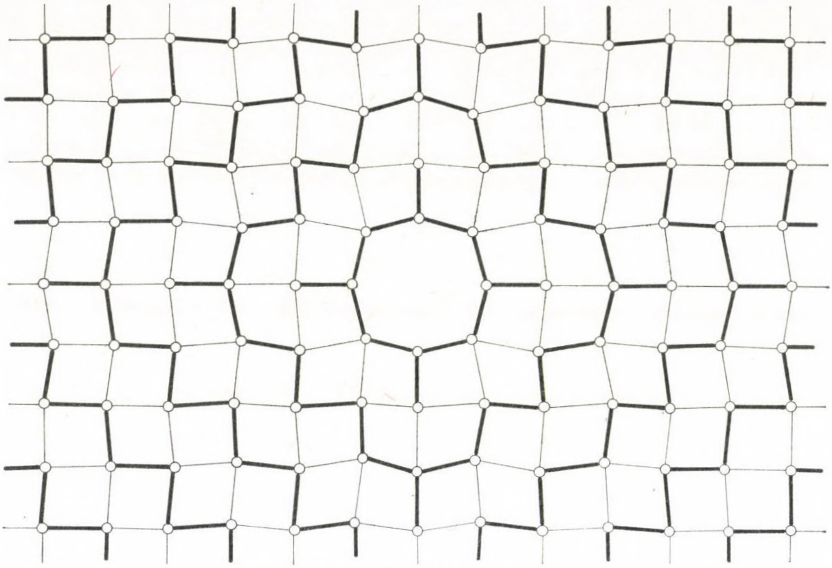


Abb. 2. Bildhafte, zweidimensionale Darstellung der Anordnung der Gitterbausteine um eine Leerstelle in einem Diamantgitter

sind die Metallatome zu den Kohlenstoffatomen verschoben und die M—C-Abstände entsprechend kurz [5]. Dasselbe Resultat wurde an unterstöchiometrischem Vanadincarbid auf Grund von röntgenographischen Untersuchungen erhalten und die long-range order Effekte aufgrund der NMR-Spektren gezeigt [7]. Auch um eine Leerstelle besteht also eine innere Verspannung, welche alternierende Verlängerungen und Verkürzungen zwischen den folgenden Bereichen verursacht, wie dies in vereinfachter zweidimensionaler bildhafter Darstellung in Abb. 2 illustriert ist.

Da bei der Herstellung der Abbildungen von einem regulären, d. h. idealisierten Raster ausgegangen wurde, sind auch diese Abbildungen nicht frei von idealisierten Einflüssen, können aber bestimmte Beziehungen veranschaulichen. Beispielsweise sind Ähnlichkeiten im Anordnungsmuster um eine Leerstelle und um einen Zwischengitterplatz erkennbar: das Bild der Abstandsverkürzungen um eine Leerstelle ist ähnlich demjenigen in der zweiten Sphäre um einen Zwischengitterplatz.

Schließlich wollen wir das Muster struktureller Inhomogenitäten besprechen, wie es durch Substitution eines regulären Gitterbausteines durch einen Fremdgitterbaustein gebildet wird. Die Auswirkungen der Substitution eines Germaniumatoms durch ein Antimonatom in einem Germaniumkristall [3] ist in Abb. 3 dargestellt. Da die Sb—Ge-Wechselwirkungen stärker sind, als die Ge—Ge-Wechselwirkungen, sind die Sb—Ge-Abstände kürzer, die benachbarten Ge—Ge-Abstände länger und die an diese angrenzenden Ge—Ge-

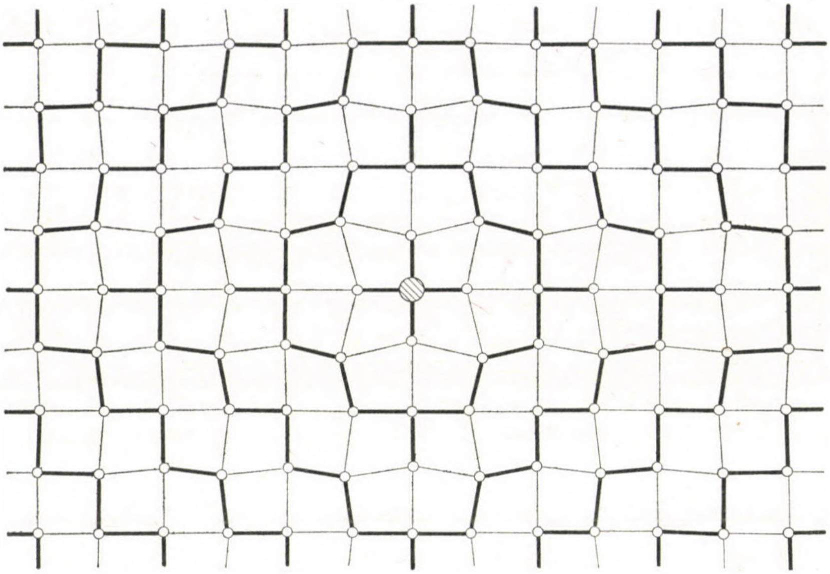


Abb. 3. Bildhafte, zweidimensionale Darstellung der Anordnung der Gitterbausteine in einem Germaniumkristall, in welchem eine Germaniumposition durch Antimon ersetzt wurde

Abstände wieder kürzer, als in der idealisierten Elementarzelle des Germaniumkristalls.

Die Meßbarkeit der Reichweiten richtet sich nach dem Ausmaß der Wechselwirkungen aller beteiligten Partner und der Deformierbarkeit des Gitters sowie nach der verwendeten experimentellen Methode. So ist die spektrale Aufspaltung der Acceptorzustände in Galliumphosphid-Kristallen nach Einbau von Sauerstoff oder Schwefelatomen bis auf eine Entfernung von 2 nm nachweisbar [8], die Verfolgung des Einflusses von Al-Atomen in Siliziumdioxid mit Hilfe der LEED-Methode bis über 6 nm [9] und der Effekt der Fluoreszenzlöschung bis zu Entfernungen von 150 nm feststellbar [10].

4. Struktur-modifizierte und modifizierende Zentren

Jede »Störstelle« ist also Zentrum einer charakteristischen Strukturmodifizierung als Folge der Wechselwirkung zwischen Störstelle u. umgebendem Gitter. Zur Illustration möge der Vergleich mit der Lösungschemie dienen, wo die Modifizierung der gelösten Teilchen durch das Lösungsmittel leicht gemessen werden kann. Die Modifizierung eines Ions durch das Lösungsmittel zeigt sich beispielsweise in der Variation der ^{23}Na chemischen NMR-Verschiebung in $NaClO_4$-Lösungen gleicher Konzentration in verschiedenen Lösungsmitteln [11]. In diesen Fällen besteht eine lineare Relation zwischen der chemischen

Verschiebung und der Donorzahl der Lösungsmittel. Aber auch bei gleicher unmittelbarer Umgebung eines Ions, z. B. von ^{59}Co in Trisäethylendiaminkobalt(III) wird die chemische Verschiebung vom Lösungsmittel dadurch beeinflußt, daß die Lösungsmittelumgebung über die Ligandenhülle eine Modifizierung des Koordinationszentrums bewirkt [12]. Darüber hinaus spielen Konzentration und Anwesenheit anderer Lösungsbestandteile eine entscheidende Rolle.

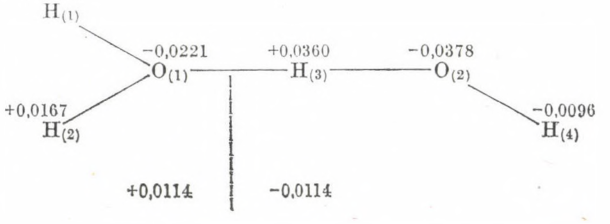
In einem Kristall wird jede »Störstelle« (»Defekt«) ebenfalls durch die ihn umgebenden Gittereigenschaften modifiziert. Ein Gitterbaustein an einem Zwischengitterplatz ist einer anderen Umgebung unterworfen, als an einem regulären Gitterplatz und hat daher unterschiedliche Eigenschaften. Selbst eine Leerstelle erfährt ihre charakteristische Prägung durch Wechselwirkungen mit dem sie umgebenden Gitter.

Demnach modifiziert jeder »Defekt« seine Umgebung und wird selbst durch diese modifiziert.

Zur Klarstellung der Begriffe ist es daher sinnvoll, an Stelle von »Störstelle« bzw. »Defekt« die Bezeichnung **„Strukturmodifiziertes und modifizierendes Zentrum"** zu wählen, wofür die Abkürzung **„SMM-Zentrum"** gebraucht werden kann.

Auch flüssiges Wasser würde ohne »strukturmodifizierende Zentren« nicht existieren [1, 13]. Als solche fungieren die durch Eigenionisation im thermodynamischen Gleichgewicht vorliegenden Wasserstoffionen und Hydroxidionen, sowie »Hohlräume«, welche mit Gasmolekülen »besetzt« sein können. In destilliertem Wasser kommt bei Zimmertemperatur ein strukturregulierendes Zentrum auf etwa 44 000 Wassermoleküle. Die Eigenionisation kann als Ergebnis der kooperativen Effekte zwischen den Wassermolekülen im Sinne des erweiterten Donor-Acceptor-Modells aufgefaßt werden [13].

Selbst im idealisierten dimeren Wassermolekül ist die Ladungsdichteverteilung unsymmetrisch [14]. Nur zwei der 4 Wasserstoffatome, nämlich $H_{(1)}$ und $H_{(2)}$ sind äquivalent und zwar stärker sauer, als in einem monomeren Wassermolekül. Hingegen ist die Azidität von $H_{(4)}$ zufolge der hohen Elektronendichte geringer, als im Monomeren. Die Bindungen $H_{(1)}$——$O_{(1)}$, $H_{(2)}$——$O_{(1)}$ und $H_{(3)}$——$O_{(2)}$ sind länger und die Bindung $O_{(2)}$——$H_{(4)}$ kürzer als m isolierten H_2O-Molekül. Daher muß die Anlagerung weiterer Wassermole-



küle zu unsymmetrischen Strukturen führen, wobei auch die Äquivalenz von $H_{(1)}$ und $H_{(2)}$ verloren gehen muß. Die bei der Bildung polymerer Wassermoleküle auftretenden kooperativen Effekte bewirken die weitere Verkürzung von $O_{(1)}$——$H_{(3)}$ und die weitere Verlängerung z. B. von $H_{(3}$——$O_{(2)}$. Diese mit steigender Molekülgröße wachsenden Bindungsabstände können dazu führen, daß Heterolyse unter Bildung eines Protons und eines Hydroxidions eintritt, welche jeweils an Wasserpolymere gebunden sind. Ihre Präsenz in flüssigem Wasser als Ergebnis kooperativer Effekte ist für die Stabilität der Flüssigkeit erforderlich. Sie sind SMM-Zentren, welche die Flüssigkeitsstruktur erst ermöglichen. Außerdem liegen in flüssigem Wasser Hohlräume vor, welche mit Gasmolekülen »besetzt« sein können [13] und welche als SMM-Zentren Strukturgradienten im flüssigen Wasser errichten.

In Analogie zur Eigenionisation des Wassers kann in einem Kristall die Stabilität von Leerstellen und Zwischengitterplätzen als Ergebnis kooperativer Wechselwirkungen zwischen den Gitterbausteinen aufgefaßt werden. Wie die Konzentration der Wasserstoffionen und der Hydroxidionen in reinem Wasser hängt die Konzentration der SMM-Zentren in einem gegebenen Kristall von der Temperatur ab. Das Produkt aus Leerstellenkonzentration c_1 und Konzentration der Zwischengitterplätze c_z ist konstant

$$c_1 \cdot c_z = K.$$

Mit steigender Temperatur nehmen Gleichgewichtskonstante K und Leerstellenkonzentration zu. Bei gegebener Temperatur bedingt Erhöhung von c_1 Erniedrigung von c_z und umgekehrt. Erhöhung der Leerstellenkonzentration bedeutet zugleich Erhöhung ihrer Mobilität, worauf wir noch zurückkommen werden.

Die Leerstellenkonzentration c_1 in Metallen ist bei Zimmertemperatur in der Größenordnung von 10^{-5} und beim Schmelzpunkt um etwa 2 Größenordnungen höher [15]. Die Aktivierungsenergien zur Bildung einer Leerstelle w betragen etwa 1 eV, zur Bildung eines Zwischengitterplatzes hingegen etwa 4 eV. In Metallen mit dichtester Kugelpackung ist daher die Leerstellenkonzentration größer als diejenige der Zwischengitterplätze [16]. Für die Beweglichkeiten innerhalb der festen Phase ist daher in erster Linie die Leerstellendichte maßgeblich. Die Anzahl der Leerstellen N_1, ist im Vergleich zur Gesamtzahl der Gitterbausteine N durch die folgende Gleichung gegeben [17]:

$$c_1 = \frac{N_1}{N} \equiv e^{-w/kT}$$

In Ionenkristallen kann die Zahl der SMM-Zentren bedeutend höher sein, z. B. beträgt diese in einem TiO-Kristall etwa 15% [18, 19] und in einem

Kristall von α-Silberjodid (welches oberhalb 140 °C stabil ist) können sich die Silberionen »irgendwo« im Kristall befinden, so daß der Kationenanteil des Kristalls als »quasigeschmolzen« im Anionennetzwerk aufgefaßt werden kann [17].

5. Das Strain-Field-Konzept

Es wurde darauf hingewiesen, daß jedes SMM-Zentrum nicht nur unter einem gewissen Spannungszustand steht, sondern zugleich einen solchen auf seine Umgebung ausübt. Die weitreichenden Effekte sind kontinuierlich. Ein Kontinuum wird gewöhnlich mit Hilfe des Feldbegriffes beschrieben. Das Feld, welches ein SMM-Zentrum unmittelbar umgibt, ist das sogenannte »strain-field« [20, 21]. Dieses Feld ist der Ausdruck des inhomogenen Wirkens von Kräften in entgegengesetzten Richtungen.

Die Wirkungen des strain-field, welches ein SMM-Zentrum umgibt, mögen mit denjenigen des Coulomb-Feldes in der Umgebung eines Ions verglichen werden. Die Hydratstruktur in der Umgebung eines Ions wird als Ausdruck der Wechselwirkungen zwischen Feld und Lösungsmittel aufgefaßt. Analog kann in einem Kristall die strukturelle Anordnung der Gitterbausteine in der Umgebung eines SMM-Zentrums als Ausdruck der Wechselwirkungen zwischen strain-field und Gitter aufgefaßt werden. Ähnlich, wie der Aufbau einer Solvathülle sowohl durch die Natur des Ions, als auch durch die Lösungsmitteleigenschaften geprägt ist, so wird die strukturelle Anordnung der Gitterbaustene sowohl durch die Natur des SMM-Zentrums, als auch durch die Gittereigenschaften bestimmt.

Für Halbleiterkristalle wurde gefunden, daß das strain-field auf Grund der Aufspaltung der Acceptorzustände fast unabhängig ist von der Größe des SMM-Zentrums. Die Aufspaltung hängt vor allem von den wechselseitigen elektronischen Effekten (Donor-Acceptor-Wechselwirkung) ab [8].

6. Wechselwirkungen zwischen SMM-Zentren

Da ein strain-field prinzipiell räumlich nicht begrenzt ist, müssen Wechselwirkungen zwischen den SMM-Zentren durch die sie umgebenden strain-fields erfolgen.

SMM-Zentren können einander anziehen oder abstoßen, sich in bestimmten Regionen anreichern [22, 23] und so innerhalb des Kristallgitters mikroskopische Raumbereiche unterschiedlicher Konzentration und unterschiedlicher Anordnung der SMM-Zentren errichten. Es wäre ein Irrtum eine Random-Verteilung der SMM-Zentren innerhalb des Kristallverbandes anzunehmen. Vielmehr coexistieren strukturelle Inhomogenitäten in Mikrobereichen des

Gitters [23—25]. Diese sind röntgenographisch oder mit Hilfe von Dampfdruckmessungen nachweisbar [23—25]. In vielen Fällen entziehen sich die Mikrophasen dem experimentellen Nachweis dadurch, daß sie entweder nur in kleinen Mengen vorhanden sind oder im Röntgendiagramm durch starke Linienverbreitungen verhüllt sind. Ihre Existenz bedeutet, daß ein Realkristall, welcher thermodynamisch ein homogenes System darstellt, strukturell durch ein Muster von Inhomogenitäten charakterisiert sein muß. Dieses Muster ist Träger von Qualitäten z. B. Informationen, welche weder statistisch noch meßtechnisch in ihrer Charakteristik erfaßt werden können.

7. Dynamische Aspekte

Neben lokalen Schwingungen der Bausteine, welche Oszillationen der Elektronendichten bewirken [26—28], sind die SMM-Zentren nicht an bestimmten Stellen des Gitters fixiert. Wie schon erwähnt, nehmen ihre Beweglichkeiten mit steigender Konzentration zu. Die die SMM-Zentren umgebenden Strukturgradienten entsprechen Gradienten des chemischen und elektrochemischen Potentials, welche die Triebkräfte für die in jedem Realkristall erfolgenden Platzwechselreaktionen darstellen. Jede räumliche Veränderung bewirkt strukturelle Veränderungen innerhalb mikroskopischer Bereiche und weitere Platzwechselvorgänge. Trotz solcher räumlicher Veränderungen bleiben die makroskopischen Eigenschaften des Kristalles und seine charakteristische Informationsspeicherung erhalten (Unter Informationsspeicherung verstehen wir allgemein die von außen im Kristall induzierten Veränderungen, deren Feststellung Informationen über den Ursprung der Veränderungen ergibt [29]. Beide sind gegenüber den Veränderungen in Mikrobereichen invariant.

Die Regelmäßigkeiten durch welche im Gleichgewicht sowohl die makroskopischen Eigenschaften, als auch der Informationsgehalt erhalten bleiben, beruhen auf einer bestimmten Ordnung innerhalb des Systems. Eine Ordnung ist nicht nur durch statische Anordnung gegeben, sondern auch durch Regelmäßigkeiten von Ereignissen, wie sie z. B. für dissipative Strukturen kennzeichnend sind. Im Kristall befindet sich ein Nebeneinander und Miteinander von sowohl statischen, als auch dynamischen Ordnungsaspekten.

In Übereinstimmung mit dem Ordnungsbegriff in der Biologie [31] ist der Ordnungszustand eines Systems umso höher,

1. je kleiner die Effekte durch Energieaufnahme,
2. je größer der Widerstand gegenüber Veränderungen,
3. je größer die Fähigkeit zur Informationsspeicherung,
4. je größer die Unabhängigkeit der Information von der Bewegung der Teilchen.

Der höchste Ordnungszustand in einem Kristall ist der dynamische Ordnungszustand, da er unabhängig ist gegenüber den tatsächlich Positionen der SMM-Zentren, welche durch die dynamische Ordnung kontrolliert werden.

SMM-Zentren sind nicht gleich. Leerstellen sind allgemein widerstandsfähiger gegen Veränderungen und haben höhere Beweglichkeiten, als andere SMM-Zentren. Die anderen Gitterbausteine sind in einem Zustand niederer Ordnung (eher statisch als dynamisch) und die Elektronen in einem noch niedrigeren. Im Rahmen dieser Darstellung wollen wir bewußt auf die unterschiedlichen Eigenschaften von Elektronen im sogenannten Leitfähigkeitsband und den sogenannten inneren Elektronen nicht eingehen. Die Gitterbausteine erscheinen in einem Netz feiner Wechselwirkungen eingesponnen, welche den dynamischen Veränderungen des Systems unterworfen sind. Dynamik bedeutet also nicht Bewegung mehr oder minder unabhängiger Teilchen, sondern ihr geordnetes Verhalten innerhalb des vorgegebenen komplexen Systems. Die dynamische Ordnung ist unabhängig von den jeweiligen Positionen der einzelnen Gitterbausteine, bzw. SMM-Zentren und sie repräsentiert die Information welche für das System charakteristisch ist. Was konstant bleibt, ist weder die lokale analytische Zusammensetzung, noch die Lagen der Gitterbausteine, sondern der charakteristische Ordnungszustand des Kollektivs. Sobald die dynamischen Veränderungen in sich ruhen, können wir von einer dynamischen Ordnung sprechen, welche ohne grobe äußere Einwirkung nicht verloren geht, also eine Art primitives Gedächtnis hat.

Der dynamische Ordnungszustand kann weder gemessen, noch mit Hilfe der Statistik erfragt werden, weil er qualitativen Charakter hat und daher nur am charakteristischen Reaktionsverhalten des Gesamtsystems erkannt werden kann: jede Veränderung des Ordnungszustandes bedingt entsprechende Veränderungen von beobachtbaren makroskopischen Eigenschaften.

Der dynamische Ordnungszustand enthält Ordnungselemente welche im Zuge der physikalischen oder der bloß gedanklichen Zerlegung des komplexen Systems in seine Bestandteile unwiderruflich verloren gehen [30]. **Was durch die Zerlegung an Präzision im Detail gewonnen werden mag, geht hiebei an Zusammenhangserkenntnis (Information) irreversibel verloren.** Daher kann das dynamische Ordnungsmuster nur im ungebrochenen Zusammenhang des realen Zustandes erfaßt werden. Es ist daher **prinzipiell unmöglich, Struktur und Eigenschaften der Materie allein aus der Kenntnis der Eigenschaften der Teilchen und ihrer unmittelbaren Wechselwirkungen abzuleiten.** Vielmehr müssen die Ordnungszustände des komplexen Systems, dem sie unterworfen sind, berücksichtigt werden. Wir können nur jedoch beschreiben, wie die dynamische Ordnung das Wechselwirkungsgefüge des Systems benützt und damit modifiziert und verändert. Damit kommen wir zu einem Primat des Qualitativen über das Quantitative.

Ordnung hat immer dynamische Aspekte. Im Prinzip läßt sich Ordnung nur unter Austausch mit der Umgebung aufrechterhalten und zwar nur im Ungleichgewichtszustand. **Die Aufrechterhaltung des thermodynamischen Gleichgewichtszustandes erfordert das Zusammenwirken mikroskopischer Ungleichgewichtszustände,** ohne welche der dynamische Charakter des makroskopischen Gleichgewichtszustandes nicht möglich wäre. Demnach bestehen kaum prinzipielle, aber sehr wohl entscheidende graduelle Unterschiede, vor allem betreffs der Komplexität zwischen konservativen und dissipativen Strukturen. Beide bedürfen grundsätzlich, wenn auch in stark unterschiedlicher Weise der Zufuhr von Energie.

Diese Aussagen stehen im Gegensatz zu dem in der Strukturlehre gebräuchlichen Ordnungsbegriff, nach dem als Ordnung die Primitivordnung im fiktiven Idealkristall angesehen und Abweichungen hievon als Manifestationen der Unordnung aufgefaßt werden [31]. Aufgrund dieser Philosophie wäre Austausch und Speicherung von Information auf Zustände der Unordnung beschränkt, im Einklang mit anderen unhaltbaren Aussagen, wie etwa derjenigen, daß der Realkristall ein Maximum an Unordnung repräsentiere [32].

8. Erscheinungen im Oberflächenbereich

Die Oberflächenbausteine haben niedrigere Koordinationszahlen, als die übrigen Gitterbausteine. Daher sind die internuklearen Abstände an der Oberfläche kürzer, als die mittleren Abstände im Kristall [2, 31]. Die von der Oberfläche ausgehenden Strainfields bewirken strukturelle Inhomogenitäten, vor allem in den Oberflächenbereichen. Selbst im Kristall eines Edelgases tragen die unter der Oberfläche liegenden Schichten zur Oberflächenenergie bei [34] und in einem Alkalihalogenidkristall ist der Einfluß der Oberfläche noch in der fünften Schichte feststellbar [35]. Die Meßbarkeit von Oberflächeneffekten erstreckt sich gegenwärtig auf Bereiche bis zu 10 nm [36].

Die Gitterkontraktionen im Oberflächenbereich bewirken beträchtliche Spannungen so daß Krater und Risse entstehen müssen, auch dann, wenn etwa durch Polieren eine ebene Oberfläche angestrebt wird. Die Bildung eines Kraters oder Risses führt zunächst zur Vergrößerung der Oberfläche und damit zu zusätzlichen Kontraktionen mit entsprechend hohen Oberflächenenergien. Vor allem an den Kraterrändern kommt es zu starken Krümmungen, welche mit den sich daraus ergebenden Gitterdeformationen im Oberflächenbereich in übertriebener Form bildhaft in zweidimensionaler Darstellung in Abb. 4 illustriert sind. Daraus ergibt sich die Notwendigkeit von Leerstellen mit innerer Oberflächenspannung, welche der äußeren Oberflächenspannung ein Gegengewicht bieten. In Abb. 4 scheint zwischen zwei Kratern nur eine Leerstelle auf, da zur Herausarbeitung des wesentlichen nur wenige Netzebenen

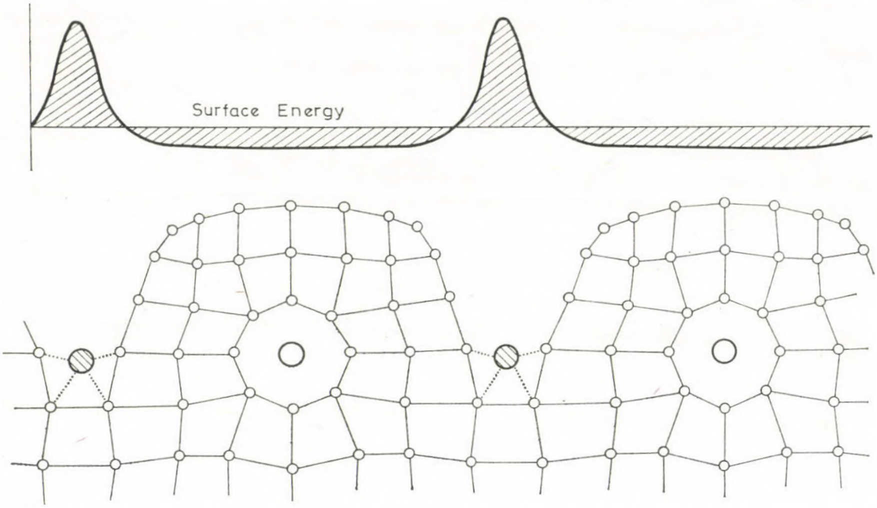


Abb. 4. Bildhafte, vereinfachte, zweidimensionale Darstellung der Anordnung von Gitterbausteinen in einem Oberflächenbereich. Die Kraterregionen entsprechen den höchsten lokalen Oberflächenenergien. Zur Stabilisierung der Gitterkontraktion und Krümmung der Oberfläche dienen Leerstellen. Der besseren Übersichtlichkeit halber wurde die Krümmung über betont und nur eine Leerstelle eingetragen

zwischen zwei Kratern eingezeichnet wurden. Tatsächlich ist die Anzahl der Netzebenen zwischen zwei Kratern wesentlich größer und mit ihr die Anzahl der Leerstellen im Oberflächenbereich. Ein Oberflächenbereich bedarf umso stärkerer Stabilisierung je stärker die Oberflächenkrümmung. Dementsprechend nimmt die Zahl der Leerstellen mit zunehmender Krümmung zu. Die lokale Leerstellenkonzentration nimmt mit abnehmendem Krümmungsradius der Oberfläche zu, und damit die Beweglichkeiten der Leerstellen [37, 38].

Die Bildung zusätzlicher Leerstellen im Zuge der Kraterbildung kann als Ergebnis von Gitterkontraktionen an der Oberfläche gedeutet werden. Diese entspricht stärkeren kooperativen Effekten zwischen den Gitterbausteinen als im Kristallinneren. Zur Bildung der Leerstellen müssen Gitterbausteine in energetisch günstigere Bereiche des Systems wandern. Bevorzugt sind hiebei die Tiefen von Kratern und Rissen. Die Einlagerung eines Bausteines in einen Krater führt zur Verminderung der lokalen Oberflächenenergie und nach der ersten und dritten Regel des erweiterten Donor-Acceptor-Konzeptes [2] zu Verlängerungen der benachbarten internuklearen Abstände im Krater. Hiedurch wird der Krater verengt. Die Veränderungen der internuklearen Abstände bleiben nicht auf diesen Bereich beschränkt, sondern setzen sich vor allem innerhalb des Oberflächenbereiches unter gleichzeitiger Wanderung von Leerstellen fort und zwar derart, daß die Kraterränder geweitet werden. Dieses Wechselspiel bewirkt alternierende Verengungen und Verbreiterungen, also

Pulsationen im Kraterbereich, deren Bedeutung an anderer Stelle näher ausgeführt werden wird.

Diese Effekte werden umso ausgeprägter sein, je größer die zusätzliche Leerstellenzahl und je größer die Zahl der in die Krater aus dem Gitter einfließenden Gitterbausteine, so daß eine Art plastischen Fließens eintritt. Durch die Summe aller Effekte werden erhebliche Energiebeträge bei der Bildung und der damit verbundenen (teilweisen) Auffüllung der Krater in deren Bereichen lokal in Freiheit gesetzt. Tatsächlich wird die Emission von Exoelektronen bei der Bildung neuer Oberflächenbereiche oder bei der Zerkleinerung von Kristallen beobachtet [39, 40]. Die photographische Registrierung der Emission der Exoelektronen ermöglicht sogar die topographische Erkennung von Kratern [39].

In nicht stöchiometrisch zusammengesetzten Festkörpern tragen die Fremdbausteine entscheidend zur Oberflächenstabilisierung bei. In den Oberflächenbereichen sind die Löslichkeiten schwer löslicher Fremdbausteine größer, als in anderen Kristallbereichen. Diese wandern daher in die Oberflächenzonen, wo sie sich anreichern und jeweils charakteristische Anordnungen einnehmen. So ist beispielsweise die Verteilung der im Oberflächenbereich von Iridium angereicherten Sauerstoffatome von der Entfernung von der Phasengrenzfläche abhängig, wobei in den unterschiedlichen Netzebenen die charakteristischen Merkmale des Inhomogenitätsmusters erhalten bleiben [41].

Demnach zeigt eine Kristalloberfläche ein hochdifferenziertes und dynamisch sich änderndes Oberflächenmuster. Die bekannten Inhomogenitäten sind nicht nur, wie bisher angenommen, topologischer Natur [42—44], sondern sie enthalten auch die Strukturinformation der sie einhüllenden Phase in integrierter flach-dreidimensionaler Form. Prinzipiell ist jeder Punkt des Gesamtsystems — wenn auch in unterschiedlicher Weise an der Oberfläche repräsentiert, welche somit an jedem Punkt der Oberfläche ein von diesem aus gesehenes Abbild der gesamten Phase bietet. Deshalb kann es nicht zielführend sein, die Eigenschaften eines Punktes isoliert als Eigenschaften desselben verstehen zu wollen.

9. Allgemeine Gesichtspunkte

Die entscheidende Rolle der dynamischen Eigenschaften wurde bisher zu wenig beachtet, da man den Idealkristall als höchstgeordnet den Betrachtungen zugrunde gelegt hat, welcher jedoch nur ein Bild einer gedachten Matrix vermittelt, auf welcher die qualitativen Eigenschaften erst »eingetragen« sein müssen. Der Kristall wird erst durch die dynamische Ordnung zum Informationsträger mit primitivem Erinnerungsvermögen.

Damit stehen die Veränderungen der Festkörper, wie sie durch Änderungen der Umgebung hervorgerufen werden, zu diesen über die Änderungen des dynamischen Ordnungszustandes in Beziehungen, welche auch für den Praktiker von Interesse sind. Beispielsweise wird die dynamische Ordnung durch Temperatur, Druck, Oberflächenbehandlung, Korngröße, Adsorption von Strahlung, umgebende Fehler oder durch mechanische Deformationen verändert, wodurch z. B. Oberflächenenergie, Reaktivität, katalytische und epitaktische Eigenschaften, Löslichkeit, Leitvermögen, Verhalten bei plastischer oder elastischer Deformation, Härte, Sprödigkeit, Adhäsion, entsprechend verändert werden. Über derartige Beziehungen soll in weiteren Arbeiten berichtet werden.

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ADSORPTION PROPERTIES OF HUNGARIAN RHYOLITE TUFFS CONTAINING MORDENITE AND CLINOPTILOLITE

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At 293 K, up to pressures of about 10^5 Pa carbon dioxide is bound practically exclusively in the pores of the zeolite component of rock samples. The mordenite (M) content and the clinoptilolite (C) content in each of four samples from various deposits were determined by comparing their CO_2 adsorption capacities with that of mordenite and clinoptilolite reference samples of known purity. The samples were converted into the H-form by deammoniation of the ammonium forms. The sample containing C in H-form has a greater adsorption capacity for Kr, N_2, SO_2 and CO_2 than the original rock. The capacity increases even further upon acid treatment. This is due to changes in the free pore dimensions. C-samples treated with acid are energetically more heterogeneous, their interaction with Kr and N_2 is much stronger. On the basis of characteristic energies obtained according to the Pore-Filling Theory and the isosteric heats of adsorption determined at low coverages, conclusions are drawn concerning the types of adsorptive interaction energies on H-C and on C treated with acid.

Introduction

Zeolite containing rocks are much less expensive than synthetic zeolites, hence their extensive application in industry and environment protection is to be expected. A series of adsorbents, even catalysts can be prepared by suitable treatment of rocks rich in zeolites. Like other substantial deposits of zeolite the world over, the sedimentary rocks of the Tokaj range contain two important varieties of zeolite, *viz.* clinoptilolite and mordenite; great amounts of these are present as rock constituents in microcrystalline form [1, 2].

In order to be able to utilize sedimental deposits of volcanic origin (rhyolite tuffs) as catalysts or adsorbents, first of all the nature of the component zeolite must be known. This requires the knowledge of its adsorption and ion exchange properties, chemical composition and dispersity as well as its secondary pore system, mineral composition, mechanical strength, *etc.* Thus the exact definition of the zeolite phase is of primary importance: this phase is principally responsible for the adsorption and catalytic properties of the given rock.

The physical and chemical properties of zeolites are relatively easy to change by means of ion exchange. In this way their molecular sieve properties can be modified with comparative ease [3], as can be their adsorption selectivity [4], catalytic [5] and some other properties. Among the modifications, the so-called H-zeolites, *i.e.* the decationized forms, represent a fundamental type of zeolite catalysts. Our studies concern mainly these H-forms.

In this paper we discuss the determination by gas adsorption, in comparison with ion exchange, of the zeolite content of Hungarian pyroclastic rocks which contain clinoptilolite or mordenite. Besides this we report on some characteristic features of adsorption on clinoptilolite.

Experimental

Geological and chemical characterization of the rocks

The sites in the Tokaj region, where the samples were collected, are listed in Table I together with a petrographical characterization [6] and the zeolite types (M for mordenite, C for clinoptilolite content) found in the rock by means of X-ray diffraction. In each sample substantial amounts of quartz (crystobalite) are also present.

Table I

Site, short description and main mineral constituents of the rock samples studied

No Mark	Site	Geological description	Main mineral component
I	Bodrog-keresztúr	Light green, hard, compact devitrified pumiceous zeolitic rhyolite tuff	M
II	Mezőzombor	Light green, hard, zeolitic, volcanic ooze tuff	M
III	Mezőzombor	Greenish grey zeolitic rhyolite tuff impregnated with hydrohaematite	M
IV	Mezőzombor	Greenish grey, microporous, hydrohaematitic zeolitic rhyolite tuff	M
V	Mád	Light greenish grey, hard, cemented zeolitic pumice	C
VI	Sátoraljaújhely	Dark greenish grey, dense, layered rhyolite tuff	C
VII	Mád	Greenish grey, crumbly, fibrous, pumiceous vitreous tuff	C
VIII	Tolcsva	Greenish light grey, hard, fine-grained, zeolitic, layered pyroclastic sandstone	C

The chemical composition of samples M I-IV is detailed in Table II, that of samples C V-VIII, in Table III. The Si to Al ratio is generally greater, due to contamination with silicon rich compounds, than in mordenite or clinoptilolite generally.

As reference substance we used a practically pure synthetic mordenite (M-NORTON, Norton Chem. Proc. Prod. Div., Worchester, Mass., U.S.A.) and a rock containing *ca.* 90% clinoptilolite (C-HECTOR, San Bernardino Co., Calif., U.S.A.) [7].

Table II

Chemical composition of the mordenite-containing rock samples studied

Component	M-I		M-II		M-III		M-IV	
	(wt.%)	$\left(\frac{\text{mmol}}{\text{g}}\right)$	(wt.%)	$\left(\frac{\text{mmol}}{\text{g}}\right)$	(wt.%)	$\left(\frac{\text{mmol}}{\text{g}}\right)$	(wt.%)	$\left(\frac{\text{mmol}}{\text{g}}\right)$
SiO_2	73.35	12.2	75.90	12.0	72.51	12.0	75.51	12.6
Al_2O_3	11.08	1.08	11.16	1.09	11.13	1.09	11.22	1.10
Fe_2O_3	0.90	0.056	0.70	0.044	1.4	0.087	1.2	0.075
H_2O	5.97	3.31	4.47	2.48	6.77	3.76	5.32	2.95
$\frac{Si}{Al}$	5.65		5.78		5.50		5.73	
	(wt.%)	$\left(\frac{\text{meq}}{\text{g}}\right)$	(wt.%)	$\left(\frac{\text{meq}}{\text{g}}\right)$	(wt.%)	$\left(\frac{\text{meq}}{\text{g}}\right)$	(wt.%)	$\left(\frac{\text{meq}}{\text{g}}\right)$
Na_2O	1.33	0.42	1.10	0.36	1.44	0.46	0.90	0.28
K_2O	5.48	1.16	5.33	1.12	4.89	1.04	4.12	0.88
MgO	0.15	0.074	0.77	0.38	0.82	0.40	0.88	0.44
CaO	1.70	0.60	0.54	0.18	1.05	0.38	0.88	0.32
$\Sigma \frac{\text{meq}}{\text{g}}$		2.25		2.04		2.28		1.92
Ion exchange capacity $\left(\frac{\text{meq}}{\text{g}}\right)$		0.74		0.55		0.75		0.66

Pretreatment of samples

Zeolites in the samples mentioned before were converted to the H-form either by deammoniation of the ammonium ion exchanged sample or by treatment with hydrochloric acid.

After comminution of the rock sample, 100 g of the particle size fraction between 1.0 and 1.6 mm was refluxed in 2 *N* aqueous ammonium nitrate (400 mL) for 4 hours. This operation was repeated twice. In the course of this treatment a great part of the mobile cations in the rock sample was replaced by ammonium ions. These ammonium ions were subsequently removed by heating the sample under reduced pressure and thus the H-form was obtained (in consequence of the process NH_4-zeol → NH_3 + H-zeol). The extent of ion exchange was determined by allowing the ammonia liberated from the sample upon heating to 1000 K to be absorbed by acid of known concentration and back-titrating the acid. These ion exchange figures, referring to unit mass of the so-called air-dry NH_4-form, are given in the last lines in Tables II and III.

With acid-resistant zeolites — as mordenite and clinoptilolite are — an acid treatment can also be used without the risk of destroying the crystal lattice. Acid treatment was carried out with 1 *N* hydrochloric acid in the same way as ion exchange with ammonium.

Methods

Before determining the adsorption isotherms the samples were kept at a pressure of about 0.1 Pa and at a temperature of 623 K for 8 hrs. Due to this treatment, the samples became completely dehydrated and deammoniated into the H-form. In what follows, the ad-

Table III

Chemical composition of the clinoptilolite-containing rock samples studied

Component	C-V		C-VI		C-VI		C-VIII	
	(wt.%)	$\left(\frac{\text{mmol}}{\text{g}}\right)$	(wt.%)	$\left(\frac{\text{mmol}}{\text{g}}\right)$	(wt.%)	$\left(\frac{\text{mmol}}{\text{g}}\right)$	(wt.%)	$\left(\frac{\text{mmol}}{\text{g}}\right)$
SiO_2	72.87	12.13	76.01	12.65	76.02	12.65	76.83	12.79
Al_2O_3	12.36	1.21	9.27	0.91	12.14	1.19	11.45	1.12
Fe_2O_3	1.14	0.07	1.60	0.10	1.21	0.08	1.17	0.07
H_2O	6.97	3.87	7.48	4.15	6.13	3.40	6.29	3.50
$\frac{Si}{Al}$	5.01		6.95		5.31		5.7	
	(wt.%)	$\left(\frac{\text{meq}}{\text{g}}\right)$	(wt.%)	$\left(\frac{\text{meq}}{\text{g}}\right)$	(wt.%)	$\left(\frac{\text{meq}}{\text{g}}\right)$	(wt.%)	$\left(\frac{\text{meq}}{\text{g}}\right)$
Na_2O	0.78	0.25	0.88	0.28	0.49	0.16	0.36	0.12
K_2O	2.49	0.53	2.06	0.44	1.72	0.36	1.33	0.28
MgO	1.57	0.78	0.10	0.05	1.13	0.56	0.82	0.41
CaO	1.78	0.64	2.57	0.92	1.14	0.40	1.72	0.62
$\Sigma\frac{\text{meq}}{\text{g}}$		2.20		1.69		1.48		1.43
Ion exchange capacity $\left(\frac{\text{meq}}{\text{g}}\right)$		1.19		1.07		0.65		0.66

sorbed amount of gas is related to one gram of sample thus pretreated. Adsorption isotherms were determined in a BET apparatus.

X-ray diffraction was measured with a Phillips PW-1050 large angle powder diffractometer using a $\lambda = 0.1141$ nm Cu K_α radiation filtered through a nickel foil.

Determination of the zeolite content of rhyolite tuffs

The determination of the zeolite content of any substance, *e.g.* rock samples or supported zeolite catalysts, which also contain other crystalline or amorphous components, is feasible if a property is measured which is peculiar to the zeolite alone, or which is in a direct and unequivocal relationship with the zeolite content. Thus there are cases when ion exchange capacity, adsorption capacity, the heat of wetting, or even the catalytic activity in a test reaction, are found to give valid conclusions concerning the zeolite content.

Often no quantitative conclusions can be drawn from X-ray powder diffractograms because the intensities of reflections are not necesserily proportional to the zeolite content due to some loss of short-range order [8]. Uncertainties arise also for zeolites present in nature exclusively, *e.g.* clinoptilolite, because no 100% pure standard reference samples of the same composition as the specimens to be studied are available. (The intensities of the individual reflections vary also with the cationic composition.) Moreover, some reflections due to the concomitant minerals may coincide with peaks characteristic of zeolites. Thus, various approximations should be used when X-ray diffraction is employed [9]. We find that it is advisable to compare quantitative data obtained by X-ray diffraction with results of other methods, for testing the reliability of the former.

As for the determinations of the zeolite contents of rocks, which we are going to describe, attention should be paid to the presence of various minerals and to the chemical composition of the zeolites which influence the ion exchange and adsorption.

Ion exchange

Total alkali and alkaline earth contents do not allow conclusions concerning the zeolite content of the various rocks because a significant amount of these ions is in the concomitant minerals and not in the zeolite phase. Neither can the zeolite content be derived from the total amount of exchangeable cations, *i.e.* from the total ion exchange capacity of the samples, because ion exchange is possible also with the non-zeolitic phase.

The ion exchange capacity of a rock sample is the amount of cation equivalents referred to 1 g air-dry rock sample (in equilibrium with a vapour pressure of 2000 Pa, at 293 K) that can be exchanged for ammonium ions upon the treatment described in the Experimental (*cf.* last line in Tables II and III).

Adsorption of carbon dioxide

If the adsorption capacity of the zeolite itself in the rock is determined, *i.e.* the sorption capacity of concomitant minerals is negligible, the zeolite content can be inferred from the adsorption capacity of rock samples. For this inference to be valid it is necessary that a suitable adsorbate should be chosen, which adsorbs only in the zeolite-micropores and practically not at all on the outer surface, and on other components of the rock. This latter condition can be checked by independent testing of the individual components involved (or of substances with similar structures) for adsorption properties under specific conditions. We have found that carbon dioxide adsorption up to about 10^5 Pa (p_r of to 2×10^{-2}) and 293 K practically satisfies all the requirements.

Preliminary studies have shown that the sorption capacity thus measured depends on the chemical composition of the zeolite, on the nature and distribution of the cations. Therefore, these uncertainties can be eliminated by measurements with samples in the H-form. Then the deviations of the sorption capacities of the rock samples can be regarded as being due to the different zeolite contents.

When preparing the H-form, *i.e.* in the course of the removal of water and ammonia from the zeolites investigated, their pore system becomes accessible without any damage of the crystal lattice of mordenite or of clinoptilolite. Upon adsorption, the micropores free from water and cations become saturated with the adsorptive. The adsorption isotherm is, generally, of type I. Between the boiling point at atmospheric pressure and the critical temperature of the adsorptive, these isotherms can be described with sufficient accuracy on the basis of the Pore-Filling Theory, by the equation

$$a = a_0 \mathrm{e}^{-\left(\frac{A}{E}\right)^n} \tag{1}$$

in which a is the adsorbed amount of gas, a_0 is the adsorbed amount of gas at saturation pressure, n is a small integer, E is the so-called characteristic energy, and A is the differential molar adsorption work to be calculated according to

$$A = RT \ln \frac{f_s}{p} \tag{2}$$

in which f_s is the fugacity of the adsorptive at saturation pressure and p is the equilibrium pressure [10].

CO_2 adsorption isotherms recorded up to 10^5 Pa ($p_r \approx 2 \times 10^{-2}$) at 293 K can be described by Eq. (1), and are linear when $\log a$ is plotted against A^3 (Fig. 1). The intercept of the extrapolated straight line gives the amount of adsorbed gas (a_0) at saturation pressure; its slope defines the characteristic energy E (*cf.* Table IV).

For the sake of comparison, carbon dioxide adsorption capacities and characteristic energies of the reference samples M-NORTON and C-HECTOR, both in H-form, were also determined (*cf.* last line in Table IV).

The characteristic energies E in Table IV differ for rock samples which contain mordenite and clinoptilolite but are practically independent of the adsorption capacities of rock samples with a given zeolite. (It should be noted that in our experience the characteristic energy E varies with the cation introduced by ion exchange.) This is in agreement with the fact that the adsorption of carbon dioxide occurs predominantly on the same mineral component, *i.e.* on the H-zeolite of the rock samples. The zeolite content of rock samples can be determined on the basis of both ion exchange and adsorption capacity when the values found are related to some suitable standard of both mordenite and clinoptilolite.

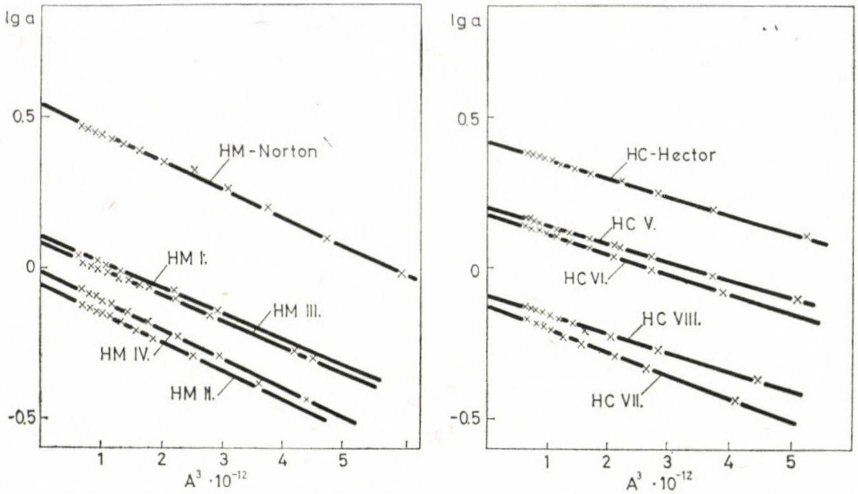

Fig. 1. Adsorption isotherms of carbon dioxide on rock samples which contain H-mordenite (HM) or H-clinoptilolite (HC), recorded at 293 K and plotted as log *a vs.* $A^3 \left(a, \frac{\text{mmol}}{\text{g}}; A, \frac{\text{J}}{\text{mol}}\right)$

Table IV

Characteristics of carbon dioxide adsorption on sample containing H-*mordenite* (HM) *or* H-*clinoptilolite* (HC)

Mark	E $\left(\frac{\text{kJ}}{\text{mol}}\right)$	n	a_0 $\left(\frac{\text{mmol}}{\text{g}}\right)$	Mark	E $\left(\frac{\text{kJ}}{\text{mol}}\right)$	n	a_0 $\left(\frac{\text{mmol}}{\text{g}}\right)$
HM-I	16.7	3	1.25	HC-V	19.3	3	1.61
HM-II	16.7	3	0.89	HC-VI	19.7	3	1.47
HM-III	16.7	3	1.25	HC-VII	18.8	3	0.71
HM-IV	16.7	3	0.98	HC-VIII	19.7	3	0.80
HM-NORTON	16.7	3	3.44	HC-HECTOR	19.7	3	2.59

Table V

Zeolite content (%) *of rock samples determined on the basis of ion exchange and adsorption capacities*

	M-I	M-II	M-III	M-IV	C-V	C-VI	C-VII	C-VIII
Ion exchange	32	24	32	28	53	48	29	30
Adsorption	36	26	36	29	56	51	25	28

With the ion exchange capacity taken from the literature [11] as 2.32 meq/g for mordenite, and 2.23 meq/g for clinoptilolite (calculated for the air-dry NH_4-forms) the figures given in the first line of Table V characterize the zeolite content of the samples tested.

The practically 100% pure HM-NORTON mordenite and the 90% pure HC-HECTOR clinoptilolite specimens were the reference standards for adsorption capacity *(cf.* last line in Table IV). The zeolite contents thus obtained are shown in the second line of Table V.

The two zeolite contents, determined by different techniques agree rather well, especially when also the mineral inhomogeneity of the rocks is considered.

Characterization of the clinoptilolite structure by gas adsorption isotherms

For this study, samples from Rátka in the Tokaj region were used. This is a deposit rich in clinoptilolite, whose content calculated from ammonium exchange capacities and carbon dioxide adsorption amounts to 63 and 60%, respectively. The chemical composition of the native rock, the product ion exchanged with a solution of ammonium chloride, and the product treated with a 1 *N* hydrochloric acid, are given in Table VI. These samples were tested for krypton and nitrogen adsorption at 77 K, for carbon dioxide adsorption at 195 K, and for sulfur dioxide at its boiling point at atmospheric pressure, *i.e.* at 263 K (relevant isotherms are shown in Fig. 2).

Table VI

Chemical composition of the clinoptilolite-containing native rock before and after treatment with 1N hydrochloric acid and ion exchange with NH_4Cl

Component	Native rock		Sample treated with 1 *N* HCl		NH_4^+-ionic form	
	(wt.%)	$\left(\frac{mmol}{g}\right)$	(wt.%)	$\left(\frac{mmol}{g}\right)$	(wt.%)	$\left(\frac{mmol}{g}\right)$
SiO_2	80.3	13.4	85.4	14.2	83.7	13.9
Al_2O_3	11.4	1.1	9.7	1.0	12.4	1.2
Fe_2O_3	1.1	0.7	0.07	0.05	1.2	0.07
$\frac{Si}{Al}$	6.1		7.17		5.8	
	(wt.%)	$\left(\frac{meq}{g}\right)$	(wt.%)	$\left(\frac{meq}{g}\right)$	(wt.%)	$\left(\frac{meq}{g}\right)$
Na_2O	0.27	0.09	0.27	0.09	0.19	0.06
K_2O	3.26	0.69	2.61	0.55	1.98	0.42
MgO	0.67	0.33	0.23	0.10	0.27	0.13
CaO	2.89	1.02	1.00	0.36	0.30	0.11
$\Sigma \frac{meq}{g}$		2.13		1.0		0.72

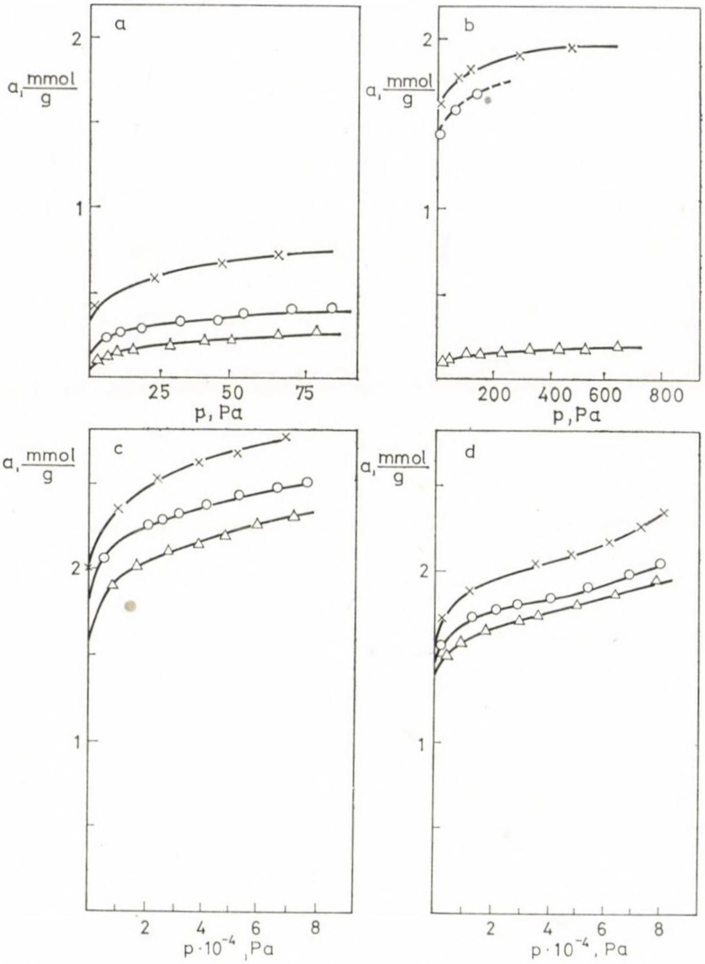

Fig. 2. Adsorption isotherms for the clinoptilolite-containing Rátka deposit (Δ), for its H-form prepared from the ammonium form by means of thermal decomposition (○) and for its H-form prepared by means of acid treatment (×); *a)* krypton adsorption isotherms at 77 K; *b)* nitrogen adsorption isotherms at 77 K; *c)* carbon dioxide adsorption isotherms at 195 K; *d)* sulfur dioxide adsorption isotherms at 263 K

Krypton and nitrogen are the most poorly adsorbed on the untreated rock samples. The adsorbed amounts of krypton and nitrogen show that the outer surface of clinoptilolite crystallites in native rock samples are mainly responsible for this adsorption. (The specific surface calculated from krypton adsorption isotherms is 25 m^2/g, therefore, the clinoptilolite crystallite size is 100 nm, in good agreement with electron microscopy (Fig. 3) and with studies relevant to diffusion kinetics [12]).

After deammoniation, subsequent to ammonium ion exchange, the adsorption capacity of the rock sample is increased. It is interesting that this

Fig. 3. Electron micrograph of a rock sample containing clinoptilolite (Rátka). The mark represents 1 μm

increase is substantially greater for nitrogen than for krypton. The reason is that the free pore size of clinoptilolite has become greater in consequence of cation removal and the space filled by the proton bound to the lattice oxygen is very small. This has the effect that krypton, with its larger critical diameter ($d_{cr} = 0.39$ nm) cannot whereas the somewhat smaller nitrogen ($d_{cr} = 0.37$) can just enter the clinoptilolite pores at 77 K. Of course, this entering proceeds very slowly indeed, owing to the very slight difference in size between the pores and nitrogen molecules. Even after two hours no equilibrium with respect to nitrogen is reached; this is why this "isotherm" is shown by a dotted line in Fig. 2b.

The adsorption capacity increases further in the course of treatment with hydrochloric acid, because, in addition to partial ion exchange, some of the $\geqslant$Al—O—Si$\leqslant$ bonds are hydrolyzed and, due to hydrolysis of the four bonds around aluminium, the latter is also dissolved from the zeolite lattice (and most probably from other components of the rock sample, too). In consequence of this, the internal surface of clinoptilolite becomes accessible for both krypton and nitrogen.

The micropores of the three samples at the temperatures of the experiment are accessible for both carbon dioxide and sulfur dioxide. Also in this

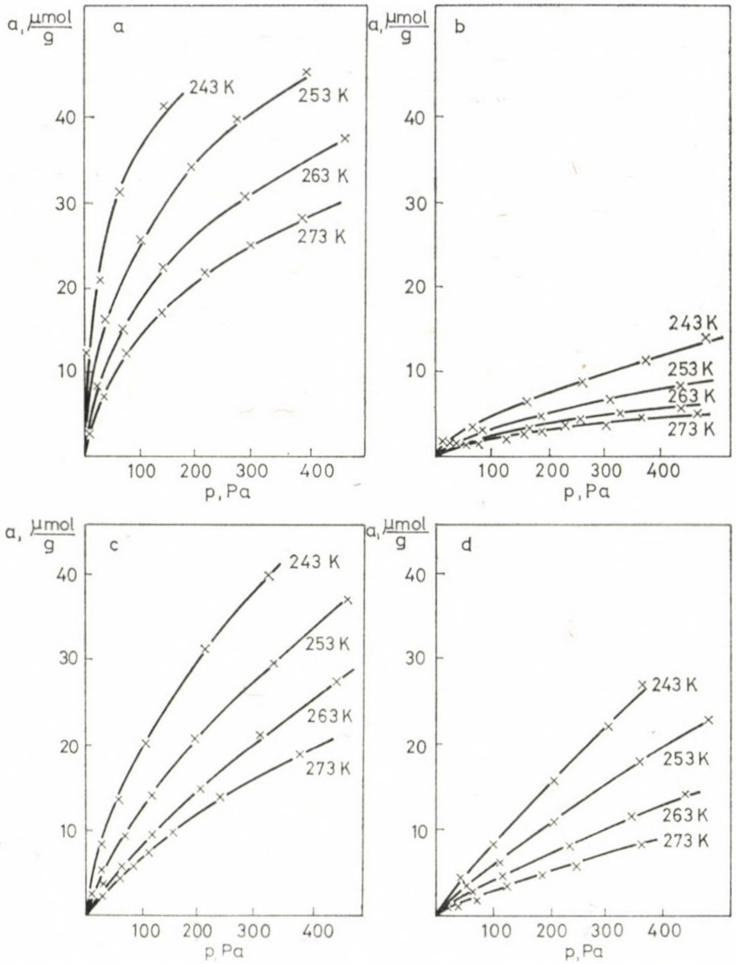

Fig. 4. Adsorption isotherms at 243, 253, 263 and 273 K, relevant to the adsorption of, *a)* nitrogen on H-clinoptilolite prepared by acid treatment, *b)* nitrogen on H-clinoptilolite prepared from its ammonium form, *c)* krypton on H-clinoptilolite prepared by acid treatment, *d)* krypton on H-clinoptilolite prepared from its ammonium form

instance the H-form offers greater pore volumes for the adsorbate than the original sample, containing relatively large alkali and alkaline earth cations. Consequently, the adsorption capacity of the H-form is somewhat greater. A further small increase of adsorption capacity is the result of treatment with hydrochloric acid since dissolution of aluminium also occurs beside protonic ion exchange and this produces further pores or makes others accessible (*cf.* uppermost curves in Figs 2c and 2d).

The treatment with acid or the thermal decomposition of the NH_4-form results in derivatives with different Si to Al ratios, cationic composition and

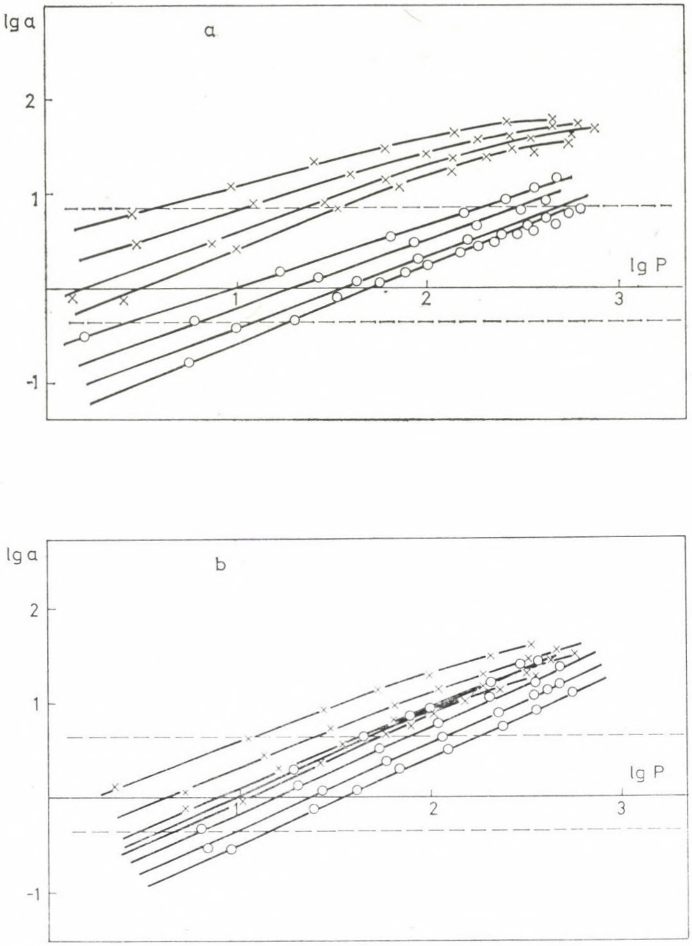

Fig. 5. Plot of log *a vs.* log *p* from adsorption isotherms $\left(a, \frac{\mu\text{mol}}{\text{g}}; p, \text{Pa}\right)$ for; *a)* adsorption of nitrogen, *b)* adsorption of krypton on H-clinoptilolite prepared by acid treatment (×) and from its ammonium form by thermal decomposition (○)

sorption capacities. While chemical analysis gives an overall composition of the rock, the adsorption properties correlate with the zeolite phase.

The energy of interaction between the adsorbate and zeolite depends, on the one hand, on the nature of the adsorbate, and on the other hand, on the crystal structure of zeolite and on the type and amount of cations in the zeolite lattice. Therefore, the clinoptilolite samples pretreated in two different ways are characterized with the isosteric adsorption heats of krypton and nitrogen. These heats were calculated from adsorption isotherms determined at 243, 253, 263 and 273 K (Fig. 4).

The isotherms refer to the clinoptilolite phase alone, because adsorption on the most active concomitant, montmorillonite, under these conditions is less by several order of magnitude; at these temperatures, far above 77 K, there is no significant difference between the adsorption of krypton and nitrogen. This also suggests that both adsorb in pores.

According to **Barrer** and **Paterson** [13], adsorption isotherms on synthetic H-mordenite at filling lower than 0.5%, can be described by Freundlich's equation

$$a = Kp^{\frac{1}{n}} \tag{3}$$

in which a is the adsorbed amount, p is the equilibrium pressure, K and n are constants.

The $\log a$ *versus* $\log p$ representation of the isotherms in Fig. 4 have linear initial sections (Fig. 5) supporting the validity of Eq. (3). The parameters of the straight lines give the constants of Eq. (3) (*cf.* Table VII). The validity of Henry's law ($n \approx 1$) can be concluded at low krypton saturations of both clinoptilolite derivatives.

The isosteric heat of adsorption, q_{st}, was calculated as usual, on the basis of the Clausius-Clapeyron equation, since the isotherms as determined represent real equilibria:

$$q_{\mathrm{st}} = H_g - H_a = -R\left(\frac{\partial \ln p}{\partial \frac{1}{T}}\right)_a$$

in which H_g is the molar enthalpy of the gas phase, H_a that of the adsorbate.

Table VII

Constants of Freundlich's equation

T (K)	From nitrogen adsorption isotherms on H-clinoptilolite prepared			
	from its NH_4-form		by acid treatment	
	K	n	K	n
273	0.048	1.21	0.563	1.12
263	0.060	1.31	0.795	1.16
253	0.087	1.45	1.096	1.31
243	0.126	1.54	1.380	1.78
	from krypton adsorption isotherms			
273	0.076	1.06	0.209	1.04
263	0.102	1.07	0.276	1.04
253	0.162	1.08	0.437	1.16
243	0.235	1.09	0.725	1.22

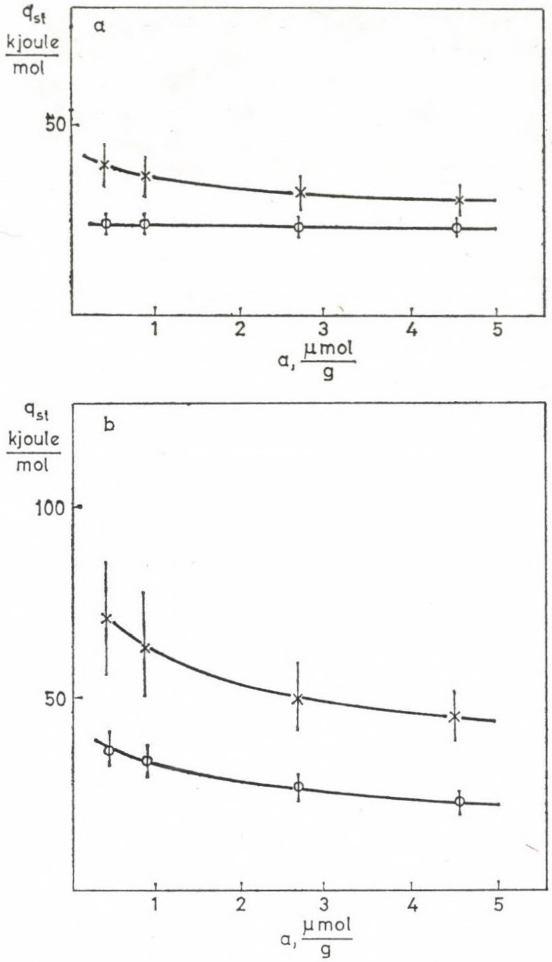

Fig. 6. **Isosteric heat of adsorption as a function of the amount of gas adsorbed; *a)* heat of krypton adsorption, *b)* heat of nitrogen adsorption on H-clinoptilolite prepared by acid treatment (×) and from its ammonium form by thermal decomposition (○)**

The *p* values pertinent to the *a* values were obtained from Fig. 5 at various temperatures. That range of *a* (broken line in Fig. 5) where the isosteric heats of adsorption were calculated is determined as follows. The lower limit is given by *a* when this and the corresponding equilibrium pressure *p* could be accurately measured; the upper limit is given by the value at which Freundlich's isotherm equation is still valid, *i.e.* where the curves in Fig. 5 are linear. Figure 6 shows the isosteric heat of adsorption as a function of the coverage by nitrogen or krypton on H-clinoptilolite samples prepared by acid treatment or from the ammonium form by heat treatment.

Discussion

At low coverages, the heat of adsorption is the sum of various energies of interaction, such as dispersion, short-range repulsion and electrostatic interaction [14].

Dispersive attraction and repulsion at small distance will always be in evidence, irrespective of the nature of adsorbent and adsorbate. Dispersive energy in zeolites derives mainly from the interaction between lattice oxide ions and adsorbate; owing to the smaller number and lower polarizability of cations, the dispersive energy of these is not significant.

The various alkali and alkaline earth ions are only partly shielded by the oxide ions of the zeolite; in their local electrostatic field also the polarization is effective. On the other hand, the protons are almost completely shielded by the oxide ions of the lattice, therefore, the polarization component in the interaction energy is much smaller in the H-forms than in the alkali or alkaline earth forms.

The interaction of dipole or quadrupole molecules with the electrostatic field of the cations adds the so-called dipole or quadropole energy to the energy of adsorption.

Figure 6a demonstrates that the isosteric heat of adsorption of krypton is greater on an acid treated adsorbent than on an H-form made from the NH_4-form. The decrease of adsorption heat with increasing adsorption points to the surface heterogeneity. The dissolution of aluminium results in energetically different adsorption sites where more lattice oxygen can surround the adsorbed krypton atoms. As a consequence of this, also the dispersive interaction energy may become greater. Heterogeneity, and greater heats of adsorption are caused by alkali and alkaline earth cations which remain in the zeolite after acid treatment. Krypton may become adsorbed also in the electrostatic field of these; then also polarization forces are exerted besides dispersive ones.

The heterogeneity of the adsorption energy more pronounced for polarizing force of the cations, and for greater polarizability and dipole or quadrupole moment of the adsorbate molecule [15]. Just because of this, our clinoptilolite samples prove to be more heterogeneous towards the quadrupole nitrogen than towards krypton and also adsorb nitrogen with greater strength (*cf.* Figs 6a and 6b). The adsorption heat of nitrogen on acid-treated samples is significantly higher than that of krypton. This difference cannot be explained by supposing stronger dispersive and polarizing interactions; it may be the result first of all of strong cation-quadrupole interaction.

At large coverages, i.e. at $a/a_0 = 1/e$, when $A = E$ [*cf.* Eq. (1)], characteristic energy E indicates the strength of interaction; E has been determined (*cf.* Table IV) for the adsorption of carbon dioxide both on mordenite and clinoptilolite. Inspite of the many similarities of these two zeolites (similar Si to Al ratios, similar ion exchange capacities, specific pore volumes, dominance of four- or five-membered tetrahedron rings in their crystal structures), their characteristic energies E are different: 16.7 kJ/mol for mordenite, and 19.7 kJ/mol for clinoptilolite, both determined with samples in the H-form. In such cases [14], the electrostatic interaction with the quadrupole carbon dioxide being weak, the dispersive energy can be the most important component of interaction energy. This dispersive energy is greater in clinoptilolite which has smaller pores, thus the adsorbate interacts with a greater number of lattice oxide ions than in the larger pores of mordenite.

*

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MASSENSPEKTREN ALICYCLISCHER VERBINDUNGEN, IX*

3- UND 4-ACETOXYHETERACYCLOHEXANE

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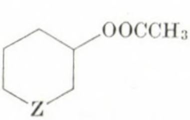
Die massenspektrometrische Fragmentierung der bifunktionellen 3- und 4-Acetooxyheteracycloalkane mit O, S, SO_2 und NCH_3 als Heteroatom bzw. als Heteroatomgruppierung ist diskutiert und mit dem massenspektrometrischen Abbau der entsprechenden monofunktionellen Heteracyclohexane und des Acetoxycyclohexans verglichen worden. Dabei zeigte sich, daß beide funktionellen Gruppen den Abbau determinieren, daß aber auch beide funktionellen Gruppen sich beim massenspektrometrischen Abbau gegenseitig beeinflussen.

Die deutlichen Unterschiede im Fragmentierungsverhalten der 3-substituierten und der 4-substituierten Acetoxyheteracyclohexane erlauben eine gute Unterscheidung der jeweiligen Isomeren mit Hilfe ihrer Massenspektren.

Das massenspektrometrische Fragmentierungsverhalten des monofunktionellen Acetoxycyclohexans [2, 3] und der monofunktionellen Heteracyclohexane [4—7] ist gut bekannt. Demgegenüber liegen zum massenspektrometrischen Abbau bifunktioneller Verbindungen, insbesondere zur Fragmentierung der Acetoxyheteracyclohexane, kaum Untersuchungen vor [4, 8, 9].

Wir haben daher im Rahmen unserer systematischen Untersuchungen zum Nachweis intramolekularer Wechselwirkungen in Heteracycloalkanderivaten die Massenspektren einer repräsentativen Reihe von 3-Acetoxyheteracyclohexanen **1** und von 4-Acetoxyheteracyclohexanen **2** aufgenommen und diskutiert. (Das Massenspektrum von 3-Acetoxyoxacyclohexan **1d** ist bereits von Budzikiewicz und Grotjahn [9] diskutiert worden).



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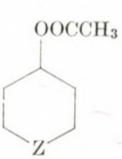

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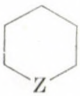

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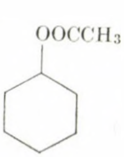

4

a: Z = S
b: Z = SO_2
c: Z = NCH_3
d: Z = O

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* VIII. Mitt., vgl. [1]

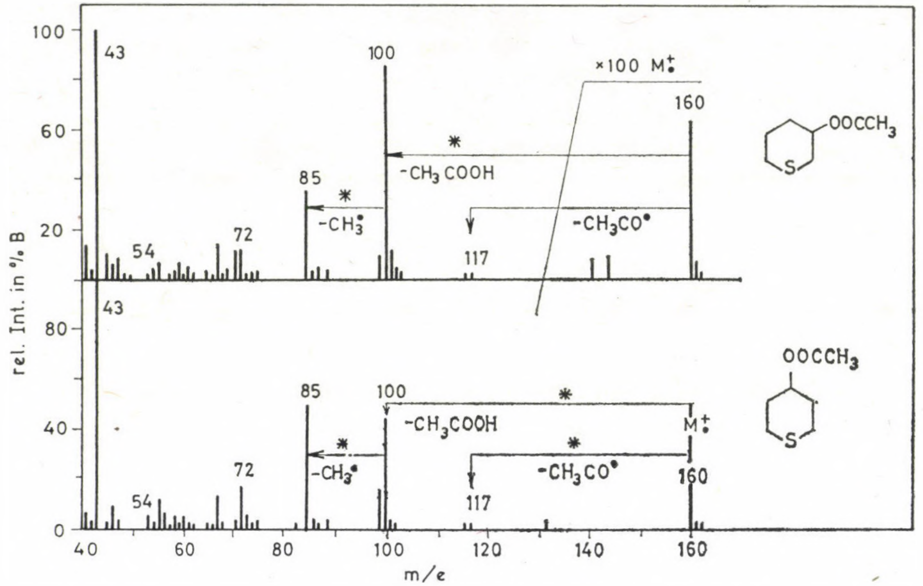


Abb. 1. 70 eV-Massenspektren von 3-Acetoxythiacyclohexan **1a** und von 4-Acetoxythiacyclohexan **2a**

Dabei interessierten einmal Gemeinsamkeiten und Unterschiede in der Fragmentierung dieser Verbindungen im Vergleich zu den Heteracyclohexanen **3** und zum Acetoxycyclohexan **4** sowie Unterschiede im massenspektrometrischen Abbau zwischen den Stellungsisomeren **1** und **2**.

Acetoxythiacyclohexane 1a und 2a

Abbildung 1 zeigt die 70 eV-Massenspektren von 3-Acetoxythiacyclohexan **1a** und von 4-Acetoxythiacyclohexan **2a**. Die Molekülionenpeaks liegen bei der Massenzahl 160 und haben eine Intensität von 0,2% bezogen auf $\%\Sigma_{39}$ (Verbindung **1a**) bzw. von 4,8% (Verbindung **2a**). Beide Intensitätswerte liegen zwischen denen für Thiacyclohexan (10,6%) und für Acetoxycyclohexan (0,01%). Der größere Betrag für $M^{+.}$ im Spektrum von **2a** weist darauf hin, daß hier eine geringere Beeinflussung zwischen der Thioäthergruppierung und der Acetoxygruppe vorhanden ist als in **1a**.

Die intensiven Fragmente 100 entstehen aus M^{+} durch Eliminierung von Essigsäure. Der weitere Abbau von 100 führt zum Fragment 85 (Methylradikalabgabe) und aufgrund von Retro-Diels-Alder-Spaltungen zu den Fragmenten 72 bzw. 54. Die Basisfragmente 43 ($CH_3CO^{\urcorner +}$) entstehen aus M^{+} durch Oniumspaltung innerhalb der Acetoxygruppe.

Als Folge der Abspaltung der Acetoxygruppe als Acetoyxradikal werden die Fragmente 101 gebildet, die aber nur eine geringe Intensität aufweisen.

Deutliche Unterschiede bestehen in den Intensitäten der wichtigsten Fragmente in den Spektren von **1a** und **2a**. Der Molekülionenpeak sowie die Fragmentpeaks 85, 72 und 43 haben in den Spektren von **2a** die größere Intensität als im Spektrum von **1a**. Für die Fragmente 101, 100 und 54 trifft dagegen das umgekehrte zu.

Acetoxythiacyclohexan-1,1-dioxide 1b und 2b

Abbildung 2 zeigt die 70 eV-Massenspektren von 3-Acetoxythiacyclohexan-1,1-dioxid **1b** und von 4-Acetoxythiacyclohexan-1,1-dioxid **2b**. Die Blockierung der freien Elektronenpaare am Schwefel führt dazu, daß in den Spektren der Sulfone **1b** und **2b** im Gegensatz zu **1a** und **2a** kein Molekülionenpeak vorhanden ist.

Der Abbau der Acetoxygruppe führt zu den Fragmenten 149 (M-$\mathrm{CH_3CO}]^+$) und 132 (M-$\mathrm{CH_3COOH}]^+$).

Der Peak 133 im Spektrum von **1b** weist darauf hin, daß bei 1,3-Anordnung von Acetoxygruppe und Sulfongruppe auch die Abspaltung von Acetoxyradikalen auftritt.

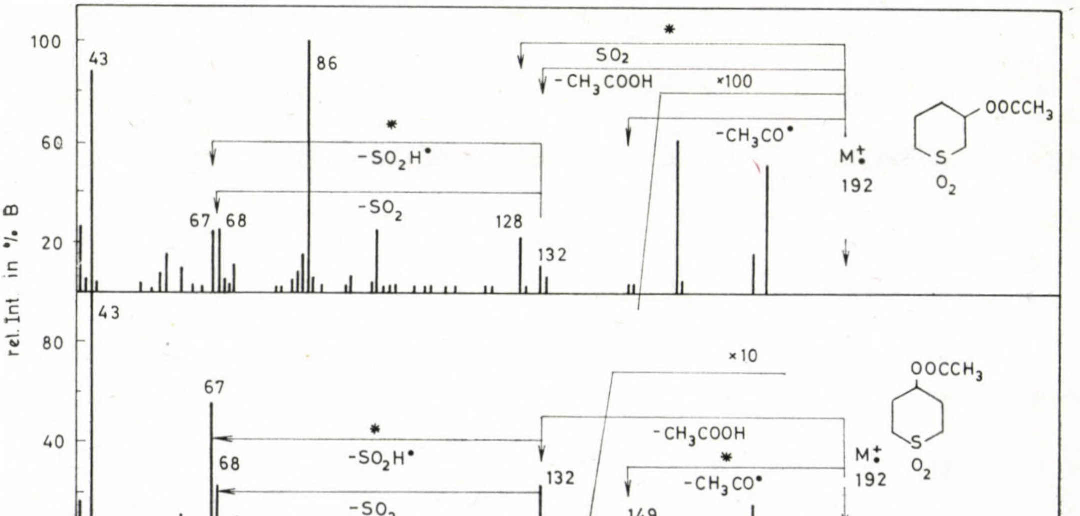


Abb. 2. 70 eV-Massenspektren von 3-Acetoxythiacyclohexan-1,1-dioxid **1b** und von 4-Acetoxythiacyclohexan-1,1-dioxid **2b**

Der Abbau von 132 erfolgt in beiden Spektren durch SO_2- und $SO_2H^\bullet$-Abgabe unter Bildung der Bruchstücke 68 bzw. 67. Ähnlich wie in den Spektren von **1a** und **2a** haben auch in den Spektren von 4-Acetoxythiacyclohexan-1,1-dioxid **2b** der Molekülionenpeak und die diskutierten Fragmente 149, 132, 68, 67 und 43 eine größere Intensität als im Spektrum von **1b**.

Acetoxy-*N*-methylazacyclohexane 1c und 2c

Abbildung 3 zeigt die 70 eV-Massenspektren von 3-Acetoxy-*N*-methylazacyclohexan **1c** und von 4-Acetoxy-*N*-methylazacyclohexan **2c**.

Die Molekülionenpeaks liegen bei der Massenzahl 157 und haben eine Intensität von 0,1% (**1c**) bzw. von 4,4% (**2c**). Beide Intensitätswerte liegen zwischen denen für Acetoxycyclohexan **4** (0,01%) und *N*-Methylazacyclohexan **3c** (7,5%) [6].

In den Spektren beider Verbindungen hat das Basisfragment die Massenzahl 43.

Die Hauptfragmentierungswege führen zu den Bruchstücken $M\text{-}CH_3COOH]^+$, $M\text{-}CH_3COO]^+$ und $M\text{-}CH_3CO]^+$. Bedingt durch eine transanulare Ladungsstabilisierung erfolgt die Abspaltung der Acetoxygruppe beim Abbau des 4-Acetoxy-*N*-methylazacyclohexans vorzugsweise als Acetoxyra-

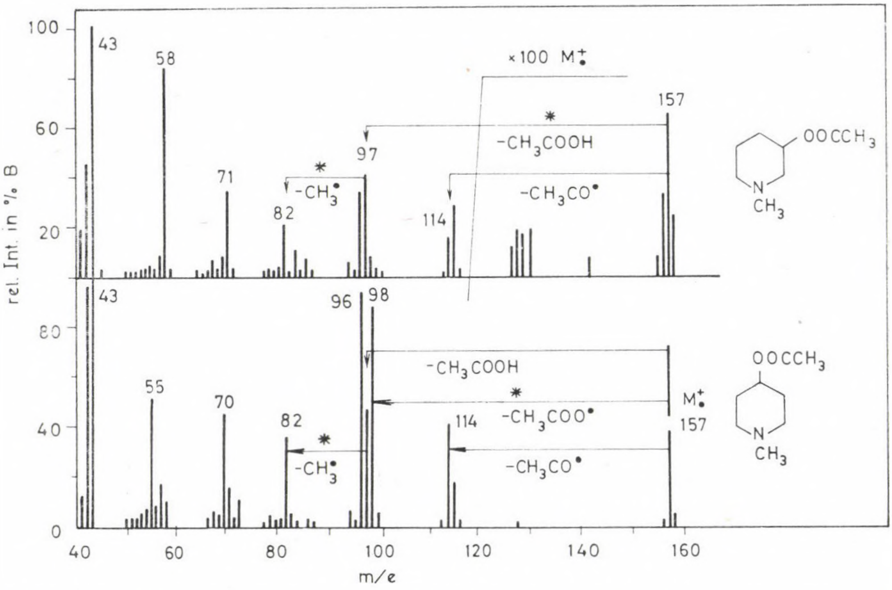


Abb. 3. 70 eV-Massenspektren von 3-Acetoxy-*N*-methylazacyclohexan **1c** und von 4-Acetoxy--*N*-methylazacyclohexan **2c** dikal unter Bildung des Fragmentes 98 und nur zum geringeren Teil durch Abspaltung von Essigsäure (unter Bildung von 97).

Zerfallsreaktionen des Fragmentes 97 sind wiederum die Methylradikalabgabe (Bildung des Fragmentes 82) und die Retro-Diels-Alder-Reaktion (Fragmente 69 und 54).

Die für *N*-Methylazacyclohexan **4c** charakteristischen Bruchstücke 71 ($C_4H_9N^{\urcorner +}$), 70 ($C_4H_8N^{\urcorner +}$) und 58 ($C_3H_8N^{\urcorner +}$) sowie M-$H^{\urcorner +}$ sind in beiden Spektren vorhanden.

Die Intensitätswerte von M^+ und der diskutierten Bruchstücke 114, 97, 82, 69, 54 und 70 sind jeweils in den Spektren von **2c** größer als in den Spektren von **1c**.

Die charakteristischen Unterschiede besonders in den Intensitäten der Fragmente 55, 58, 70, 71, 96 und 98 ermöglichen eine gute Unterscheidung der Verbindungen **1c** und **2c** an Hand ihrer Massenspektren.

Acetoxyoxacyclohexane 1d und 2d

Der massenspektrometrische Zerfall des 4-Acetoxyoxacyclohexans **2d** fügt sich, wie aus Abb. 4 hervorgeht, ebenso wie der Zerfall des 3-Acetoxyoxacyclohexans **1d** [9] in das Zerfallsschema der diskutierten Acetoxyheteracyclohexane ein.

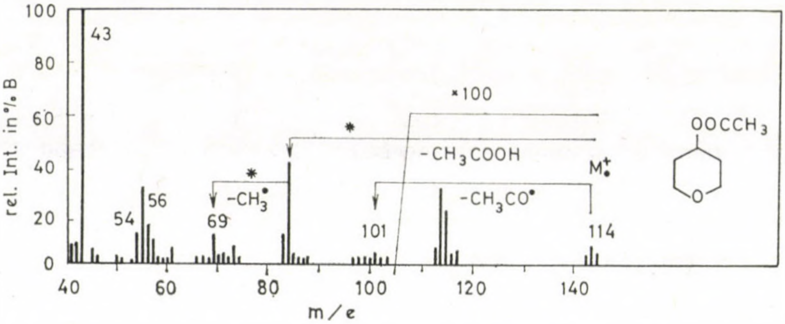
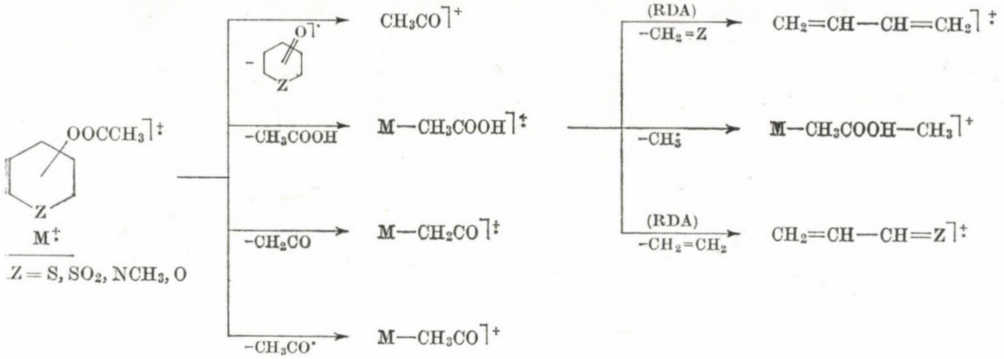


Abb. 4. 70 eV-Massenspektrum von 4-Acetoxyoxacyclohexan **2d**

Diskussion

Eine vergleichende Betrachtung zum massenspektrometrischen Abbau der Acetoxyheteracyclohexane **1** und **2** führt zu folgenden Resultaten:

Wie aus den Niedervoltspektren (12 eV) der untersuchten Verbindungen hervorgeht, verläuft die massenspektrometrische Fragmentierung aller Acetoxyheteracyclohexane grundsätzlich nach einem einheitlichen Schema:



Dabei wird die Fragmentierung in hohem Maße durch den Abbau der Acetoxygruppe geprägt. Dies äußert sich einmal in den meist hohen Intensitäten der Fragmente M-$CH_3CO^{\rceil +}$ und M-$CH_3COOH^{\rceil +}$ und zum anderen in der Intensität der Basisfragmente $CH_3CO^{\rceil +}$.

Der Einfluß der Ringheteroatome zeigt sich in den Spektren der Thiacyclohexanderivate **1a** und **2a** in der Anwesenheit zahlreicher schwefelhaltiger Bruchstücke wie z. B. $CHS^{\rceil +}$, $CH_2S^{\rceil +}$, $CH_3S^{\rceil +}$, $C_2H_2S^{\rceil +}$, $C_2H_3S^{\rceil +}$, $C_2H_4S^{\rceil +}$, $C_2H_5S^{\rceil +}$ [4, 7]. Ein Vergleich der Intensitäten dieser Bruchstücke mit den Intensitäten im Spektrum des Thiacyclohexans **4a** zeigt jedoch eine deutliche Abnahme der Werte an.

In den Spektren der Thiacyclohexan-1,1-dioxide **1b** und **2b** wird der Einfluß der Sulfongruppe durch Abspaltungsreaktionen von SO_2 und von SO_2H' (aus dem Fragment 132) dokumentiert. Auch in den Spektren der Acetoxy-*N*-methylazacyclohexane weisen stickstoffhaltige Bruchstücke bei den Massenzahlen 71, 70 und 58 mit zum Teil beträchtlicher Intensität auf die Anwesenheit der *N*-Methylgruppe hin.

Die Stabilisierung der Molekülionen hängt sowohl von der Art als auch von der Stellung des Ringheteroatoms ab. Aus den Intensitäten von $M^{+}_{\cdot}$ läßt sich nachstehende Reihe abnehmender Stabilisierung ableiten:

$$\text{S-4} > \text{CH}_3\text{N-4} > \text{S-3} > \text{CH}_3\text{N-3} > \text{O} > \text{CH}_2 > \text{SO}_2$$

In den Massenspektren der Acetoxythiacyclohexane und der Acetoxy-*N*-methylazacyclohexane wird bei 1,4-Anordnung von Ringheteroatom und Acetoxygruppe das Molekülion besser stabilisiert als bei 1,3-Anordnung.

Zur (halbquantitativen) Abschätzung des Einflusses der Heteroatome auf den massenspektrometrischen Abbau wurden die Intensitäten der durch das Ringheteroatom und der durch die Acetoxygruppe verursachten Bruchstücke summiert, vgl. hierzu [10]. Dabei wurde die nachstehende Reihenfolge abnehmender Stabilisierung gefunden:

$$\text{S-3} > \text{CH}_3\text{N-3} > \text{S}-4 > \text{CH}_3\text{N-4} > \text{OOCCH}_3 > \text{SO}_2-4 > \text{SO}_2-3$$

Es zeigt sich, daß auch die Stabilisierung der positiven Ladung während des massenspektrometrischen Abbaus sowohl von der Anzahl der freien Elektronenpaare als auch von der Stellung des Heteroatoms (relativ zur Acetoxygruppe) abhängt. Aus der gefundenen Reihenfolge sowie auch aus den Intensitäten insbesondere der $M\text{-CH}_3\text{COOH}^{\urcorner +}$-Bruchstücke kann der Schluß gezogen werden, daß in den Massenspektren der Acetoxythiacyclohexane, der Acetoxy-*N*-methylazacyclohexane und der Acetoxyoxacyclohexane der Abbau der Acetoxygruppe durch das Heteroatom in 3-Stellung stärker beeinflußt wird als durch das Heteroatom in 4-Stellung.

Die bereits diskutierten deutlichen Unterschiede beim massenspektrometrischen Abbau der 3-substituierten und der 4-substituierten Acetoxyheteracyclohexane, vgl. Abbildungen **1** bis **3**, erlauben eine gute massenspektrometrische Unterscheidung der einzelnen Isomeren. Insgesamt kann festgestellt werden, daß die massenspektrometrische Fragmentierung der bifunktionellen Acetoxyheteracyclohexane sowohl durch das Ringheteroatom als auch durch die Acetoxygruppe geprägt wird.

Veränderungen in den Intensitäten charakteristischer Bruchstücke in den Spektren der Acetoxyheteracyclohexane im Vergleich zu den entsprechenden monofunktionellen Heteracyclohexanen und zum Acetoxycyclohexan weisen auf Wechselwirkungen zwischen dem Ringheteroatom und der Acetoxygruppe hin.

Experimenteller Teil

Zur Darstellung der untersuchten Verbindungen sei auf die Arbeiten [11—14] verwiesen.

Die Aufnahme der Massenspektren erfolgte mit einem Massenspektrometer der Firma Varian MAT (CH-6) bei 70 und bei 12 eV. Ionenquelle IXE 5, Temperatur 200 °C, Emissionsstrom 30 μA, indirekter Einlaß.

*

Wir danken Herrn Chem.-Ing. L. Goetz für die Aufnahme der Massenspektren.

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AMINOPHTHALAZINONE DERIVATIVES, VII*

REACTION OF CHLOROPHTHALAZINONE WITH SECONDARY AMINES STUDY OF THE STERIC EFFECT, II

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In the aminolysis of chlorophthalazinone (**1a**) with secondary amines, the yield of *N*-substitution (**1** → **5**, **1** → **7**) is significantly affected by the steric structure of the amine. In the cyclic secondary amines substituents at the C-2 position give rise to a strong steric hindrance. The possibility for *N*-substitution gradually decreases with increasing size of the ring, while in the case of open-chain secondary amines it varies suddenly as a function of the position of the NH group in the chain.

Chlorophthalazinone (**1a**, CPA), being resistant to nucleophilic reagents (amines) owing to its structure of vinyl halide character, can be made to react with aminoalcohols directly [1] and with amines containing no OH group in glycol solution [2]. In the case of aminoalcohols it is autocatalysis, in glycol medium the catalytic effect of the solvent which facilitates the *N*-substitution (reactions **1** → **5** and **1** → **7**). The catalytic effect (explained by the formation of the reactive alcohol adduct of type **3**) was confirmed unambiguously by observations made during aminolysis experiments with the slightly nucleophilic aniline. FLITSCH [3] and our observations have equally shown that CPA fails to react when refluxed with aniline, when, however, ethylene glycol is added to the solution in an amount less than the stoichiometric quantity (0.2 mole of glycol for 1 mole of CPA), anilinophthalazinone is formed *via* **1a** → → **3a** → **9** in 83% yield. In other cases somewhat more glycol may be necessary, since the side reaction (formation of glycol ether accompanied by elimination of HCl: **1a** → **3a** → **8**) consumes more or less glycol.**

In the aminolysis of CPA (**1a**), the steric requirement of the substituents of the reacting amine has an important role. According to earlier examinations with aminoalcohols [1] and with primary alkyl- and aralkylamines [2] in glycol solutions, the aminophthalazinone derivatives are obtained in high yields (in the main, 70–95%), when the environment of the terminal amino group is sterically entirely free; however, even the presence of a methyl group at α

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* Part VI, see Acta Chim. Acad. Sci. Hung., **105**, 175 (1980)

** Besides ensuring the catalytic action, the use of glycol solution has the advantage that owing to its high boiling point it facilitates the maintaining of the optimum temperature of the reaction mixture.

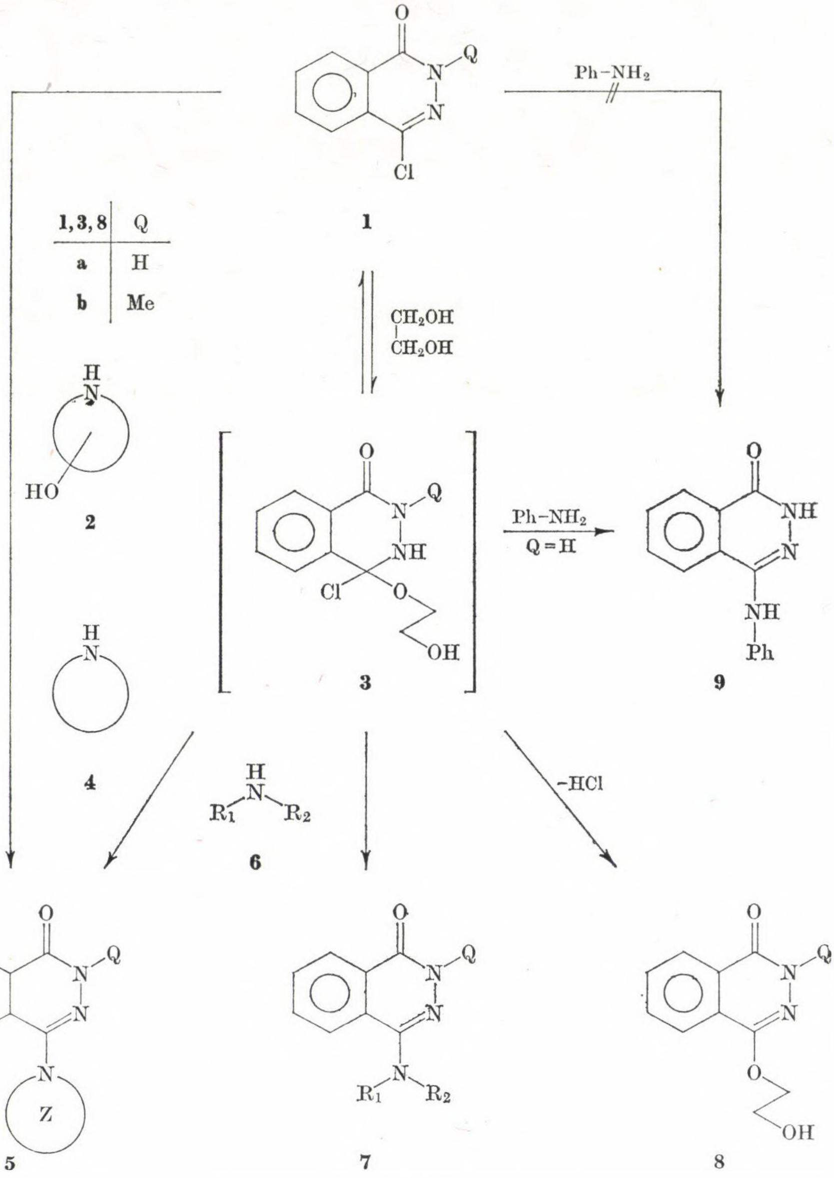


Fig. 1

position greatly reduces the degree of conversion. The purpose of the present work was to establish the effect of steric factors on the yield of coupling reactions with secondary amines.

Reaction **1a** → **5** was tried with four aminoalcohols derived from piperidine (**2**) (see Table I), and the phthalazinone derivatives **5a**—**5c** were obtained

Table I

Reaction of chlorophthalazinone with piperidine and morpholine derivatives (**1** → **5** *and* **1** → **3** → **5**)

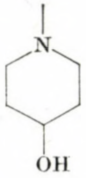
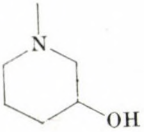
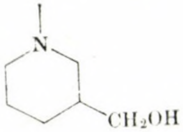
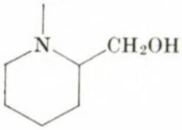
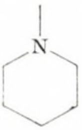
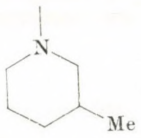
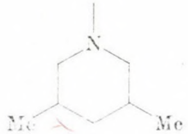
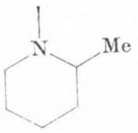
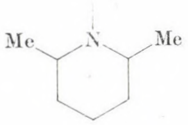
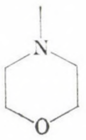
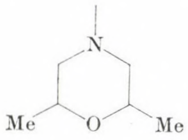
Cyclic secondary amine	Ethylene glycol	Product (*5*)	Z-	Reaction time, h	Yield, %
4-Hydroxypiperidine	—	**a**		12	86.5
3-Hydroxypiperidine	—	**b**		12	83.8
3-Piperidinemethanol	—	**c**		12	92.6
2-Piperidinemethanol	— +	**d**		60	— —
Piperidine	+	**f**		10	74.9
4-Methylpiperidine	+	**g**		10	76.7

Table I (cont.)

Cyclic secondary amine	Ethylene glycol	Product (5)	Z-	Reaction time, h	Yield, %
3-Methylpiperidine	+	**h**		10	76.0
3,5-Dimethylpiperidine	+	**i**		10	75.8
2-Methylpiperidine	+	**j**		50	2.4
2,6-Dimethylpiperidine	+	**k**		60	—
Morpholine	+	**l**		25	74.7
2,6-Dimethylmorpholine	+	**m**		25	72.4

according to the autocatalytic process (yields: 84—93%), but no *N*-substitution could be achieved with 2-piperidinemethanol, even in the presence of glycol.

An essentially similar steric hindrance has been found in the *N*-substitution reactions using other piperidine derivatives in glycol solutions (Table I). Thus, CPA reacts with piperidine, 3- and 4-methylpiperidine, as well as with 3,5-dimethylpiperidine to nearly the same extent and in satisfactory yields (75—77%), that is, methyl substituents at the C-3, C-4 or the C-3,5 positions cause no steric hindrance during coupling. The same holds for morpholine and 2,6-dimethylmorpholine; in these reactions **5l** (75%) and **5m** (72%) are obtained in nearly identical yields. Methyl substituents at the α position, however, exert significant steric hindrance, therefore coupling can be achieved only in 2% yield with 2-methylpiperidine, and 2,6-dimethylpiperidine entirely resists coupling with CPA under the experimental conditions employed.

In cyclic secondary amines, increase in the size of the ring results in a *gradual* decrease in yield (see Table II). In open-chain secondary amines the reactivity varies *suddenly*, depending on the position of the NH group in the chain and the steric requirement of the substituents (Table III). *N*-Methylbutylamine (NH at C-2) can be coupled in a medium yield, but *N*-methylcyclohexylamine, also containing a C-2 NH group, has a coupling ability of about one order of magnitude lower, owing to the less favourable steric construction.

An even stronger steric hindrance is found in diethylamine (NH at C-3), which is coupled to the phthalazinone skeleton only in 1.4% yield. Further increase in steric shielding may lead to complete failure of the *N*-substitution. *N*-Ethylbutylamine and particularly dipropylamine (NH at C-4) represent the limit where, owing to steric factors hindering coupling, the other possible process, glycol ether formation **3** → **8** becomes exclusive.

In order to monitor the aminolysis of CPA in ethylene glycol solution, a valuable method providing rapid information, suitable for use in the case of amines with boiling points lower than that of the solvent, was developed. The essence of the procedure is that the boiling point of the CPA-amine-glycol systems, measured in the liquid increases as a function of the decreasing amine concentration. The hydrochloric acid liberated during the *N*-substitution (coupling) is bound practically by the free amine, since the basicity of aminophthalazinone derivatives is very low. For this reason, the *N*-substitution reactions (**1** → **3** → **5** and **1** → **3** → **7**) consume 2 equivalents of amine, whereas the side reaction accompanied by elimination of hydrochloric acid (**1** → **3** → **8**) requires 1 equivalent of amine only. When 1 mole of CPA is allowed to react with 2 moles of amine, and *N*-substitution occurs exclusively, the internal boiling point of the solution attains or slightly exceeds the boiling point of glycol (196 °C); on the other hand, when a significant amount of glycol ether

Table II

Influence of the size of the ring on the yield of the reactions **1** → **3** → **5** *in glycol solution*

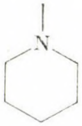
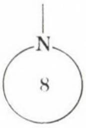
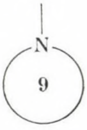
Cyclic imine (*4*)	Product (*5*)	Z-	Reaction time, h	Yield, %
Pyrrolidine	e		5	96.2
Piperidine	f		10	74.9
Hexamethyleneimine	n		15	58.9
Heptamethyleneimine	o		15	38.0
Octamethyleneimine	p		15	20.6

Table III

Reaction of open-chain secondary amines with chlorophthalazinone in glycol solution (**1** → **3** → **7**; reaction time: 60 h)

Secondary amine (*6*)	Site of NH group in the chain	Product (*7*)			Yield, %
			R_1	R_2	
N-Me-butylamine	2	**a**	Me-	Bu-	56.0
N-Me-cyclohexylamine	2	**b**	Me-	C_6H_{11}-	6.5
Diethylamine	3	**c**	Et-	Et-	1.4
N-Et-butylamine	3	**d**	Et-	Bu-	—
Dipropylamine	4	**e**	Pr-	Pr-	—

is also formed beside the *N*-substitution, the maximum boiling point of the mixture can be far below the boiling point of glycol.

In Fig. 2, the boiling point curves of some CPA-amine-glycol systems are shown as a function of the reaction time. The relatively rapidly substituted amines which give a satisfactory yield produce steep curves (—×—×—) and can well be distinguished from the flat (—○—○—) curves of amines being less reactive owing to their less favourable steric structure. The two types of curves indicate not only the predominating nature of *N*-substitution or glycol ether formation, but also show that *N*-substitution is the faster process.

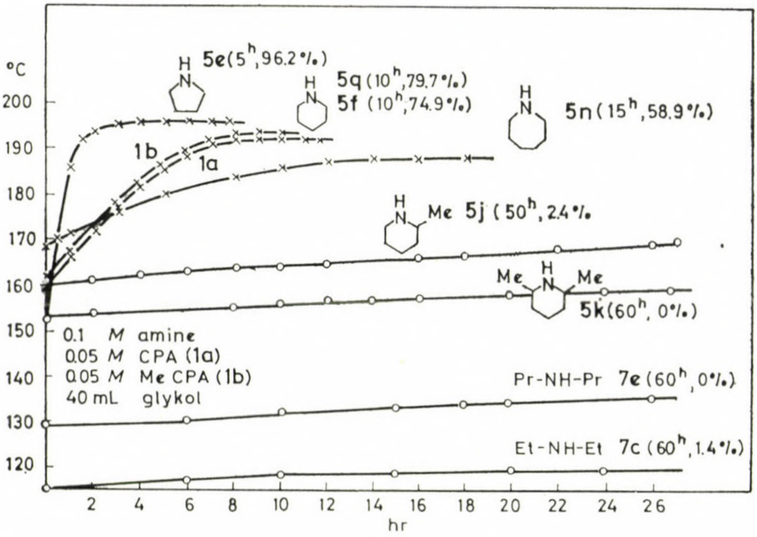


Fig. 2. Boiling point curves of some CPA (**1a**)-amine-glycol systems measured in the liquid

2-Methyl-4-chlorophthalazinone (**1b**, Me-CPA) has nearly the same reactivity as CPA. This can well be seen from the parallel boiling point curves of **1a** and **1b** in the reaction with piperidine. The glycol adduct **3b** formed in glycol solution gives the product **5q** through *N*-substitution and subsequent glycol elimination (79.7%; the better yield is also reflected in the higher maximum of the boiling point curve); the product of the side reaction is 2-methyl-4-phthalazonyl glycol ether (**8b**).

The experimental data unambiguously confirm that the F-strain [4] occurring during the nucleophilic attack of the amine strongly hinders the reaction. The influence of the steric construction on reactivity is particularly striking when pyrrolidine, a compound most suitable for coupling (yield in 5 h: 96%, no glycol ether is formed), is compared with diethylamine having nearly the same basicity and nucleophilic character (yield only 1.4% of **7c** after refluxing for 60 h; the main product is the glycol ether and unchanged CPA can also be recovered). Since pyrrolidine is significantly more suitable for coupling in this reaction, it is evident that in the given case the *N*-substitution (**1** → **5** and **1** → **7**) depends primarily on the steric structure of the amine rather than on its basicity or nucleophilic character. Cyclic secondary amines can be, in general, coupled in a better yield that open-chain secondary amines with the same number of atoms, since a ring is sterically more favourable than the open form, where free rotation may allow the development of disadvantageous conformers increasing thereby the steric shielding of the imino group.

Experimental

M.p.'s were determined with a Boetius micro melting point determining apparatus. The IR spectra were recorded in KBr pellets with UR-10 and IR-75 (Carl Zeiss, Jena) spectrophotometers.

2-Methyl-4-chlorophthalazinone (1b)

4-Chlorophthalazinone (**1a**) (18.0 g; 0.1 mole) was dissolved in a mixture of Methyl Cellosolve (100 mL) and aqueous (100 mL) potassium hydroxyde (28 g; 0.5 mole), with mild heating. The solution was cooled in water and dimethyl sulfate (37.8 g; 0.3 mole) was added to it dropwise under mechanical stirring. After allowing to stand for a short time, the mixture was diluted with water to 2 litres and the crystals which separated were filtered off. A further crop can be obtained from the mother liquor on concentration. The combined crude product (15.4—17.7 g; 79.1—91.0%) was recrystallized from aqueous ethanol after clarification with carbon. Colourless needles separated from the solution; on standing in suspension, they recrystallized into plates, m.p. 128—129 °C (*lit.* [5] m.p. 127—128 °C).

$C_9H_7ClN_2O$ (194.6). Calcd. Cl 18.2. Found Cl 18.4%.

IR: νCO_{amide} 1655, $\nu C{=}N$ 1576 (?) 1,2-disubst. Ar 769 cm^{-1}.

4-Anilino-1(2*H*)-phthalazinone (9)

A mixture of aniline (10 mL) and chlorophthalazinone (1.80 g; 0.01 mole) was refluxed in an atmosphere of nitrogen gas in the presence of ethylene glycol (0.124 g; 2 mmoles) for 20 hrs. Aniline was removed by steam distillation, and the somewhat sticky residue was rubbed with a cold mixture of dioxan and water (1 : 1). The crude product (2.32—2.39 g) was crystallized from ethanol or ethyl acetate to give colourless plates (1.98 g; 83.4%), m.p. 257—258 °C (lit. [3] m.p. 258 °C).

$C_{14}H_{11}N_3O$ (237.3). Calcd. C 70.9; H 4.7; N 17.7. Found C 70.8; H 4.6; N 17.7%.

IR: νNH 3320, νNH_{amide} 3250—2800, νCO_{amide} 1642, $\nu C{=}N$ 1588, δNH 1531, 1,2-disubst. Ar 775, monosubst. Ar 695, 759 cm^{-1}.

4-(4-Hydroxypiperidino)-1(2*H*)-phthalazinone (5a)

A mixture of chlorophthalazinone (4.50 g; 0.025 mole) and 4-hydroxypiperidine (5.05 g; 0.05 mole) was heated to 170—180 °C in nitrogen gas atmosphere for 12 hrs. The melt which crystallized on cooling was mixed with some water, the crude product (5.30 g; 86.5%; m.p. 220—224 °C, halogen-free) was filtered off and washed with water. Colourless needles were obtained on recrystallization from much water after clarification with carbon. M.p. 223—224 °C.

$C_{13}H_{15}N_3O_2$ (245.3). Calcd. N 17.1. Found N 17.2%.

IR: νOH 3425, νNH_{amide} 3250—2600, $\nu CH_2(N)$ 2820, νCO_{amide} 1653, $\nu C{=}N$ 1588, $\nu C{-}O$ 1058 or 1065, 1,2-disubst. Ar 748 cm^{-1}.

4-(3-Hydroxypiperidino)-1(2*H*)-phthalazinone (5b)

On the analogy of the preparation of **5a**, heating of chlorophthalazinone (4.50 g; 0.025 mole) and 3-hydroxypiperidine (5.05 g; 0.05 mole) for 12 hrs in nitrogen gas atmosphere at 170—180 °C, yielded the crude product (5.13 g; 83.8%; m.p. 188—190 °C, halogen-free). When crystallized from water, colourless needles or prisms were obtained, m.p. 194—196 °C.

$C_{13}H_{15}N_3O_2$ (245.3). Calcd. N 17.1. Found N 17.1%.

IR: νOH 3330, νNH$_{\text{amide}}$ 3250—2600, νCH$_2$(N) 2805, νCO$_{\text{amide}}$ 1658, νC=N 1586, νC—O 1075 or 1062, 1,2-disubst. Ar 762 cm^{-1}.

4-(3-Hydroxymethylpiperidino)-1(2*H*)-phthalazinone (5c)

In a ground-glass conical tube a mixture of 3-piperidinemethanol (2.30 g; 0.02 mole) and chlorophthalazinone (1.80 g; 0.01 mole) was heated for 12 hrs to 170—180 °C under reduced pressure (66—80 mbar). The hard resin became a paste on treatment with water, then solidified again. The crude product (2.40 g; 92.6%; m.p. 180—183 °C) was crystallized from much water or aqueous ethanol to obtain colourless prisms, m.p. 183—185 °C.

$C_{14}H_{17}N_3O_2$ (259.3). Calcd. N 16.2. Found N 16.3%.

IR: νOH 3390, νNH$_{\text{amide}}$ 3300—2600, νCH$_2$(N) 2785, νCO$_{\text{amide}}$ 1642, νC=N 1578, νC—O 1022, 1,2-disubst. Ar 758 cm^{-1}.

4-(2-Hydroxymethylpiperidino)-1(2*H*)-phthalazinone (**5d**) could not be prepared from 2-piperidinemethanol and chlorophthalazinone either according to the procedure applied in the preparation of **5c** or in glycol solution (60 h).

Aminolysis of chlorophthalazinone (1a, CPA) in glycol solution

Instructions for effecting the aminolysis and purifying the reaction product

A mixture of CPA, the amine and glycol was gently boiled in a flask equipped with a reflux condenser and a thermometer reaching into the liquid (the ground joints were greased) until the increase of boiling point measured in the liquid stopped. After dilution with water (750 mL of water for 40 mL of glycol), the crude product was filtered off, and the by-product phthalazonyl glycol ether (**8a**) and eventual CPA contamination were removed by extraction with hot water (100 mL of H_2O for 1.0 g of crude product). Extraction was repeated until constant m.p. and negative Beilstein test were attained. Products **5** and 7 were crystallized from a suitable solvent to achieve further purification.

4-Pyrrolidino-1-(2*H*)-phthalazinone (5e)

A mixture of chlorophthalazinone (9.00 g; 0.05 mole) and pyrrolidine (7.1 g; 0.1 mole) was refluxed in ethylene glycol (40 mL) for 5 hrs. The crude product separated on dilution with water (10.34 g; 96.2%; m.p. 187—189 °C, halogen-free) and was crystallized from ethanol to obtain colourless plates, m.p. 189—190 °C.

$C_{12}H_{13}N_3O$ (215.3). Calcd. N 19.5. Found N 19.6%.

IR: νNH$_{\text{amide}}$ 3300—2600, νCH$_2$(N) 2858, νCO$_{\text{amide}}$ 1648, νC=N 1571, 1,2-disubst. Ar 776 cm^{-1}.

4-Piperidino-1(2*H*)-phthalazinone (5f)

A mixture of ethylene glycol (40 mL), piperidine (8.52 g; 0.1 mole) and CPA (9.00 g; 0.05 mole) was refluxed for 10 hrs. The crude product which separated on dilution with water (10.3 g, halogen-free) was purified by extraction with hot water to give colourless flat needles (8.58 g; 74.9%), m.p. 197—197.5 °C (from ethanol).

$C_{13}H_{15}N_3O$ (229.3). Calcd. N 18.3. Found N 18.2%.

IR: νNH$_{\text{amide}}$ 3300—2600, νCH$_2$(N) 2829, νCO$_{\text{amide}}$ 1641, νC=N 1581, 1,2-disubst. Ar 741 cm^{-1}.

4-(4-Methylpiperidino)-1(2*H*)-phthalazinone (5g)

A mixture of 4-methylpiperidine (9.92 g; 0.1 mole) and CPA (9.00 g, 0.05 mole) was refluxed in ethylene glycol (40 mL) for 10 hrs. The crude product (10.2 g, halogen-free) was extracted with hot water, to give 9.32 g (76.7%) of **5g**, m.p. 208—210 °C. Colourless prisms from ethanol, m.p. 210—211 °C.

$C_{14}H_{17}N_3O$ (243.3). Calcd. N 17.3. Found N 17.4%.

IR: νNH_{amide} 3300—2600, $\nu CH_2(N)$ 2810, νCO_{amide} 1650, $\nu C{=}N$ 1582, 1,2-disubst. Ar 779 cm^{-1}.

4-(3-Methylpiperidino)-1(2*H*)-phthalazinone (5h)

In ethylene glycol solution (40 mL), a mixture of 3-methylpiperidine (9.92 g; 0.1 mole) and CPA (9.00 g; 0.05 mole) was refluxed until the elevation of the boiling point measured in the solution stopped (10 h). The crude product precipitated on the addition of water (10.8 g, halogen-free); it was extracted with hot water and **5h** (9.24 g; 76%) was crystallized from aqueous ethanol to give colourless elongated plates, m.p. 180—181 °C.

$C_{14}H_{17}N_3O$ (243.3). Calcd. N 17.3. Found N 17.3%.

IR: νNH_{amide} 3300—2600, $\nu CH_2(N)$ 2840, νCO_{amide} 1645, $\nu C{=}N$ 1582, 1,2- disubst. Ar 754 cm^{-1}.

4-(2-Methylpiperidino)-1(2*H*)-phthalazinone (5j)

A mixture of CPA (18.00 g; 0.1 mole) and 2-methylpiperidine (19.84 g; 0.2 mole) was refluxed in glycol solution (80 mL) for 50 hrs. The halogen-free crude product isolated after dilution with water was suspended in ethanol (200 mL), heated to the boiling temperature and, after cooling, the undissolved phthalazonyl glycol ether **(8a)** was filtered off. The evaporation residue of the alcoholic mother liquor was extracted with cold chloroform. The extract crystallized from aqueous alcohol as colourless flat needles (0.59 g; 2.4%), m.p. 157—159 °C.

$C_{11}H_{17}N_3O$ (243.3). Calcd. N 17.3. Found N 17.4%.

IR: νNH_{amide} 3300—2600, νCH_2 2799, 2848, νCO_{amide} 1660, $\nu C{=}N$ 1588, 1,2-disubst. Ar 779 cm^{-1}.

4-(3,5-Dimethylpiperidino)-1(2*H*)-phthalazinone (5i)

3,5-Dimethylpiperidine (11.32 g; 0.1 mole) and CPA (9.00 g; 0.05 mole) were refluxed in glycol solution (40 mL) for 10 hrs. The halogen-free crude product which separated on dilution with water (11.3 g) was purified by extraction with hot water as described in the Instructions above, to give 9.74 g (75.8%) of **5l**; thick needles from aqueous ethanol, m.p. 208—210 °C.

$C_{15}H_{19}N_3O$ (257.3). Calcd. N 16.3. Found N 16.4%.

IR: νNH_{amide} 3300—2600, νCH_2 2812, 2834, νCO_{amide} 1645, $\nu C{=}N$ 1582, 1,2-disubst. Ar 771 cm^{-1}.

When 2,6-dimethylpiperidine was treated as described above, the product obtained after refluxing for 60 hrs was a mixture of glycol ether and CPA; no *N*-substituted product **(5k)** could be isolated.

4-Morpholino-1(2*H*)-phthalazinone (5l)

A mixture of ethylene glycol (40 mL), morpholine (8.71 g; 0.1 mole) and CPA (9.00 g; 0.05 mole) was refluxed for 25 hrs and the cold solution was diluted with water. The crystals which separated (10.4 g, halogen-free) were filtered off and purified by extraction with hot water to give 8.63 g (74.7%) of **5l**; colourless needles, m.p. 240—241.5 °C (from ethanol).

$C_{12}H_{13}N_3O_2$ (231.3). Calcd. N 18.2. Found N 18.3%.

IR: νNH_{amide} 3300—2600, $\nu CH_2(N)$ 2848, νCO_{amide} 1659, $\nu C{=}N$ 1586, 1,2-disubst. Ar 748 cm^{-1}.

4-(2,6-Dimethylmorpholino)-1(2*H*)-phthalazinone (5m)

2,6-Dimethylmorpholine (11.52 g; 0.1 mole) was allowed to react with chlorophthalazinone (9.00 g; 0.05 mole) in glycol (40 mL) solution. After stabilization of the boiling point measured in the solution (25 h), the material which separated on dilution with water (11.3 g) was filtered off and extracted with hot water (*cf.* Instructions) to remove the by-products and to obtain 9.38 g (72.4%) of **5m**; colourless prisms, m.p. 265—268 °C (from ethanol).

$C_{14}H_{17}N_3O_2$ (259.3). Calcd. N 16.2. Found N 16.2%.

IR: νNH_{amide} 3300—2600, $\nu CH_2(N)$ 2849, νCO_{amide} 1650, $\nu C{=}N$ 1582, 1,2-disubst. Ar 766 cm^{-1}.

4-Hexamethyleneimino-1(2*H*)-phthalazinone (5n)

Hexamethyleneimine (9.92 g; 0.1 mole) and chlorophthalazinone (9.00 g; 0.05 mole) were refluxed in glycol solution (40 mL) for 15 hrs. The crude product which separated on the addition of water (9.5 g) was extracted with hot water. The halogen-free product melted at 201—203 °C (7.17 g; 58.9%). Colourless plates from ethyl acetate, m.p. 203—204 °C.

$C_{14}H_{17}N_3O$ (243.3). Calcd. N 17.3. Found N 17.4%.

IR: νNH_{amide} 3300—2600, $\nu CH_2(N)$ 2848, νCO_{amide} 1645, $\nu C{=}N$ 1579, 1,2-disubst. Ar 782 cm^{-1}.

4-Heptamethyleneimino-1(2*H*)-phthalazinone (5o)

Heptamethyleneimine (5.66 g; 0.05 mole) and CPA (4.50 g; 0.025 mole) were refluxed in ethylene glycol (20 mL) for 15 hrs, to give, after dilution with water, a crude product (6.5 g) strongly contaminated with CPA. After boiling with water three times, the sticky substance was mixed with ethanol (70 mL), the solution was filtered, the filtrate was evaporated to dryness and the residue was extracted with hot ethyl acetate. The substance extracted crystallized from aqueous ethanol in the form of colourless prisms (2.44 g; 38%), m.p. 192—194 °C.

$C_{15}H_{19}N_3O$ (257.3). Calcd. N 16.3. Found N 16.4%.

IR: νNH_{amide} 3300—2600, $\nu CH_2(N)$ 2842, νCO_{amide} 1648, $\nu C{=}N$ 1580, 1,2-disubst. Ar 778 cm^{-1}.

4-Octamethyleneimino-1(2*H*)-phthalazinone (5p)

A mixture of ethylene glycol (10 mL), octamethyleneimine (5.09 g; 0.04 mole) and CPA (3.6 g; 0.02 mole) was refluxed for 15 hrs. The emulsion formed on dilution with water was mixed with hydrochloric acid in an amount required to obtain a clear solution, and the insoluble crystalline product (2.6 g) was filtered off. A suspension of this product in ethanol (50 mL) was shortly boiled, cooled, and filtered; the substance filtered off consisted of a mixture of **1a** and **8a**. The evaporation residue of the filtrate was repeatedly extracted with hot water (*cf.* Instructions). The purified **5p** (1.12 g; 20.6%) crystallized from ethyl acetate in the form of colourless prisms, m.p. 173—174 °C.

$C_{16}H_{21}N_3O$ (271.4). Calcd. N 15.5. Found N 15.4%.

IR: νNH_{amide} 3300—2600, $\nu CH_2(N)$ 2842, νCO_{amide} 1648, $\nu C{=}N$ 1578, 1,2-disubst. Ar 777 cm^{-1}.

2-Methyl-4-piperidino-1(2*H*)-phthalazinone (5q; Q = Me, Z = piperidyl-)

(a) Halogen-free **5q** was prepared from 2-methyl-4-chlorophthalazinone (**1b**) (9.73 g; 0.05 mole) by refluxing it with piperidine (8.52 g; 0.1 mole) in glycol solution (40 mL) for 10 hrs. The crude product (9.70 g; 79.7%) precipitated on the addition of water, m.p. 92—95 °C; it was crystallized from aqueous ethanol to give colourless prisms, m.p. 95—96 °C.

(b) Piperidinophthalazinone (**5f**) (2.29 g; 0.01 mole) was dissolved in a mixture of Methyl Cellosolve (20 mL) and water (5 mL) in the presence of potassium hydroxyde (2.8 g; 0.05 mole). Dimethyl sulfate (3.78 g; 0.03 mole) was added in small portions to the cold solution, under mechanical stirring. After standing for 1 h, the solution was diluted with water and evaporated to dryness on a rotary evaporator. The crude product (2.10 g; 86.3%), m.p. 93—95 °C, was suspended in water, filtered off and recrystallized from aqueous ethanol. The substance obtained was identical with that prepared according to method *(a)*.

$C_{14}H\ N_3O$ (243.3). Calcd. N 17.3. Found N 17.4%.

IR: νCH_2 2820, νCO_{amide} 1648, $\nu C{=}N$ 1579, 1,2-disubst. Ar 782 cm^{-1}.

2-Methyl-1(2*H*)-phthalazonyl-4-(2-hydroxyethyl)ether (8b)

The product (1.7 g; 15.4%) obtained by evaporation of the aqueous-glycolic mother liquor from the preparation of **5q** according to method *(a)*, was crystallized from ethanol to give colourless needles, m.p. 153—154 °C.

$C_{11}H_{12}N_2O_3$ (220.2). Calcd. C 60.0; H 5,5; N 12.7. Found C 60.2; H 5.4; N 12.8%.

IR: νOH 3338, νCO_{amide} and $\nu C{=}N$ 1632, 1580, $\nu C{-}O$ 1083, 1,2-disubst. Ar 735 cm^{-1}.

4-(*N*-Methyl-n-butylamino)-1(2*H*)-phthalazinone (7a)

CPA (9.00 g; 0.05 mole) and *N*-methyl-*n*-butylamine (8.72 g; 0.1 mole) were refluxed in ethylene glycol (40 mL) for 60 hrs. The air-dry crude product (9.3 g) which separated on the addition of water was extracted with chloroform. The extract (6.48 g; 56%) gave colourless needles when crystallized from aqueous ethanol; m.p. 114.5—116 °C.

$C_{13}H_{17}N_3O$ (231.3). Calcd. N 18.2. Found N 18.2%.

IR: νNH_{amide} 3300—2600, $\nu CH_2(N)$ 2838, νCO_{amide} 1650, $\nu C{=}N$ 1580, 1,2-disubst. Ar 754 cm^{-1}.

4-(*N*-Methylcyclohexylamino)-1(2*H*)-phthalazinone (7b)

Analogously to the preparation of **7a**, a practically halogen-free reaction product (6.0 g) was obtained from *N*-methylcyclohexylamine (0.1 mole). Compound **7b** (0.84 g; 6.53%), isolated by extraction with ethanol (100 mL), was crystallized from aqueous ethanol to give colourless needles, m.p. 168—169 °C.

$C_{15}H_{19}N_3O$ (257.3). Calcd. N 16.3. Found N 16.4%.

IR: νNH_{amide} 3300—2600, νCO_{amide} 1655 sh, 1642, $\nu C{=}N$ 1578, 1,2-disubst. Ar 782 cm^{-1}.

4-Diethylamino-1(2*H*)-phthalazinone (7c)

CPA (9.00 g; 0.05 mole) and diethylamine (7.3 g; 0.1 mole) were refluxed in glycol (40 mL) for 60 hrs. Compound **7c** (0.15 g; 1.4%) was extracted from the crude product with ethyl acetate; colourless needles from aqueous ethanol, m.p. 134—135 °C.

$C_{12}H_{15}N_3O$ (217.3). Calcd. N 19.3. Found N 19.2%.

IR: νNH_{amide} 3300—2600, νCH_2 2828, νCO_{amide} 1655, $\nu C{=}N$ 1582, 1,2-disubst. Ar 782 cm^{-1}.

N-Ethyl-*n*-butylamine and di-*n*-propylamine failed to give the coupled products (**7d**, **7e**) with CPA when refluxed for 60 hrs in ethylene glycol. The crude product which separated on the addition of water was a mixture of **1a** and **8a**.

*

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REACTIONS OF METHYL 3-ARYL-2-PROPYONATES WITH NUCLEOPHILIC NITROGEN COMPOUNDS

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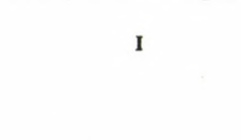
Benzylamine reacts with methyl 3-phenyl-(**IVa**) and methyl 3-(*p*-methoxyphenyl)-(**IVb**)2-propynoates to give the corresponding *N*-benzyl-3-aryl-2-propynoic amides (**Va** and **b**). On the other hand, methyl 3-(*p*-chlorophenyl)-2-propynoate (**IVc**) give methyl (*Z*)-β-benzylamino-*p*-chlorocinnamate (**VIa**).

p-Methylaminobenzene and *p*-methoxyaminobenzene react with **IVa—c** to give the corresponding methyl (*Z*)-β-(arylamino)cinnamates (**VIb—g**). Similarly, *o*-phenylenediamine gave with **IVc**, methyl (*Z*)-β-(*o*-aminoanilino)-*p*-chlorocinnamate (**VII**).

Benzoylhydrazine reacts with **IVa** and **b** to give the corresponding 1*H*-3-aryl-1-benzoyl-5-hydroxypyrazole (**VIIIa** and **b**); **VIIIa** was converted into the known 3-phenylpyrazol-5-one by the action of concentrated hydrochloric acid.

Benzamidine hydrochloride and **IVa—c** in the presence of aqueous sodium carbonated give the corresponding methyl (*Z*)-β-benzamidinocinnamates (**IXa—c**).

Although the reactions of nucleophilic nitrogen compounds with esters of propiolic acid and acetylenedicarboxylic acid have been extensively investigated [1], few examples are reported for similar reactions with esters of 3-aryl-2-propynoic acid. For example, it has been reported that ethyl 3-phenyl-2-propynoate reacts with *n*-butylamine [2] to give a mixture of ethyl *cis*-β-(*N*-*n*-butylamino)cinnamate (**I**) and *N*-(*n*-butyl)-3-phenyl-2-propynoic amide (**IIa**). Also, in a recent publication [3] from this laboratory, it was demonstrated that ethylenediamine and ethanolamine exclusively attack the ester grouping of methyl 3-aryl-2-propynoates to give the corresponding di-(*N*-methylene-3-aryl-2-propynoic amides) (**III**) and *N*-hydroxyethyl-3-(*p*-chloro-



I

$$\mathrm{Ar{-}C{\equiv}C{-}CONHCH_2R}$$

II

(a) $\mathrm{Ar = C_6H_5}$, $\mathrm{R = (CH_2)_2CH_3}$

(b) $\mathrm{Ar = C_6H_4Cl\text{-}}p$, $\mathrm{R = CH_2OH}$

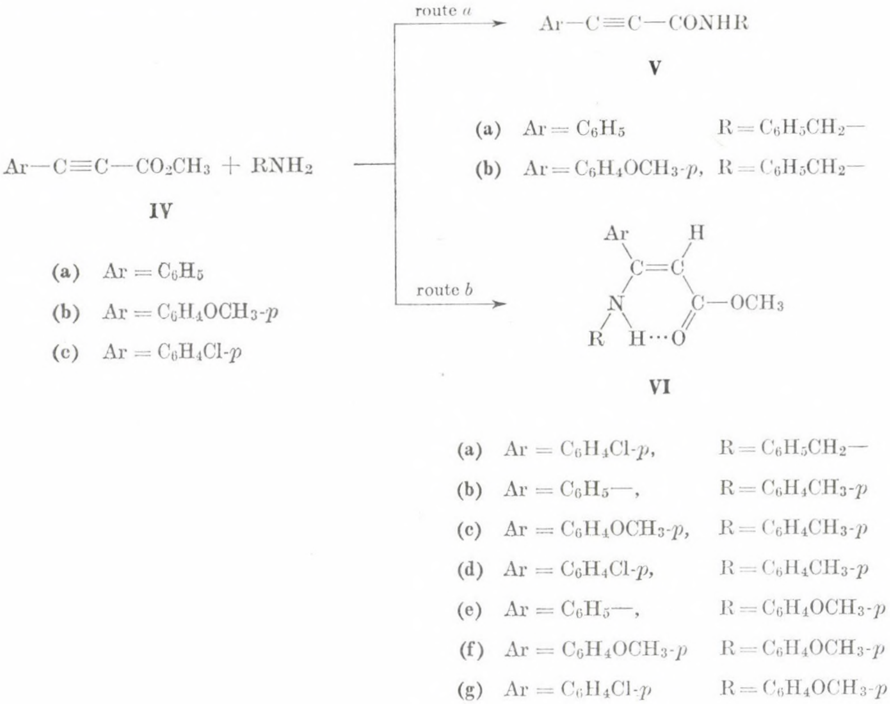
$$\mathrm{(Ar{-}C{\equiv}C{-}CONH{-}CH_2{-})_2}$$

III

phenyl)-propynoic amide (**IIb**), respectively. The present work was aimed at extending the study of the reactions of methyl 3-aryl-2-propynoates with benzylamine, various amino-derivatives such as *p*-methylaminobenzene, *p*-methoxyaminobenzene and *o*-phenylenediamine, benzoylhydrazine and benzamidine hydrochloride in order to establish the structure and/or configuration of the products as well as the scope of the reactions.

a) *Reactions with benzylamine*

When methyl 3-aryl-2-propynoates (**IVa—c**) were allowed to react with an equimolar amount of benzylamine in methanol, they gave rise to the corresponding *N*-benzyl-3-aryl-2-propynoic amides (**Va** and **b**) in the case of **IVa** and **IVb**, and methyl (*Z*)-*β*-benzylamino-*p*-chlorocinnamate (**VIa**) in the case of **IVc**. In the first case, benzylamine attacked the ester grouping (route *a*), whereas in the latter case nucleophilic attack, by the amine, at the *β*-acetylenic carbon atom occurred (route *b*).



$Ar—C{\equiv}C—CO_2CH_3 + RNH_2$

IV

(a) $Ar = C_6H_5$
(b) $Ar = C_6H_4OCH_3\text{-}p$
(c) $Ar = C_6H_4Cl\text{-}p$

$Ar—C{\equiv}C—CONHR$

V

(a) $Ar = C_6H_5$ $R = C_6H_5CH_2—$
(b) $Ar = C_6H_4OCH_3\text{-}p,$ $R = C_6H_5CH_2—$

VI

(a) $Ar = C_6H_4Cl\text{-}p,$ $R = C_6H_5CH_2—$
(b) $Ar = C_6H_5—,$ $R = C_6H_4CH_3\text{-}p$
(c) $Ar = C_6H_4OCH_3\text{-}p,$ $R = C_6H_4CH_3\text{-}p$
(d) $Ar = C_6H_4Cl\text{-}p,$ $R = C_6H_4CH_3\text{-}p$
(e) $Ar = C_6H_5—,$ $R = C_6H_4OCH_3\text{-}p$
(f) $Ar = C_6H_4OCH_3\text{-}p$ $R = C_6H_4OCH_3\text{-}p$
(g) $Ar = C_6H_4Cl\text{-}p$ $R = C_6H_4OCH_3\text{-}p$

The structure of **Va** and **b** was confirmed by analytical data, infrared and electronic spectroscopy (*cf.* Table I).

The structure of **VIa** was established from its analytical data and infrared spectroscopy which was devoid of a band at *ca.* 2200 cm^{-1} ($\nu_{C\equiv C}$) (*cf.*

Table I

N-Benzyl-3-aryl-2-propynoic amides (**Va** *and* **b**) *and methyl (Z)-β-benzylamino-p-chlorocinnamate* (**VIa**)

Compound	m.p. (°C)	Yield (%)	Formula	Analysis: Calcd., Found			Infrared spectra (cm^{-1})			Electronic spectra	
				C	H	N	ν_{NH}	$\nu_{C=C}$	$\nu_{C=O}$	γ_{max} (nm)	log ε
Va	104—5*	70	$C_{16}H_{13}NO$	81.68 81.70	5.57 5.53	5.95 5.46	3260	2220	1630	258	4.5
Vb	104—5**	60	$C_{17}H_{15}NO_2$	76.96 76.50	5.70 5.66	5.28 5.20	3260	2210	1635	277 291	4.4 4.3
VIa	77—8*	75	$C_{17}H_{16}ClNO_2$	67.66 68.05	5.34 5.68	4.64 4.19	3280	—	1640		

* From methanol
** From benzene

Table I). Its configuration as *Z* was established from the fact that $\nu_{C=O}$ has a lower value when compared with $\nu_{C=O}$ of α,β-unsaturated esters [4]. This suggested chelation of the C=O group by the NH group and this is only compatible with a *Z*-configuration of the product.

It is worth noting that ethylenediamine, ethanolamine [3] and *n*-butylamine [2] have been reported to give with methyl (or ethyl) 3-phenyl-2-propynoate, *N*-substituted-3-phenyl-2-propynoic amides. These results together with those obtained in the case of benzylamine may, therefore, establish that aliphatic primary amines attack the ester grouping of acetylenic esters preferentially to give derivatives of 3-aryl-2-propynoic amides. However, formation of **VIa** from methyl 3-(*p*-chlorophenyl)-2-propynoate (**IVc**) and benzylamine may be explained on the basis that the presence of a chlorine atom (with its -*I* effect) in the *p*-position of the phenyl group adjacent to the —C≡C— group makes the latter more susceptible to be attacked by the nucleophile.

b) *Reactions with primary aromatic amines and o-phenylenediamine*

Addition of an equimolar amount of *p*-methylaminobenzene or *p*-methoxyaminobenzene to a methanolic solution of each of **IVa, b** or **c** followed by refluxing for 5 hrs gave methyl (*Z*)-β-(arylamino)cinnamates (**VIb—g**), as a result of a nucleophilic attack on the β-acetylenic carbon atom (route *b*).

The structure of **VIb—g** was confirmed by analytical data, infrared and electronic spectroscopy (*cf.* Table II). Again, the low values of $\nu_{C=O}$ and ν_{NH} in these compounds suggested that hydrogen bonding between the C=O and NH groups is involved and this established configuration of the products as *Z*.

Table II

Methyl (Z)-β-(p-tolylamino) and (p-methoxyphenylamino)-cinnamates **(VI b—d)** *and* **(VIe—g)**

Compound	m.p. (°C)	Yield (%)	Formula	Analysis: Calcd., Found			Infrared spectra (cm^{-1})		Electronic spectra	
				C	H	N	ν_{NH}	$\nu_{C=O}$	λ_{max} (nm)	log ε
VIb	90—1*	52	$C_{17}H_{17}NO_2$	76.38 76.81	6.41 6.44	5.24 5.36	3240	1670	245 320	4.05 4.1
VIc	79**	47	$C_{18}H_{19}NO_3$	72.72 73.03	6.44 6.38	4.71 4.32	3240	1660	246 320	4.05 4.3
VId	104***	68	$C_{17}H_{16}ClNO_2$	67.66 67.26	5.34 5.30	4.64 4.28	3240	1685	250.5 322	4.15 4.2
VIe	86—7***	64	$C_{17}H_{17}NO_3$	72.08 72.50	6.05 6.01	4.94 4.58	3280	1670	252 323	4.2 4.2
VIf	83****	83	$C_{18}H_{19}NO_4$	69.00 69.49	6.11 6.26	4.47 3.98	3240	1650	249 320	4.05 4.15
VIg	120****	76	$C_{17}H_{16}ClNO_3$	64.25 64.34	5.07 5.41	4.40 3.99	3240	1660	256.5 325	4.2 4.3

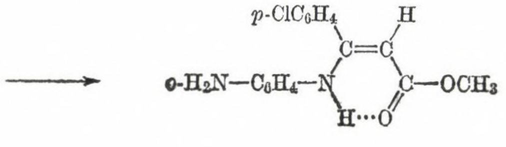
* From methanol
** From light petroleum (b.p. 80—100 °C)
*** From light petroleum (b.p. 40—60 °C)
**** From light petroleum (b.p. 60—80 °C)

Formation of the *Z*-isomers in these additions is consistent with (i) the previous findings that the addition of primary amines to acetylenes conjugated with carbonyl groups proceeds exclusively so that the C=O and NH substituents are placed in *Z* position to each other [1, 5], and (ii) with the well-established rule of trans-nucleophilic additions [6] on the other hand.

Similarly, *o*-phenylenediamine reacted with methyl 3-(*p*-chlorophenyl)-2-propynoate (**IVc**) in methanol at room temperature to give methyl (*Z*)-β-(*o*-aminoanilino)-*p*-chlorocinnamate (**VII**), whose structure was confirmed by its analytical data, infrared and NMR spectroscopy. Thus its infrared spectrum shows $\nu_{C=O}$ at 1650 cm^{-1} and ν_{NH} in the region of 3430—3220 cm^{-1} and its

$$p\text{-}ClC_6H_4{-}C{\equiv}C{-}CO_2CH_3 + o\text{-}H_2N{-}C_6H_4{-}NH_2 \longrightarrow$$

IVc



VII

NMR spectrum shows signals at δ 5.05 (s, 1H, olefinic), 3.7 (s, 3H, CO_2CH_3) and 6.4—7.2 (m, 8H, aromatic). Again, compound **VII** showed chelation effects as is evident from the low value of $\nu_{C=O}$ as compared with $\nu_{C=O}$ of α,β-unsaturated esters [4]. This may also establish the configuration of the product as *Z*.

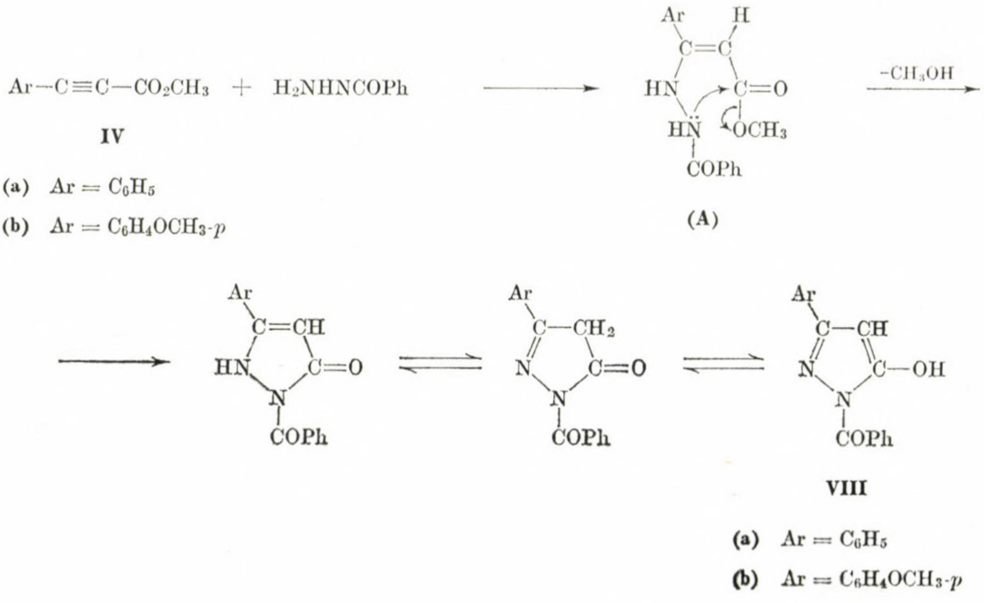
These results show that primary aromatic amines and diamines add to methyl 3-aryl-2-propynoates according to route *b*, *i.e.* nucleophilic *trans* attack at the β-acetylenic carbon atom *(cf.* ref. [1, 5, 6]) to give the (*Z*)-compounds.

c) *Reaction with benzoylhydrazine*

Refluxing a solution of methyl 3-phenyl- (**IVa**) and methyl 3-(*p*-methoxyphenyl)- (**IVb**) 2-propynoates with an equimolar amount of benzoylhydrazine in methanol gave the corresponding 1*H*-3-aryl-1-benzoyl-5-hydroxypyrazoles (**VIIIa** and **b**) whose structure was confirmed by analytical data, infrared and electronic spectroscopy *(cf.* Table III). Furthermore, **VIIIa** was hydrolyzed with concentrated hydrochloric acid *(cf.* Experimental) to give the known [7] 3-phenylpyrazol-5-one.

The absence of a band at 1705—1710 cm^{-1}, which is characteristic of the C=O group of pyrazolones [8], in the spectra of **VIII** suggested that they most probably exist in the enolic form indicated.

The reaction of the acetylenic esters (**IVa** and **b**) with benzoylhydrazine seems to take place by an initial attack on the β-acetylenic carbon atom by



IV

(a) Ar = C_6H_5

(b) Ar = $C_6H_4OCH_3$-*p*

(**A**)

VIII

(a) Ar = C_6H_5

(b) Ar = $C_6H_4OCH_3$-*p*

Table III

1*H*-3-*Aryl*-1-*benzoyl*-5-*hydroxypyrazoles* (**VIIIa** *and* **b**)

Compounds	m.p. (°C)	Yield (%)	Formula	Analysis: Calcd., Found C	H	N	Infrared spectra (cm^{-1}) ν_{NH}	$\nu_{C=O}$	Electronic spectra γ_{max} (nm)	log ε
VIIIa	243–5	57	$C_{16}H_{12}N_2O_2$	72.72 72.34	4.58 4.65	1.060 1.018	3180	1670	223	4.5
VIIIb	250	61	$C_{17}H_{14}N_2O_3$	69.38 69.09	4.79 4.84	9.52 9.14	3160	1670	220 269	4.6 4.4

the NH_2 group o-benzoylhydrazine to give intermediate A (not isolated) which then gives **VIII** *via* ring closure. This postulate is consistent with the previous finding [9] that aroylhydrazines add to the acetylenic bond of dimethyl acetylenedicarboxylate to give the hydrazones of oxalacetic ester [9].

d) *Reaction with benzamidine hydrochloride*

The acetylenic esters (**IVa–c**) react with benzamidine hydrochloride in the presence of aqueous sodium carbonate *(cf.* Experimental) to give the corresponding methyl (*Z*)-*β*-benzamidinocinnamates (**IXa–c**) whose structures were confirmed by analytical data, infrared and electronic spectroscopy. Thus, their infrared spectra *(cf.* Table IV) show strong bands for C=O (chelated) and NH groups and are devoid of bands at *ca.* 2200 cm^{-1} ($\nu_{C\equiv C}$), which indicates that the nucleophile attacked preferentially the *β*-acetylenic carbon

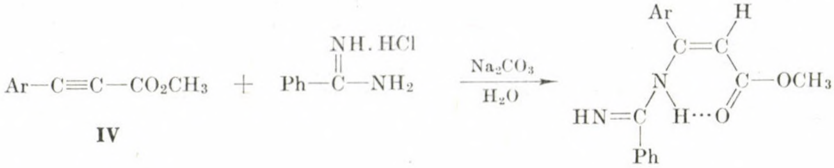
Table IV

Methyl (*Z*)-*β*-*benzamidinocinnamates* (**IXa–c**)

Compound	m.p. (°C)	Yield (%)	Formula	Analysis: Calcd., Found C	H	N	Infrared spectra (cm^{-1}) ν_{NH}	$\nu_{C=O}$	Electronic spectra λ_{max} (nm)	log ε
IXa	144*	71	$C_{17}H_{16}N_2O_2$	72.84 72.54	5.75 5.61	10.00 10.14	3260	1675	230 260	4.6 4.3
IXb	202*	77	$C_{18}H_{18}N_2O_3$	69.67 69.33	5.85 5.33	9.03 8.69	3280	1675	238 261	4.5 4.4
IXc$^+$	192**	63	$C_{17}H_{15}ClN_2O_2$	64.86 64.41	4.80 4.83	8.90 8.42	3260	1675	239 254	4.4 4.5

* From benzene-ethanol mixture
** From ethanol
$^+$ Cl: Calcd. 11.28; Found 11.73%

atom. Their electronic spectra (*cf.* Table IV) may reflect their structural analogy.



IV

IX

(a) Ar = C_6H_5—

(b) Ar = $C_6H_4OCH_3$-*p*

(c) Ar = C_6H_4Cl-*p*

Experimental

All melting points are uncorrected. Infrared (KBr discs) and electronic (in ethanol) spectra were recorded on Unicam SP 1200, Beckman IR 20 and Beckman DK-2 Ratio-Recording spectrophotometers, respectively. ^{1}H-NMR spectra (in $CDCl_3$) were recorded on a Varian XL-100-VFT system using TMS as an internal standard.

General procedure for the addition of benzylamine to methyl 3-aryl-2-propynoates (IVa—c)

Benzylamine (1.0 g, 0.01 mol) in methanol (10 mL) was added to a solution of methyl 3-aryl-2-propynoate (**IV**) (0.01 mol) in methanol (10 mL) and the reaction mixture was allowed to stand at room temperature for one to two days until crystallization occurred. The solid product was then filtered off and recrystallized from a suitable solvent to give *N*-benzyl-3-aryl-2-propynoic amides (**Va** and **b**) and methyl (*Z*)-*β*-benzylamino-*p*-chlorocinnamate (**VIa**). The results are given in Table I.

General procedure for the addition of primary aromatic amines to methyl 3-aryl-2-propynoates (IVa—c)

p-Methylaminobenzene or *p*-methoxyaminobenzene (0.01 mol) in methanol (10 mL) was added to a solution of the acetylenic ketone (**IV**) (0.01 mol) in methanol (10 mL) and the reaction mixture was refluxed for 5 hrs on a boiling water bath. The reaction mixture was then allowed to stand at room temperature overnight, whereby a crystalline product was obtained. Upon filtration and crystallization from the appropriate solvent, methyl (*Z*)-*β*-(*p*-tolylamino) or (*p*-methoxyphenylamino)cinnamate derivatives (**VIb**—**d** or **VIe**—**g**) were obtained. The results are given in Table II.

Addition of o-phenylenediamine to methyl 3-(*p*-chlorophenyl)-2-propynoate (IVc)

o-Phenylenediamine (0.54 g, 0.005 mol) in methanol (10 mL) was added to a solution of **IVc** (0.98 g, 0.005 mol) in methanol (10 mL) and the reaction mixture was allowed to stand at room temperature for 24 hrs. The solid that precipitated was filtered off and recrystallized from light petroleum (b.p. 80—100 °C) to give methyl (*Z*)-*β*-(*o*-aminoanilino)-*p*-chlorocinnamate (**VII**) (60% yield), m.p. 159—160 °C.

$C_{16}H_{15}ClN_2O_2$. Calcd. C 63.47; H 4.95; Cl 11.73; N 9.25. Found C 63.63; H 5.11; Cl 11.69; N 8.90%.

General procedure for the addition of benzoylhydrazine to methyl 3-aryl-2-propynoates (IVa and b)

Benzoylhydrazine (0.01 mol) in methanol (20 mL) was added to a solution of the methyl 3-aryl-2-propynoates (**IVa** or **b**) (0.01 mol) in methanol (10 mL) and the reaction mixture was refluxed for 8 hrs on a boiling water-bath. The solution was then concentrated and the solid that precipitated was filtered off and recrystallized from benzene-ethanol to give 1*H*-3-aryl-1--benzoyl-5-hydroxypyrazole (**VIIIa** or **b**). The results are given in Table III.

Conversion of 1*H*-1-benzoyl-5-hydroxy-3-phenylpyrazole (VIIIa) into 3-phenylpyrazol-5-one

1*H*-1-Benzoyl-5-hydroxy-3-phenylpyrazole (**VIIIa**) (1.0 g) in concentrated hydrochloric acid (10 mL) was refluxed for 2 hrs and the solid precipitated upon cooling of the reaction mixture was filtered off and dissolved in water (5 mL). Neutralization of the aqueous solution of the hydrochloride with sodium carbonate gave a precipitate which was filtered off and dried. Recrystallization of the product from ethanol gave 3-phenylpyrazol-5-one (0.5 g), m.p. and mixed m.p. with an authentic specimen [7] 235 °C.

General procedure for the addition of benzamidine hydrochloride to methyl 3-aryl-2-propynoates (IVa—c)

Benzamidine hydrochloride (1.6 g, 0.01 mol) in methanol (20 mL) was added to a solution of methyl 3-aryl-2-propynoate (**IVa**, **b** or **c**) (0.01 mol) in methanol (20 mL). Aqueous sodium carbonate (0.53 g, in the least amount of water) was then added to the reaction mixture dropwise over 15 min. The reaction mixture was refluxed on a boiling water-bath for 5 hrs, concentrated and the precipitated solid was filtered off. Recrystallization from a suitable solvent gave the corresponding methyl (*Z*)-β-benzamidinocinnamate (**IXa**, **b** or **c**). The results are given in Table IV.

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RECENSIONES

E. W. Flick: *Household and Automotive Chemical Specialties*

Noyes Data Corp., 1979, 390 pages

The book forms a volume of the series of patent and formulation collections known also in Hungary, and containes the full formulation of 545 very useful household chemical and motor car tending preparations. Descriptions are divided into three parts. In the first part percentage composition of basic materials needed for the preparation are given, the second part contains important information in conjunction with the compounding of the preparation, while in the third part, the compilers of the volume summarize the substantial merits of the use of the preparation. The volume is organized in four main parts. The first part contains the formulations of household chemical preparations, the second those of motor-car tending agents. In the third part the chemical structure of the additives marked with a trade name in the formulation, or its approximate description, is given, and in the fourth part also the companies manufacturing the components of the given trade name.

Household chemical preparations, to mention only the most important, comprise detergents of general use, detergent compositions for laundries, carpet cleaning and tending preparations, leather and plastics cleaners, floor and furniture revivers and parquet polishes, and dishwasher and washing compositions of a wide variety. The second part of the volume contains formulations of preparations suitable for the cleaning and polishing of motorcars and for the cleaning of the engine block, formulations of cleaning agents for the tending of tyres and of many other car tending specialties.

The book will be a useful aid for chemists and chemical engineers engaged in research and development in the field of household chemistry, because its study makes them acquainted with a series of new preparations, and the knowledge of their properties of utilization and the prices of the additives offers a possibility to modify the formulations of their products manufactured already.

B. Losonczi

J. I. Duffy: *Printing Inks*

Development since 1975 Chemical Technology Review No. 139
336 pages, Noyes Data Corporation. New Jersey, USA, 1979

This book, similarly to other volumes of this series, is an elaborated patent collection relevant to a period of a special field. It covers practically all the US patents concerning printing inks, their manufacture, application and linked branches, having appeared between January 1, 1976, and the end of 1978. (Previous titles on this subject were published in 1972 and 1976.)

The book classifies the patents by subject matter in the following groups:

1. *Conventional printing inks*, their binders and auxiliary materials.

2. *Duplicating inks;* in addition to conventional *(e.g.* hectographic and carbon) inks, materials of chemical copying systems (self-copying paper sets), thermal copying papers, and the inks of electrostatic (*e.g.* xerox) copying.

3. *Pigments, dyestuffs.* Numerous mono- and polyazo, phthalocyanine, indoline, metal complex and other colouring substances, fluorescent **materials** (mainly pigments), to be used in lacquers, printing inks, textile printing dyes, or for the colouring of plastics (PVC, polyamide, cellulose esters and ethers, *etc.*).

4. *Inks of jet printing* (printing with an ink jet deflected by electrical or magnetic field) on non-adsorbent surfaces (on plastics, glass, metal too); preparation of magnetic pigments suitable for this purpose; nozzle cleaning with ultrasound.

5. *Radiation curable inks,* primarily binding materials, polymerization photoinitiators of UV-curing inks, electric conductive inks of this type, suitable for the manufacture of printed circuits.

6. *Textile printing:* printing dyestuffs, thickeners, marking inks, finishing processes and materials. The chapter deals in detail with the inks for thermal transfer printing, in spreading use.

7. The chapter "*Specialty inks and applications*" covers thermochromic dyes (particularly on liquid crystal basis), ball-point pen inks, marking pen inks, electrical resistor inks and other problems of application techniques, of which *e.g.* a plasticsantifoaming printing ink is recommended for use in the manufacture of embossed plastics floor and wall tiles.

8. *Company Index, Inventor Index* and the list of patents according to registration number close the volume.

The book contains the cited patents in an edited form.

This form offers more than an abridgement, because it discusses all the essential contents of the patents, enumerates materials used, formulations and operations, but at the same time does not simply quote the text of the patent. It is to the advantage of the book that the author deliberately omits the complicated language, generally characteristic of patents and justified primarily from the aspect of patent rights, as well as the perpetual repetitions in the Claims. Thus, the edited form is easier to survey and understand than the original patent.

The author does not qualify the patents and does not take stands concerning their realizability.

The book summarizes technical problems that arose in recent years in this field and their alternative solutions, making thus possible a retrospective assessment, and with a relatively short delay the survey of present status; it may give inspiration, and can be used as a concentrated source for novelty investigation, naturally only with respect to the USA.

The book gives useful information to specialists engaged in applied research and technological development in the relevant industrial branches.

J. HALABRIN

M. W. RANNEY: *Oil Shale and Tar Sands Technology* (Recent Developments)

Pp. 429., Noyes Data Corp., Park Ridge, New Jersey, 1979

Technologies, granted patent protection in the U.S.A., between March 1975 and December 1978, for the processing of oil shales and tar sands are presented in this book, with many details and in a manner well suited for the expert reader. Nearly all the technologies dealt with here have the recovery of fluid energy carriers, of hydrocarbons, as their purpose. The professional and economical significance of this book can be judged by some data there pointed out, viz. that mineral oil recoverable from the shale deposits detected up to now is estimated at 27×10^9 tons (19×10^9 of this in the U.S.A.), and, essentially bituminous, heavy oils in tar sands may amount to 3.6×10^{12} tons in the U.S.A. and to 13×10^{12} tons in Canadian deposits. Thus the importance of an economically and technologically efficient recovery cannot be overemphasized.

This book sorts out the relevant patent specifications in five groups. The first three deal, respectively, with the distillation of shales ex situ, *i.e.* quarried and removed from deposits; with recovery of hydrocarbons from shale deposits *in situ*, *i.e.* processing without mining operations; and with refinery and purification of the crudes and gases thus produced. Two chapters deal with tar sand processing: in one the *in situ* technologies are collected, *i.e.* flooding with hot water, extraction with solvents, combustion *in situ*. The final chapter contains separation techniques applied to sands *ex situ.*

The presentation of the specifications is sufficiently detailed; understanding is facilitated by means of drawings and flow-charts. This book offers technological information that cannot be found in professional journals or in scientific monographs. The timeliness of the publication of this book happens to be emphasized also by the fact that noteworthy deposits of oil shale have been detected in Hungary.

J. Tóth

F. Rosenberger: *Fundamentals of Crystal Growth* I

Macroscopic Equilibrium and Transport Concepts Springer Series in Solid-State Sciences, Vol. 5
Springer-Verlag, Berlin—Heidelberg—New York, 1979, 530 pages

The intention of the Author is to give a three-volume foundation to the interdisciplinary field of crystal growth. Recently crystal growth has acquired autonomy and covers a broad spectrum of knowledge from solid state physics and chemistry, thermodynamics, statistical mechanics, surface physics and chemistry, analytical and preparative chemistry, fluid dynamics, crystallography, electrochemistry and technology. Owing to the difficult accessibility of facts scattered over a wide field, this interdisciplinary science raises many difficulties for both professors and students. Based upon his abundant experience in teaching this subject, and in growing crystals, the Author attempts a balanced presentation of knowledge needed for the control of crystal growth processes.

In the present first volume essentially the physico-chemical foundations are laid in five chapters, *viz.* 1. Thermodynamics, 2. Phase equilibria and phase diagrams, 3. Crystal growth and phase diagrams. 4. Mass and heat transfer, 5. Segregation.

The subject matter for the chapters is chosen with the discernment of the experienced crystal grower with due care for the unity of theory and practice. Problems to be solved by the reader are given at the end of each chapter, together with ample reference to the literature.

The second volume, being prepared, intends to discuss the kinetics and morphology of crystal growth together with theoretical considerations and models pertinent to this topic.

In the third volume a presentation of the techniques of crystal growth is planned. The possibilities offered by various techniques forcing the expert to make a compromise will be discussed.

The approach evident in the first volume is up-to-date indeed. The Author endeavours to lay the foundation for the understanding of every process during crystal growth, therefore, various transport phenomena, and phase diagrams describing the behaviour of several substances are discussed in detail. Distinct and clear definitions are attempted with success, often discrepancies in interpretations in earlier literature are pointed out. The multitude of drawings and photographs, the logical deduction of equations and accurate cross-references make this book easily readable and most valuable.

It is felt that these three volumes, of which the first is available, will become a standard work for experts active in the practice of crystal growth as well as for professional teaching personnel.

R. Voszka

INDEX

PHYSICAL AND INORGANIC CHEMISTRY

ORGANIC CHEMISTRY

Printed in Hungary

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NEW DATA TO THE MECHANISMS OF THE PERKOW-ARBUZOV REACTION

(PRELIMINARY COMMUNICATION)

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

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The reactions of trialkyl phosphite with α-halogenoacetophenones are known to involve two pathways, resulting in oxo-phosphonates and vinyl phosphates. In spite of numerous efforts, the mechanism of the reactions has not been fully elucidated [1—6].

On the basis of the kinetic data gathered in these reactions we came to the conclusion that there should be only one intermediate common for both the ketophosponate and vinyl phosphate directions [7].

Now we present a series of crossover experiments showing that it is the phosphonium salt $Q^+ X^-$ that is formed in the reaction of trimethyl phosphite with α-bromoacetophenone (Scheme 1).

In the mixture of a chloroacetophenone and a bromoacetophenone, the latter being substituted in the aromatic ring in another way than the former, the ratio of the vinyl phosphates and ketophosphonates is different from the mathematical sums of the quantities obtained in the reactions of each halogenoacetophenones with trimethyl phosphite (Tables I and II). The direction of the changes is such as if the bromoketone obtainable from the chloroketone by halogen exchange and, conversely, the chloroketone formed from the bromoketone by similar exchange had also been present in the reaction mixture.

The reactions were run at 70°C with an excess of trimethyl phosphite using 2.5 mmoles of the halogenoacetophenones in each experiment. Analyses were made by GLC [7]. The extent of the exchange reaction was calculated and shown in the Tables.

As the possibility of a halogen exchange between α-halogenated acetophenones in the absence of trimethyl phosphite was excluded by separate experiments, the result can only** be explained by supposing an ion exchange reaction

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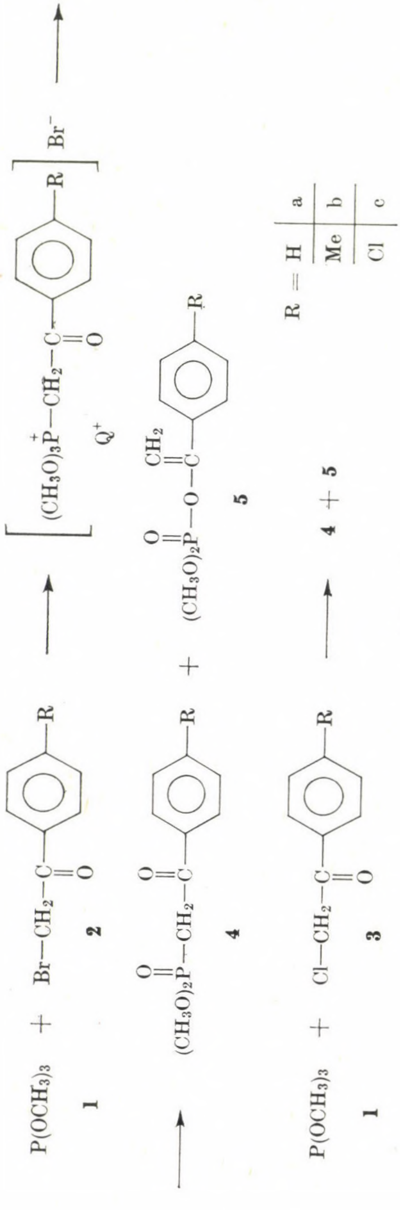
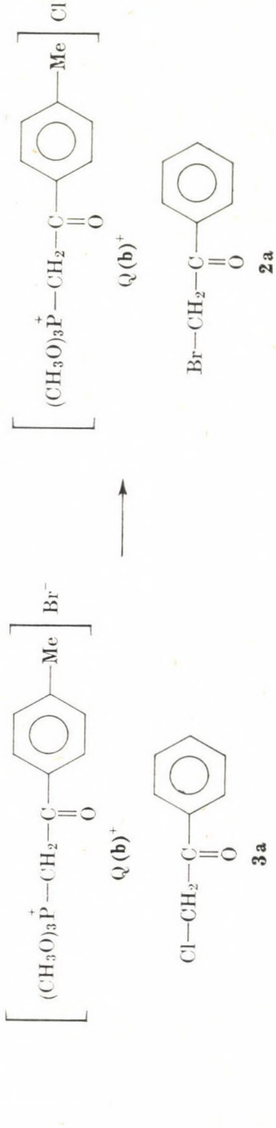
[*] To whom correspondence should be addressed.

[**] The existence of the halophosphonium-enolate ion pair intermediate [7] is questionable, since no appreciable amount of dehalogenation of α-halogenoacetophenones can be observed during the Arbuzov—Perkow reaction even in the presence of an acid catalyst [5].



Scheme 1



Scheme 2

Table I

Starting compd. Products, mmole	3a	2a	3b	2b	3a + 2b	Crossed reaction, in mmole, %
		in benzene				
5a	2.50	1.33	—	—	2.44	
4a	0	1.17	—	—	0.06	0.13
5b	—	—	2.50	0.93	1.01	5
4b	—	—	0	1.57	1.49	
		in chlorobenzene				
5a	2.50	1.00	—	—	2.38	
4a	0	1.50	—	—	0.12	0.20
5b	—	—	2.50	0.63	0.78	8
4b	—	—	0	1.87	1.72	
		in acetonitrile				
5a	2.44	0.66	—	—	1.97	
4a	0.06	1.84	—	—	0.53	0.58
5b	—	—	2.41	0.31	0.81	23
4b	—	—	0.09	2.19	1.69	
		in nitrobenzene				
5a	2.41	0.43	—	—	1.81	
4a	0.09	2.07	—	—	0.68	0.70
5b	—	—	2.38	0.27	0.85	28
4b	—	—	0.12	2.23	1.65	

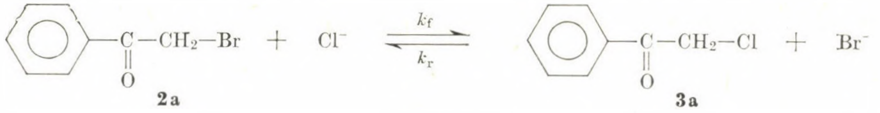
Table II

Starting compd. Products, mmole	3a	2a	3c	2c	2a + 3c	Crossed r., in mmole %	2c + 3a	Crossed r. in mmole, %
		in benzene						
5a	2.50	1.33	—	—	1.40		2.44	
4a	0	1.17	—	—	1.10	0.16	0.06	0.13
5c	—	—	2.50	1.60	2.44	6	1.65	5
4c	—	—	0	0.90	0.06		0.85	
		in chlorobenzene						
5a	2.50	1.00	—	—	1.10		2.38	
4a	0	1.50	—	—	1.40	0.18	0.12	0.19
5c	—	—	2.50	1.38	2.42	7	1.46	8
4c	—	—	0	1.12	0.08		1.04	
		in acetonitrile						
5a	2.44	0.72	—	—	1.20		2.00	
4a	0.06	1.78	—	—	1.30	0.66	0.50	0.65
5c	—	—	2.47	0.90	2.05	26	1.32	26
4c	—	—	0.03	1.60	0.45		1.18	
		in nitrobenzene						
5a	2.41	0.70	—	—	1.21		1.95	
4a	0.09	1.80	—	—	1.29	0.70	0.55	0.67
5c	—	—	2.45	0.88	2.00	28	1.30	27
4c	—	—	0.05	1.62	0.50		1.20	

between ionic halogen of the phosponium bromide and the chloroacetophenone starting material (Scheme 2 for the reaction between the salt from **2b** and **3a**).

The extent of the exchange reaction depends on the solvent polarity and temperature, and it can be as high as 28% in nitrobenzene at 70°C.

The mechanism of the exchange reaction shown in Scheme 2 has also been substantiated by the data obtained in exchange reactions between lipophylized chloride or bromide ion (using triethylbenzylammonium chloride, TEBAC, or tetrabutylammonium bromide, TBAB) and α-bromo- and α-chloroacetophenones, respectively (Scheme 3).



Scheme 3

The exchange reactions in benzene at ambient temperature are faster by about two orders of magnitude ($k_f \approx 5$ dm^{3}mol^{-1}s^{-1}; $k_r \approx 5 \times 10^{-3}$ dm^{3}mol^{-1}s^{-1}) than the rate of the Perkow-Arbuzov reaction ($k = 1.8 \times 10^{-5}$ dm^{3}mol^{-1}s^{-1}) with the same halogenacetophenones and an equilibrium ($K \approx$ $\approx 10^3$) is attained.

It is important to note that in the Arbuzov-type reaction of phosphites with halogens MICHALSKI *et al.* succeeded in confirming the existence of halogenophosphonium salt intermediates [8].

^{31}P-NMR measurement at ambient temperature to check the charged intermediate have remained unsuccessful, probably owing to the low concentration of the intermediate.

A number of experiments were also made in acetonitrile at 70°C to study the effect of the added nucleophile on the product ratio (measured after a fourhour reaction time, Table III).

Table III

Reaction	Added salt mole, %		Products mole, %				Product ratio 5 : 4	Dealkylation mole, %
2c + **1**	—		**5c**	29	**4c**	71	0,41	0
	TEBAC	40		14		36	0.67	40
	TBAB	40		13		47	0.28	40
3a + **1**	—		**5a**	98	**4a**	2	49	0
	TEBAC	40		58		2	29	40
	TBAB	40		38		22	1.7	40

It can be seen from Table III that the added ion other than the leaving ion in the halogenoacetophenone does influence the product ratio. The aim of finding connection between the nucleophilicity of the added anion and the direction of the decomposition of Q^+ has not been reached, however, because of at least two complicating factors: there are fast exchange reactions between the halogeno-acetophenones and the added ions and, on the effect of the added salt, both products undergo decomposition to give dealkylated product with rates different from each other.

Moreover, Table III shows that a quantitative dealkylation of the products occurs which, at the same time, comprises a new method of preparing acids from phosphonic or phosphoric acid esters [9].

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SYNTHESIS OF HETEROCYCLES *VIA* LACTONES*

A NEW ROUTE FOR THE SYNTHESIS OF *N*-β-PHENETHYLTETRAHYDROISOQUINOLINE ALKALOIDS

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A convenient synthesis of *N*-β-phenethyl-1,2,3,4-tetrahydroisoquinoline alkaloids is described. Condensation of the bromo esters **I a—b** with β-phenethylamines **II a—c** afforded the *N*-β-phenethyl-3-isoquinolones **III a—c**. Lithium aluminium hydride reduction of the isoquinolones **III a—c** in refluxing tetrahydrofuran gave substituted *N*-β-phenethyl-1,2,3,4-tetrahydroisoquinolines **IV a—c**.

Recently we have reported new total syntheses of tetrahydroisoquinoline [2, 3], *N*-benzyltetrahydroisoquinoline [4, 5], tetrahydroprotoberberine [6, 7, 8] and hexadehydroyohimbane [9] alkaloids making efficient use of 3-isochromanones. In the course of our further experiments on isoquinoline alkaloids, we have achieved a new, convenient, two step reaction sequence for the synthesis of *N*-β-phenethyl-1,2,3,4-tetrahydroisoquinolines starting from readily available 3-isochromanones. These results are reported in this paper.

The required bromo esters **Ia, b** [2—5, 7—9] were prepared from 3-isochromanones [10, 11]; they were then condensed with the β-phenethylamines **IIa—c** to afford the tricyclic lactams **IIIa—c** which were reduced with lithium aluminium hydride to the corresponding *N*-β-phenethyltetrahydroisoquinolines **IVa—c** (Scheme 1).

Experimental

All m.p. 's are uncorrected and were recorded in open capillaries on a 'Toshniwal' m.p. apparatus. IR spectra were recorded on a JASCO model IR-S spectrophotometer. NMR spectra were obtained on a Thompson Packard (TPV 60) spectrometer using TMS as the internal standard. Mass spectra were recorded on an Atlas AEI MS 902 spectrometer at 70 eV.

General procedure for the preparation of the bromo esters

The appropriate substituted 3-isochromanone was dissolved in ethanolic hydrogen bromide at 0—5 °C with constant stirring. After stirring for 30—45 min, the mixture was allowed to warm to room temperature and set aside for 24 h. The excess solvent and reagents were then removed at 5 mm-Hg and 20 °C to get the corresponding bromo ester.

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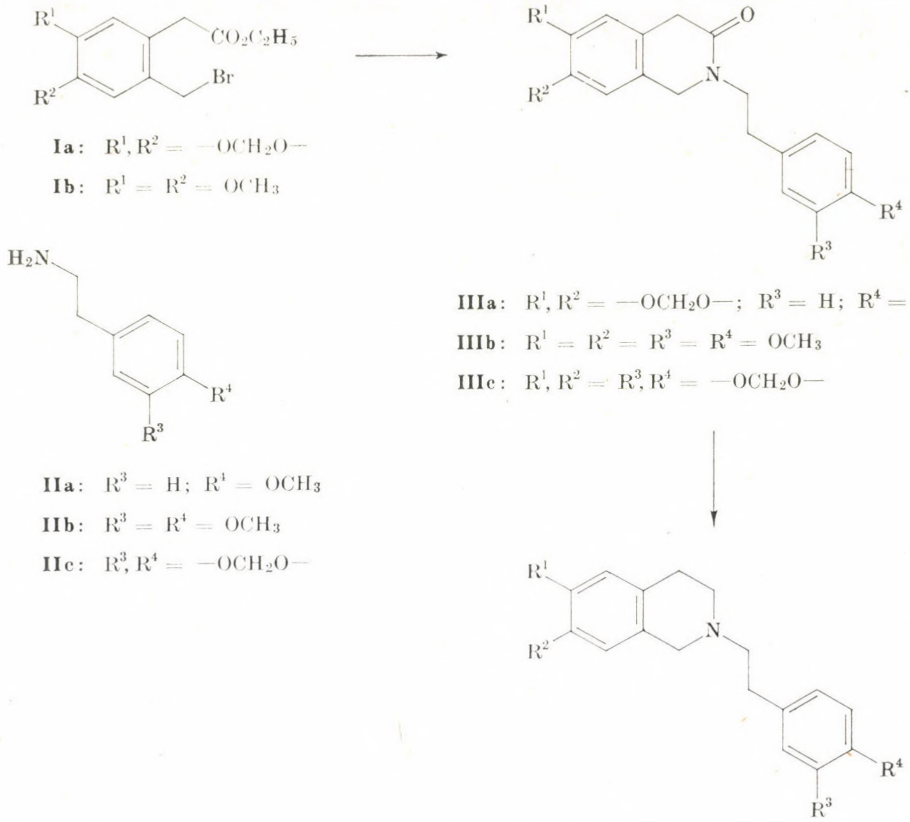
* Part IX, See ref. [1]



Ia: $R^1, R^2 = -OCH_2O-$

Ib: $R^1 = R^2 = OCH_3$

IIa: $R^3 = H$; $R^4 = OCH_3$

IIb: $R^3 = R^4 = OCH_3$

IIc: $R^3, R^4 = -OCH_2O-$

IIIa: $R^1, R^2 = -OCH_2O-$; $R^3 = H$; $R^4 = OCH_3$

IIIb: $R^1 = R^2 = R^3 = R^4 = OCH_3$

IIIc: $R^1, R^2 = R^3, R^4 = -OCH_2O-$

IVa: $R^1, R^2 = -OCH_2O-$; $R^3 = H$; $R^4 = OCH_3$

IVb: $R^1 = R^2 = R^3 = R^4 = OCH_3$

IVc: $R^1, R^2 = R^3, R^4 = -OCH_2O-$

2-(4-Methoxy-β-phenethyl)-6,7-methylenedioxy-1,2,3,4-tetrahydro-3-isoquinolone (III a)

Ethyl 2-bromomethyl-4,5-methylenedioxyphenyl acetate [8] **Ia** (3.0 g) dissolved in dioxan (12 mL) containing K_2CO_3 (1.5 g) and KI (0.5 g), was mixed with 4-methoxy-β-phenethylamine **II a** (1.50 g) dissolved in dioxan (16 mL). The mixture was refluxed on a water bath for 60 h. After the reaction mixture had cooled, dioxan was distilled off at reduced pressure and the residue extracted with $CHCl_3$ and the organic layer washed with 6N HCl, three times with water and dried (Na_2SO_4). Removal of the solvent in vacuum left a dark red syrup which was crystallized from MeOH to give **III a** (2.75 g; 84%), m.p. 155—160 °C.

IR (Nujol) : 1620 (six-membered lactam), 1520, 1490, 1380, 1270, 1190, 1045, 840, 730 cm^{-1}.

Mass spectrum (*m/e*) : 325 (M^+), 324, 309, 281, 277, 267, 266, 215, 192, 191, 179, 167, 163, 149, 147, 135 (base), 121, 107, 91, 57, *etc.*

$C_{19}H_{19}O_4N$ (325). Calcd. C 70.02; H 5.8; N 4.30. Found C 69.7; H 5.34; N 4.62%.

N-(4-Methoxy-β-phenethyl)-6,7-methylenedioxy-1,2,3,4-tetrahydroisoquinoline (IV a)

To a suspension of LAH (3.20 g) in THF (20 mL), a solution of the above isoquinolone (1.6 g) dissolved in THF (12 mL) was added in portions over 30 min, with stirring and cooling in an ice bath. The mixture was then refluxed on a water bath for 6 h. After cooling, the mixture was diluted with an excess of water and the gel which formed was separated by decantation. The solution thus obtained was then repeatedly extracted with EtOAc, the extract washed with water and dried. The solvent was removed under reduced pressure to give the isoquinoline **IV a** as a powder; after recrystallization from $CHCl_3$, the product was 1.00 g (60%), m.p. 92 °C.

IR (Nujol): 1600, 1360, 840 cm^{-1}.

Mass spectrum (m/e): 313 (M^+), 314 $(M + 1)^+$.

$C_{19}H_{23}O_3N$ (313). Calcd. C 72.9; H 7.3; N 4.33. Found C 72.81; H 7.41; N 4.33%.

N-(3,4-Dimethoxy-β-phenethyl)-6,7-dimethoxy-1,2,3,4-tetrahydro-3-isoquinolone (III b)

Ethyl 2-bromomethyl-4,5-dimethoxyphenyl acetate [3] (**I b**) (2.93 g) dissolved in dioxan (20 mL) containing K_2CO_3 (1 g) and KI (0.3 g), was condensed with 3,4-dimethoxy-β-phenethylamine **II b** (1.80 g) dissolved in dioxan (30 mL). The mixture was refluxed at 100 °C for 74h and cooled. The dioxan was evaporated under reduced pressure and the mixture diluted with water. Extraction with $CHCl_3$, washing with 6*N* HCl, then with water, drying (Na_2SO_4) and evaporation of the solvent gave a syrup which was crystallized from MeOH-hexane to obtain (**III b**) as a light brown powder, 3.10 g (81.1%), m.p. 92—95 °C.

IR ($CHCl_3$): 1640 cm^{-1} (six-membered lactam).

NMR ($CDCl_3$)δ: 3.66—4.16 (broad, 18H); 6.66—6.88 (m, 4H); 7.30 (s, 1H).

Mass spectrum (m/e): 371 (M^+), 372 $(M + 1)^+$, 352, 330, 326, 235, 224, 206, 170, 182, 165 (base), 164, 152, 150, 135, 129, 107, 91, 79, 66, 51.

$C_{21}H_{25}O_5N$ (371). Calcd. C 67.8; H 6.6; O 21.5. Found C 67.72; H 6.61; O 21.23%.

N-(3,4-Dimethoxy-β-phenethyl)-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline (IV b)

The above isoquinolone (**III b**) was reduced in refluxing THF, as above, to afford **IV b** in 71% yield; m.p. 82—89 °C ($CHCl_3$); R_f 0.44 ($CHCl_3$).

$C_{21}H_{27}O_4N$ (357). Calcd. C 70.5; H. 7.5; N 3.8. Found C 70.2; H 7.69; N 3.72%.

The hydrochloride had m.p. 124—130 °C.

$C_{21}H_{24}NO_4Cl$ (389.5). Calcd. C 64.69; H 6.16; N 3.59; Cl 9.11. Found C 64.72; H 6.11; N 3.64; Cl 9.00%.

N-(3,4-Methylenedioxy-β-phenethyl)-6,7-methylenedioxy-1,2,3,4-tetrahydro-3-isoquinolone (III c)

To a well stirred solution of ethyl 2-bromomethyl-4,5-methylenedioxyphenylacetate [8] (**I a**) (150 mg) in DMF (5 mL) containing Et_3N (0.5 mL) there was added 3,4-methylenedioxy-β-phenethylamine (**II c**) (280 mg). The mixture was refluxed at 100 °C for 60 h. The cooled solution was diluted with water and extracted with $CHCl_3$ (30 mL). The $CHCl_3$ extract was washed with dilute HCl (10 mL), water (40 mL), dried (Na_2SO_4) and the solvent evaporated to leave a gummy material. Crystallization from $CHCl_3$ gave **IV c** (230 mg; 68%), m.p. 140—142 °C; R_f 0.79 (EtOH).

IR (Nujol): 1610, 1480, 1420, 1330, 1100, 940, 830, 735 cm^{-1}.

$C_{19}H_{17}O_5N$ (339). Calcd. C 66.86; H 5.57; N 4.10. Found C 66.91; H 5.60; N 4.17%.

N-(3,4-Methylenedioxy-β-phenethyl)-6,7-methylenedioxy-1,2,3,4-tetrahydroisoquinoline (IV c)

The above isoquinolone (**III c**) was reduced in refluxing THF with LAH to afford **IV c** in 65% yield, m.p. 146—149 °C (dec.).

$C_{19}H_{19}NO_4$ (315). Calcd. C 70.15; H 5.84; N 4.30. Found C 70.25; H 5.92; N 4.12%.

*

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STUDY OF THE TRANSFORMATIONS OF DIOLS AND CYCLIC ETHERS, XLVII*

TRANSFORMATION OF 1,3-BUTANEDIOL ON SOME SUPPORTED METAL CATALYSTS (NEW DATA ON THE MECHANISM OF DEHYDRATION)

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The dehydration of 1,3-butanediol was studied on supported Ag, Co and Cu catalysts. The differences between the effects of these catalysts were interpreted. Intermediates of the transformations were detected, which provide new support for the reaction mechanism proposed earlier. Correlations were established between the selectivites of the reactions, the mass velocity and the temperature.

Introduction

Detailed accounts were given previously of the results of research into the directions [1—3], the stereochemistry [4—6] and the mechanisms [7, 8] of the dehydration of diols with various structures on certain metals, mainly copper. On that basis, the scheme of transformation of 1,3-butanediol (**I**) can be outlined as in Fig. 1. The initial step is dehydrogenation, which is followed by the dealdolization of the intermediate hydroxy-oxo compounds (**II** and **III**) (the formation of **IV** or **VIII** and **IX**), and dehydration (the formation of **V** or **X**). The third reaction step is the hydrogenation of the unsaturated compounds. The end-products are 2-butanone (**VI**), butanal (**XI**), 2-butanol (**VII**), 1-butanol (**XII**), ethanol (**IX**), acetone (**IV**) and acetaldehyde (**VIII**).

The validity of the outlined processes was confirmed on Cu, Cu/SiO_2 and Raney-type Cu catalysts [3, 7, 8]. Our investigations with a supported platinum catalyst [2] and on various Raney catalysts [9, 10] showed a similar picture.

The subject of the present studies was the transformation of 1,3-butanediol on certain supported metal catalysts, and the dependence of the transformations on the mass velocity and temperature, with a view to obtaining new data in support of the above mechanism, and to generalizing this mechanism to other metal catalysts. A catalyst which, under suitable conditions, selectively converts 1,3-butanediol to 2-butanone would permit a new type of preparation of the latter compound. The investigations included commercially available industrial catalysts.

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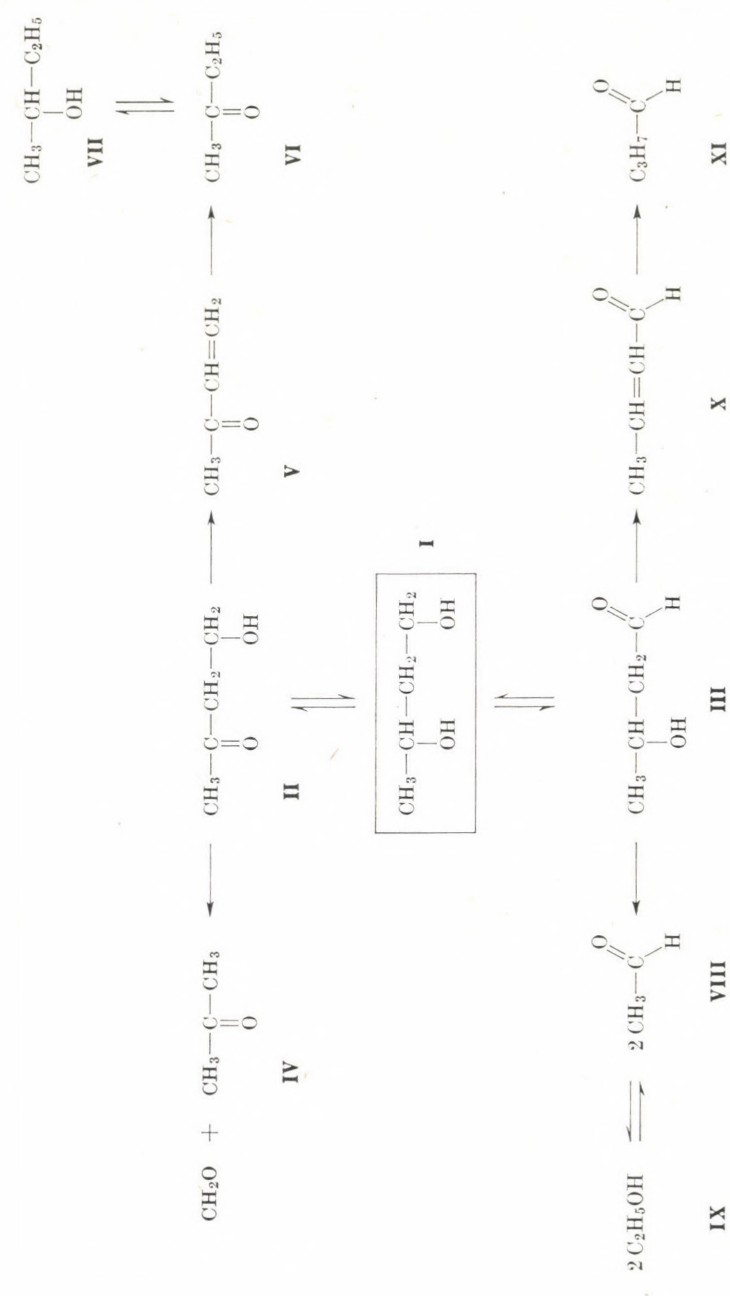

Fig. 1. Scheme of transformation of 1,3-butanediol (**I**) on metal catalysts

Experimental

Catalysts

Co-KG (KG = Merck Kieselguhr with a particle size of 2×10^{-4}—3×10^{-4} m): The support was suspended in $Co(NO_3)_2$ solution, evaporated to dryness under constant stirring, and then heated in a tube reactor at 573 K for 4 h in a stream of air. It was next reduced in a stream of hydrogen with a rate of 5×10^{-7} m^3 s^{-1} at 473 and 573 K for 1 h, and then at 673 K for 4 h. The metal content of the catalyst was 20%.

Cu-KG 1: The support was suspended in $Cu(NO_3)_2$ solution and evaporated to dryness under constant stirring. After decomposition (673 K, 4 h), reduction was performed in a hydrogen stream of 5×10^{-7} m^3 s^{-1} at 423, 473, 523 and 553 K, for 1 h at each temperature. The metal content of the catalyst was 5%.

Cu-KG 2, *Cu-COS*, *Ag-COS* (COS = BDH Cab-O-Sil M5 support): These catalysts were prepared as in Ref. [11]. In the case of Cu-KG 2 and Ag-COS, the metal hydroxide or oxide was precipitated onto the support with NaOH solution, while in the case of Cu-COS a solution of NH_4OH was used. Activation was carried out as described for Cu-KG 1. In all three cases the metal content of the catalyst was 20%.

$CuO/ZnO/Cr_2O_3$: Leuna catalyst L-1930, with a copper content of 38%.

$CuO/ZnO/Al_2O_3$: Leuna catalyst L-1950, with a copper content of 24%. Both Leuna catalysts were activated as described for Cu-KG 1.

Investigation methods

The investigations were performed with the apparatus described previously [12].

Products were analyzed with a Chrom 41 gas chromatograph, with the application of a flame ionization detector, on 2.4 m columns, with nitrogen as carrier gas. The analytical conditions and the retention times are listed in Table I.

The 1,3-butanediol used in the study was a product of BDH. It was purified by fractionation, and was gas-chromatographically pure.

Table I

Chromatographic analysis data

	Compound	Retention time (s)
Partition liquid: 15% CWAX 1500*	I	228
Carrier gas rate: 1×10^{-6} m^3 s^{-1}	II	102
	III	66
Temperature: 453 K		
	IV	234
Partition liquid: 15% diphenylformamide*	V	540
	VI	432
	VII	672
Carrier gas rate: 7.5×10^{-7} m^3 s^{-1}	VIII	120
	IX	252
Temperature: 338 K	X	1210
	XI	366
	XII	1083

* Solid support: silanized Merck Kieselguhr with a particle size of 2×10^{-4}—3×10^{-4} m

Table II

Product composition (mol %) from the catalytic transformation of 1,3-*butanediol* (I)

Expt.	Catalyst	Temp. (K)	Mass velocity*	Conversion (%)	Mol percent of compounds formed											
					II	III	IV	V	VI	VII	VIII	IX	X	XI	XII	Unidentified
1	Cu-KG 1	498	4	93	0	0	3	0	31	0	11	29	0	19	6	1 (1)**
2	Cu-KG 2	483	31	90	0	0	4	6	39	0	14	20	0	11	6	0
3	Co-KG	523	31	92	0	0	8	0	26	0	40	14	0	12	0	0
4	Cu-COS	484	36	98	0	0	4	0	47	0	16	14	4	7	8	0
5	Ag-COS	476	50	42	0	0	4	0	32	2	21	16	0	15	0	10 (2)
6	L-1930	503	64	100	21	1	7	6	29	0	12	10	0	9	5	0
7	L-1950	498	4	100	0	0	2	0	49	4	4	23	0	8	10	0
8	L-1930	523	550	78	19	0	8	5	31	0	13	9	0	10	5	0
9			300	100	2	2	12	0	49	0	14	9	0	9	3	0
10			130	100	14	2	11	0	39	0	12	9	0	9	4	0
11			120	100	10	2	12	0	39	0	14	9	0	10	4	0
12			80	100	13	2	12	0	38	0	13	9	0	8	5	0
13	L-1930	503	640	69	21	0	7	6	30	0	11	10	0	9	6	0
14			330	97	11	0	9	5	33	0	14	10	0	11	7	0
15			160	99	12	1	4	4	37	0	12	11	0	12	7	0
16			80	100	14	1	7	5	35	0	12	11	0	11	4	0
17	L-1930	473	16	100	0	0	6	0	50	0	5	14	0	9	16	0
18		498	4	100	0	0	9	0	51	4	5	14	0	7	10	0
19		523	4	100	0	0	12	0	51	4	6	13	0	7	7	0
20		548	4	100	0	0	16	0	53	3	5	11	0	3	4	5 (1)
21	L-1950	473	4	100	0	0	2	0	43	1	7	24	0	9	14	0
22		498	4	100	0	0	2	0	49	4	4	23	0	8	10	0
23		523	4	100	0	0	5	0	45	3	8	27	0	4	3	5 (1)
24		548	4	100	0	0	15	0	42	3	10	23	0	3	0	4 (1)

* units: $kg_{diol}\ kg_{cat}^{-1}\ s^{-1}\ 10^{-5}$

** the numbers in parantheses are the numbers of unidentified compounds

Results and Discussion

The characteristic experimental results are to be seen in Table II. The transformations occurring under various conditions on the different catalysts were compared on the basis of the selectivities shown in Tables III—V. The following conclusions may be drawn from the experimental data:

Table III
Selectivity of transformation of **I** *on various catalysts*

Expt.	Catalyst	Temp. (K)	Mass velocity*	Conversion (%)	Selectivities (%)					
					P_{C4}^{**}	P_D	$S_{C4} + S_{II}$	S_D	P	S
1	Cu-KG 1	498	4	93	31	25	39	4	56	43
2	Cu-KG 2	483	31	90	20	21	54	5	41	59
3	Co-KG	523	31	92	16	37	36	11	53	47
4	Cu-COS	484	36	98	22	18	55	5	40	60
5	Ag-COS	476	50	42	18	23	42	5	41	47
6	L-1930	503	64	100	17	12	63	8	29	71
7	L-1950	498	4	100	21	15	62	2	36	64

* For units, see Table II

** P denotes the selectivity of products formed by dehydrogenation at the primary hydroxy group and S that at the secondary hydroxy group. C4 refers to products with the same number of carbon atoms as in the starting diol and D refers to products formed by dealdolization.

$$P_{C4} = 100\,\frac{[\mathbf{X}] + [\mathbf{XI}] + [\mathbf{XII}]}{100 - 0.5\,[\mathbf{VIII}] - 0.5\,[\mathbf{IX}]}\,.$$

The other selectivities were calculated in a similar way. P_D refers to $0.5\,[\mathbf{VIII}] + 0.5\,[\mathbf{IX}]$; S_D to **IV**, P_{C4} to $\mathbf{X} + \mathbf{XI} + \mathbf{XII}$, S_{C4} to $\mathbf{V} + \mathbf{VI} + \mathbf{VII}$ and S_{II} to **II**

Table IV
Dependence of the transformation of **I** *on the mass velocity* (catalyst: L—1930)

Expt.	Temp. (K)	Mass velocity*	Conversion (%)	Selectivities (%)						
				P_{C4}	P_D	S_{C4}	S_D	S_{II}	P	S
8	523	550	78	17	12	41	9	21	29	71
9		300	100	16	13	55	14	2	29	71
10		130	100	17	12	44	11	16	29	71
11		120	100	16	15	44	14	11	31	69
12		80	100	15	14	42	14	15	29	71
13	503	640	69	17	12	40	8	23	29	71
14		330	97	20	12	43	13	12	32	68
15		160	99	21	13	47	5	14	34	66
16		80	100	17	13	46	8	16	30	70

* For units, see Table II

(1) Essentially the same processes take place on the catalysts examined. It also proved possible to detect intermediates of the transformations (**II**, **III**, **V** and **X**, see Table II). These data are in accordance with the mechanism proved earlier for the transformation of **I** [7, 8], and at the same time mean the generalization of this mechanism to a group of supported metal catalysts.

(2) The Leuna catalysts proved more selective as regards (a) dehydrogenation of the secondary hydroxy group; (b) conversion of **II** and **III** to products containing four carbon atoms (S_{C4}, P_{C4}; see Table III); (c) reduction of the oxo compounds formed to alcohols (see **VI**/**VII**, **VIII**/**IX** and **XI**/**XII** in Table II).

For the interpretation of (2a), it must be taken into consideration that, under the experimental conditions employed, the direct catalytic dehydrogenation of the hydroxy groups is accompanied by hydrogen transfer reactions [8, 13, 14] (Fig. 2). The donor or acceptor molecules taking part in the hydrogen transfer processes must be adsorbed on active sites of the catalyst that are close to one another, which assumes a sterically crowded transition complex

Table V
Temperature dependence of the transformation of **I**

Expt.	Catalyst	Temp. (K)	Mass velocity*	Conversion (%)	Selectivities (%)					
					P_{C_4}	P_D	S_{C_4}	S_D	P	S
17	L-1930	473	16	100	28	10	55	7	38	62
18		498	4	100	19	10	61	10	29	71
19		523	4	100	15	11	61	13	26	74
20		548	4	100	8	8	61	17	16	78
21	L-1950	473	4	100	27	18	53	2	45	55
22		498	4	100	22	15	61	2	37	63
23		523	4	100	9	21	58	6	30	64
24		548	4	100	4	20	54	18	24	72

* For units, see Table II

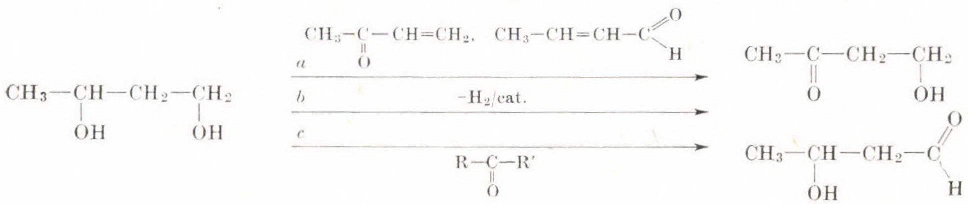

Fig. 2. Various modes of dehydrogenation of **I**. *Path a:* hydrogen transfer between unsaturated oxo compounds and **I**. *Path b:* catalytic dehydrogenation. *Path c:* hydrogen transfer between oxo compounds and **I**

4]. In the hydrogen transfer reaction, therefore, the sterically less hindered imary hydroxy group may be expected to be the more reactive, while the rect catalytic dehydrogenation will be faster in the case of the secondary ydroxy group than for the primary one [15]. Our experimental data also ow that on the Leuna catalysts the direct catalytic dehydrogenation of **I** redominates ($S : P \simeq 2 : 1$); in contrast, on the other catalysts the hydrogen ansfer processes also come into the foreground ($S : P \simeq 1 : 1$; see Table III).

In connection with dehydration (2b), it may be stated that, since the electivities of the transformations proceeding on two catalysts with strongly differing acidities (Cu-KG 2, Cu-COS; see Table VI) are almost the same, fundamentally the selectivity cannot be a function of the acidic sites. At the same time, the basic sites on oxide catalysts are also known to play an important role in dehydration reactions [17—19]. From this respect it is to be expected that the Leuna catalysts will exhibit higher dehydrating activities, since their surfaces are more basic.

Table VI

Surface acidities and basicities of silica-supported copper catalysts and Leuna catalysts [16]

Catalyst	Surface acidity (equiv. kg^{-1})	Surface basicity (equiv. kg^{-1})
Cu-KG 2	0.04	0.0
Cu-COS	0.09	0.57
L-1930	0.38	0.16
L-1950	0.25	0.13

The shift in the oxo compound/alcohol ratio for the end-products on the Leuna catalysts (point 2c) may be explained in that the hydrogen formed in the direct dehydrogenation is utilized for direct catalytic hydrogenation of the oxo compounds. (It is known that hydrogen is adsorbed much better on Cr_2O_3 or on ZnO than on copper [20, 21]).

(3) With increasing mass velocity, **II** accumulates to an increasing extent in the product, while at the same time the individual selectivity values do not change (Table IV). This is in accordance with the results of our earlier kinetic measurements, which indicated that the dehydration of **II** is the slowest step in the sequence $\mathbf{I} \rightarrow \mathbf{II} \rightarrow \mathbf{V}$ [13].

(4) With increasing temperature, the rate of dehydrogenation of the secondary hydroxy group increases to a greater extent than that of the primary

hydroxy group. In spite of this, it did not prove possible to increase the selectivity of formation of 2-butanone (VI), because of the simultaneous increase in the rates of the dealdolization processes (P_D, S_D).

*

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INVESTIGATION OF NUCLEOTIDE-METAL ION SYSTEMS, I

INTERACTION OF Co^{2+} IONS WITH ADENINE AND ITS NUCLEOTIDES

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The following compounds have been prepared by a novel method: $CoCl_2$.adenine.$3H_2O$; CoCl.AMP.$4H_2O$; $CoADPH.4H_2O$ and $CoATPH_2.4H_2O$. The ultraviolet, visible and infrared spectra of these compounds have been studied and conclusions drawn on structures in the solid and dissolved state. Concerning the metal — ligand bonds, it is supposed that mainly phosphate groups are involved in the coordination, but in the Co^{2+}-adenine, Co^{2+}-ADP and Co^{2+}-ATP systems, in addition to the Co—O bonds, Co—N bonds are also formed with the N_7 atom and the $C_6—NH_2$ group.

Introduction

The coordination of metal ions in adenine nucleotides can occur at the following sites: at the adenine ring (at the $C_6—NH_2$ group and/or at the N_7 atom), and at the phosphate chain. If we exclude the formation of polynuclear complexes, three sorts of bonding can be imagined, depending on the experimental conditions:

$$\begin{matrix} A-R-P \\ \quad\quad | \\ \quad\quad M \end{matrix} \qquad \begin{matrix} A-R \\ |\quad\ | \\ M-P \end{matrix} \qquad \begin{matrix} A-R-P \\ | \quad\quad \\ M \quad\quad \end{matrix}$$

(a) (b) (c)

Alkali, alkaline earth metals, and metals in the first transition series form with ATP mainly structures corresponding to (a) [1], structure (b) contributes only 12% [1, 2], the formation of structure (c) could not be detected in metal-nucleotide systems.

Co^{2+} ions form 1 : 1 complexes with adenine [3]. According to infrared [4] and ^1H-NMR [5] investigations, both the NH_2-group and N_7 atom are involved in the coordination.

Opinions differ concerning the structure of metal nucleotides. On the basis of difference spectra [6] and infrared investigations [7, 8], it is supposed that only β and γ phosphate groups participate in coordination, adenine and ribose do not influence the spectra. On the other hand, MO calculations [9], ^{1}H-NMR [10, 11] and relaxation investigations [12] as well as thermodynamic considerations [13] lead to the conclusion that ATP is a quadridentate ligand.

The pK values of adenine and its nucleotides [13—16], and the stability constants for the Co^{2+} compounds [3, 13, 14, 17] are known from the literature.

From all these it becomes clear that different authors applying identical methods obtain different results for the structure. The aim of our work was to isolate the Co^{2+} compounds of adenine and its nucleotides in a crystalline form and to contribute to the better knowledge of these complicated systems by their physico-chemical study.

Experimental

The compounds studied were prepared from the 1 : 1 mixture of the aqueous solutions of $CoCl_2 \cdot 6H_2O$ and the appropriate base. The solutions were cooled to about 5 °C, mixed, and the metal compound was precipitated under constant stirring by cooled acetone. The product was filtered, washed with alcohol and dried over P_2O_5. Analytical data and compositions are given in Table I.

Table I

Ligand*	C(%)		H(%)		Co(%)		H_2O(%)		Cl(%)	
	calcd.	found	calcd.	found	calcd.	found	calcd.	found[2*]	calcd.	found
Adenine	18.8[3*]		3.5	3.5	18.5	17.8[4*]	13.5	16.9	22.2	21.5
AMP-5'	23.5	23.5	3.9	4.4	11.5	11.4[5*]	15.0	14.1	6.9	6.2
ADP-5'	21.6[3*]		3.8	3.8	10.6	10.4[4*]	8.7	13.0	—	—
ATP-5'	18.2	18.2	3.4	3.7	8.9	8.8[5*]	10.9	8.0	—	—

Suggested composition of the compounds:
$CoCl_2 \cdot adenine \cdot 3H_2O$, $CoCl \cdot AMPH \cdot 4H_2O$, $Co \cdot ADPH \cdot 4H_2O$, $Co \cdot ATPH_2 \cdot 4H_2O$.
* data always refer to the 5'-phosphate derivatives,
[2*] thermogravimetric data,
[3*] determination of carbon is uncertain,
[4*] data obtained by complexometric titration,
[5*] measured spectrophotometrically

The spectra of the solutions were taken on a Specord UV-VIS spectrometer; reflectance curves were recorded on a Beckman DU spectrophotometer at ambient temperature, using bidistilled water and MgO as reference materials. Infrared spectra were recorded on a spectrophotometer of the type UR-10 (Zeiss, Jena) in KBr pellets.

pH-metric titrations were performed with a Radelkis OP 205 pH-meter, with a combined glass electrode of the type OP 807. Solutions of a concentration of 5×10^{-2} mol/dm^3 were used.

Thermoanalytical measurements were performed on a Paulik—Paulik—Erdey (MOM, Hungary) Derivatograph, applying a heating rate of 6 °C/min.

Results

pH-*metric titrations*

The aim of these measurements was to determine the composition of the complexes formed and to obtain information about the role of the pH.

In the systems AMP.Na_2—Co^{2+}, ADP.Na_2—Co^{2+} and ATP.Na_2—Co^{2+} the sharp pH-jump characteristic for the presence of the free ligand, when applying one equivalent of base, did not occur; instead of that a buffer region appeared, which was shifted to different extents, indicating the formation of 1 : 1 complexes. Upon increasing the base concentration, a characteristic change of colour can be observed. In the AMP.Na_2—Co^{2+} system, the initial pink colour turned into blue upon the addition of one equivalent of base (pH = = 7.5—8); in the ADP.Na_2—Co^{2+} system it turned into violet and blue upon adding three or four equivalents of base (pH = 7.5—8), respectively, whereas in the ATP.Na_2—Co^{2+} system also a blue colour appeared upon the addition of four equivalents of base (pH = 10.5). No precipitation was observed in either case. The pink → blue colour transition found clearly indicates a change in the composition (see *e.g.* [19]) and the symmetry of the molecules formed in the solution. This is also supported by the experimental fact that we have succeeded in the isolation of various crystalline products having different spectral characteristics from the ATP.Na_2—Co^{2+} system at different pH (see in a further paper).

Ultraviolet spectra

The ultraviolet absorption spectra of nucleotides and their Co^{2+} compounds are practically identical, but neither differ very much the spectra of the different nucleotides (see Table II). The spectra are only slightly influenced by

Table II

Ultraviolet spectroscopic data of the basic substances and their Co^{2+} *complexes*

Compound	Band maximum nm (lg ε)
Adenine	208 (4.26) 260 (4.14)
Co^{2+}-	208 (4.25) 260 (4.15)
AMP.Na_2	207 (4.28) 259 (4.16)
Co^{2+}-	208 (4.28) 260 (4.15)
ADP.Na_2	207 (4.27) 259 (4.15)
Co^{2+}-	208 (4.26) 260 (4.13)
ATP.Na_2	207 (4.30) 260 (4.13)
Co^{2+}-	208 (4.27) 260 (.412)

the pH. As neither ribose, nor phosphate absorbs significantly in the 340—210 nm region, the bands in the spectra can be assigned to the $\pi \rightarrow \pi^*$ transitions of the adenine ring.

Visible spectra

The bands of the spectra in mixtures and solutions at about 620 and 514 nm can be assigned to the

$$^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)\,(\nu_2) \text{ and } {}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)\,(\nu_3)$$

transitions, respectively. The intensity of the former is significantly lower, due to its being a two-electron transition. The LEVER [20] method permits approximate calculation of the RACAH parameter B and the energy of the ν_1 band. On the basis of the ν_2 and ν_3 bands, $B = 870$ cm^{-1}, which corresponds to a nepheloauxetic ratio of $\beta = 0.78$. The first d—d band, ν_1, $[{}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)]$ is to be expected at around 7650 cm^{-1}. For the Co^{2+}—AMP, Co^{2+}—ADP and

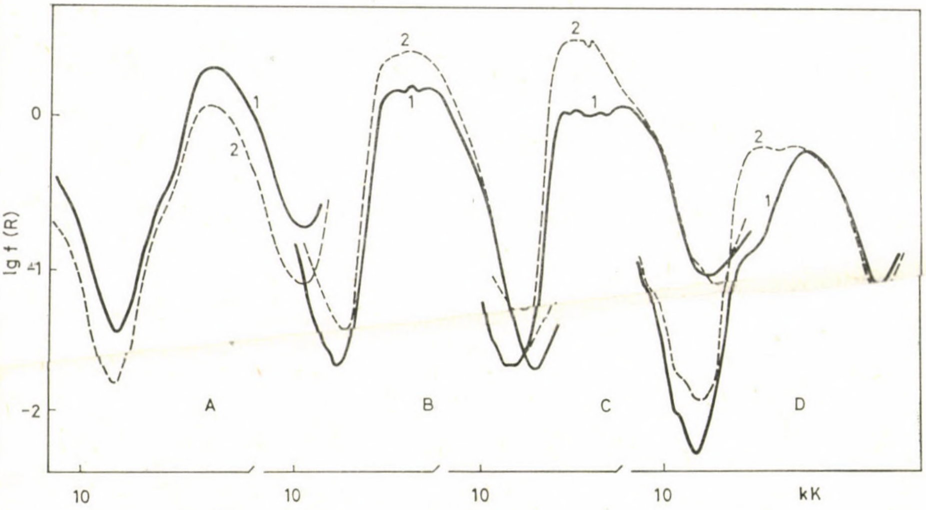
Table III
Data of visible spectra of Co^{2+} *nucleotide systems*

Compound	Band maxima nm and lg ε				Geometry
Co^{2+}-adenine	R*	—	549	~ 650	pO
	R**	—	550	~ 650	pO
Co^{2+}-AMP	E	~ 490	514 0.88	~ 615	pO
	R*	—	—	581	pT
	R**	—	—	581	pT
Co^{2+}-ADP	E	~ 490	514 0.87	~ 620	pO
	R*	—	515	633	pO + (pT)
	R**	—	500	633	pT + (pO)
Co^{2+}-ATP	E	~ 494	514 0.83	~ 615	pO
	O	~ 495	514 0.88	—	pO
	R*	—	521	658	pO
	R**	—	543	613	pO + (p

E: 1 : 1 mixture of Co^{2+} and base,
O: aqueous solution of the solid metal salt,
R*: reflectance spectrum before drying,
R**: reflectance spectrum after drying for 24 hrs,
pO: pseudo-octahedral,
pT: pseudo-tetrahedral

o^{2+}—ATP systems, identical *B* values can be calculated, and these values re near to those calculated for the hydrated ions, thus proving that in the bove compounds the Co—O bonds predominate (Table III).

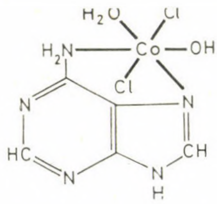
The structure of reflectance spectra is more complicated (Fig. 1). The pectra of Co^{2+}-adenine are practically the same before and after drying. he structure is a distorted octahedron with a very low symmetry; structure **I** probable. There is no significant difference in the case of Co^{2+}—AMP either; ccording to the spectrum, the structure is distorted tetrahedral (structure **II**). he spectrum of Co^{2+}—ADP is complex: the wet substance contains both, trahedral and octahedral species (structure **III**) while in the dry state the trahedral form predominates. Before drying, Co^{2+}—ATP has a distorted ctahedral structure (structure **IV**), which, however, becomes mixed tetra- edral + octahedral after drying. The rate of reversible water adsorption nanges in the sequence Co^{2+}—ATP > Co^{2+}-adenine > Co^{2+}—ADP > > Co^{2+}—AMP, in parallel with the change of solubility.



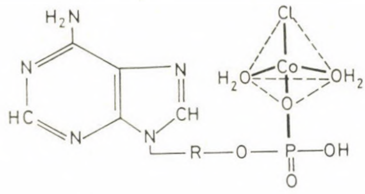
ig. *1*. Reflectance spectra. A: $CoCl_2$.adenine.$3H_2O$; B: CoCl.AMPH.$4H_2O$; C: Co.ADPH·$4H_2O$; D: Co.$ATPH_2$.$4H_2O$; 1 (——): before drying; 2 (- - -): after drying for 24 h

nfrared spectra

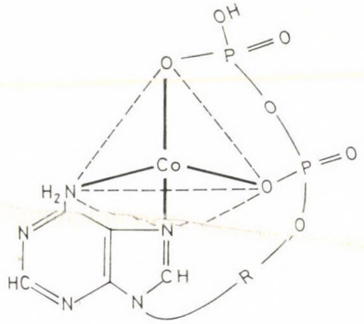
The characteristic frequencies for the basic substance and Co^{2+} com- lexes are contained in Table IV.



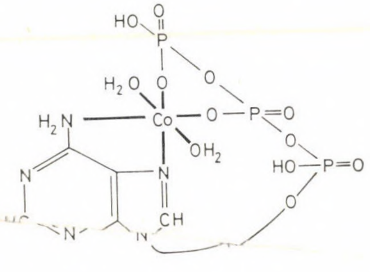
I



II



III



IV

From the spectra of AMP.Na$_2$, ADP.Na$_2$, ATP.Na$_2$ and the appropriat metal complexes a similarity is apparent, except in the regions characteristi for the phosphate group.

In the case of ADP.Na$_2$ and ATP.Na$_2$, the bands of the asymmetri stretching of the P—O—P group are to be found at 933 and 902 cm^{-1}, whic are shifted by 18 cm^{-1} to higher frequencies for Co^{2+}—ATP, in accordan with the literature [21]. The characteristic bands of P—O and C—O grou lie between 1070 and 1120 cm^{-1}; this band is shifted by 15—30 cm^{-1} to low frequencies for the metal salts. The vibration of the P=O group is betwee 1210 and 1260 cm^{-1}. The frequency of the PO$_3^{2-}$ group in free bases is to b found between 970 and 990 cm^{-1}; this band is hardly or not at all observed i the spectra of metal salts. The stretching band of the C=N group appea between 1660 and 1650 cm^{-1} in the spectra of AMP.Na$_2$, ADP.Na$_2$ an ATP.Na$_2$ and is significantly shifted for Co^{2+}—ADP and Co^{2+}—ATP to th region of 1690—1700 cm^{-1}. This shift is probably to be explained by the forma tion of a charged C=N$^+$ group [21]. The character of the spectrum is n much changed in the region of lower wavenumbers; the bands of the free bas in the spectra of metal salts are diffuse and lower in intensity.

Table IV

Infrared frequencies of the ligands and their Co^{2+} *compounds*

Adenine	Co-adenine	AMP	Co-AMP	ADP	Co-ADP	ATP	Co-ATP
3310 s	3330 s	3400 s	3350 s	3340 s	3350 s	3360 s	3350 s
3125 s	3170 s	3200 s	3180 s	3200 s	3200 s	3165 s	3150 s
2980 m							
2800 m							
2690 m							
2600 m							
				1698 s		1714 s	
1678 s	1670 s	1660 s	1660 m	1650 s	1696 s	1652 m	1698 s
1610 s	1638 m	1613 m	1610 m	1610 s	1616 m	1616 m	1618 w
	1570 m	1580 w	1580 w			1560 w	1570 w
	1520 w	1489 w	1490 w	1486 m	1515 m	1500 w	1519 m
	1470 m						
1424 m	1407 m	1428 w	1430 w	1426 m	1428 m	1418 w	1432 w
1373 m	1370 m	1340 w	1344 w				
1340 m	1350 m	1303 w	1304 w				
1314 s	1332 m	1217 w	1218 w	1228 s	1220 s	1259 s	1222 s
1257 m	1223 m	1110 s	1112 s				
1129 m	1110 m	1085 s	1072 s	1112 s	1095 s	1110 s	1080 s
1026 m		979 m	989 m	972 m			
	960 w			938 s	936 s	902 m	920 m
942 s	928 m	797 w	795 w	824 m	822 w	816 w	824 w
915 m	910 w	725 w	712 w	724 m	723 w		
798 m	790 m	640 w	638 w	643 w	637 w	641 m	636 w
724 m	736 m	535 w	544 w	535 m	525 m	520 m	520 m
645 s			496 w			495 m	
622 m							
	607 m						
	573 w						
	554 w						
541 m	542 m						

Band intensities, s: strong, m: medium, w: weak

Based on these data, the assumption can be made that the base-metal interaction influences mainly the phosphate groups, but the participation of the N atoms of the adenine ring in the coordination cannot be excluded either, especially in the ADP, ATP and adenine compounds.

*

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STUDIES ON PYRIDAZINE DERIVATIVES, V*

ETHOXYCARBONYLATION REACTION OF PYRIDAZINYLHYDRAZONES

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The reaction of pyridazinylhydrazones **I** with diethyl pyrocarbonate may give the exo- **(II)** and endo-*N*-(ethoxycarbonyl) **(III)** derivatives. In general, the more stable compounds **III** are formed, but in one case **(Ig)**, the exo-acyl derivative **(IIg)** could also be prepared. The structures of the compounds were established spectroscopically.

In the course of a study on the structure-activity relations of antihypertensive pyridazinylhydrazones (**I**) [2], the synthesis of the *N*-(ethoxycarbonyl) derivatives (**II**) appeared desirable. Of compounds **I**, only the reaction of **Ig** with diethyl pyrocarbonate yielded the pale yellow exo-*N*-(ethoxycarbonyl) derivative **IIg**; compounds **Ia—f** were converted into the red endo-*N*-(ethoxy-carbonyl) derivatives **IIIa—f** under the given reaction conditions (Fig. 1). Compound **IIg** isomerized to the endo-*N* derivative **IIIg** on short refluxing in diethyl ether.

The structures of the new compounds were elucidated on the basis of their IR and ^{1}H-NMR spectra. As the spectroscopic parameters of the isomers **IIg—IIIg** are significantly different, it was possible to determine the structures of all *N*-(ethoxycarbonyl) derivatives, even if only one of the isomers was available (Table I).

In the IR spectrum of **IIIg**, the carbonyl frequency is lower because conjugation results in a lower bond order, while in the spectrum of **IIg** the higher value is due to the $-I$ effect of the heteroaromatic ring. In the ^{1}H-NMR spectrum of **IIg** the chemical shift of the H-5 atom is higher by more than 1 ppm than that in the spectrum of **IIIg**, which can be attributed to the aromatic structure and the anisotropic effect of the near-by ethoxycarbonyl group; the chemical shifts of H-4 do not exhibit significant differences. Accordingly, the difference in the chemical shifts of the H-5 and H-4 atoms is lower by more than 1 ppm in structures of type **III** than in the isomers of type **II**. As the H-5 and H-4 values strongly depend also on the substituents X, R' and R", it is

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[*] Part IV, see Ref. [1]

Table I

Characteristic IR and ^{1}H-NMR data

Compound No.	IR data, cm^{-1} (KBr)		^{1}H-NMR data, $\delta_{TMS} = 0$ ppm			
			ArH		Ethoxycarbonyl group	
	Amide-I band	Other signals	δH-5 d(1H)[a, i]	δH-4 d(1H)[a, i]	δCH_3 t(3H)[b]	δCH_2 qa(2H)[b]
III a	1680	1710[f] 1305[g] 1070[g]	6.77	6.48	1.35	4.30
III b	1700	1720[f] 1320[g] 1080[g]	6.73	6.47	1.36	4.30
III c	1690	1730[f] 1335–10[g] 1080[g]	6.75	6.49	1.35	4.30
III d	1690	1525[h] 1350[h] 850[h]	7.73	7.62	1.37	4.40
III e	1685	—	6.73	6.46	1.35	4.27
III f	1680	—	6.66	6.41	1.35	4.20
III g	1670	—	6.79	6.58	1.35	4.25
II g	1740	—	7.77	6.48	1.35	4.38
IV a	1710[p]	3240[r]	7.70	7.40	—	—
			7.75[j]	7.60	—	—
IV b	1680[s]	3250[t]	7.55	7.30	—	—
			7.70[j]		—	—

s = singlet
d = doublet
t = triplet
qa = quartet
m = multiplet

[a] *A* or *B* part of an *AB*-multiplet
[b] $J = 7$ Hz
[c] *A* or *B* part of an *AA'BB'* multiplet (2–2H)
[d] Ethoxycarbonyl group of the R" substituent
[e] chemical shifts of the phenyl ring, calculated by *AB*-approximation; H–2,6 < H–3,5, $J = 9$ Hz
[f] $\nu C{=}O$ band of ester group
[g] $\nu C{-}O$ band of ester group

of compounds **IIIa–g**, **IIg** *and* **IVa**, **b**

(CDCl$_3$ solution, at room temperature)

X subst.		R' and R'' substituents					
δNCH$_2$ *m*(4H)[c]	δOCH$_2$ *m*(4H)[c]	δCH$_3$ (R')	δCH$_3$ (R'')	δOCH$_2$[d] (R'')	δCH$_2$ (R'')	δCH (R')	δArH[e] (R'')
—	—	1.95 *s*(3H)	1.20[d] *t*(3H)[b]	4.10 qa(2H)[b]	2.80[a,k] 3.50[a,k]	—	—
—	—	1.90 *s*(3H)	1.40[n] *s*(9H)	—	2.89[a,l] 3.41[a,l]	—	—
—	—	1.86 *s*(3H)	1.24[d] *t*(3H)[b]	4.12 *qa*(2H)[b]	100–150 Hz *m*(4H)[m]	—	—
—	—	—	—	—	—	8.24 *s*(1H)	7.86[c] 8.24[c]
—	—	1.90 *s*(6H)		—	—	—	—
—	—	—	—	—	90–170 Hz *m*(10H)[o]	—	—
3.15	3.75	1.85 *s*(6H)		—	—	—	—
3.20	3.75	2.05 *s*(6H)		—	—	—	—
—	—	2.20 *s*(3H)	1.35 *t*(3H)[b]	4.30 *qa*(2H)[b]	—	—	—
—	—	2.30 *s*(3H)	1.30 *t*(3H)[b]	4.25 *qa*(2H)[b]	—	—	—
—	—	2.20 *s*(3H)	1.35 *t*(3H)[b]	4.30 *qa*(2H)[b]	—	—	—
—	—	2.15 *s*(3H)			—	—	—

[h] $\nu_{as}NO_2$, $\nu_s NO_2$ and $\nu C-N(O_2)$ bands

[i] $J = 10$ Hz (**IIIa–g**), $J = 11$ Hz (**IIg**)

[j] ^{1}H-NMR data measured in DMSO-d solution at room temperature

[k] *d*, $J = 15$ Hz (1H)

[l] *d*, $J = 16$ Hz (1H)

[m] A_2B_2 multiplet

[n] *t* -butyl group

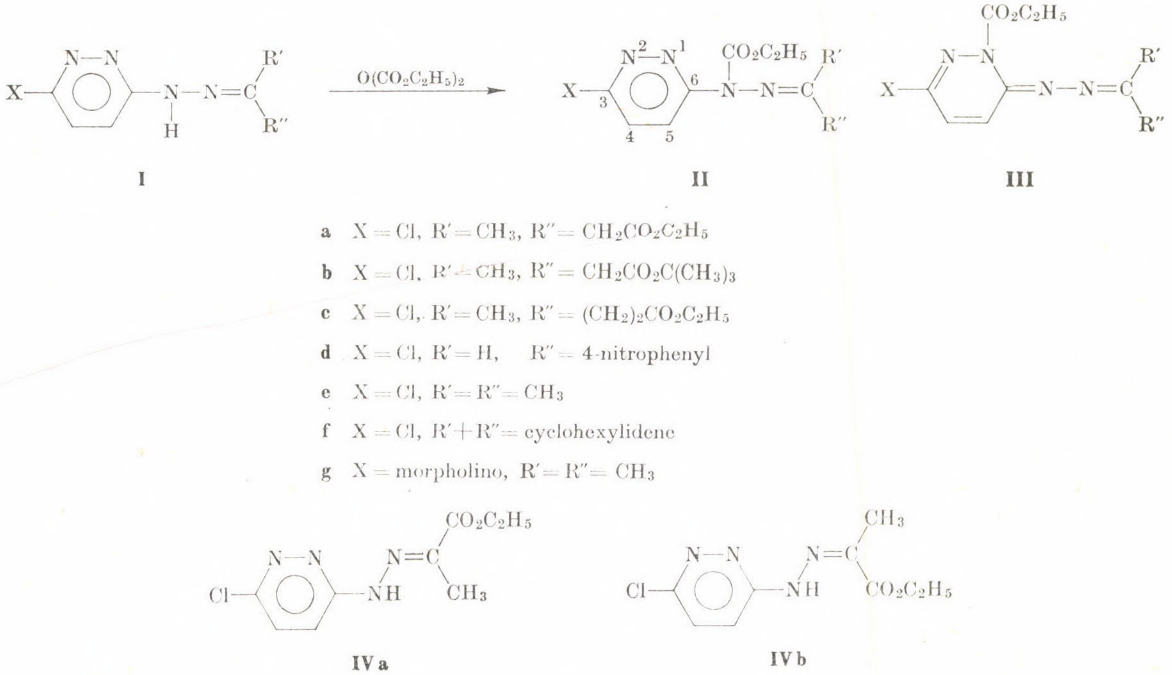
[o] R' and R'' groups

[p] $\nu C=O$ band of ester group (vs, sharp)

[r] νNH band (b)

[s] $\nu C=O$ band of ester group (b)

[t] νNH band (sharp)



a X = Cl, R′ = CH_3, R″ = $CH_2CO_2C_2H_5$
b X = Cl, R′ = CH_3, R″ = $CH_2CO_2C(CH_3)_3$
c X = Cl, R′ = CH_3, R″ = $(CH_2)_2CO_2C_2H_5$
d X = Cl, R′ = H, R″ = 4-nitrophenyl
e X = Cl, R′ = R″ = CH_3
f X = Cl, R′ + R″ = cyclohexylidene
g X = morpholino, R′ = R″ = CH_3

Fig. 1

Synthesis of the *N*-(ethoxycarbonyl) derivatives

A mixture of the pyridazinylhydrazone (**I**) (5 mmoles), diethyl pyrocarbonate (11 mmoles) and tetrahydrofuran (15 mL) was refluxed for 2 h and then allowed to stand overnight. The solvent was removed in vacuum and the red oil obtained was purified by chromatography on a Brockmann-I Al_2O_3 column with dichloromethane eluant, and then crystallized.

1-(Ethoxycarbonyl)-3-chloro-6(1*H*)-(4-nitrobenzylidenehydrazono) pyridazine (IIId)

A mixture of **Id** (1.39 g; 5 mmoles), diethyl pyrocarbonate (2.43 g; 15 mmoles) and tetrahydrofuran (30 mL) was refluxed for 14 h. The unchanged starting material was removed by filtration and the filtrate was evaporated to dryness in vacuum. The crude product was recrystallized.

1-(Ethoxycarbonyl)-3-chloro-6(1*H*)-(2-propylidenehydrazono)pyridazine (IIIe)

A mixture of **Ie** (2 g; 11 mmoles), diethyl pyrocarbonate (5.6 g; 35 mmoles) and dichloromethane (30 mL) was allowed to stand for 2 days. The solvent was removed in vacuum and the oily residue was allowed to stand in a refrigerator for 2 days. The solidified material was rubbed with diethyl ether (5 mL) and the crude product was recrystallized.

1-(Ethoxycarbonyl)-3-chloro-6(1*H*)-(cyclohexylidenehydrazono)pyridazine (IIIf)

A mixture of **If** (1.48 g; 6.6 mmoles), diethyl pyrocarbonate (2.27 g; 14 mmoles) and tetrahydrofuran (20 mL) was refluxed for 6 h and allowed to stand overnight. The solvent was removed in vacuum and the crude product was recrystallized.

Table II

1-*Ethoxycarbonyl-6(1H)-hydrazonopyridazines* (**IIIa—g**)

Compound No.	Method Solvent	Melting point °C	Yield %	Formula
III a	isopropanol-gasoline 1 : 1	124—125	31	$C_{13}H_{17}ClN_4O_4$ (328.76)
III b	isopropanol-diethyl ether 1 : 1	126—128	25	$C_{15}H_{21}ClN_4O_4$ (356.78)
III c	diethyl ether	83—85	22	$C_{14}H_{19}ClN_4O_4$ (342.78)
III d	dichloromethane	202—204	28	$C_{14}H_{12}ClN_5O_4$ (349.74)
III e	isopropanol-gasoline 2 : 8	134—136	55	$C_{10}H_{13}ClN_4O_2$ (256.69)
III f	diethyl ether	114—116	19	$C_{13}H_{17}ClN_4O_2$ (296.76)
III g	diethyl ether	172—174	60	$C_{14}H_{21}N_5O_3$ (307.35)

their difference which can be used for making distinction between the isomers:

$$\Delta\delta\ \text{H-5, 4 } (\mathbf{IIIg}) = 0.21 \text{ ppm},$$

$$\Delta\delta\ \text{H-5, 4 } (\mathbf{IIg}) = 1.29 \text{ ppm}.$$

Each product obtained by the ethoxycarbonylation of compounds **Ia**—**f** was found to be homogeneous. In the knowledge of the ^{1}H-NMR data of the isomers **IIg** and **IIIg**, it was established that all the ethoxycarbonylated derivatives, except **IIg**, were endo-*N* derivatives of type **III**; the $\Delta\delta$ H-5, 4 shift difference was < 0.3 ppm for all compounds.

E-1-(3-Chloro-6-pyridazinyl)-2-ethoxycarbonyl-ethylidenehydrazine (**IVa**) having a structure related to **Ia** is converted, under conditions similar to those given above, not into the ethoxycarbonyl derivative, but partial isomerization also takes place; the pure *Z*-isomer (**IVb**) has been isolated in 1% yield.

In the IR spectrum of the *Z*-isomer, the carbonyl frequency is lower by 30 cm^{-1} and the νNH band is sharper owing to the intramolecular chelate structure; furthermore, in the ^{1}H-NMR spectrum the chemical shift of the NH proton is greater than in the case of the *E*-isomer. The pyridazine protons appear at nearly the same field strength in the spectra of both isomers, which fact precludes the possibility of endo-exo tautomerism. In compounds **Ia**—**d**, the ^{1}H-NMR spectra did not indicate a mixture of geometric isomers (these do not exist in **Ie**—**g**). A likely explanation is that it is only in **IV** where chelation (a strong intramolecular H-bond) can stabilize the energetically less favourable *Z*-isomeric structure; in compounds **Ia**—**d** there is no possibility for chelation, hence their *Z*-isomer is not formed at all. In theory, it can be assumed that rapid inversion or internal rotation (perhaps involving tautomerism) can lead to averaging of the chemical shifts corresponding to the isomers, but this is not probable, since isomerization requires an energy of activation in compound **IV**, too. The occurrence of geometric isomers was not observed in compounds **II** and **III** either.

Experimental

M.p. 's were measured with a Boetius melting point determining apparatus, and are uncorrected.

The microanalytical data C, H, N of all compounds were consistent with the compositions given.

IR spectra were recorded in KBr pellets with a Perkin—Elmer 577 spectrophotometer. ^{1}H-NMR spectra were obtained with a JEOL 60 HL instrument at 60 MHz at room temperature, using TMS internal standard.

The starting compounds were prepared in the known ways: **Ia**—**c** [2], **Id** [3], **Ie**, **f** [4], **Ig** [5], **IVa** [6].

1-(3-Morpholino-6-pyridazinyl)-1-(ethoxycarbonyl)-2-(2-propylidene)hydrazine (IIg)

A mixture of **Ig** (1.35 g; 5.7 mmoles), diethyl pyrocarbonate (1.57 g; 9.7 mmoles) and tetrahydrofuran (15 mL) was allowed to stand for 1 day, and then the solvent was removed in vacuum. The oily residue was allowed to stand for 2 days at —10 °C, then the solid precipitate was suspended in cold diethyl ether (2×5 mL) and filtered to give 1.05 g (60%) of the product, m.p. 70—73 °C.

1-(Ethoxycarbonyl)-3-morpholino-6(1*H*)-(2-propylidenehydrazono)pyridazine (IIIg)

Compound **IIg** (0.25 g; 0.65 mmoles) was refluxed in diethyl ether 5 mL for 10 mins and the precipitate **IIIg** was filtered off after cooling.

Compounds **IIIa**—**g** are summarized in Table II.

Z-1-(3-Chloro-6-pyridazinyl)-2-[(ethoxycarbonyl)-ethylidene]hydrazine (IVb)

A mixture of isomer *E* (**IVa**) (1.46 g; 6 mmoles), diethyl pyrocarbonate (3.24 g; 20 mmoles) and tetrahydrofuran (25 mL) was refluxed for 10 h. The solvent was removed in vacuum, the residue was rubbed with diethyl ether (10 mL) and the precipitate (*E*-isomer) was filtered off. The above procedure was repeated twice with the filtrate. The *Z* isomer was obtained in a yield of 0.014 g (1%), m.p. 122—124 °C.

*

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EFFECT OF UREA, THIOUREA AND SELENOUREA ON THE HYDROGEN OVERVOLTAGE AT THE GALLIUM ELECTRODE

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The effect of urea, thiourea and selenourea on the rate of hydrogen evolution at the dropping gallium electrode has been investigated in 1 mol/dm^3 $HClO_4$ solution. It has been established that the additives investigated increase the rate of hydrogen evolution at constant overvoltage and at a given concentration (10^{-3}mol/dm^3) in the order: urea $<$ thiourea $<$ selenourea.

The adsorption of thiourea (TU) at several metal electrodes has been investigated [1—4]. At the gallium electrode **Bagockaja** *et al.* measured the effect of thiourea adsorption on the rate of electrolytic hydrogen evolution and on the structure of the double-layer [4]. Contrary to findings at the mercury electrode, they established that additive of thiourea in neutral or acid solution changes the rate of hydrogen evolution the gallium electrode, and the structure of the electrode/electrolyte boundary layer changes too, as indicated by an increase in capacity. Thiourea and its *N*-substituted derivatives reduce the corrosion of iron, exert an inhibitor effect [5], for the explanation of which it is assumed that iron — thiourea complexes are formed at the iron surface. IR investigations suggest that thiourea is bonded to the metal by its sulphur atom [6]. The strong interaction between the sulphur atom of thiourea and metal is indicated also by the finding that the adsorption of thiourea at the solution/air interface is lower than at the solution/metal interface, as contrary to most of the organic compounds, thus also to urea (U) of similar structure than thiourea, which is adsorbed in the same measure at the solution/air and solution/metal interfaces [7].

It seems probable that the difference found in the adsorption of urea and thiourea is reflected also in the effect of these compounds on electrode processes. At the solid or liquid gallium electrode, thiourea additive in $HClO_4$ solution increases the rate of hydrogen evolution, *i.e.* it participates as a catalyst in the process.

According to literature data, the difference in adsorption behaviour of urea and thiourea can be attributed to a difference in bond strength between metal-oxygen and metal-sulphur. It is therefore to be expected that these compounds will affect also the rate of electrode processes in a different measure. A larger difference in adsorptive properties than that found between urea and thiourea is to be expected between urea and selenourea (SeU) and it is to be expected that the latter will diminish in a larger measure the rate of hydrogen evolution than thiourea.

Starting from theses assumptions, the effect of urea, thiourea and selenourea on the rate of hydrogen evolution has been studied at the dropping gallium electrode in a 1 mol/dm^3 $HClO_4$ solution.

Experimental

The dropping gallium electrode described earlier [8] has been used for the investigations, modifying the measuring cell so that sampling for the measuring of drop weight shall not interfere in the recording of the polarization curve. In our investigations the current — time curves belonging to the single potential values have been recorded on a PAR 170 instrument by the potentiostatic method, and from these curves $\bar{I}$, the mean value of current belonging to the given potential, has been determined, from which current density **j** has been calculated using the following formula [9]:

$$\mathbf{j} = 5/3 \frac{\bar{I}}{S_{max}} .$$

S_{max}, the maximal surface of the drop, can be calculated from the weight of the gallium drop, when density is known. In our measurements the value of S_{max} was about 0.1 cm^2.

From the pairs of values current density (**j**)-overvoltage (η), experimentally obtained, the (η) — lg **j** curves have been plotted. Measurements were carried out with a dropping electrode made of gallium of 99.9999 purity, at 32 °C, in pure and additive-containing $HClO_4$ solutions of 1 mol/dm^3 concentration, saturated with hydrogen. Perchloric acid solutions were prepared from bidistilled water and 70 w% perchloric acid (Merck) of analytical grade. Twice recrystallized urea and thiourea (Reanal), and selenourea (Merck) of analytical grade were used as additives. Before the beginning of the measurements, solutions were further purified by electrolysis for about 14—16 hours at a current density of 10^{-3}A/cm^2 on a gallium cathode used for this special purpose.

Polarization curves were recorded in the current density region from 10^{-4} to 10^{-2} A/cm^2.

Figure 1 shows the lg **j** — η curves plotted from data measured for 1 mol/dm^3 pure $HClO_4$ solution and such containing 10^{-3}mol/dm^3 urea, thiourea or selenourea as additive. As can be

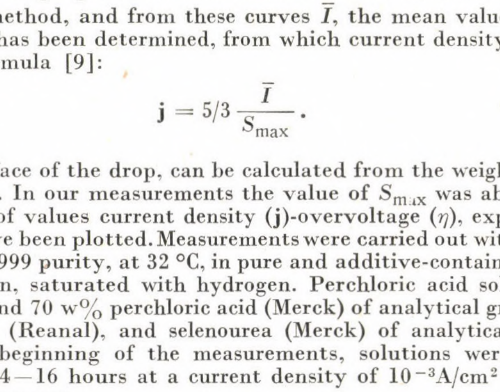

Fig. 1. η — lg **j** curves at the dropping gallium electrode in 1 mol/dm^3 $HClO_4$ solution, containing as additive in 10^{-3} mol/dm^3 concentration (1) selenourea, (2) thiourea, (3) urea, and (4) no additive

noted from the figure, urea diminishes in the smallest measure hydrogen overvoltage, $\Delta\eta = 8-10$ mV, the polarization curve measured in the presence of urea runs parallel to the curve measured in pure $HClO_4$ solution, the value of $\partial\eta/\partial$ lg j in the potential range -0.6 to 0.8 V is in both cases 0.103 V. The decrease in overvoltage produced by 10^{-3}mol/dm^3 thiourea is considerably larger, $\Delta\eta \approx 175$ mV, and a still larger decrease in overvoltage of 190 mV is caused by selenourea of the same concentration. It should be noted that in the presence of selenourea additive the reproducibility of the measurements is worse than in the two preceding cases, because of the instability of selenourea. It can be seen from the aforeasid that the catalytic effect of the three additives investigated, the decrease in overvoltage and the increase in the rate of hydrogen evolution which can be characterized with the Δ lg **j** value, changes in the order U < TU < SeU(Δ lg **j** is the difference of the lg **j** value measured in $HClO_4$ + additive solution and the lg **j** value measured in pure $HClO_4$ solution at $\eta =$ constant). Δ lg **j** values are summarized in Table I. lg **j** — η curves obtained for solutions of $HClO_4$ + TU or SeU composition reveal two sections of different slope. In the case of thiourea the two sections intersect at -0.72 V, at lower overvoltages $\partial\eta/\partial$ lg **j** ≈ 0.084 V, while at higher overvoltages the slope is 0.180 V. The break of the polarization curve obtained for the solution containing selenourea is at $\eta = -0.74$ V, the value of the slope in the potential range of $\eta > -0.74$ V is 0.096 V, while at overvoltage values of $\eta < -0.74$ V, 0.170 V. In the case of the additives investigated the break observed on the polarization curves is presumably due to the desorption of these substances from the electrode surface.

Discussion

It has been mentioned in the experimental part that of the additives investigated urea has the least effect on the rate of hydrogen evolution. Thiourea has a considerably greater one, and selenourea has the strongest catalytic effect. The molecules of these compounds differ in so far that oxygen, sulfur or selenium is linked to the carbon atom, and, of their physical constants, mole polarization increases in the order U < TU < SeU [10, 11], *i.e.* the catalytic effect of the additives increases parallel to their polarizability (see Table I). Presumably, with increasing polarizability primarily the adsorption of the additives changes, and that additive is the better catalyst, for which the change in free enthalpy of adsorption is higher. Correlation between the polarizability of the additive and its adsorption or catalytic effect indicates that adsorption is determined in first approximation by dispersive forces.

Table I

η(V)	Δ lg j j = A/cm^2		
	Urea	Thiourea	Selenourea
-0.75	0.09	1.66	1.95
-0.70	0.08	1.76	2.00
-0.65	0.08	1.69	1.90
$\bar{\alpha}_e^*$ 10^{24} (cm^3)	5.715 (10)	9.805 (11)	—

* Values calculated using the refractive index measured at $\lambda = 564.1$ nm.

This seems to be supported by the slight difference between the dipole moment of the $C = X$ bond of urea (4.59 D) and of thiourea (4.89 D) [12] ($X = O$, S, Se), owing to which the energy of the gallium - dipole interaction may be nearly identical in the two cases.

In addition to the difference in dispersive forces, to the increase in catalytic activity in the order $U < TU < SeU$, the difference in chemical interaction $Ga \leftrightarrow X = C$ also play a part.

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PREPARATION, STABILITY AND OXYGEN STOICHIOMETRY IN PEROVSKITE-TYPE BINARY OXIDES

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Binary oxides of perovskite-type corresponding to the following stoichiometric compositions have been prepared by the explosion method. It has been found that in reductive atmosphere (10% H_2 + 90% He), the binary oxides show higher thermal stability in comparison with respective single oxides of transition metals. The stability increases as follows: $LaNiO_{2.98} < LaCoO_{3.00} < LaFeO_{3.22}$. The reduction of binary oxides proceeds *via* intermediate stages at which compounds with different oxygen stoichiometry are formed.

Introduction

Perovskite-type binary oxides with the general formula ABO_3 (where A is a trivalent rare earth element and B is a transition metal ion) are important as model systems in the search for a correlation between the chemical property of a solid and its catalytic activity [1, 2]. From practical point of view these oxides are considered potential catalysts for exhaust gases in catalytic mufflers and electrodes for high-temperature fuel cells [3—12] where the above oxides can be substituted for coinage metals. Based on the surface structure of perovskites, it is assumed that square array B—O—B ion system is a catalytically active surface. The contribution of the lattice oxygen to the catalytic reaction consists in the reduction of the surface with the formation of anion vacancies [2, 13].

It has been established that depending on the method used for the preparation of perovskite-type binary oxides, samples with considerable differences in surface areas [10, 14, 15] and in oxygen stoichiometry [16—18] are obtained. The observed differences in catalytic activity of a given binary oxide result from using different methods for its synthesis [14, 19, 20]. In our previous paper [15], a new explosion method has been described for the synthesis of perovskite-type binary oxides using $LaCoO_3$ as an example and the method was compared with other methods known from literature. It has

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been shown that our method enables to obtain phase-homogeneous product with a relatively high surface area which is the result of a comparatively low final temperature of calcination.

The present study was aimed at determining the optimum conditions of syntheses of $LaFeO_3$ and $LaNiO_3$ using the explosion method as well as at examining the thermal stability in reductive atmosphere and oxygen stoichiometry for both the above compounds and $LaCoO_3$.

Experimental

$LaFeO_3$ and $LaNiO_3$ were synthesized by the explosion method described in our earlier paper [15]. To the aqueous solutions of lanthanum(III) and iron(III) as well as lanthanum(III) and nickel(II) nitrates a saturated solution of ammonium bicarbonate was added until $pH = 7.0$ was reached. The precipitate was dissolved in glacial acetic acid and then concentrated (using a vacuum evaporator) to about 300 cm^3 what made 30% of the starting volume. After transferring the solution in to a quartz evaporating dish, a further evaporation was carried out until spontaneous explosion reaction started. The products obtained as a result of explosion were dark-red and black, respectively, for $LaFeO_3$ and $LaNiO_3$. The above products were heated at 533 K for 2 h in a vacuum system under a pressure of 1.33 Pa. Further calcination was carried out at 773 K in air flowing with a rate of 30 dm^3/h for 15 and 20 h, respectively, for $LaNiO_3$ and $LaFeO_3$. Lanthanum(III) cobaltate prepared in our earlier study [15] was also subject to examination. The following oxides: Fe_2O_3, Co_3O_4 and NiO were also prepared using the same procedure as that applied for binary oxides, in order to compare their thermal stabilities with those of corresponding binary oxides. During all the thermal treatments the temperature was maintained with an accuracy of $\pm$ 5 K.

The lanthanum and iron content of the prepared samples was determined by EDTA titration and the nickel content electrogravimetrically. The surface area of the samples was measured by gas-chromatographic technique using a Perkin—Elmer Sorptometer Model 212 C. Helium was used as a carrier gas and nitrogen as an adsorbate. The X-ray analysis was carried out on a diffractometer TUR-M-62 with a goniometer HZG-3 made in GDR. Iron-filtered Co K_α radiation and nickel-filtered Cu K_α radiation were used, respectively, for $LaFeO_3$ and $LaNiO_3$. Thermogravimetric studies were performed using Sartorius microthermobalance "Gravimat" Model 4133 under experimental conditions as follows: starting weight of a sample 0.05 g, atmosphere 10% H_2 + 90% He, flow rate 3 dm^3/s heating rate 0.33 K/s. Magnetic measurements were carried out by the Faraday method at 293 K at magnetic field intensity up to 9700 Oe using the apparatus described elsewhere [21]. The Mohr's salt was applied as a standard. All reduced samples underwent an evacuation before the magnetic measurements.

Results and Discussion

Results of X-ray examination of $LaCoO_3$ used in this study were given in our earlier publication [15], therefore diffraction patterns of the above compound are not presented in this paper. However, other experimental data concerning $LaCoO_3$ published previously [15] will be given in a further part of the paper in parentheses for comparison with the other binary oxides.

It was found, on the grounds of diffraction curves shown in Figs 1a and 2a that in addition to main reflections originating from $LaFeO_3$ and $LaNiO_3$ phases, also reflections corresponding to some phases of oxide substrates are observed. Relatively low intensities of all reflections in the diffraction patterns

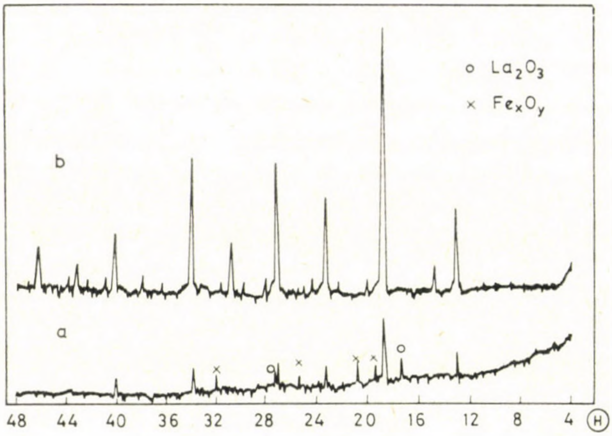

Fig. 1. X-ray curves for $LaFeO_3$: a — material after the explosion, b — material after the explosion preliminary calcinated at 573 K for 2 h at p = 1.33 Pa and then at 773 K for 20 h

proves very poor crystal order of the obtained products. Further thermal treatment has led to an increase in reflections ascribed to the phase of a given perovskite and disappearance of reflections belonging to phases of simple oxides. We have established that the lowest temperature at which monophase products of $LaFeO_3$ and $LaNiO_3$ are obtained is 773 K (identical as in the case of $LaCoO_3$ synthesis). Calcination time necessary to prepare phase-homogeneous samples was 15 and 20 h, respectively, for $LaNiO_3$ and $LaFeO_3$ (10 h for $LaCoO_3$). X-ray curves for samples showing reflections corresponding to the literature data on $LaFeO_3$ [22] and $LaNiO_3$ [23] are given in Figs 1b and 2b. Chemical analysis testifies to a very good stoichiometric agreement since in the case of $LaNiO_3$ lanthanum content was 56.22% and nickel content 23.61% what corresponds to a La: Ni ratio of 1.004. In the case of $LaFeO_3$ lanthanum

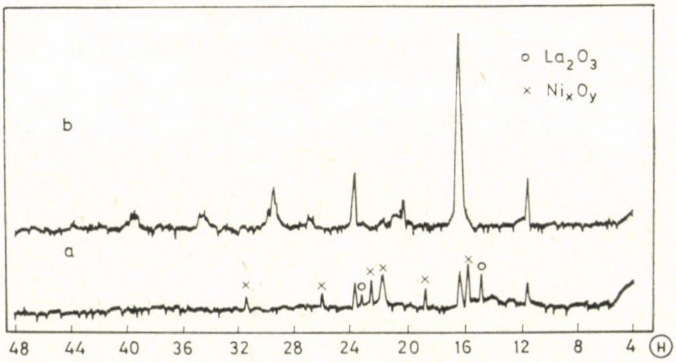

Fig. 2. X-ray curves for $LaNiO_3$: a — material after the explosion, b — material after the explosion preliminary calcinated at 573 K for 2 h at p = 1.33 Pa and then at 773 K for 15 h

content was equal to 57.02% and iron content to 22.64% what makes the ratio of La: Fe = 0.995. (Lanthanum content in $LaCoO_3$ amounted to 56.10% and cobalt content to 24.66% what gives the ratio of La: Co = 0.965). Surface areas of the prepared samples were 25.9 and 22.7 m^2/g, respectively, for $LaFeO_3$ and $LaNiO_3$ (34.6 m^2/g for $LaCoO_3$). One can notice, while comparing surface areas of samples prepared by explosion and ceramic methods that the former method gives the product with a surface area which is *e.g.* for $LaNiO_3$ larger by one order of magnitude than that obtained by the latter method (0.98 m^2/g).

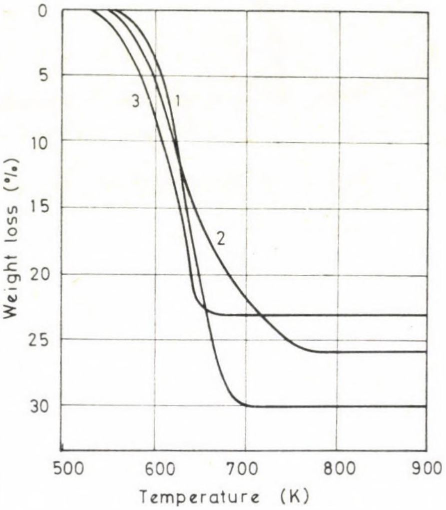

Fig. 3. TG curves for Fe_2O_3(1), $Co_3O_{3.89}$(2) and $Ni_{0.93}O$(3) in 10% H_2 + 90% He at 3 dm^3/s and 0.33 K/s

Curves of thermogravimetric analysis (TG) carried out in reductive atmosphere (10% H_2 + 90% He) are shown in Fig. 4. In the case of $LaCoO_3$ and $LaNiO_3$ the shape of TG curves is similar. The reduction proceeds in two steps. The first step of $LaNiO_3$ reduction occurs in the temperature range of 480—640 K, followed by a shoulder between 640 and 740 K proving the stability of partially reduced sample. The second stage of reduction starts above 740 K and ends at 900 K. These is no weight change above 900 K, and the total weight loss is 9.66 wt.%. The thermogravimetric curve for $LaCoO_3$ shows a similar two-step course of reduction and differs from that for $LaNiO_3$ only in temperature values which are about 100 K higher for each reduction steps, indicating the higher thermal stability of $LaCoO_3$ in comparison with $LaNiO_3$. The total weight loss was 9.75% wt. in the case of $LaCoO_3$. The thermogravimetric curve recorded by SIS *et al.* [24] during heating of a stoichiometric lanthanum(III) cobaltate in reductive atmosphere (10% H_2 + 90% N_2) is similar to our curves. On the other hand, $LaFeO_3$ gives a different

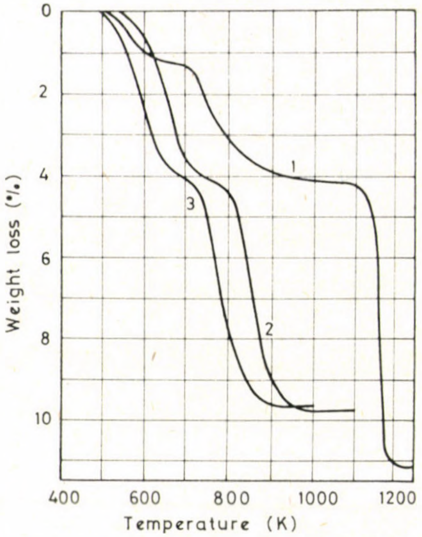

Fig. 4. TG curves for $LaFeO_{3.22}$(1), $LaCoO_{3.00}$(2) and $LaNiO_{2.98}$(3) in 10% H_2 + 90% He at 3 dm^3/s and 0.33 K/s

thermogravimetric curve *(e.g.* curve 1, on Fig. 4). In this case the first step of reduction occurs in the temperature range of 520—580 K. Above this temperatures the sample is stable up to 720 K and then the second step of reduction is observed up to 870 K. Within the temperature region of 870—1140 K a long plateau occurs which indicates the high thermal stability of $LaFeO_3$. The last compound undergoes reduction in a narrow temperature range (between 1140 and 1220 K) and the maximum weight loss is 11.20 wt.%. The presence of La_2O_3 and a respective metal was identified in the final product by X-ray analysis. The above products are formed according to the following overall process:

$$LaMeO_3 \rightarrow 1/2\, La_2O_3 + Me + 3/4\, O_2. \qquad (1)$$

Basing on the above reaction and on the determined values of weight loss caused by reduction process, starting compositions of the investigated binary oxides were calcinated and they appeared to be as follows: $LaFeO_{3.22}$, $LaCoO_{3.00}$ and $LaNiO_{2.98}$. Deviations from oxygen stoichiometry in $LaFeO_{3.22}$ and $LaNiO_{2.98}$ result from the presence of Fe^{4+} and Ni^{2+} in these compounds [25]. It is proper to add that the observed weight loss which amounts to 1.31 wt.% for $LaFeO_{3.22}$ at 580 K is in a good agreement with the determined value of excess oxygen.

Results of the thermogravimetric analysis of single oxides Fe_2O_3, Co_3O_4 and NiO which were also prepared by the explosion method are presented in Fig. 3. The above oxides are reduced to the corresponding metal at 550, 690 and

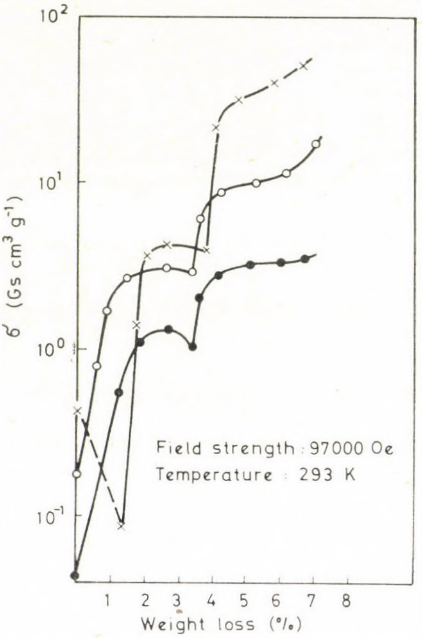

Fig. 5. Magnetic moment as a function of reduction degree (expressed as weight loss in %) for $LaFeO_{3.22}$(×), $LaCoO_{3.00}$(○) and $LaNiO_{2.98}$(●)

770 K for NiO, Fe_2O_3 and Co_3O_4, respectively, and the shape of curves indicates a one-step reduction. The fact that maximum weight loss occurs for single oxides at lower temperatures than for corresponding binary oxides of perovskite-type proves higher thermal stability of the binary oxides. Starting compositions of single oxides calculated on the grounds of weight losses are as follows: $Fe_2O_{3.00}$, $Co_3O_{3.89}$ and $Ni_{0.93}O$. Results of magnetic measurements for $LaFeO_{3.22}$, $LaCoO_3$ and $LaNiO_{2.98}$ which were reduced before the measurements to a specified reduction degree are given in Fig. 5. All the presented results were obtained at 293 K at a field intensity of 9700 Oe. Dependence of magnetic moments on the reduction degree of $LaCoO_3$ and $LaNiO_{2.98}$ have similar character and the shape of the curve for $LaCoO_{3.00}$ is close to that obtained by SIS *et al.* [24] for stoichiometric $LaCoO_3$. The weight loss value at the initial stage of reduction of $LaFeO_{3.22}$ (1.3 wt.% — see thermogravimetric curve in Fig. 3) for which the minimum value of magnetic moment was observed is equivalent to the determined amount of excess oxygen. In the whole investigated range of weight losses observed for $LaCoO_{3.00}$, $LaNiO_{2.98}$ and $LaFeO_{3.22}$ an irregular increase occurs in magnetic moment values which is caused by not uniform process of metallic phase formation (Fe, Co and Ni, respectively). In order to determine quantitatively by magnetic method the concentration

of a given metallic phase in a sample, the following empirical dependence, established by **Heukelom** *et al.* [26] was applied:

$$\frac{1}{\sigma} = \frac{1}{\sigma_\infty} + \frac{1}{\sigma_\infty (\varkappa H)^{0.9}}$$

where: σ — specific magnetization of a sample at H field intensity
σ_∞ — saturation of magnetization
$\varkappa$ — a constant

The $1/\sigma_\infty$ value for a sample under study is obtained by plotting the dependence $1/\sigma$ *vs.* $1/H^{0.9}$ and extrapolating the straight line to $1/H^{0.9} = 0$. Basing on the known values of saturation of magnetization at 293 K which are 218.0, 161 and 54.39 for Fe, Co and Ni [26], respectively, and on saturation of magnetization value of a given sample, percentages of metallic phases in investigated samples were calculated.

Results of magnetization measurements of selected samples with determined weight loss are shown in Fig. 6. A criterion of selection of samples analyzed for metallic phase content was the shape of curve representing the dependence of magnetic moment on weight loss (Fig. 5). Concentration of metallic phases determined for samples with specified reduction degrees was used to calculate the contribution of each component (Table I) and to establish the scheme of reduction of binary oxides under study. The obtained results of magnetic and thermogravimetric studies show that the overall reduction process described by equation (1), leading to the formation of La_2O_3 and a

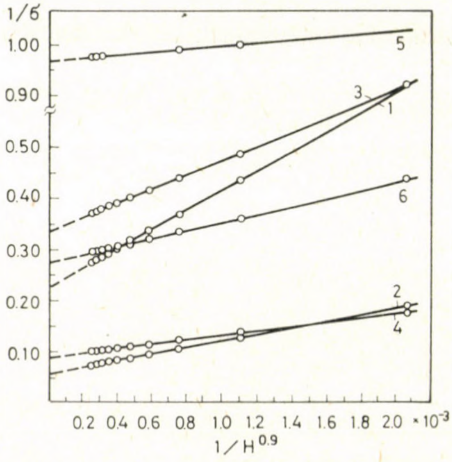

Fig. 6. Determination of σ_∞ value by extrapolation method for samples with percentage of weight loss as follows: $LaFeO_{3.22}$ — 2% (1), $LaFeO_{3.22}$ — 4.55% (2); $LaCoO_{3.00}$ — 1.38% (3), $LaCoO_{3.00}$ — 5.18% (4); $LaNiO_{2.98}$ — 1.77% (5), $LaNiO_{2.98}$ — 5.00% (6)

Table I

Stoichiometric composition of the investigated samples as established on the grounds of weight loss and metallic phase content

Weight loss, %	Metallic phase content, %	Stoichiometric composition
0	0	$LaCoO_{3.00}$
1.38	1.85	$LaCo_{0.92}O_{2.79}$
5.18	6.96	$LaCo_{0.71}O_{2.20}$
0	0	$LaNiO_{2.98}$
1.77	1.90	$LaNi_{0.92}O_{2.73}$
5.00	6.71	$LaNi_{0.72}O_{2.23}$
0	0	$LaFeO_{3.22}$
2	2.04	$LaFe_{0.91}O_{2.70}$
4.55	7.91	$LaFe_{0.66}O_{2.31}$

respective metal, in fact occurs via intermediate compounds with different oxygen deficiency, what can be expressed by the equation as follows:

$$LaMeO_3 \rightarrow LaMe_xO_{3-y} + (1-x)\,Me + 1/2\,y\,O_2 \qquad (2)$$

where: $Me = Fe$, Co or Ni.

At the first stage of reduction, *i.e.* below weight losses of 3.25 wt.% for $LaCoO_{3.00}$ and $LaNiO_{2.98}$ and 3.6 wt.% for $LaFeO_{3.22}$, x and y are between the following values: $0 < x \leq 0.92$ and $0 < y \leq 0.5$. When weight loss exceeds 3.25 wt.% for $LaCoO_{3.00}$ and $LaNiO_{2.98}$, and 3.6 wt.% for $LaFeO_{3.22}$, the second stage of reduction is observed (Fig. 5) which corresponds to an increase in σ value. There is no clear maximum at the above reduction stage, therefore the values of weight loss of 5.18, 5.00 and 4.55% (based on shape of curves shown in Fig. 3) were chosen as representative of this stage, for $LaCoO_{3.00}$, $LaNiO_{2.98}$ and $LaFeO_{3.22}$, respectively. On the grounds of these values and concentrations of metallic phase, the stoichiometric compositions given in Table I were determined. They show that reactions occurring at the second stage of reduction can be also described by Eq. (2). However, above the discussed values of weight loss, the obtained data do not lead to univocal conclusions.

Conclusions

1. Optimum conditions of $LaFeO_3$ and $LaNiO_3$ syntheses were determined for the explosion method, elaborated earlier to prepare $LaCoO_3$. Both for $LaFeO_3$ and for $LaNiO_3$ the optimum temperature of synthesis is 773 K and calcination time 15 and 20 h for $LaFeO_3$ and $LaNiO_3$, respectively.

2. Under the applied conditions of synthesis binary oxides with the following composition were obtained: $LaFeO_{3.22}$, $LaCoO_{3.00}$ and $LaNiO_{2.98}$.
3. In all cases under study, binary oxides show higher thermal stability in comparison with respective single oxides (Fe_2O_3, $Co_3O_{3.89}$ and $Ni_{0.93}O$).
4. The order of thermal stability is the following: $LaNiO_{2.98} < LaCoO_{3.00} < LaFeO_{3.22}$
5. In a reductive atmosphere, the reduction of the above compounds does not give directly La_2O_3 and the respective metal (Fe, Co or Ni) but proceeds *via* intermediate compounds of different oxygen deficiency.

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STUDIES ON POLYMER GEL — BINARY MIXTURE SYSTEMS, I

THE EFFECT OF THE SELF-ASSOCIATING COMPONENT ON PARTITION EQUILIBRIA

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The effect of the self-association of one of the diffusible components upon the equilibrium of a gel—binary mixture system is discussed for the systems PVA—water—dodecyl-trimethyl-ammonium bromide, and PVA—water—saccharose. Consistently with theoretical calculations, the curves characteristic of selective solvatation are strongly convergent in this case; but data found and data calculated for sorption in infinitely dilute solutions differ by nearly one order of magnitude.

Introduction

Extensive studies in our laboratories were carried out in recent years in order to elucidate the fundamental factors which affect the phenomena of swelling and sorption. Already the first results were promising, at least as far as two fundamental aspects were concerned. On the one hand it could be shown that sorption isotherms obtained for gels of a small degree of cross-linking and of low polymer concentration are the same — within limits of experimental error — as the solvation isotherms referred to a solution at infinite dilution [1]. The equivalence of the two phenomena was verified later for other systems, too [2]. On the other hand it was found that, generally, it is only in very simple cases that parameters noted in theoretical work [3, 4, 5] prove suitable for a quantitative description of total and preferential sorption. For, in the course of detailed experimentation we have found that the shape of sorption isotherms in strongly polar systems is often decisively affected by the structure of the solvent mixture used, besides the χ_{ij} interaction parameters and the molar volumes of the diffusible components. Thus detailed study of poly(vinyl alcohol) — water — aliphatic alcohol systems has shown that the association-state of the solvent mixture plays a significant role in the θ-state conformation of poly(vinyl alcohol) (PVA), in other words the polymer molecule must, so to say to fit to the structure of the mixture [6, 7, 8]. The results of these experiments also draw attention to the fact that — contrarily to the theoretical treatments, based on the supposition of completely or partially disordered states, currently used — a rather more suitable theoretical way is open perhaps by considering the interaction between the variously coupled systems and by considering how this interaction affects the two "main" components, *viz.* the polymer molecules and the molecules of the solvent mixture. However, the opening up of such a way of looking at this matter is for the future because at present we are hindered by the relative complexity of the systems and by some theoretical difficulties.

In this paper we present a report on the effect of the association of one of the diffusible components on the gel — binary mixture equilibrium, by way of using an obvious model: dodecyl-trimethyl-ammonium bromide, DTAB, a surfactant soluble in water. Earlier studies have shown that this substance does not interact with PVA, as do anionactive surfactants [9], thus association of the surfactant molecules will be the principal process to affect partitioning equilibrium. For the sake of comparison also the partitioning of saccharose a non-associable component that has about the same molar volume as DTAB, is considered.

Experimental

Substances

PVA, (Rhodoviol 60/20) average relative molecular mass 2.10^5, acetate content 3 mole per cent, was used. Prior to the preparation of the gel the polymer was purified in the usual way to remove acetate groups [8].

DTAB, (Serva, Heidelberg) was several times recrystallized from an acetone—benzene mixture.

Saccharose, commercial product, was recrystallized from aqueous solutions.

The succinic dialdehyde, SDA, used for cross-linking, was prepared from 2,5-dimethoxy--tetrahydrofurane by means of hydrolysis with concentrated hydrochloric acid. SDA was recovered by extraction with ether; this crude product was distilled under atmospheric then under reduced pressure. SDA was stored as a concentrated solution in water. The composition of this solution was determined by titration with a 0.1 N solution of H_2SO_4 in the presence of $NaHSO_3$.

In all cases solutions were prepared with distilled water.

Preparation of the gel

Three series of gels, denoted by A, B, and C were prepared from PVA solutions containing 4, 8, and 10 per cent by weight of the polymer, respectively at various ratios of PVA to SDA. First, the calculated amount of SDA to the intensively agitated solution of the polymer, then hydrochloric acid to reach $pH = 1.5$ was added.

0.5 cm thick layers from the homogeneous mixture were poured into plexi glass frames made for this purpose. After completion of the gelation process the gel-plates were cut into pieces to edge lengths of 1.5 to 2.0 cm and then these were extracted with distilled water. The purity of the water in equilibrium with the gel pieces was checked by interferometry. Characteristics of the gels are collected in Table I. In this paper only studies on gels of the series B and C are discussed.

Determination of the weight degree of swelling

The mass of the gel pieces taken out of the swelling medium was weighed on an analytical balance, after careful drying of their surface with blotting paper. The non-volatile diffusible component of the gels was extracted with distilled water and then the specimens were dried in vacuum at 333 K, then also the dry polymer mass was weighed. The ratio of swollen mass to dry one is the weight degree of swelling; the reciprocal of this quantity is the weight fraction of polymer in the gel.

Table I

Characteristics of PVA hydrogels

Ser. n°.	A		B		C	
	ϱ_c	W_3^0	ϱ_c	W_3^0	ϱ_c	W_3^0
1	0.0029	3.80	0.0013	6.10	0.0010	5.80
2	0.0051	5.10	0.0043	11.40	0.0031	10.00
3	0.0077	7.00	0.0071	13.30	0.0130	15.00
4	0.0100	8.10	0.0100	15.40	0.0120	18.10

ϱ_c ratio of amounts (moles) of SDA and PVA in the system (in the case of the polymer this means that mass calculated on the basis of the molecular mass of the monomer unit)

W_3^0 polymer content (per cent by weight) of gel in equilibrium with pure water.

Sorption measurements

From gel-plates of known composition samples were weighed on an analytical balance into test tubes, 10 mL capacity each, and provided with rubber stoppers, so as to have 0.1 . . . 0.2 g the polymer in the system. Also on an analytical balance, DTAB, or saccharose, solutions were weighed on to the gels so that a 50 : 1 ratio of total solution with the mass of water in the gel included to the mass of the dry polymer should be obtained. The test tubes were then carefully sealed and kept at 298 K till equilibrium was established (separate studies showed five days to be needed for this).

The composition of the solution in equilibrium with the swollen gel was determined with a liquid-interferometer type ITR-2 and with the help of a calibration curve. The sensitivity was ± 0.002 per cent by weight for one scale division when cuvettes of 0.5 or 1.0 cm were used. The instrument was kept at constant 298 ± 0.1 K temperature during measurements. The interferometer scale was read to an accuracy of ± 1 division. All in all, according to numerous tests carried out with many systems, the concentrations of the solutions could be determined to an accuracy of ± 0.01 per cent by weight.

Calculation of the data characteristic of the sorption

Sorption parameter γ_w for one of the components (for solute in our case) was calculated on the basis of the equation

$$\gamma_w = \frac{W_{\mathrm{i},2} - W_{\mathrm{e},2}}{100\, m_\mathrm{p}}\, m_0$$

where $W_{\mathrm{i},2}$ is the initial concentration of the solute in the system (per cent by weight) referred to the m_0 mass of the solution; $W_{\mathrm{e},2}$ is the equilibrium concentration in the supernatant; m_p is the mass of the polymer in the system.

If the sorption isotherm *i.e.* the $\gamma_w = \mathrm{f}(W_\mathrm{e})$ function and the dependence of the q_w weight degree of swelling on equilibrium concentration is known then the $W_{\mathrm{g},k}$ concentration in the gel of the diffusible component k partitioned between solution and gel phases can be given as

$$W_{\mathrm{g},k} = W_{\mathrm{e},k} + \frac{100\, \gamma_{w,k}}{q_w - 1}\,,$$

the material balance relevant to the system being here utilized. On the basis of this equation the partitioning isotherm $W_\mathrm{g} = \mathrm{f}(W_\mathrm{e})$ can be constructed from experimental data.

Results

As fundamental experimental data the sorption isotherms of DTAB and of saccharose are shown in Figs 1 and 2; the dependence of S_r values $\left(\frac{\text{g solution bound}}{\text{g polimer}}\right)$ on the equilibrium concentration of DTAB in the PVA—DTAB—water system, is shown in Fig. 3. Composition corresponding to

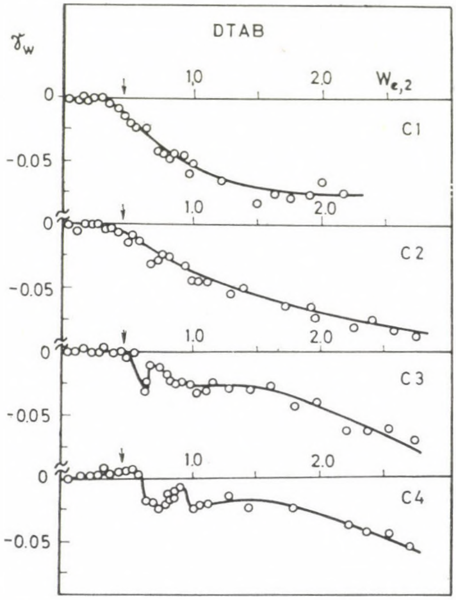

Fig. 1. The sorption of DTAB on C-type PVA hydrogels

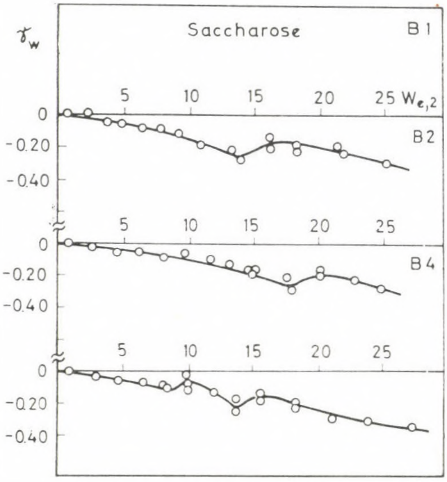

Fig. 2. The sorption of saccharose on B-type PVA hydrogels

critical micelle-formation concentration, c.m.c. [10] is marked by arrows on the DTAB isotherms. Figure 4 shows partitioning isotherms for the DTAB—water system, calculated from smoothed sorption isotherms. For saccharose, it is only a former experience [11] that allows us to say that q_w monotonously decreases, though by decrements hardly surpasses experimental error, in a concentration range which is comparable with that of DTAB.

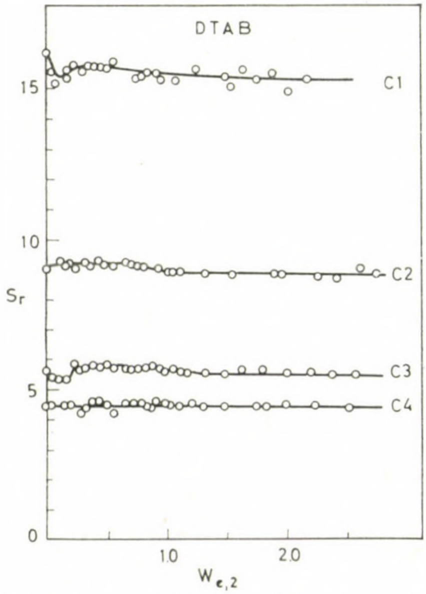

Fig. 3. The dependence of S_r values on DTAB equilibrium concentration for C-type PVA hydrogels

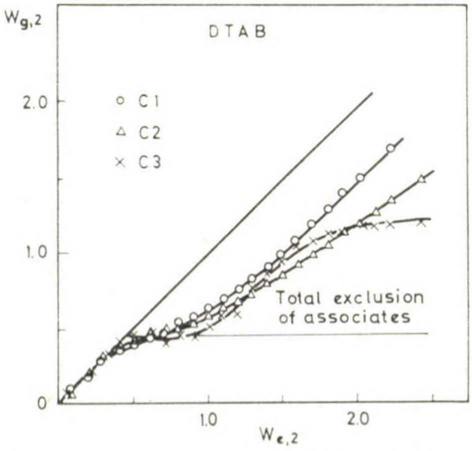

Fig. 4. Partitioning isotherms of DTAB on PVA hydrogels

Based upon sorption isotherms relevant either to DTAB or to saccharose, it can be said that their shape — at least in the majority of the cases tested — partly satisfies expectation: for DTAB, the sorption isotherm passes into the negative range in the region of c.m.c. due to the exclusion from the gel the associates formed; for saccharose the entire sorption isotherm relevant to the range of compositions studied runs in the negative domain.

We should like to emphasize here that in this work we do not deal with the anomalous, by theoretical approach not yet interpretable sections of the sorption isotherms. This may be reserved for future communications in which also more recent experiences will be reported.

Discussion

In a previous communication [12] we have shown that the term for the chemical potential of the solvent in the binary gel-phase should contain minimum two members of chemical potential (principle of compensation). That means that the change with volume of the Helmholtz-energy of the semi-open system (gel-phase) can be resolved — owing to a consideration of the processes that take place — into two pressure or chemical potential components with opposite sings. For the diffusible component 1

$$\mu_1 = \mu_1^0 + \Delta P(V)\, \bar{V}_1 \tag{1}$$

where $\Delta P(V) = \left(\frac{\partial \Delta A}{\partial V}\right)_{T, n_2}$, and

$$\bar{V}_1 = \left(\frac{\partial V}{\partial n_1}\right)_{n_2},$$

the partial molar volume of the solvent. (Here we wish to note that with systems of this type we calculate only with changes of volume due to the effect of a change in the amount of the diffusible component; thus, having an unequivocal correlation between V and n_1 in an incompressible system, we can generally write $A = \mathrm{f}(V(n_1))$. Therefore, and using the chain-rule, the term $\left(\frac{\partial \Delta A}{\partial V}\right) \cdot \left(\frac{\partial V}{\partial n_1}\right)$ gives the chemical potential of component 1. Formally, this is the product of pressure and of the partial molar volume of the solvent.)

When a binary mixture is in equilibrium with the gel phase instead of a pure solvent, the discussion proceeds essentially on the same line. In the simplest case the concentrations of the diffusible components in the external mixed phase and in the gel-volume occupied by the solvent are the same.

Generally, for component 1

$$\mu_1(c_2) = \mu_{1,\mathrm{el}}(c_3) + \mu_{1,\mathrm{mix}}(c_2, c_3)\,. \tag{2}$$

Here c_2 stands for the other component, c_3 for the polymer-concentration in the gel and $\mu_{1,\mathrm{el}}(c_3)$ for that part of the chemical potential which is due to the elastic response of the network and $\mu_{1,\mathrm{mix}}(c_2, c_3)$ for that part of it which is due to the mixing of the components. Since the equilibrium requires equality of the chemical potentials of both diffusible components in both subsystems we must have

$$\mu_1 = \mu_{1,\mathrm{mix}}(c_2, c_3) + P_{\mathrm{el}}(V)\,\overline{V}_1, \quad \text{and}$$

$$\mu_2 = \mu_{2,\mathrm{mix}}(c_1, c_2) + P_{\mathrm{el}}(V)\,\overline{V}_2\,. \tag{3}$$

In equation (1) the standard value of the chemical potential of the solvent was taken to be the value of the pure component referred to $P_{\mathrm{el}} = 0$. Since some polymer is always present in the gel, that part of μ_1 in the ternary subsystem which depends on c_3 cannot be left out of account. Therefore in this case choosing the standart chemical potential of components *1* and *2* is difficult. Of course the $c_3 \to 0$ transition can be a formal solution but principally it is not realizable in the case of networks. Further difficulties are caused (and this approaches reality the most closely) by the different interactions of the diffusible components with the polymer in the gel phase, or by composition difference of the two parts of the system due to other factors, *i.e.* the phenomenon of selective solvation (sorption) emerges. From the point of a quantitative description here the only expedient method would be a determination of the extreme value of the function which expresses the Helmholtz-energy of the overall system by means of all the important parameters. Lack of concrete thermodynamical data on the one hand, involved mathematical difficulties on the other, would not allow this determination to succeed but in single cases and at the price of gross simplifications.

POUCHLY *et al.* [5] have calculated a few cases according to the Flory-Huggins model of solutions, with an extension so as to account also for the various aspects of association-solvatation of the components of the solvent. These calculations have shown that a negative selective sorption in respect of the diffusible component with greater molecular volume may be expected when no specific interaction between the components is effective. Obviously, this is a trivial consequence also of Eq. (1). Then total sorption (degree of swelling) decreases monotonously with the concentration of the component with greater molar volume (partial "deswelling" effect). If one of the components is capable of self-association and it solvates the polymer chain when the other component behaves like an indifferent solvent then solvatation isotherms start in the positive domain and change sign later on. Also an extreme or limit value is found for the dependence of degree of swelling from the composition of the mixture: the maximum is located near the sorption azeotrope.

The authors cited above have proposed a suggestive illustration which emphasizes the essential features of the several typical cases; their proposal will be used here with slight alterations.

Fundamentally, two features of a ternary system of this type must be expressed by an adequate illustration. One is how the degree of swelling (total sorption) changes or how the volume fraction of the polymer changes as a function of the composition of the mixture; the other is how the difference of concentrations changes between the two parts of the system (preferential sorption) as a function of the composition of the mixture and polymer content.

Expressed in weight fractions, the preferential sorption according to the authors quoted can be written

$$\varepsilon_{w,2} = w_2' - w_{2,0}$$

where $w_2' = \frac{w_2}{w_1 + w_2}$; the index 2 refers to the dissolved substance, *i.e.* DTAB or saccharose in our cases, the index 0 refers to the space where no polymer is present. Thus the corresponding points, *i.e.* those which characterize the equilibrium, can be plotted, suitably on a $w_3 = f(w_2')$ diagram. When the w_3 *vs* w_2' function is plotted for gels at various degrees of cross-linking and the points are joined in vertical direction, w_3 as the function of w_2' is obtained. The value for $w_3 = 0$, or when polymer concentration is zero, corresponds to a given $w_{2,0} \cdot \varepsilon_{w,2}$ can be determined from the deviation of the former curve from the vertical line set up at this point and also how this depends on w_3 can be read off immediately. Joining the correlated points in horizontal direction produces the levels of the osmotic pressures which are nearly the same, *i.e.* the osmotic isobars for the networks.

If one of the components is likely to form self-associates then the vertical curves characteristic of selective sorption will converge, according to numerical calculations [5]. No results in connexion with further studies of this question are to be found in the literature.

Considering the system DTAB—water, it seems to be clear (*cf.* partitioning isotherms on Fig. 4) that there exists a range of concentrations of DTAB which corresponds to a fairly good approximation to the domain where DTAB-micelles are nearly completely excluded. The beginning of the range of concentration which corresponds to this exclusion is in the vicinity of the critical concentration of micelle formation of the surfactant. On the other hand we see a surprising tendency, already observed on the sorption isotherms, that the less the degree of crosslinking the lower the DTAB-concentration at which exclusion begins. A probable explanation is that the homogeneity of gels changes with increasing degree of cross linking, or that part of the micelles penetrates into the gel. Another experience worth mentioning is that non-associated DTAB molecules, though considerably more voluminous than water, are not excluded from the gel. This effect can be interpreted as a competitive interaction between DTAB and PVA; that includes an effect, attributable to compounds of this type, perhaps favourable for PVA, that modifies the structure of water.

The ternary diagrams discussed in detail in the preceding part are shown for DTAB–water, or saccharose–water systems, on Figs 5 and 6. In both instances we left the small, though measurable change of the weight degree of swelling out of account. There exists a sharp difference between the two systems in the same range of concentrations: the lines characteristic of

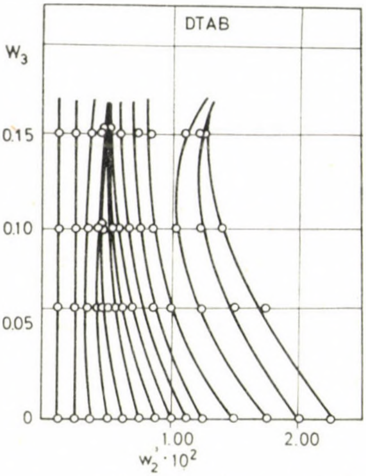

Fig. 5. The selective sorption curves and the approximate osmotic isobars for PVA — water — DTAB systems

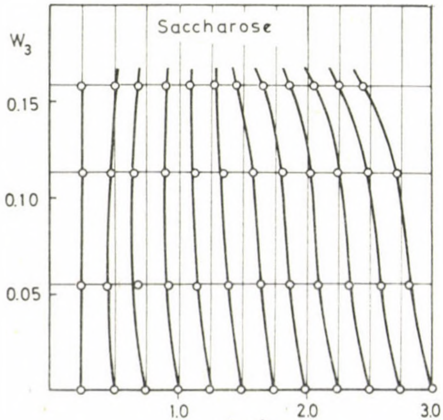

Fig. 6. The selective sorption curves and the approximate osmotic isobars for PVA — water — saccharose systems

selective sorption of DTAB are definitely convergent: the position of the greatest density of lines corresponds quite well to c.m.c. Thereby the partitioning behaviour of ternary systems of this type has been experimentally shown the first time.

The more detailed calculations of the authors referred to deal with systems which are infinitely dilute in respect of the polymer. A quantity, can be defined in this case which is characteristic for the selective sorption,

$$A_{w,2} = \lim_{w_3 \to 0} \left(\frac{\varepsilon_{w,2}}{w_3} \right) \tag{5}$$

and it is calculable as a function of the composition of the mixture with certain simplifying assumptions. If no specific interactions, *e.g.* strong dipole—dipole, or hydrogen bonding effect operate in the system, then, approximately,

$$A_{w,2} = \frac{\bar{r}_1 - \bar{r}_2}{\bar{r}_1 w_{1,0} + \bar{r}_2 w_{2,0}} w_{1,0} w_{2,0} \tag{6}$$

Here $\bar{r}_1$ and $\bar{r}_2$ represent the average (by weight!) size of the associates formed from components 1 and 2, expressed with volumes of the base-segment of the lattice model. (Since in the present case the densities of the components do not greatly differ from unity, which corresponds to water, and because Eq. (6) is an approximative one it was not necessary to correct the data for the densities of the components.)

If component 1, *i.e.* water, is selected to be the basic unit, then

$$\bar{r} = \frac{\bar{r}_2}{\bar{r}_1}, \text{ and}$$

$$A_{w,2} = \frac{1 - \bar{r}}{w_{1,0} + \bar{r} w_{2,0}} w_{1,0} w_{2,0} \,. \tag{7}$$

Since for systems studied $w_{2,0} \leqslant w_{1,0}$, and $w_{1,0} + w_{2,0} = 1$,

$$A_{w,2} = \frac{(1 - \bar{r}) w_{2,0}}{1 + \bar{r} w_{2,0}} \,. \tag{8}$$

The appropriate molecular mass (308 for non-associated DTAB) being taken in consideration, in the concentration range below c.m.c. $\bar{r} \approx 17$, and above c.m.c. the data given in Table II are relevant. The later are calculated for bi-disperse systems, with molecular mass 15400 [13] and micellar concentration of $w_{2,0} - w_{2,0\,\text{c.m.c}}$, and for a constant concentration, $w_{2,0\,\text{c.m.c}}$ of non-associated DTAB.

Table II

Change of $\bar{r}$ in the concentration range above c.m.c. (calculated data)

$w_{2,0} - w_{2,0\,\mathrm{c.m.c.}}$	$\bar{r}$
5.10^{-4}	700
15.10^{-4}	760
35.10^{-4}	780
55.10^{-4}	790

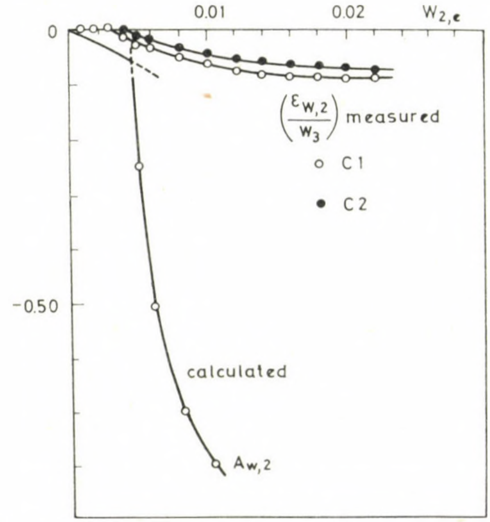

Fig. 7. Measured and calculated sorption isotherms for DTAB

The application of equation (8) is illustrated by Fig. 7, where the deviations of data found from data calculated is nearly of one order of magnitude. In the concentration range $0 < w_e < 0.01$, partitioning isotherms give a relatively real picture of the presently accepted view of the self-association of such substances [14], thus the great discrepancy between data calculated and data found cannot be explained on the basis of gel structure. We attempted the $w_3 \rightarrow 0$ extrapolation from available data, but this did not significantly improve the situation on Fig. 7, either.

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INFLUENCE OF PHOTOGRAPHIC AND PHOTOMETRIC EFFECTS ON THE SPECTROGRAPHIC EVALUATION, VIII*

OPTIMIZATION OF THE EVALUATION IN THE SPECTROGRAPHIC ANALYTICAL METHOD DEVELOPED FOR PURPOSES OF POLLUTION CONTROL

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Optimization of the evaluation in the spectrographic analytical method developed for purposes of pollution control is described. Results in reducing errors in density measurements, in increasing the range of density measurements and also in the calibration of emulsion (included the independence of evaluation by *l*-transformation from the type of microdensitometer as well as the photographic and photometric relationships established for spectral lines and the background), and computer programmes elaborated for spectrographic evaluation by the application of mathematical statistical methods have been used. In this way, while the precision of analytical results has been maintained, the accuracy of analysis could be increased in a concentration range of 0.5—1 order of magnitude wider as compared to conventional procedures.

1. Introduction

As in previous papers of this series [1—7] it has been presented the light intensity range measured by photographic method as well as the accuracy of intensity measurements are determined by the interaction of photographic and photometric factors. Reducing the random and systematic errors of density measurements the measuring range of the conventional type microdensitometers can be doubled, *i.e.* up to density 4.0 [2, 3]. The range of the blackening curve applicable for light intensity measurement used to be narrower than the measuring range of the microdensitometer: density S_{LL}, representing the upper limit of the straight section of blackening curve, is influenced by the type of spectrum (line, or continuous), conditions of its recording, and the photographic emulsion as well (first of all its γ-value) [5]. In the case of

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densities lower than those of S_{LL} the l-transformation can be used with unchanged precision even in the extended range [4, 6]. The slope of the blackening curves determined by line spectra is higher than the γ-value referring to the continuous spectra. The difference of the two γ-values depends on the type and condition of emulsion and decreases with the increase of background density [7].

Our previous publication reported on the efficiency of the spectrographic analytical method elaborated for pollution control serving for the determination of 15 elements in the case of conventional evaluation [1]. This serves as the basis of comparison to the optimization to be reached by the up-to-date microdensitometer of wide measuring range [3] and by using the above theoretical results.

2. Experimental

The complete calibration of the described analytical method serving for pollution control [1] was repeated so, as on the spectra recorded on the spectral plate type ORWO WU 3 the density was measured with the up-to-date microdensitometer type G II—MFKI [3]. In order to be able to examine the influence of emulsion, the spectra of calibration samples have been recorded also on a spectral plate, type Agfa-Gevaert 23 D 50, under the given experimental conditions, and this plate was also completely evaluated by measuring the density values with G II-MFKI microdensitometer.

Efficiency of analytical methods have been characterized, in this case too, by the following evaluating parameters:

a) $c_{max}-c_{min}$ concentration ranges corresponding to the linear section of analytical curves,

b) B_X slopes of these analytical curves,

c) s_c/c [%] relative standard deviation values characteristic of the relative precision of the method,

d) $\underline{c}$ values of detection limits,

e) Δc [%] values characteristic of the accuracy of the method, differences between concentrations calculated and measured are determined on the analysis of samples of known composition.

3. Results

On the two types of spectral plates applied to the experiments the γ-values determined with G II-MFKI microdensitometer are plotted against the wavelength on Fig. 1. It can be seen that γ-values on the spectral plate type Agfa-Gevaert 23 D 50 are considerably higher than those on ORWO WU 3. Under the given experimental conditions, S_{LL} values could not always be determined, however, according to data available $S_{LL} \geq 2.50$ at each wavelength, on both plates. The average k-value of plate type WU 3 is 0.47, while that of plate type 23 D 50 is 0.30 in the wavelength range examined.

Table I and II demonstrate the evaluating parameters of the analytical methods in the case of evaluation of two plate types by microdensitometer G II-MFKI. To make better comparison $\Delta \log c_x$ logarithm concentration

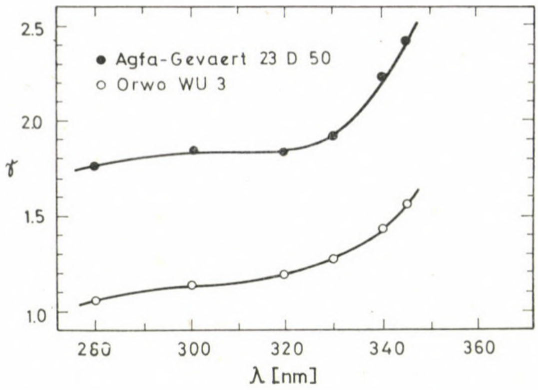

Fig. 1. Variation of γ-values as a function of wavelength (Orwo WU 3 and Agfa-Gevaert 23 D 50 spectral plates, G II — MFKI microdensitometer)

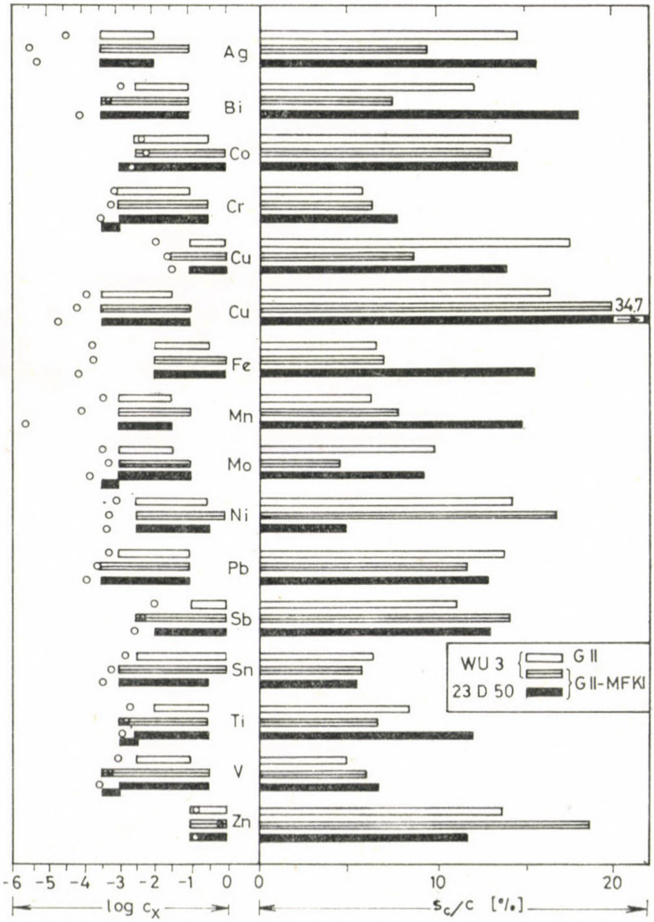

Fig. 2. Δ log c_X linear parts of analytical curves, $\underline{c}$ detection limits (represented with circles) and s_c/c relative precision values obtained by spectral plates and microdensitometers of different types

Table I

Valuating parameters of the analytical method in the case of Orwo WU 3

Line pair Parameter	Ag 328 Pd 325	Bi 306 In 303	Co 345 Pd 325	Cr 302 Pd 302	Cu 282 In 303	Cu 327 In 325	Fe 302 Pd 302
$c_{\max}$ [%]	0.1	0.1	1.0	0.316	1.0	0.1	1.0
$c_{\min}$ [%]	0.000316	0.000316	0.00316	0.001	0.0316	0.000316	0.01
B_X	0.714	0.885	0.938	0.959	0.978	0.863	0.707
s_c/c [%]	9.4	7.5	13.0	6.3	8.6	19.9	7.0
$\underline{c}$ [ppm]	0.03	6.1	71	6.5	364	0.6	(2.1)
Δc [%] I.	—	4.7	—	10.6	—	21.2	10.3
II.	9.5	3.1	36.6	18.9	—	13.4	—

ranges corresponding to the linear range of the analytical curves, s_c/c [%] standard deviation values and $\underline{c}$ detection limit values are plotted side by side element by element in Fig. 2. Values obtained by conventional microdensitometer Zeiss G II from plate type WU 3 have also been shown on the figure [1]. In addition to this, in the above three cases the average linear $\overline{\Delta \log c_X}$ range of the analytical curves, the value of the mean $\overline{s_c/c}$ [%] standard deviation* and the average Δc [%] difference of concentrations determined in control samples from the correct value (Table III) were also calculated. The last line of the table demonstrates that from among the $2 \times 15 = 30$ concentration measurements to be performed in the two control samples in how many cases can the determination be performed.

4. Conclusions

4.1. *Extension of the limit of measurement*

The extension of the upper measuring limit of the microdensitometer involves a considerable increase in the linear range of the analytical curve best utilized for analysis. One can see on the plate type ORWO WU 3 that the analytical curves determined by microdensitometer G II-MFKI frequently are continued towards high concentrations even then, if using conventional G II apparatus, already a bending can be observed or the densities are too high, and not measurable, resp. However, when applying photographic emulsion of higher γ-value — due to photographic and photometric causes detailed earlier — linear analytical curves can be obtained only in narrower concentra-

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* The unexpectedly high values of standard deviation observed at copper determination have been left out from calculation of the average value.

spectral plates measured by means of G II — MFKI microdensitometer

Mn 279 / Pd 302	Mo 313 / Pd 325	Ni 300 / Pd 302	Pb 283 / In 303	Sb 287 / In 303	Sn 286 / Pd 302	Ti 336 / Pd 325	V 318 / Pd 325	Zn 330 / In 325
0.1	0.1	1.0	0.1	1.0	1.0	0.316	0.316	1.0
0.001	0.001	0.00316	0.000316	0.00316	0.001	0.001	0.000316	0.1
1.069	0.951	0.864	0.751	1.030	0.961	0.946	0.927	0.822
8.0	4.4	16.6	11.5	14.0	5.8	6.7	6.0	18.6
0.9	5.3	4.8	2.5	47	6.1	18	5.9	6020
17.3	5.0	2.4	34.1	0.5	2.0	20.0	12.3	—
6.0	—	5.3	39.8	20.0	2.7	16.1	22.6	—

tion range even with microdensitometers of wide measuring range. Namely, the S_{LL}-values gained by microdensitometer G II-MFKI do not differ essentially for the two plate types, but because of the greater γ-value, the range of logarithm intensity measured in emulsion type 23 D 50 is, evidently narrower. This fact is extremely disadvantageous, if only conventional microdensitometer is available, as in this case at higher γ-value the measurable concentration range is quite narrow. This is represented by the analytical curves of Cr spectral lines at 302.16 nm (Fig. 3).

At the comparison of $\overline{\Delta \log c_X}$ values given in Table III one has to take into consideration that due to the different intensities of the analytical

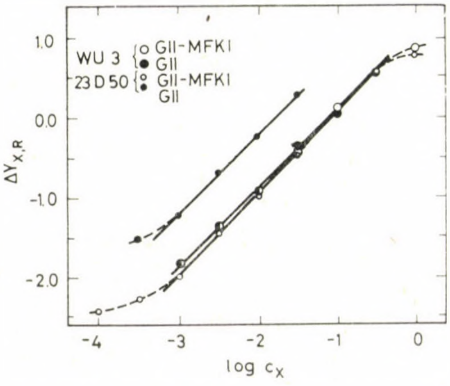

Fig. 3. Analytical curves of Cr 302.16 nm/Pd 302.80 nm line-pair as determined on Orwo WU 3 and Agfa-Gevaert 23 D 50 spectral plates by means of G II and G II — MFKI microdensitometers, resp. (In the case of spectral plate type 23 D 50 and G II microdensitometer, only the Pd 292.25 nm reference line of lowest density could be measured, this causing displacement of the corresponding analytical curve)

Table II

Valuating parameters of analytical method in the case of Agfa-Gevaert

Line pair	Ag 328	Bi 306	Co 345	Cr 302	Cu 282	Cu 327	Fe 302
Parameter	Pd 325	In 303	Pd 325	Pd 302	In 303	In 325	Pd 302
c_{max} [%]	0.01	0.1	1.0	0.316	1.0	0.1	1.0
c_{min} [%]	0.000316	0.000316	0.001	0.001	0.1	0.000316	0.01
B_{X}	0.839	0.867	1.083	0.994	0.973	0.864	0.749
s_c/c [%]	15.6	17.9	14.5	7.7	13.8	34.7	15.5
$\underline{c}$ [ppm]	0.06	0.8	21	3.0	320	0.2	(0.8)
Δc [%] I.	—	11.3	—	5.9	—	20.2	17.6
II.	6.6	35.1	—	0.5	—	16.4	—

lines, exposure conditions optimal for all spectral lines can not be found. Thus, from the photographically measurable intensity range in the case of the single spectral lines various intervals can be utilized even by microdensitometers of wide measuring range. At the multi-element determination, the extension of measuring range is advantageous also from this point of view. In the case of high concentrations, the slope of the analytical curve may be decreased also by self-absorption in addition to photometric effects, this can, however, be truly judged if the measured density values are lower than S_{LL}.

Above mentioned are illustrated by presenting some analytical curves, too. Density of spectral line Sn 286.33 nm can be regarded as optimum from the point of view of exposure of the plate ORWO WU 3, the highest measurable density falls close to S_{LL} when applying microdensitometer G II, so the analytical curve is linear from the highest concentrations downwards through 2.5 orders of magnitude and by 3 orders in the case of microdensitometer G II-MFKI (Fig. 4a). On the figure it can be seen that on the plate Agfa-Gevaert 23 D 50 the high densities can not be measured reliably — because of the scattered light — and to this fact can be attributed the bending of analytical curve towards high concentrations. The mean differences observed in the three compared cases are well demonstrated by the analytical curves of Ni 305.08 nm (Fig. 4b). The analytical curve got on ORWO WU 3 plate of lower γ-value by means of microdensitometer G II-MFKI is linear even to the highest measurable concentrations, while it bends at a concentration lower by one order of magnitude when evaluating by the G II apparatus. On the Agfa-Gevaert 23 D 50 plate linear range was found to be higher by a half order of magnitude comparing to the latter case. At last, the analytical curves of Pb 283.31 nm spectral line demonstrate on Fig. 4c the unambigously observable self-absorption. In all the three cases, the densities are lower than S_{LL}.

23 *D* 50 *spectral plates measured by means of G II — MFKI microdensitometer*

$\frac{\text{Mn 279}}{\text{Pd 302}}$	$\frac{\text{Mo 313}}{\text{Pd 325}}$	$\frac{\text{Ni 300}}{\text{Pd 302}}$	$\frac{\text{Pb 283}}{\text{In 303}}$	$\frac{\text{Sb 287}}{\text{In 303}}$	$\frac{\text{Sn 286}}{\text{Pd 302}}$	$\frac{\text{Ti 336}}{\text{Pd 325}}$	$\frac{\text{V 318}}{\text{Pd 325}}$	$\frac{\text{Zn 330}}{\text{In 325}}$
0.0316	0.1	0.316	0.1	1.0	0.316	0.316	0.316	1.0
0.001	0.001	0.00316	0.000316	0.01	0.001	0.00316	0.001	0.1
1.021	0.977	1.000	0.861	0.906	1.041	0.993	0.965	0.776
14.7	9.2	4.8	12.7	12.8	5.5	12.0	6.7	11.5
0.02	1.6	4.8	1.2	30	3.8	13	3.0	1458
24.6	3.7	13.2	4.5	14.3	1.5	27.8	32.8	—
—	3.5	12.3	16.2	—	5.5	28.3	36.9	—

Table III

Average values of evaluating parameters of the analytical method in the case of spectral plates and microdensitometers of different types

Spectral plate	Orwo WU 3	Orwo WU 3	Agfa-Gevaert 23 D 50
Densitometer	Zeiss G II	G II MFKI	G II–MFKI
$\overline{\Delta \log c_X}$	1.63	2.40	2.10 (2.19)*
$\frac{\overline{s_c}}{c}$ [%]	10.1	9.6	11.7
$\overline{\Delta c}$ [%]	16.7	13.9	15.4
Number of measurements	20	24	22

* In the case of background correction with two-γ-method

Comprehensively, it is to be stated that for the increase of the concentration measuring range and for the multi-element analysis it is favourable to extend the measuring range of microdensitometer and to use spectral plate of lower γ-value, as well.

4.2. *Slope of analytical curves*

In optimal case $\bar{B}_X$ is equal to 1. In the 3 compared cases the B_X values are identical within the limits of experimental errors. The minor differences can be explained first of all by the fact that the determinations have been

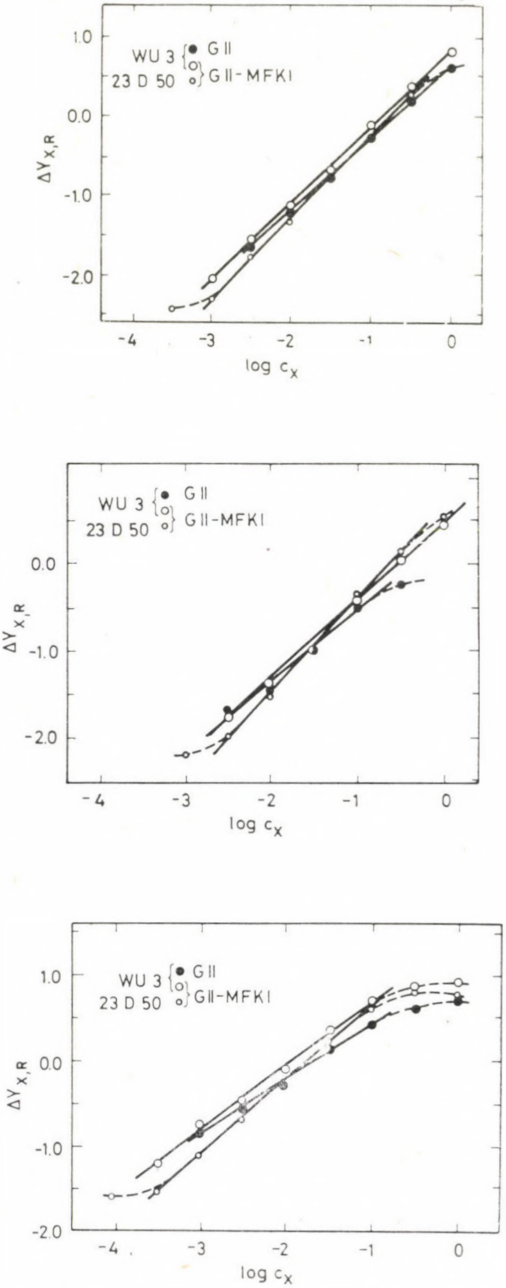

Fig. 4. Analytical curves determined on Orwo WU 3 spectral plate by means of G II and G II — MFKI microdensitometers, resp., and analytical curves determined on Agfa-Gevaert 23 D 50 spectral plate by means of the G II — MFKI microdensitometer: a) Sn 286.33 nm/Pd 302.80 nm line-pair, b) Ni 305.08 nm/Pd 302.80 nm line-pair, c) Pb 283.31 nm/In 303.94 nm line-pair

performed in different concentration ranges and on the basis of measuring points of various number. In addition to this, spectra on the plate 23 D 50 were separately recorded.

B_X-values of various elements obtained by the combination of WU 3 and G II fall within 0.9—1.1 in 5 cases, by the combination of WU 3 and G II-MFKI in 9 and 23 D 50 and G II-MFKI in 10 cases. Slope of analytical curves plotted in wider concentration range in average better approaches the optimal value.

4.3. *Relative precision*

In the three cases there is no considerable difference among the values of relative precision of concentration measurement. Value s_c/c [%] is somewhat smaller in the case of ORWO WU 3—G II-MFKI combination ensuring the widest concentration range, compared to the other cases.

4.4. *Detection limit*

Considering the detection limit values shown in Fig. 2 they seem to correspond to the lower limit* of the examinable concentration ranges, and in most cases values got on plate type 23 D 50 of higher γ-values are the lowest. In spite of this, the linear range of analytical curves obtained on the plate type ORWO WU 3 by microdensitometer G II-MFKI is frequently (Cu, Sb, Ti, V) longer towards the lower concentrations, than on the plate type 23 D 50. Probably the reason of this is that on the latter plate the difference between the γ-values of the line and continuous spectra is not negligible, thus the photographic detection gives in vain better detection, owing to the inaccurate background correction the lower section of the analytical curve is not linear. Similar observation can be made on Fig. 3, on the analytical curves of Cr 302.16 nm spectral line.

4.5. *Accuracy of analyses*

From the point of view of accuracy of analyses it can be stated that values gained on the plate ORWO WU 3 by microdensitometer G II-MFKI are the most favourable. The average deviation Δc [%] is the lowest in this case, while the number of concentrations to be determined is the greatest. This version is followed by the combination of 23 D 50 and G II-MFKI and afterwards WU 3 and G II.

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* With Ag and Fe a difference of two orders of magnitude is to be observed between the detection limit and the lower limit of concentration range. The latter case can unambigously be explained by the contamination of chemicals used, what corresponds to about 0.01% Fe-content. In the case of Ag and although in a less extent, at Cu, too, by all probability excitation problems are responsible for the differences [1].

Summarizing the earlier mentioned we can state that by extending the measuring range of the microdensitometer the linear range of analytical curve best utilizable for analysis can also be significantly increased, while the analyses can be carried out with the same precision and even higher accuracy than by means of conventional microdensitometers. The increase of γ-value of photographic emulsion brings along an improvement in the detection limit, however, the decrease of the examinable concentration range is a drawback. Knowing the characteristics of the microdensitometer being at disposal the γ-value *(i.e.* photographic emulsion) has to be chosen so as a most favourable combination of the examinable concentration range and detection limit could be achieved.

5. Extension of the linear range of the analytical curve

The analytical curve may bend from the straight line because of self-absorption at high concentrations, while at low concentrations due to the inaccurate background correction* even if all density values lie in the reliably measurable range.

In the case of a given analytical method this effect can be eliminated by choosing appropriate spectral line and photographic emulsion. However, at multi-element analysis it can not always be eliminated, occasionally we ought to apply self-absorption lines and photographic emulsion of higher γ-value. This time extension of the linear range by special correction may be necessary.

5.1. *Investigation of self-absorption analytical lines*

In the analytical chemical application of the KEREKES — CSÉTI — ÁG equation [8] suitable for the description of the self-absorption a difficulty arises, namely in the intensity range corresponding to self-absorption theoretically two concentrations may correspond to the same line intensity value. Simpler are those methods based on measuring the spectral line width, which — according to experiences — are suitable to plot unambiguous analytical curves in this case, too [9, 10, 11, 12]. Recently, VECSERNYÉS and ZÁRAY [13, 14] obtained linear analytical curves in a wide concentration range by measuring the integrated density under the line profile instead of density belonging to the peak height of spectral line. KUBOVA and PLŠKO eliminated the effect of self-absorption on the analytical curve observed at high concentrations so, that the density was measured on the wings of the line instead of its middle [15].

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* At low concentrations, one has to take into consideration also the blank value originating from the contamination of chemicals used, and eventually the interfering effect of the coincident line as well.

In the case of two unambiguously self-absorptional spectral lines: Pb 283.31 nm and Cu 327.45 nm some possibilities of analytical utilization of the self-absorption range were investigated.

To these measurements the G II-MFKI apparatus was connected to a recorder and the specimen table was moved with a sincron motor continuously. The spectrum parts were examined on ORWO WU 3 plate by means of this device. The slit-width of microdensitometer was adjusted to as narrow as possible (about 0.10 mm). Calibration of emulsion was also repeated by the registration of the two-step spectra at adequate wavelengths. Altogether 6 spectral lines were examined: Pb 283.31 nm, Cu 327.45 nm, Sn 286.33 nm, In 303.94 nm, In 325.86 nm, Pd 302.80 nm. The Sn-line is used as comparative line free from self-absorption, while palladium and indium are reference elements.

Based on the recorded spectrograms the following parameters of analytical lines have been determined:*

a) Based on the density belonging to the peak-height of the line and on the values of background densities, I_x, I_R and $\Delta I_{X,R}$ values have been calculated belonging to the peak height.

b) Line width values $d_{I/2}$, $d_{I/10}$ and d_U have been measured at the half, tenth and background level of the spectral line intensity $I_X = \mathrm{mm} \log I_x$ belonging to peak height.

c) Value of analytical line width d_a was also measured at density corresponding to the peak height of the reference line In 325.61 nm in the case of Cu 327.45 nm, further on the $d_{s/2}$ line width at the half part of peak height density.

d) On the basis of line width measured at various intensity levels as well intensity I_X belonging to peak height the approximate value of area T_X under the line profile has been calculated. As Fig. 5 shows the spectral line was divided into a triangle and two trapezoids, and their surfaces were added.

With the help of the above arbitrarily chosen parameters, the different analytical curves of the examined elements were determined. Analytical curves obtained by value pairs $\log c_X$, $\Delta I_{X,R}$ are demonstrated on Fig. 6a. In the case of Sn no self-absorption, at Pb a little, while at Cu in quite a great measure of self-absorption seen to appear. Similar observation can be made, if the analytical curves are plotted on the basis of value pairs I_X, $\log c_X$ (Fig. 6b), without reference element, and even applying value pairs $\log T_X$, $\log c_X$ the shape of curves does not show any change (Fig. 6c). Using the given approaching method

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* In the lack of adequate integrator with the help of planimeter the possibility of measuring the integrated density under the line profile was examined. However, this method proved to be extremely laborous, and its accuracy did not meet the demands, as well, consequently, later on it had not been applied.

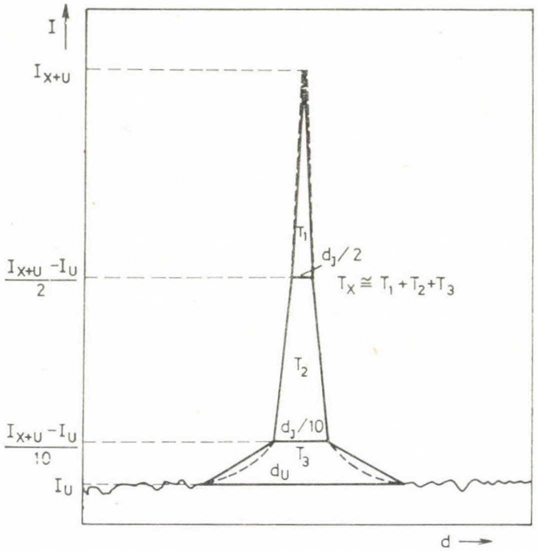

Fig. 5. Method of approximative calculation of T_X area under intensity profile of spectral lines

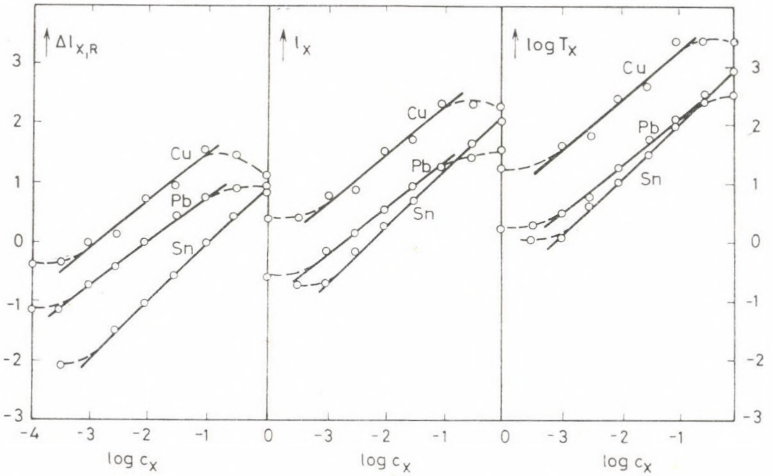

Fig. 6. a) Analytical curves of the Cu 327.47 nm/In 325.61 nm, Pb 283.31 nm/In 303.94 nm and Sn 286.33 nm/Pd 302.80 nm line-pairs plotted as a function of log c_X, $\Delta l_{X,R}$; b) Analytical curves of Cu 327.47 nm, Pb 283.31 nm and Sn 286.33 nm spectral lines plotted against log c_X, l_X values; c) Analytical curves of Cu 327.47 nm, Pb 286.33.31 nm and Sn 286.33 nm spectral lines plotted against log c_X, T_X values

by measuring the area under the line profile the self-absorption range is not applicable for analysis.

Correlations between the logarithm of line widths measured on various ways and logarithm of concentrations are represented by results obtained in the case of line Cu 327.45 nm (Fig. 7). It is to be seen that even on this way analytical curve well-applicable also in the self-absorption range was not obtained. It is, however, an interesting fact that the logarithm of line width measured at the half and tenth part of intensity I_X is constant within the limits of error in the case of low concentrations, while from the start of self--absorption it increases. Based on this observation, we tired to correct the original analytical curves so that log $d_{I/2}$ and log $d_{I/10}$ values, resp. were added to $\Delta l_{X,R}$. But this method proved to be unsuccessful. Nevertheless, even in the self-absorption range linear analytical curves have been obtained, too, if the appropriate l_X values were multiplied by the line widths. Figure 8 shows the

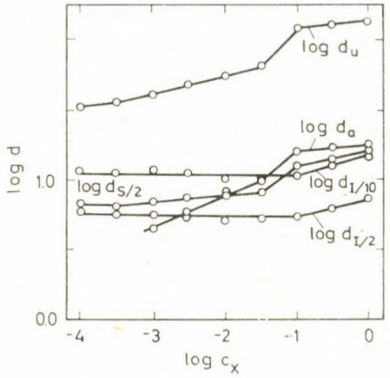

Fig. 7. Analytical curves of Cu 327.45 nm line as determined on the basis of line width logarithms measured by different procedures

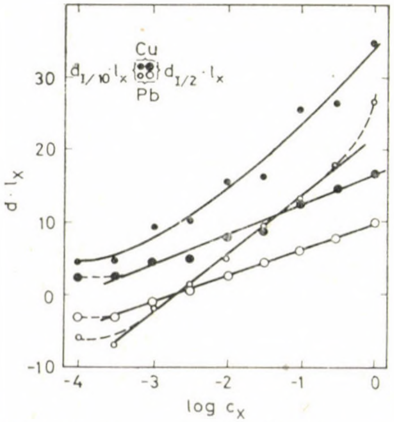

Fig. 8. Analytical curves of Cu 327.45 nm and Pb 283.31 nm spectral lines plotted against (log c_X; $d_{I/10} \cdot l_X$) and (log c_X; $d_{I/2} \cdot l_X$) values, resp.

Table IV

Valuating parameters of analytical curves as determined with dependent variables $\Delta l_{X,R}$, l_X *and*

Spectral lines	Evaluation parameters	Dependent		
		$\Delta l_{X,R}$	l_X	$\log T_X$
	c_{max} [%]	0.1—	0.1—	0.1—
Pb 283.31 nm	c_{min} [%]	0.000316	0.000316	0.001
(In 303.94 nm)	r	0.998	0.999	0.996
	B_X	0.750	0.757	0.821
	s_c/c [%]	12.3	8.1	17.3
	c_{max} [%]	1.0—	1.0—	1.0—
Sn 286.33 nm	c_{min} [%]	0.001	0.001	0.001
(Pd 302.80 nm)	r	1.000	0.999	0.991
	B_X	0.959	0.931	0.944
	s_c/c [%]	7.13	11.9	9.75
	c_{max} [%]	0.1—	0.1—	0.1—
Cu 327.45 nm	c_{min} [%]	0.001	0.001	0.001
(In 325.86 nm)	r	0.979	0.976	0.970
	B_X	0.770	0.794	0.863
	s_c/c [%]	33.7	36.5	43.4

analytical curves of Cu and Pb gained by this way. It is clear that in both cases better results were obtained by multiplication with $d_{I/2}$. The graphical representation in itself is not sufficient to the objective comparison of analytical curves, therefore the suitable regression lines were calculated with the variables used in the course of examinations. In Table IV the examined concentration range $c_{max} - c_{min}$, the value of correlation coefficient r, the slope B_X of regression lines, as well as of relative precision of concentration measurement s_c/c [%] referring to the given regression line are shown. These data unambiguously prove that under the given experimental conditions linear analytical curve is obtained also in the self-absorption range, if the logarithm intensity l_X of analytical lines is multiplied by the value of $d_{I/2}$. This value is of area character, approaching the area under the line profile expressed in logarithm intensity. Under the given circumstances decrease of peak-height caused by self-absorption was compensated by the increase of line width.

5.2. *Background correction by the two-γ-method*

According to VI-th paper of this series [7] the higher the γ-value and lower the background density are the greater is the quotient γ_{L+U}/γ_U. In this case, the difference in γ_{L+U} and γ_U values may cause error when the background correction is done by uniform γ. This is proved also by the experimental data. The average γ-value of the spectral plate Agfa-Gevaert 23 D 50 reaches about 2.0 in the examined wavelength range, and the background densities fall *line width logarithms as measured by different methods, resp. The independent variable is* log c_X *in all cases*

variable					
log d_U	log d_a	log $d_{S/2}$	$d_U \cdot l_X$	$d_{I/10} \cdot l_X$	$d_{I/2} \cdot l_X$
1.0—	—	—	1.0—	1.0	1.0
0.000316	—	—	0.000316	0.000316	0.000316
0.982	—	—	0.976	0.990	0.999
0.192	—	—	33.951	8.934	3.667
50.5	—	—	59.6	38.0	8.92
1.0—	—	—	1.0—	1.0—	1.0—
0.001	—	—	0.001	0.001	0.001
0.993	—	—	0.964	0.996	0.995
0.179	—	—	44.260	8.871	4.397
27.1	—	—	63.3	21.3	23.5
1.0—	1.0—	1.0—	1.0—	1.0—	1.0—
0.0001	0.001	0.000316	0.001	0.001	0.001
0.972	0.965	0.956	0.950	0.973	0.988
0.174	0.207	0.118	111.700	8.532	4.356
71.7	62.2	79.1	75.5	54.6	35.4

within 0.03 and 0.08. In spite of this, the average γ-value of ORWO WU 3 emulsion is only about 1.3, and the background densities are also significantly high: 0.10—0.20. Using emulsion 23 D 50 it occurred many times, that the analytical curve did not straighten towards low concentrations when working with background correction of uniform γ-value. This was not observed at plate WU 3 under the same circumstances.

Accordingly, the difference between γ_{L+U} and γ_U values can not be neglected in the case of plate 23 D 50, *i.e.* the background correction is to be performed by two-γ-method [16, 17, 18]. For this purpose, γ_{L+U} values determined experimentally are available. Considering the small background density, in the given case $\gamma_{L+U} \simeq \gamma_L$. The γ_U values were calculated indirectly, on the basis of the theoretical correlations of the previously mentioned paper [7], *i.e.* on the basis of equation $\gamma_L/\gamma_U \simeq 1.3$. The two-$\gamma$ background correction method was applied to those elements, for which it was reasonable, with values obtained on this way. Results are summarized in Table V. It is to be seen that by this method the linear range of analytical curves could be extended towards low concentrations by averagely a half order of magnitude, while the values of other evaluating parameters remained practically unchanged. These results are represented also on Fig. 9, where the analytical curves of spectral line Cr 302.16 nm are plotted in the case of uniform and two-γ background correction, resp.

Extension of measuring range of various elements got on this way, are shown in Fig. 2, also the average value $\Delta \log c_X = 2.19$ is given in brackets

Table V

Valuating parameters of the analytical method in the case of
O = Original: $\gamma_{L+U} = \gamma_U$ C = Corrected:

Spectral line pairs	Cr 302/Pd 302		Mo 313/Pd 325		Mo 315/Pd 325	
Calculation method	O	C	O	C	O	C
c_{max} [%]	0.316	0.316	0.1	0.1	1.0	1.0
c_{min} [%]	0.001	0.000316	0.001	0.000316	0.00316	0.001
B_X	0.994	1.008	0.977	0.975	0.870	0.882
s_c/c [%]	7.7	7.5	9.2	15.2	8.2	7.5
$\underline{c}$ [ppm]	3.0	3.5	1.6	1.2	4.5	3.9
Δc [%] I.	6.0	6.9	39.2	38.3	40.1	39.0
II.	0.5	2.4	36.1	36.5	47.8	50.0

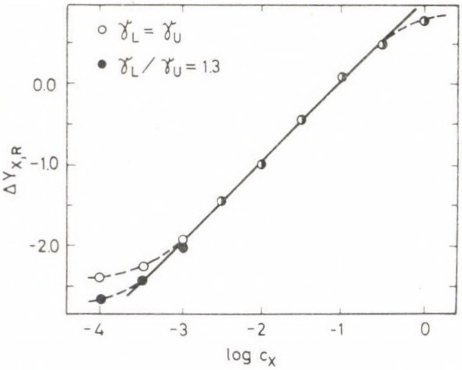

Fig. 9. Analytical curves of Cr 302.16 nm/Pd 302.80 nm line-pair in the case of background correction with uniform and two-γ method resp.

in Table III. This latter value is not much less than $\overline{\Delta \log c_X} = 2.40$ gained with a combination of ORWO WU 3 and G II-MFKI. In the case of a higher γ-value the two-γ background correction offers a possibility to utilize the achieved good detection power.

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background correction with uniform and two-γ-method, resp.
$\gamma_U = \gamma_{L+U}/1,3$ and $(k_{L+U} = k_U)$

Ni 305/Pd 302		V 318/Pd 325		Ti 337/Pd 325		Sn 317/Pd 325	
O	C	O	C	O	C	O	C
1.0	1.0	0.316	0.316	0.316	0.316	0.316	0.316
0.00316	0.001	0.001	0.000316	0.00316	0.001	0.001	0.001
0.999	0.999	0.965	1.007	0.967	0.995	1.013	1.042
7.3	9.0	6.7	8.6	7.3	11.4	6.4	5.8
9.9	9.3	2.9	3.9	9.5	10.9	3.7	3.1
8.8	9.4	33.0	31.5	24.6	22.6	35.4	34.3
21.3	27.5	36.8	31.0	30.8	29.6	46.3	43.2

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CORRELATION BETWEEN ADSORPTION PARAMETERS CHARACTERIZING BINARY AND TERNARY LIQUID MIXTURES ON HETEROGENEOUS SOLID SURFACES

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The equations for adsorption from multicomponent liquid mixtures on heterogeneous solid surfaces are discussed. These equations make possible to predict adsorption from multicomponent liquid mixtures in terms of adsorption from pairs of liquids. The experimental data for adsorption of benzene, toluene and *p*-xylene from cyclohexane and *n*-heptane on silica gel at 20 °C were used to illustrate the correlation of the adsorption parameters for binary and ternary liquid mixtures.

Introduction

In contrast to the extensive literature concerning adsorption from binary liquid mixtures [1–3], the multicomponent liquid adsorption systems have been comparatively little studied (see Ref. [2]). Recently, some papers dealing with theoretical aspects of adsorption from multicomponent liquid mixtures on solid surfaces have been published [4–9]. The majority of these papers concern liquid adsorption in the whole concentration region [5–9], whereas the earlier papers usually refer to adsorption at low concentration (see Ref. [2]).

Of great importance in the studies of multicomponent adsorption systems is the prediction of adsorption from multicomponent liquid mixtures in terms of adsorption from pairs of liquids. An advanced theoretical treatment of this problem has been given by OŚCIK [10], MINKA and MYERS [5]. OŚCIK derived an equation defining the mole fraction of the *i*-th component in the multicomponent surface phase by means of the mole fractions of this component in the different binary surface phases. The components appearing in binary liquid mixtures form the multicomponent mixture. However, MINKA and MYERS derived an equation for the mole fraction of the *i*-th component in the surface phase which contains the equilibrium constants characterizing adsorption from binary liquid mixtures on solid surfaces. In both approaches [5, 10] the adsorption process is considered by assuming the energetic homogeneity of the adsorbent surface. The exact analysis of both equations shows that they are equivalent. Importance of the works [5, 10] lie in reducing the experimental study of multicomponent adsorption systems to the study of adsorption from binary liquid mixtures on solids.

In this paper the approach of **Minka** and **Myers** [5] to study of multicomponent adsorption systems has been generalized by assuming the energetic heterogeneity of the adsorbent surface. The adsorption parameters for experimental data of adsorption from ternary liquid mixtures: *n*-heptane — cyclohexane — benzene, *n*-heptane — cyclohexane — toluene, *n*-heptane — cyclohexane — *p*-xylene and suitable binary liquid mixtures on silica gel have been compared.

Theoretical

Let us consider adsorption from *n*-component ideal liquid mixtures on heterogeneous solid surfaces. Additionally, we assume that the total number of molecules in the surface phase is constant and the molecular sizes of all components are identical. The adsorption process may be represented by a series of quasichemical reactions between a molecule of the *i*-th component $(i = 1,2 \ldots, n-1)$ and a molecule of the *n*-th component, *i.e.*

$$(i)^{\mathrm{l}} + (n)^{\mathrm{s}} \rightleftarrows (i)^{\mathrm{s}} + (n)^{\mathrm{l}} \tag{1}$$

where the symbols (i) and (n) denote molecules of the components "i" and "n", respectively; the subscripts "1" and "s" refer to the bulk and surface phases. The equilibrium constant K_{in}, describing exchange reaction (1) on a given type of adsorption sites with different adsorption energies E_i and E_n, may be expressed as follows [6]:

$$K_{in} = \exp\left(\frac{E_{in}}{RT}\right) = \frac{x_i^{\mathrm{s}} x_n^{\mathrm{l}}}{x_n^{\mathrm{s}} x_i^{\mathrm{l}}} \tag{2}$$

where

$$E_{in} = E_i - E_n \tag{3}$$

and x_i^{s} and x_i^{l} are mole fractions of the *i*-th component in the surface and bulk phases, respectively. The mole fraction x_i^{s} refers to adsorption sites with a difference of adsorption energies E_{in}.

Let us introduce $(n-1)$-dimensional distribution function $F(E_{1n}, E_{2n}, \ldots, E_{n-1,n})$ satisfying the following normalization condition:

$$\int_{\Delta} F(E_{1n}, E_{2n}, \ldots, E_{n-1,n})\, \mathrm{d}E_{1n}\, \mathrm{d}E_{2n} \ldots \mathrm{d}E_{n-1,n} = 1 \tag{4}$$

where Δ is an $(n-1)$-dimensional integration region. The function F characterizes the energetic heterogeneity of the adsorbent surface. Then, the equilibrium constant of reaction (1) for the whole adsorbent surface may be considered as an average of the constants K_{in} referring to different types of adsorption sites:

$$\bar{K}_{in} = \int_{\Delta} K_{in} F(E_{1n}, E_{2n}, \ldots, E_{n-1,n}) \, \mathrm{d}E_{1n} \, \mathrm{d}E_{2n} \ldots \mathrm{d}E_{n-1,n} =$$

$$= \frac{x_n^l}{x_i^l} \int_{\Delta} \frac{x_i^s}{x_n^s} F(E_{1n}, E_{2n}, \ldots, E_{n-1,n}) \, \mathrm{d}E_{1n} \, \mathrm{d}E_{2n} \ldots \mathrm{d}E_{n-1,n} \tag{5}$$

Expressing the integral appearing in Eq. (5) in a similar way as in Ref. [7], we have:

$$\bar{K}_{in} = \left(\frac{x_{i,t}^s}{x_{n,t}^s}\right)^{1/m} \left(\frac{x_n^l}{x_i^l}\right) \qquad \text{for } i = 1, 2, \ldots, n-1 \tag{6}$$

where m is the parameter characterizing the energetic heterogeneity of the adsorbent surface and it is greater than zero. The symbol $x_{i,t}^s$ denotes the mole fraction of the i-th component in the whole surface phase. For m equal to unity, Eq. (6) becomes Eq. (2), which is valid for homogeneous adsorbent surfaces. The system of equations (6) gives:

$$x_{i,t}^s = (\bar{K}_{in} x_{in}^l)^m \Big/ \left[1 + \sum_{j=1}^{n-1} (\bar{K}_{jn} x_{jn}^l)^m\right] \tag{7}$$

$$\text{for } i = 1, 2, \ldots, n-1$$

and

$$x_{n,t}^s = 1 \Big/ \left[1 + \sum_{j=1}^{n-1} (\bar{K}_{jn} x_{jn}^l)^m\right] \tag{8}$$

where

$$x_{in}^l = x_i^l / x_n^l \,. \tag{9}$$

Equation (7) has been obtained in Ref. [7] by considering the kinetics of adsorption from liquid mixtures on solid surfaces. For $m = 1$, Eq. (7) reduces to the expression which has been obtained by MINKA and MYERS [5] for homogeneous solid surfaces. In conclusion it can be said that Eq. (7) has been derived on the basis of Eq. (5), which defines the equilibrium constant for a heterogeneous surface as an average of the equilibrium constants referring to homogeneous surface patches.

Up to now, an other approach to liquid adsorption on heterogeneous solid surfaces was used [3, 6, 8, 9]. It was assumed that the mole fraction of the i-th component in the whole surface phase, $x_{i,t}^s$, is an average of the mole fractions x_i^s referring to the homogeneous surface patches, *i.e.*

$$x_{i,t}^s = \int_{\Delta} x_i^s F(E_{1n}, E_{2n}, \ldots, E_{n-1,n}) \, \mathrm{d}E_{1n} \, \mathrm{d}E_{2n} \ldots \mathrm{d}E_{n-1,n} \tag{10}$$

$$\text{for } i = 1, 2, \ldots, n-1$$

Starting from Eq. (10) and using the method reported in Ref. [6, 8], the following expression for $x_{i,t}^{s}$ may be derived:

$$x_{i,t}^{s} = \frac{\bar{K}_{i1} x_{in}^{l}}{z} \cdot \frac{(\bar{K}_{1n} z)^m}{1 + (\bar{K}_{1n} z)^m} \qquad \text{for } i = 1, 2, \ldots, n-1 \tag{11}$$

where

$$z = x_{1n}^{l} + \sum_{j=2}^{n-1} \bar{K}_{j1} x_{jn}^{l} \tag{12}$$

where m is the heterogeneity parameter analogous to that appearing in Eq. (7). Equation (11) has been derived by applying the following assumptions:
(i) the difference of adsorption energies

$$E_{j1} = E_j - E_1 \qquad \text{for } j = 2, 3, \ldots, n-1 \tag{13}$$

is identical for all homogeneous surface patches,
(ii) the equation of MINKA and MYERS [5], written in the following form:

$$x_i^{s} = \frac{K_{i1} x_{in}^{l}}{z} \cdot \frac{K_{1n} z}{1 + K_{1n} z} \tag{14}$$

was used in the integral (10),
(iii) the energy distributions characterizing adsorption of binary liquid mixtures "$i + n$", for $i = 1, 2, \ldots, n-1$ have the same quasigaussian shape and are shifted along the energy axis only.

Equation (11) has been derived by assuming a quasigaussian distribution, which was introduced by SIPS [11] for description of gas adsorption on heterogeneous solid surfaces. Next, this distribution has been applied in the theory of adsorption from binary liquid mixtures on heterogeneous solid surfaces [12, 13].

Both Eqs (7) and (11), derived by using the different procedures, in the case of adsorption from binary liquid mixtures give an identical expression:

$$x_{1,t}^{s} = (\bar{K}_{12} x_{12}^{l})^m / [1 + (\bar{K}_{12} x_{12}^{l})^m] \tag{15}$$

Equations (7), (11) and (15) will be used to describe the experimental adsorption data from ternary and binary solutions. Adsorption parameters determined by means of Eq. (15) for adsorption from binary liquid mixtures will be compared with the analogous parameters evaluated according to Eqs (7) and (11) from adsorption data for ternary solutions.

Results and Discussion

Adsorption isotherms for different liquid hydrocarbon mixtures on silica gel at 20 °C were used to examine Eqs (7), (11) and (15). These adsorption data were measured for the following ternary and binary liquid mixtures:

n-heptane(1) — cyclohexane(2)—benzene(3),
n-heptane(1)—benzene(3),
cyclohexane(2)—benzene(3),
n-heptane(1)—cyclohexane(2)—toluene(3),
n-heptane(1)—toluene(3),
cyclohexane(2)—toluene(3),
n-heptane(1)—cyclohexane(2)—*p*-xylene(3),
n-heptane(1)—*p*-xylene(3),
cyclohexane(2)—*p*-xylene(3).

The integer written at the liquid hydrocarbon denotes the number of the component in a given liquid mixture. The experimental details concerning the adsorption systems listed above are given in Ref. [14].

The excess adsorption data for binary liquid mixtures "$i + 3$" were examined by using the linear form of Eq. (15):

$$\ln x^{\mathrm{s}}_{3i,t} = m \ln \bar{K}_{3i} + m \ln x^{\mathrm{l}}_{3i} \qquad \text{for } i = 1, 2 \tag{16}$$

where

$$x^{\mathrm{s}}_{i,t} = 1 - x^{\mathrm{s}}_{3,t}; \qquad x^{\mathrm{s}}_{3i,t} = x^{\mathrm{s}}_{3,t}/x^{\mathrm{s}}_{i,t} \tag{17}$$

and

$$x^{\mathrm{s}}_{i,t} = n^{\mathrm{e}}_{i}/n^{\mathrm{s}} + x^{\mathrm{l}}_{i}. \tag{18}$$

Here n^{e}_{i} is the adsorption excess of the i-th component, and n^{s} is the total number of moles in the surface phase. Firstly, the parameter n^{s} has been evaluated for all adsorption systems with binary liquid mixtures by using the procedure described in Ref. [15]; this procedure is based on Eq. (15). Next, the values of n^{s} for adsorption of two binary liquid mixtures "1 + 3" and "2 + 3" forming the ternary mixture "1 + 2 + 3" were averaged. This average value of n^{s} was used to characterize the adsorption of binary liquid mixtures "1 + 3" and "2 + 3" and ternary mixture "1 + 2 + 3".

In Table I the average values of n^{s}, adsorption parameters $\bar{K}_{3i}$ and m for the adsorption of the binary liquid mixtures investigated are summarized. The parameters $\bar{K}_{3i}$ and m, evaluated from experimental data of adsorption from ternary liquid mixtures, are also given in Table I. These parameters were calculated according to the following linear equation:

Table I

Adsorption parameters of the straight lines presented in Figs 1—3

Liquid mixture		i	Adsorption of binary mixture			Adsorption of ternary mixture	
component "3"	component "i"		n^s [mmol/g]	$\bar{K}_{3i}$	m	$\bar{K}_{3i}$	m
Benzene	n-heptane	1	2.38	7.7	1.00	7.4	1.00
Benzene	cyclohexane	2	2.38	7.2	0.95	6.5	0.97
Toluene	n-heptane	1	1.32	21.1	1.40	15.6	1.20
Toluene	cyclohexane	2	1.32	14.0	0.91	15.0	1.00
p-xylene	n-heptane	1	1.19	19.3	1.00	19.7	1.00
p-xylene	cyclohexane	2	1.19	20.8	0.81	18.6	0.90

$$\ln x^{s}_{3i,t} = m \ln \bar{K}_{3i} + m \ln x^{l}_{3i} \tag{19}$$

where

$$x^{s}_{i,t} = 1 - x^{s}_{3,t} - x^{s}_{j,t} \qquad \text{for } i,j = 1,2 \text{ and } i \neq j. \tag{20}$$

Equation (19) has been obtained from Eq. (7). The mole fractions for the *i-th* component in the ternary surface phase were calculated according to Eq. (18), using the average parameter n^s, which has been evaluated for the adsorption of binary mixtures. Figures 1—3 present the straight lines (16) for binary mix-

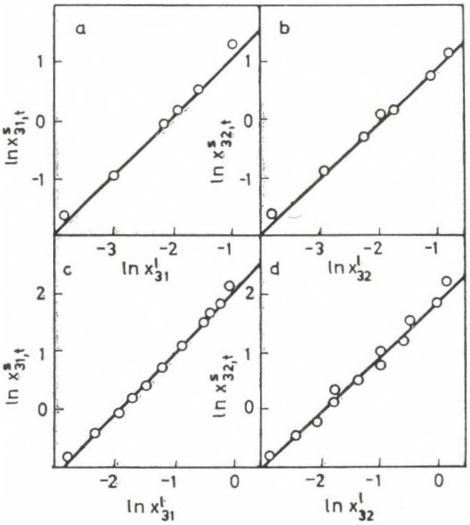

Fig. 1. Adsorption on silica gel at 20 °C for binary and ternary liquid mixtures containing n-heptane (1), cyclohexane (2) and benzene (3). Linear dependences ln $x^s_{3i,t}$ *vs.* ln x^l_{3i} for i = 1,2 plotted according to Eq. (16) for binary mixtures "3 + i" (a, b) and Eq. (19) for ternary mixture "1 + 2 + 3" (c, d)

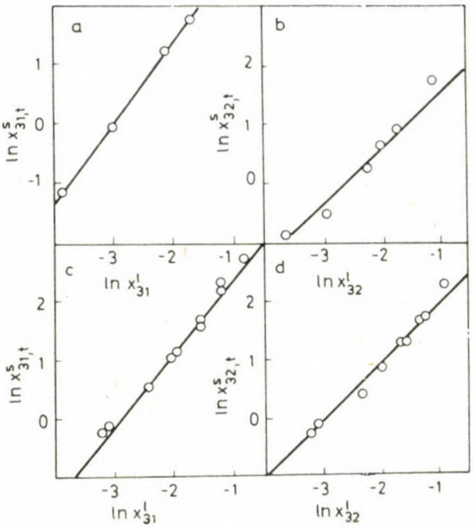

Fig. 2. Adsorption on silica gel at 20 °C for binary and ternary liquid mixtures containing *n*-heptane (1), cyclohexane (2) and toluene (3). Linear dependences $\ln x^s_{3i,t}$ *vs.* $\ln x^l_{3i}$ for $i = 1,2$ plotted according to Eq. (16) for binary mixtures "3 + *i*" (a, b) and Eq. (19) for ternary mixture "1 + 2 + 3" (c, d)

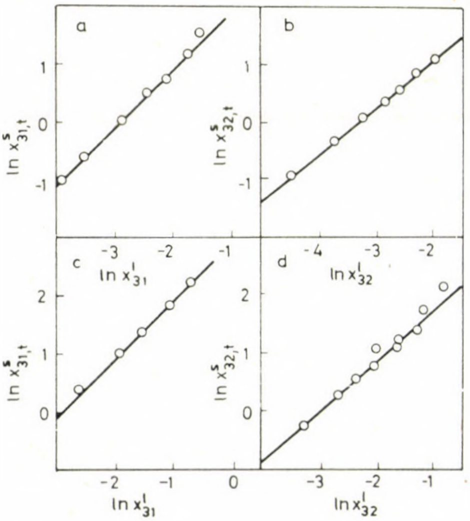

Fig. 3. Adsorption on silica gel at 20 °C for binary and ternary liquid mixtures containing *n*-heptane (1), cyclohexane (2) and *p*-xylene (3). Linear dependences $\ln x^s_{3i,t}$ *vs.* $\ln x^l_{3i}$ for $i = 1,2$ plotted according to Eq. (16) for binary mixtures "3 + *i*" (a, b) and Eq. (19) for ternary mixture "1 + 2 + 3" (c, d)

tures "1 + 3" and "2 + 3" and the linear dependences (19) for ternary solution "1 + 2 + 3". It follows from Figs 1—3 that the experimental points lie on the suitable straight lines. The results summarized in Table I indicate that the adsorption parameters m, $\bar{K}_{31}$ and $\bar{K}_{32}$ evaluated from adsorption data of binary and ternary liquid mixtures are approximately identical. This good

Table II

Adsorption parameters of the straight lines presented in Fig. 4

Liquid mixture	n^s [mmol/g]	$r = x^1_{12}$	$\bar{K}_{32}$	m
n-heptane 1 + cyclohexane 2 + + benzene 3	2.38	0.33	6.1	1.00
		1		1.00
		3		1.00
n-heptane 1 + cyclohexane 2 + + toluene 3	1.32	1	13.2	0.98
		3		1.13
n-heptane 1 + cyclohexane 2 + + p-xylene 3	1.19	1	22.2	0.95
		3		0.89

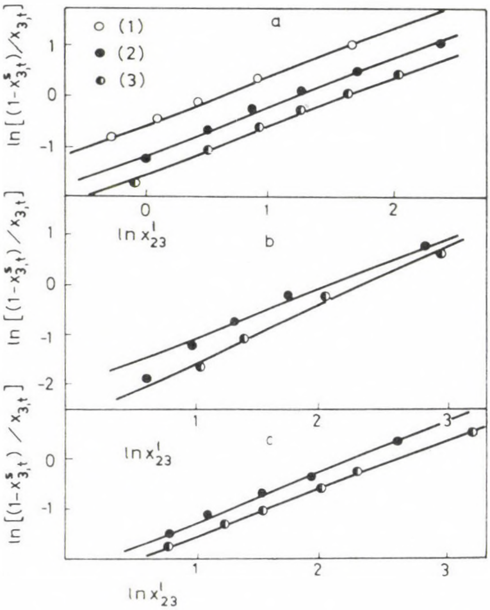

Fig. 4. Linear dependence (21) plotted for adsorption of ternary liquid mixtures: n-heptane (1) — cyclohexane (2) — benzene (3) (a), n-heptane (1) — cyclohexane (2) — toluene (3) (b), and n-heptane (1) — cylohexane (2) — p-xylene (3) (c) on silica gel at 20 °C. The circles denote experimental points for the following values of r: 0.33 (1), 1.0 (2) and 3.0 (3)

correlation between the adsorption parameters for binary and ternary liquid mixtures indicates that the prediction of adsorption from ternary mixture "1 + 2 + 3" by means of the paramters describing the adsorption of binary mixtures "1 + 3" and "2 + 3" is possible.

Now we shall examine Eq. (11) by using adsorption data for ternary liquid mixtures listed in the beginning of this section. Equation (11) may be rewritten in the following linear form:

$$\ln \frac{1 - x^{s}_{3,t}}{x^{s}_{3,t}} = m \ln [\bar{K}_{23}(1 + r\,\bar{K}_{12})] + m \ln x^{1}_{23} \tag{21}$$

where

$$r = x^{1}_{12} = \text{const}\,. \tag{22}$$

In Fig. 4 the linear dependences (21) plotted for experimental points satisfying condition (22) are presented for the adsorption systems investigated. In Table II the parameters $\bar{K}_{32}$ and m evaluated according to Eq. (21) are summarized. The parameters $\bar{K}_{3i}$ and m evaluated by means of Eq. (21) are similar to those summarized in Table I. Equations (7) and (11) lead to similar results, because the adsorption systems investigated show small heterogeneity effects.

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STUDY OF CHARGE-TRANSFER BANDS IN SILYL-SUBSTITUTED ANILINE AND PHENOL DERIVATIVES

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Several compounds containing Ar—O—Si and Ar—N—Si bonds have been studied in order to investigate the effect of the silyl substituent on the electronic spectrum. The UV spectra of the compounds have been recorded and quantum chemical calculations performed by the PPP method, using four different parametrizations. It could be established that the effect of d-orbitals in the silicon atom is small, the minor shifts in the spectra can be explained by changes in the inductive effects.

Introduction

It is well known that silicon is capable of conjugation with electron donating atoms or groups due to its empty d-orbitals. This is supported *e.g.* by the UV spectrum of trimethylsilylbenzene [1], the planar geometry of trisilylamines [2], the structure of silatranes [3], the Si-O-Si bond angle [4], and by a number of anomalous physico-chemical properties. Different authors [5, 6] agree in the fact that the effect of the d-orbitals is more pronounced in the excited state, and in properties which can be characterized by the excited state, than in the ground state. This is why one of the most useful methods for studying this effect is UV spectrophotometry. It is also known that substituents containing lone pairs can produce so called CT (charge-transfer) transitions with aromatic compounds, which appear in the UV spectra with high intensity. The existence and appearance of CT bands depend on the electronegativity of the donor and on the arrangement of the molecular orbitals in the aromatic system.

A comparison between the CT effect and the $(p-d)\pi$ effect seems to be interesting. What will be the resultant of the two effect, *i.e.* the direction of shift of the electron pair, if the donor substituent is bonded to a silicon atom and an aromatic ring?

In this work two series of compounds have been investigated, characterized by Ar-O-Si and Ar-N-Si bonds. The UV spectra were determined and quantum chemical calculations carried out by the PPP method.

Table I

Experimental ultraviolet spectra

Compounds	Solvent	λ_{max} (nm)	Assignment	ε_{max}
(I)	cH	220	p	4260
		267	α	1160
(II)	cH	241	CT	11780
		287	α	1790
(III)	EtOH	216	p	7800
		272	α	1940
(IV)	cH	245	CT	10500
		294	α	3690
(V)	Hex	220	p	5600
		276	α	1990
(VI)	Hex	212	p	68900
		244	CT	17800
		294	α	7370
(VII)	Hex	244	CT	7400
		293	α	3200
(VIII) $C_6H_5OCH_3$	cH	220		7500 [12]
		275	α	2100
(IX) $C_6H_5NHCH_3$	vapour	158.7		16000 [13]
		180	β	22500
		196	p	28000
		238	CT	12000
		283.3	α	2200
(X) $1,2\text{-}C_6H_4(OCH_3)_2$	cH	225	p	7150 [12]
		275	α	2550
(XI) $1,2\text{-}C_6H_4(NH_2)_2$	EtOH	210	p	37000 [14]
		239	CT	6500
		295	α	3200
(XII) $2\text{-}H_2NC_6H_4OCH_3$	cH	237	CT	8500 [12]
		286	α	3450
(XIII) $C_6H_5Si(CH_3)_3$	vapour	188	β	9780 [15]
		211	p	3800
		264	α	160
(XIV) $C_6H_5C(CH_3)_3$	EtOH	208	p	8500 [1]
		251	α	150
		257		200
		263		140
		266		120
(XV) $(SiH_3)_3N$	vapour	180	n-σ^*	[16]
(XVI) $(CH_3)_3N$	vapour	190.5		3900 [17]
		227.2	n-σ^*	900

cH: cyclohexane
Hex: *n*-hexane
EtOH: ethyl alcohol

Experimental

The following organosilicon compounds were prepared by methods known from the literature.

Ultraviolet spectra were recorded by a Spectromom 201 spectrophotometer; *n*-hexane, cyclohexane and ethyl alcohol were used as solvent. The data of the maxima and their assignments are shown in Table I. In the same Table UV data of other similar organic and organosilicon compounds from the literature are also listed.

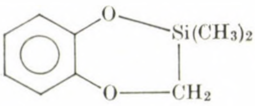
(I) $C_6H_5OSi(CH_3)_3$ [7]

(II) $C_6H_5NHSi(CH_3)_3$ [8]

(III) $1,2\text{-}C_6H_4[OSi(CH_3)_3]_2$ [9]

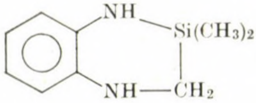
(IV) $1,2\text{-}C_6H_4[NHSi(CH_3)_3]_2$ [10]

(V)



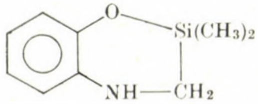
[11]

(VI)



[11]

(VII)



[11]

Calculations

Calculations were made by the PPP method, using four types of parametrization. Parameters *A* were taken from the work of Kiss and Szőke [18], parameters *B* and *C* were determined as the result of our own iterative PPP calculations [19], whereas parameters *D* were calculated from the data of Hinze and Jaffe [20]. The following bond distances were used for the calculations [21]: $r_{CC} = 139.7$ pm, $r_{CO} = 136$ pm, $r_{CN} = 142.6$ pm, $r_{SiO} = 164.8$ pm, $r_{SiN} = 172$ pm. PPP parameters are summarized in Table II.

Results and Discussion

The structure of the compounds is mirrored by their UV spectra. Compounds containing Ar-N bonds show a characteristic CT band, compounds with Ar-O bonds have a benzene-like structure, with a well-defined vibrational α-band. The spectra of the silicon derivatives differ only insignificantly from those of the carbon compounds. The differences can be explained by the conjugation of the d-orbital of the silicon atom, which causes a bathochromic

Table II

PPP parameters (eV)

	A	*B*	*C*	*D*
I_C	11.16			
γ_{CC}	11.13			
I_{Si}	1.10			
γ_{SiSi}	3.762			
β_{CC}	−2.39			
β_{SiO}	−1.25			
β_{SiN}	−1.44			
I_N	25.73	26.39	26.39	28.733
γ_{NN}	16.76	17.44	17.44	16.776
I_O	30.07	31.25	32.9	34.052
γ_{OO}	19.14	21.53	21.53	18.751
β_{CO}	−2.50	−2.17	−2.17	−2.17
β_{CN}	−2.30	−2.19	−2.19	−2.19

shift in the case of $\pi-\pi^*$ transitions (compounds **XIII** and **XIV**), whereas a hypsochromic shift appears in the case of bands of the n-σ^* type (compounds **XV** and **XVI**) (for details, see [22]).

Calculated electronic transitions and oscillator strengths are shown in Table III, compared with the experimental data.

On the basis of the results, it can be established that the PPP method yields reliable data for the Ar-O and Ar-N type compounds. Regression coefficients between measured and calculated data are the following: $r_A = 0.92$, $r_B = 0.92$, $r_C = 0.92$ and $r_D = 0.89$. At the same time, for compounds containing Ar-O-Si and Ar-N-Si bonds, neither parametrization yielded acceptable results ($r_A = 0.68$, $r_B = 0.61$, $r_C = 0.73$). The largest difference is caused in every case by the low energy value of the second electronic transition, which almost reaches the value of the α-band, and in some cases the α- and the p-bands are even reversed. With several compounds even new transitions can be observed, which cannot be explained at all. The significant electron shift of the σ system cannot be assumed either, these effects being partially considered already by parameters *B* and *C* in the iterative PPP calculation. Results concerning compound **XIII** in Table III prove the correct choice of the parameters ($\beta_{SiC} = -1.26$ eV). The difference cannot be explained by the possible assumption of an incorrect geometry. The almost free rotation of the $(CH_3)_3Si$ groups can be imagined in the mono-derivatives, and also different arrangements in the ortho-substituted compounds. But in compounds **V**—**VII** the geometry is

Table III

Experimental and calculated transitions (eV) *and oscillator strengths*

Comp.	$\Delta E_{\mathrm{exp.}}$ (f)	$^1E_{\mathrm{calc.}}$ (f)			
		A	*B*	*C*	*D*
I	4.64 (.028)	4.66 (.026)	4.63 (.065)	4.74 (.013)	
	5.64 (.102)	4.91 (.297)	4.65 (.303)	5.34 (.258)	
		6.01 (.021)	6.00 (.015)		
II	4.32 (.043)	4.55 (.047)	4.57 (.038)	4.57 (.038)	
	5.14 (.282)	4.58 (.494)	4.61 (.498)	4.61 (.498)	
		5.96 (.012)	5.99 (.009)	5.99 (.009)	
III	4.56 (.047)	4.41 (.076)	4.35 (.095)	4.59 (.021)	4.65 (.003)
	5.74 (.187)	4.53 (.341)	4.32 (.404)	5.08 (.265)	4.85 (.009)
		4.88 (.115)	4.75 (.144)	5.35 (.170)	5.01 (.004)
		5.74 (.005)	5.74 (.000)		5.40 (.032)
IV	4.22 (.088)	4.21 (.132)	4.25 (.116)	4.25 (.116)	
	5.06 (.252)	4.17 (.531)	4.23 (.529)	4.23 (.529)	
		4.77 (.270)	4.80 (.304)	4.80 (.304)	
		5.63 (.004)	5.69 (.009)	5.69 (.009)	
V	4.49 (.048)	4.55 (.002)	4.46 (.001)	4.48 (.073)	
	5.64 (.134)	4.10 (.152)	3.87 (.157)	4.83 (.044)	
		5.42 (.070)	5.18 (.058)	5.66 (.082)	
VI	4.22 (.177)	4.37 (.009)	4.39 (.010)	4.39 (.010)	
	5.08 (.427)	3.75 (.226)	3.81 (.215)	3.81 (.215)	
	5.85 (1.652)	5.07 (.075)	5.08 (.068)	5.08 (.068)	
		5.47 (.888)	5.47 (.907)	5.47 (.907)	
VII	4.23 (.077)	4.37 (.018)	4.37 (.007)		
	5.08 (.177)	3.68 (.100)	3.66 (.125)		
		5.06 (.113)	4.98 (.065)		
		5.48 (.600)	5.42 (.734)		
VIII	4.51 (.050)	4.61 (.041)	4.53 (.043)	4.69 (.025)	4.84 (.007)
	5.64 (.180)	5.70 (.252)	5.56 (.314)	5.80 (.187)	6.09 (.029)
IX	4.37 (.053)	4.39 (.059)	4.39 (.055)	4.39 (.055)	
	5.20 (.288)	5.33 (.424)	5.31 (.417)	5.31 (.417)	
	6.31 (.671)	6.33 (.392)	6.28 (.361)	6.28 (.361)	
	6.88 (.540)	6.65 (.820)	6.64 (.781)	6.64 (.781)	
	7.80 (.384)	7.58 (.649)	7.53 (.694)	7.53 (.694)	
X	4.51 (.061)	4.41 (.062)	4.30 (.065)	4.54 (.034)	4.78 (.008)
	5.51 (.171)	5.32 (.193)	5.13 (.217)	5.53 (.136)	5.97 (.031)
XI	4.20 (.077)	4.13 (.098)	4.14 (.090)	4.14 (.090)	4.60 (.029)
	5.19 (.156)	4.82 (.258)	4.83 (.251)	4.83 (.251)	5.60 (.128)
	5.90 (.839)	5.94 (1.050)	5.90 (1.015)	5.90 (1.015)	6.47 (1.186)
XII	4.33 (.083)	4.25 (.080)	4.21 (.077)	4.30 (.064)	4.69 (.019)
	5.23 (.204)	5.03 (.268)	4.96 (.251)	5.10 (.281)	5.76 (.122)
XIII	4.69 (.005)	4.79 (.006)			
	5.88 (.249)	5.74 (.232)			
	6.60	6.54 (.455)			
		6.57 (.578)			

quite unambiguos, the movement of silicon is hindered to a great extent, and these facts do not cause differences in the UV spectra: the CT- and p-bands are found at the expected frequencies. The extension of conjugation to the silicon atom results in significant differences in the electron distribution (see Table IV).

Table IV

Partial charges and bond orders (B parameters)

Compound	δ_i			p_{ij}			
	O	N	Si	C–O	C–N	Si–O	Si–N
VIII	+0.1343	—	—	0.366	—	—	—
I	+0.2038	—	−0.1069	0.326	—	0.425	—
IX	—	+0.1592	—	—	0.397	—	—
II	—	+0.2535	−0.1468	—	0.344	—	0.492

It is apparent that the partial positive charge of the nitrogen and oxygen atoms considerably increases, the C-O and C-N bond order significantly decreases, while a great negative charge is accumulated on the silicon atom, and the Si-O and Si-N bond orders assume values between 0.4 and 0.5.

On the basis of these results it can be established that in the compounds studied the $(p-d)\pi$ effect is small, *i.e.* silicon does not take part in the conjugation. This is also supported by the fact that if silicon is not considered in the calculation, a better agreement with the experimental data can be achieved. In this case, of course, the results agree with those calculated for compounds **VIII**—**XII**, and the regression coefficients are the following: $r_A = 0.90$, $r_B = 0.88$, $r_C = 0.91$, $r_D = 0.90$.

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OXIDATION-REDUCTION REACTIONS BETWEEN SODIUM SULFINATE AND VARIOUSLY OXIDIZED DERIVATIVES OF DISULFIDES AND SULFINIC ESTERS

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The reactions of variously oxidized disulfides with sodium sulfinate were investigated in dimethylformamide solutions. The α-disulfones were found to be convertible into thiolsulfonates. In addition to the decomposition of disulfide trioxides, direct reaction also takes place in about 23%. Under proper experimental conditions, thiolsulfonates can be reduced into disulfides. In the case of thiolsulfinates, disproportion is also accompanied by the direct reaction occurring to a limited extent (6%). The mechanisms of reactions can be interpreted on the basis of literature analogies.

On the basis of our previous paper [1] and other researches, it is partly confirmed, partly considered probable that variously oxidized derivatives of disulfides react with the sulfinate anion under suitable reaction conditions. Since no literature data are available regarding the details, we decided to make a systematic investigation of these reactions.

Reactions of α-disulfones with sulfinic acid salts

Studies on these reactions were required for explaining the reaction taking place between sulfonyl chlorides and sulfinic acid salts. Corson and Pews [2] allowed *p*-toluenesulfonylchloride to react with *excess* sodium *p*-toluenesulfinate in acetonitrile and obtained mainly thiolsulfonate and sodium sulfonate, together with some disulfone (I):

$$ArSO_2-Cl + 3\ ArSO_2Na \rightarrow ArS-SO_2-Ar + 2\ ArSO_3Na + NaCl \qquad (I)$$

Corson and Pews [2] described, on the basis of their work and papers of earlier authors [3—5] that *one mole* of *p*-toluenesulfonyl chloride [3, 4] or iodide [5] reacted with *one mole* of sodium *p*-toluenesulfinate to yield the disulfone (II):

$$Ar-SO_2Cl + ArSO_2Na \rightarrow ArSO_2-SO_2-Ar + NaCl \qquad (II)$$

However, these authors [2] assumed that the disulfone was not an intermediate, but the two reactions proceeded independently, since in a separate experiment the disulfone could not be converted into the tiolsulfonate by treatment with excess sodium *p*-toluenesulfinate.

According to this assumption, the reaction of *p*-toluenesulfonyl chloride with sodium *p*-toluenesulfinate takes place in about 95% through the attack of the oxygen atom in the sulfinate at the sulfonyl sulfur atom, leading to the formation of a sulfinyl-sulfonyl anhydride. The course of this favoured reaction was also confirmed in kinetic measurements by KICE and GUARALDI [6]. Along with this reaction, the formation of the disulfone takes place only in about 5% (III):

$$\mathrm{Ar{-}SO_2{-}Cl + ArSO_2Na} \begin{array}{l} \xrightarrow{5\%} \mathrm{Ar{-}SO_2{-}SO_2{-}Ar + NaCl} \\ \xrightarrow[95\%]{} [\mathrm{Ar{-}SO_2{-}O{-}SO{-}Ar}] + \mathrm{NaCl} \end{array} \qquad \text{(III)}$$

As the next step, a "*statu nascendi*" reaction of the sulfinyl-sulfonyl anhydride with sodium sulfinate is assumed resulting in the formation of disulfide trioxide and sodium sulfonate (IV):

$$\mathrm{Ar{-}SO_2{-}O{-}SO{-}Ar + Ar{-}SO_2Na \rightarrow Ar{-}SO_2{-}SO{-}Ar + Ar{-}SO_3Na} \qquad \text{(IV)}$$

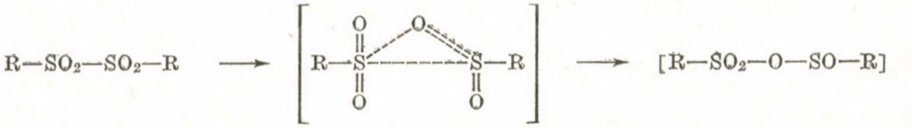
On heating the disulfide trioxide is isomerized into sulfenyl-sulfonyl anhydride which reacts with sodium sulfinate (with the sulfinate anion) to give thiolsulfonate and sulfonic acid [7, 8] (V):

$$\mathrm{Ar{-}SO_2{-}SO{-}Ar \rightarrow (Ar{-}SO_2{-}O{-}S{-}Ar]}$$

$$\mathrm{[Ar{-}SO_2{-}O{-}S{-}Ar) + Ar{-}SO_2Na \rightarrow ArSO_2{-}S{-}Ar + Ar{-}SO_3Na} \qquad \text{(V)}$$

In an earlier paper [1] we described that the reaction between *p*-toluenesulfonyl chloride and excess sodium *p*-toluenesulfinate at elevated temperatures in dimethylformamide gave *only* thiolsulfonate and sodium sulfonate as the end-products; therefore, it seemed interesting to examine the above recation more closely under such conditions.

One mole of *p*-tolyldisulfone was allowed to react with two moles of sodium *p*-toluenesulfinate. In contrast with the unsuccessful experiments of CORSON and PEWS [2], when the reaction was effected in dimethylformamide, *p*-tolylthiolsulfonate and sulfonic acid could be isolated (the latter in the form of the *S*-benzyl-isothiuronium salt). According to our assumption, the occurrence of the reaction was made possible by the transisomerisation of the disulfone on the effect of heating in a strongly polar solution, as described by KICE and FAVSTRITSKY [9], yielding sulfinyl-sulfonyl anhydride which, on the effect of two moles of sodium sulfinate, transformed into thiolsulfonate, probably through the disulfide trioxide and sulfenyl-sulfinyl anhydride (VI, IV, V):

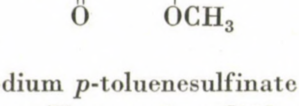

(VI)

In order to elucidate better the part-processes of this conversion, the reaction of disulfide trioxides with sodium sulfinate was studied.

Reactions of disulfide trioxides and sulfinic esters with sulfinic acid salts

According to the experiments of Bredereck *et al.* [7] and Kice and Pawlowski [8], disulfide trioxides react with sulfinic acid in acetonitrile to give thiolsulfonate and sulfonic acid. Similarly, when we effected the reaction in dimethylformamide with sodium sulfinate, the formation of thiolsulfonate and sodium sulfonate was observed. Since these reaction products were also obtained by the heating of disulfide trioxides, the course of the reaction was examined by heating a solution of disulfide trioxide in dimethylformamide in the absence of sodium sulfinate, to determine the amounts of products formed. In contrast with the observations of Kice and Pawlowsky [8], who used dioxane and found also disulfide, in our experiment only thiolsulfonate and sulfonic acid could be detected.* The amounts of thiolsulfonate formed in the two experiments were compared and the difference indicated that, in addition to the thermolysis of disulfide trioxide, the reaction between the disulfide trioxide and sulfinate anions took place in about 25–30%.

The above reaction is closely correlated with the observation of Schank *et al.* [10, 11] who found that the α-alkoxy ethers of *p*-toluenesulfinic esters,



$$\mathrm{Ar-\underset{\displaystyle O}{\underset{\|}{S}}-O-\underset{\displaystyle OCH_3}{\underset{|}{CH}}-R}$$

when heated with excess sodium *p*-toluenesulfinate during their preparation, yielded *p*-toluenethiolsulfonate. These authors [11] assumed that the formation of the thiolsulfonate took place through the sulfinic ester mentioned and sul-

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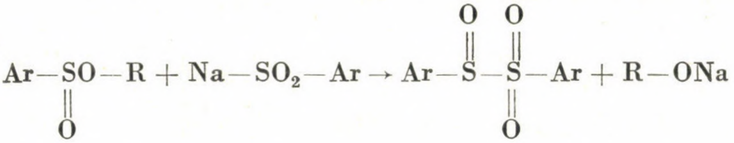
* Studying the solid-phase thermolyses of disulfide trioxides Schank and Werner [Phosphorus and Sulfur 8, 335 (1980)] observed the formation of disulfide, thiolsulfonate and sulfonic acid anhydride as well.

finic acid forming disulfide trioxide (VII), involving nucleophilic splitting of the S—O bond by the sulfinate anion (V), according to the mechanism suggested by **Kice** and **Pawlowsky** [8]: however, disulfide trioxide could be neither detected nor isolated, owing to its unstable nature.



$$\mathrm{Ar{-}\underset{\underset{O}{\|}}{S}O{-}R + Na{-}SO_2{-}Ar \rightarrow Ar{-}\overset{\overset{O}{\|}}{S}{-}\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}{-}Ar + R{-}ONa} \qquad \text{(VII)}$$

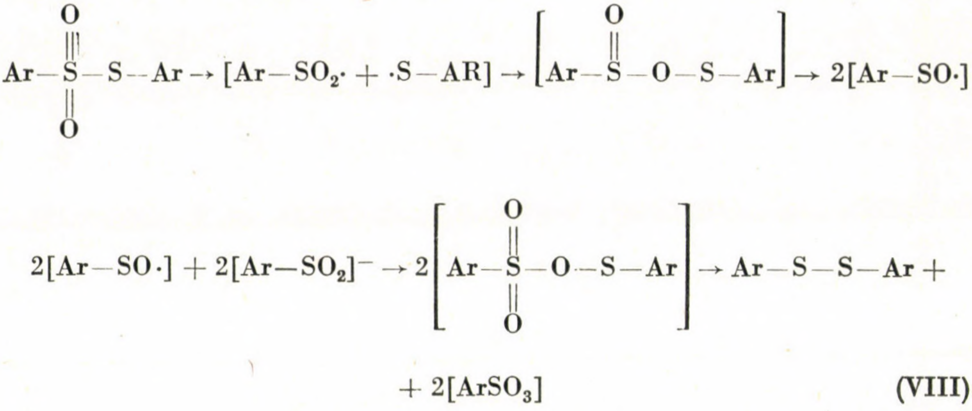
The formation of disulfide trioxide is, in our opinion, rendered probable by the analogous reaction described by **Boldyrev** *et al.* [12—14), who reported the formation of thiolsulfonate from sulfenic esters (Ar–S—O—R) and sulfinic acid or sodium sulfinate.

For a closer investigation of this reaction, *p*-toluenesulfinic methyl ester, having a simpler structure, was allowed to react with sodium sulfinate and, after processing the reaction mixture, the thiolsulfonate was obtained as expected. Since, however, sulfinic esters undergo also spontaneous decomposition into the thiolsulfonate on standing [15] or under thermal effects [11, 16], the experiments were again supplemented by blanks. The amount of thiolsulfonate was found here to be only about 5% of the amount of the thiolsulfonate formed in the reaction, thus the interaction between the sulfinic ester and the sulfinate anion leading to the formation of thiolsulfonate can be regarded as predominating (VII + V), which also confirms the recation path resulting in thiolsulfonate.

Reactions of thiolsulfonates with sulfinic acid salts

Reduction of thiolsulfonates have been effected with a number of reagents, such as hydrogen iodide/sulfurous acid [17—21], hydrogen bromide [22], sodium arsenite [23, 24], hydrogen sulfide [25, 26], metallic zinc in alcohol [27—30], metallic zinc/acid (nascent hydrogen) [27, 33, 28, 35, 31, 21, 21a, 36—37a], electrochemical methods [38—50], triphenylphosphine [51], trimethyl phosphite [52, 53], sodium cyanide [53], reduced iron [54]. However, no data indicate that sulfinic acid or sodium sulfinate have been employed for reducing thiolsulfonates. Therefore, our studies were extended to thiolsulfonates, and *one mole* of thiolsulfonate was allowed to react with two moles of sodium sulfinate in dimethylformamide to obtain disulfide and sodium sulfonate.

In respect of the course of the reaction, the works of GILBERT *et al.* [55] and KICE and FAVSTRITSKY [9] dealing with the thermolysis of thiolsulfonates and disulfones were considered (VIII):



$$\mathrm{Ar{-}\overset{O}{\underset{O}{\overset{\|}{\underset{\|}{S}}}}{-}S{-}Ar} \rightarrow [\mathrm{Ar{-}SO_2\cdot} + \mathrm{\cdot S{-}AR}] \rightarrow \left[\mathrm{Ar{-}\overset{O}{\overset{\|}{S}}{-}O{-}S{-}Ar}\right] \rightarrow 2[\mathrm{Ar{-}SO\cdot}]$$

$$2[\mathrm{Ar{-}SO\cdot}] + 2[\mathrm{Ar{-}SO_2}]^- \rightarrow 2\left[\mathrm{Ar{-}\overset{O}{\underset{O}{\overset{\|}{\underset{\|}{S}}}}{-}O{-}S{-}Ar}\right] \rightarrow \mathrm{Ar{-}S{-}S{-}Ar} + $$
$$+\ 2[\mathrm{ArSO_3}]$$

(VIII)

The fact that thiolsulfonates could be reduced into disulfides with sodium sulfinate in dimethylformamide, supplements the number of simultaneous reactions described in a previous paper [1] dealing with the reaction of thiolsulfonates with sodium halides. It means that, besides the basic reaction (IX) and the reactions verified by suitable model experiments (X, XI), the reaction of thiolsulfonates with sodium sulfinate (XII) should also be included.

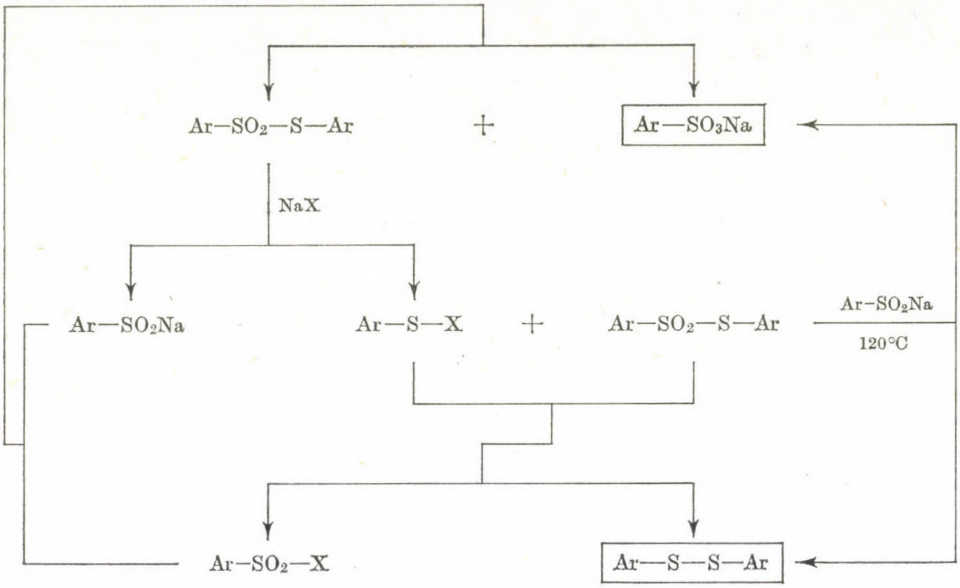
$$\mathrm{Ar{-}SO_2{-}S{-}Ar + NaX \rightarrow Ar{-}SO_2{-}Na + Ar{-}S{-}X} \tag{IX}$$

$$\mathrm{Ar{-}SO_2{-}S{-}Ar + Ar{-}S{-}X \rightarrow Ar{-}S{-}S{-}Ar + Ar{-}SO_2X} \tag{X}$$

$$\mathrm{Ar{-}SO_2{-}X + 3\ Ar{-}SO_2Na \rightarrow Ar{-}SO_2{-}S{-}Ar\ +}$$
$$\mathrm{+\ 2\ Ar{-}SO_3Na + NaX} \tag{XI}$$

$$\mathrm{Ar{-}SO_2{-}S{-}Ar + 2\ Ar{-}SO_2Na \rightarrow Ar{-}S{-}S{-}Ar + 2\ Ar{-}SO_3Na} \tag{XII}$$

In accordance with the above statements, the conversion of thiolsulfonates on the effect of alkali halides in dimethylformamide can be summarized in the following scheme (XIII). (The end-products of reactions are in frames.)



(XIII)

Reactions of thiolsulfinates with sulfinic acid salts

The reaction of thiolsulfinate with sulfinic acid was studied by KICE *et al.* [56, 57]. They established on the basis of reaction kinetic measurements that in acid media the reaction of sulfinic acid and thiolsulfinate (XIV) takes place much faster than the disproportionation (XV). The reaction of thiolsulfinate and sulfinic acid leads to the formation of thiolsulfonate (XIV), while in the disproportionation reaction disulfide is also formed beside the thiolsulfonate.

$$Ar-SO-S-Ar + 2\ Ar-SO_2H \rightarrow 2\ Ar-SO_2-S-Ar + H_2O \qquad (XIV)$$

$$2\ Ar-SO-S-Ar \rightarrow Ar-S-S-Ar + Ar-SO_2-S-Ar \qquad (XV)$$

The amount of disulfide and thiolsulfonate thus will indicate which of the two reactions is favoured. When studying the conversion of oxidized derivatives of disulfides on the effect of sodium sulfinate, it seemed to be interesting to examine the course of the above reaction in dimethylformamide solution instead of acid media. In our experiment, one mole of thiolsulfinate was allowed to react with one mole of sodium sulfinate at 75 °C, and the amount of thiolsulfonate formed in the reaction was found to be higher by about 5—6% (calculated for the starting material) than the amount that should be formed by disproportionation, thus the reaction of thiolsulfinate with sulfinic acid (XIV) reported by KICE *et al.* [56, 57], also took place in about 5—6% (calculated for the starting material) besides disproportionation. The conversion of thiolsulfonates into disulfide on the effect of sodium sulfinate occurs only at 120 °C. Simultaneous occurrence of the two reactions is confirmed by the fact that the reaction of one mole of thiolsulfinate with one mole of sodium sulfinate at temperatures higher than 120 °C leaves about 6% thiolsulfonate beside the disulfide, since some of the sodium sulfinate is consumed in the Kice reaction (XIV). When, however, sodium sulfinate is employed in excess, in accordance with reaction (XII), only the disulfide can be isolated from the reaction mixture, besides the excess of sodium sulfinate used and the sodium sulfonate formed.

Experimental

M.p.'s were measured with a Boetius micro melting point determining apparatus (Franz Küstner, Dresden), and are uncorrected. The TLC tests were effected on Kieselgel G (Merck) layer with benzene-petroleum ether (1 : 1) developing solvent and alkaline potassium permanganate for detection. The column chromatographic separations were carried out on "Kieselgel 40 für die Saulen-Chromatographie" (0.063—0.020 mm) (Merck) adsorbent, using petroleum ether-benzene solvent mixtures.

Reaction of *p*-tolyldisulfone with sodium *p*-toluenesulfinate in dimethylformamide

p-Tolyldisulfone [58] (7.75 g: 0.025 mole) and sodium *p*-toluenesulfinate (8.9 g: 0.05 mole) were heated in dimethylformamide (25 cm^3), with stirring, on an oil bath at 110 °C (±5 °C) for 24 h. Dimethylformamide was evaporated under reduced pressure produced by a water pump (about 37—39 mbar); water (50 cm^3) was added to the residue and it was extracted with benzene. The benzene solution was dried over anhydrous sodium sulfate and the benzene was evaporated, to obtain *p*-tolylthiolsulfonate (6.8 g; 97.8%). After recrystallization from petroleum ether, the m.p. was 76 °C.

S-Benzyl-isothiuronium chloride (10 g, about 0.05 mole) dissolved in water (50 cm^3) was added to the aqueous fraction; after refrigeration the *S*-benzyl-isothiuronium-*p*-toluenesulfonate was filtered off and dried (13.8 g; 81.5%), m.p. 180—182 °C.

Decomposition of di-*p*-tolyl disulfide trioxide in anhydrous dimethylformamide at 50 °C (blank test)

Di-*p*-tolyl disulfide trioxide [7] (14.72 g; 0.05 mole) was dissolved in anhydrous dimethylformamide (50 cm^3) and heated at 50 °C, with stirring for 24 h. Dimethylformamide was evaporated in vacuum 37—39 mbar, the residue was mixed with water (50 cm^3) and extracted with benzene. The benzene fraction was dried (Na_2SO_4), filtered and the solvent was evaporated to obtain *p*-tolylthiolsulfonate (7.35 g; 0.026 mole = ∼ 0.25 mole), m.p. 76 °C. According to TLC, the product was identical with an authentic sample; it was homogeneous, containing no disulfide contamination.

A solution of *S*-benzyl-isothiuronium chloride (10 g; 0.05 mole) in water (50 cm^3) was added to the aqueous fraction. The *S*-benzyl-isothiuronium-*p*-toluenesulfonate was cooled, filtered off, washed with some water and dried (14.4 g; 0.0425 mole = ∼0.05 mole).

Reaction of di-*p*-tolyldisulfide trioxide with sodium *p*-toluenesulfinate in anhydrous dimethylformamide at 50 °C

Di-*p*-tolyldisulfide trioxide (14.72 g; 0.05 mole) [7] was dissolved in anhydrous dimethylformamide (50 cm^3) and sodium *p*-toluenesulfinate (17.8 g; 0.1 mole) was added; the solution was then heated, with stirring, at 50 °C for 24 h. The solvent was evaporated in vacuum, the residue was mixed with water (50 cm^3) and extracted with benzene. The benzene fraction was dried (Na_2SO_4), filtered, and the solvent evaporated to leave di-*p*-tolyl-thiolsulfonate (10.45 g; m.p. 76 °C) as homogeneous substance identical with an authentic sample and containing no disulfide contamination (TLC). When subtracting the amount of thiolsulfonate originating from the decomposition of disulfide trioxide, the difference was 3.1 g; this quantity of thiolsulfonate was probably formed in the direct reaction between the disulfide trioxide and the sulfinate anion. Considering the amount of thiolsulfonate that can be expected theoretically in this reaction, it can be stated that the reaction with the sulfinate anion, beside the decomposition of disulfide trioxide, took place in 23%.

Decomposition of *p*-tolylsulfinic acid methyl ester in dimethylformamide (blank test)

p-Toluenesulfinic acid methyl ester [15] (8.5 g; 0.05 mole) was heated in dimethylformamide (50 cm^3) for 24 h at 100 °C. The TLC test showed the presence of some *p*-toluenethiolsulfonate. The solvent was evaporated from the reaction mixture in vacuum. After methyl *p*-toluenesulfinate had also been removed from the residue by distillation, the remaining product was *p*-tolylthiolsulfonate (0.18 g).

Reaction of *p*-tolylsulfinic acid methyl ester with sodium *p*-toluenesulfinate in dimethylformamide

p-Toluenesulfinic acid methyl ester [15] (8.5 g; 0.05 mole) and sodium *p*-toluenesulfinate [17.08 g; 0.01 mole) were heated in dimethylformamide (50 cm^3) at 100 °C for 24 h. The solvent was evaporated in vacuum, the residue was dissolved in water and extracted with benzene. The benzene fraction was dried (Na_2SO_4) and the solvent evaporated. The residue crystallized spontaneously, to give *p*-tolylthiolsulfonate (5.6 g; 46.6%), m.p. 76 °C.

Reaction of *p*-tolylthiolsulfonate with sodium *p*-toluenesulfinate in dimethylformamide

p-Tolylthiolsulfonate (13.9 g; 0.05 mole) and sodium *p*-toluenesulfinate (17.8 g; 0.1 mole) were heated in dimethylformamide (100 cm^3) in an oil bath at 120—125 °C, under stirring, for 24 h. Work-up in the usual manner, as described above, gave chromatographically uniform (TLC) *p*-tolyldisulfide (11.4 g, 92.5%). After recrystallization from petroleum ether the m.p. was 44 °C.

The aqueous fraction was mixed with a solution of *S*-benzyl-isothiuronium chloride (20 g, 0.1 mole) dissolved in water (100 cm^3). The mixture was refrigerated, then the *S*-benzyl-isothiuronium-*p*-toluenesulfonic acid salt was filtered off and dried (29.29 g; 83.6%), m.p. 180—182 °C.

Disproportionation of *p*-tolylthiolsulfinate in dimethylformamide (blank test)

p-Tolylthiolsulfinate (13.11 g; 0.05 mole) in dimethylformamide (50 cm^3) was heated on an oil bath at 75 °C, under stirring, for 24 h. The usual work-up, after removal of the benzene, gave a residue (12.97 g; 99.7%) which was found to be a mixture of thiolsulfonate and disulfide, as shown by TLC. After separation on a column, thiolsulfonate (6.6 g; 94.9%) and disulfide (5.8 g, 94.3%) were obtained.

Reaction of *p*-tolylthiolsulfinate with sodium *p*-toluenesulfinate in dimethylformamide at 75 °C

p-Tolylthiolsulfinate (13.11 g; 0.05 mole) and sodium-*p*-tolylsulfinate (17.81 g; 0.1 mole) were heated in dimethylformamide (50 cm^3) on an oil bath at 75 °C, under stirring, for 24 h. Work-up as above left a residue (13.7 g) which was found to be a mixture of disulfide and thiolsulfonate in the TLC test. When separated by the column chromatography, thiolsulfonate (7.75 g; more by 1.15 $g = 17.4\%$ than the amount obtained in the blank test) and disulfide (5.15 g) were obtained.

Reaction of *p*-tolylthiolsulfinate with sodium *p*-toluenesulfinate in dimethylformamide at 120 °C

p-Tolylthiolsulfinate (13.11 g; 0.05 mole) and sodium *p*-tolylsulfinate (8.99 g; 0.05 mole) were heated in dimethylformamide (50 cm^3) on an oil bath at 120 °C, under stirring, for 24 h. Processing of the reaction mixture in the usual manner gave a substance (13.42 g) which proved to be the disulfide containing thiolsulfonate, as shown by TLC. When separated on a chromatographic column, thiolsulfonate (0.81 g; about 6% of the amount formed in the former experiment) and disulfide (10.35 g) were obtained.

Reaction of *p*-tolylthiolsulfinate with excess sodium *p*-toluenesulfinate in dimethylformamide at 120 °C

p-Tolylthiolsulfinate (13.11 g; 0.05 mole) and sodium *p*-tolylsulfinate (17.98 g; 0.1 mole) were heated in dimethylformamide (100 cm^3) on an oil bath at 120 °C under stirring for 24 h. As usual, the solvent evaporated in vacuum, the residue mixed with water and extracted with benzene. After drying (Na_2SO_4), evaporation of the benzene left a substance (11.8 g; 95.7%) which was found to be disulfide, according to TLC. After recrystallization from petroleum ether, m.p. 44 °C.

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QUANTUM CHEMICAL CALCULATIONS ON PHENYLSILATRANES

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Quantum chemical calculations by the CNDO/2 method have been carried out on the three crystallographic modifications of 1-phenylsilatrane. In the calculations, the geometric data determined by the X-ray diffraction technique were employed. The results verify the existence of bonding between the silicon and nitrogen atoms (WIBERG index 0.35—0.39) and the role of the d orbitals in the bond structure of the molecules.

Introduction

Quantum chemical calculations on silatranes $[\mathrm{RSi(OCH_2CH_2)_3N}]$ have been carried out by few researchers up to now. Such calculations are complicated because of the large size of the molecules; they require an efficient computer and a significant amount of its working time. Up to now, conformational calculations have been effected on some molecules (1-methylsilatrane [1,2], 1-methyl-2-carba-silatrane [3]), and the structure of 1-hydrosilatrane has been investigated by means of the CNDO/2 method [4]. In all these works, the authors established that in silatranes the *endo* form and the sp^3d hybrid state of the silicon atom are energetically more favoured, than the *exo* form and the sp^3 hybrid state of the silicon atom. It should be noted, however, that the data used in the calculations by these authors were not the experimentally determined geometric ones; furthermore, in the CNDO/2 method the parametrisation of the Si—H bond is not justified. In the present work, the results of quantum chemical calculations on the three crystallographic modifications of 1-phenylsilatrane by the CNDO/2 method are discussed.

Calculations

It is known that there are three different crystallographic modifications of 1-phenylsilatrane. In the liquid state and in solution all the three modifications are present, undergoing interconversion into one another by rapid ring inversion; however, the three modifications can be prepared separately by suitable selection of the crystallization conditions. X-ray diffraction structure determinations have been carried out for all the three modifications [5–7] and the geometric data are available. The main data are shown in Table I.

These experimental data (bond distances, bond angles) were utilized in our quantum chemical calculations.

Table I

Geometric data of the three crystallographic modifications of phenylsilatrane

	α [5]	β [6]	γ [7]
Si–N	219.3 pm	215.6 pm	213.2 pm
Si–C	188.2 pm	190.8 pm	189.4 pm
Si–O average	165.6 pm	165.7 pm	165.6 pm
O–C average	143.9 pm	142.3 pm	142.5 pm
C–C average	149.8 pm	148.7 pm	154.5 pm
C–N average	147.4 pm	146.9 pm	147.3 pm
NSiC	177.9°	177.0°	179.0°
OSiO average	118.5°	118.6°	118.8°
SiOC average	123.4°	122.8°	123.5°
OCC average	111.2°	110.0°	107.9°
CCN average	107.2°	107.1°	105.4°
CNC average	113.8°	113.6°	113.1°

It presented a difficulty that in the case of the α-form, TURLEY and BOER [5] did not determine the sites of hydrogen atoms in the molecule. Therefore, the coordinates of hydrogen atoms were calculated for the tetrahedral arrangement in the case of methylene groups and for the trigonal arrangement when the hydrogen atoms are attached to the aromatic ring, using 100 pm distance for the C–H. The order-disorder structure [5] allowed different arrangements of the ring; one of them was chosen arbitrarily for the calculations. In the original CNDO/2 program [8], an erroneous formula was given for the calculation of the y component of the pd atom dipole; in the program employed by us it was corrected as follows:

$$\mu_{\mathrm{pd}}(y) = \frac{-2.5416 \cdot 10^{-29}}{3} \sum_{A} \frac{5376}{2\sqrt{5}\, Z(A)} \left[P_{3\mathrm{d}_{yz}(A),\, 3\mathrm{p}_z(A)} + \right.$$

$$\left. + P_{3\mathrm{d}_{xy}(A),\, 3\mathrm{p}_x(A)} - P_{3\mathrm{d}_{x^2-y^2}(A),\, 3\mathrm{p}_y(A)} - 1/3 P_{3\mathrm{d}_{z^2}(A),\, 3\mathrm{p}_y(A)}\right]$$

(in Cm units).

Not only spd-based calculations were carried out, but also other calculations, where the effect of the d-orbitals of silicon were neglected (sp basis).

Results and Discussion

The energy values obtained for the three modifications are listed in Table II.

The results shows that the energy values in the α- and β-modifications practically agree with each other (the difference is 80 kJ/mole), while the data for the γ-modification significantly differ from these (by 500 and 420 kJ/mole). In another calculation the C—H bond distance was increased to 105 and 108 pm. In this case, a significantly more negative value was obtained for the energy, thus the C—H distance has an important role in the total energy of the molecule. Since the positions of hydrogen atoms determined by X-ray diffraction are rather uncertain, no conclusion regarding the rapid and ready interconversion of the three modifications can be drawn from the energy values. In Table III, the net atomic charges are summarized.

Table II

Calculated energy values of phenylsilatranes, in J/mole units

Base	Energy	Modification		
		α	β	γ
spd	Total	$-4.444 \cdot 10^8$	$-4.443 \cdot 10^8$	$-4.439 \cdot 10^8$
	Binding	$-3.987 \cdot 10^7$	$-3.979 \cdot 10^7$	$-3.937 \cdot 10^7$
sp	Total	$-4.417 \cdot 10^8$	$-4.407 \cdot 10^8$	$-4.402 \cdot 10^8$
	Binding	$-3.720 \cdot 10^7$	$-3.619 \cdot 10^7$	$-3.575 \cdot 10^7$

Table III

Net atomic charges in phenylsilatranes

Atom	α		β		γ	
	spd	sp	spd	sp	spd	sp
Si	0.4586	1.3634	0.4553	1.3563	0.4412	1.3506
O*	−0.2981	−0.4718	−0.3003	−0.4762	−0.3001	−0.4793
C(O)*	0.1445	0.1248	0.1505	0.1214	0.1461	0.1182
C(N)*	0.0766	0.0746	0.0701	0.0609	0.0601	0.0498
N	−0.0944	−0.1812	−0.0899	−0.1815	−0.0789	−0.1742
C(Si)	−0.1074	−0.2007	−0.1100	−0.2056	−0.0975	−0.1862
C(ortho)*	0.0482	0.0329	0.0486	0.0309	0.0230	0.0004
C(meta)*	−0.0203	−0.0026	−0.0217	−0.0092	−0.0532	−0.0367
C(para)*	0.0225	0.0188	0.0169	0.0103	0.0402	0.0312

* Average values

It is seen that the calculations in which the d orbitals are neglected cannot be used, the net atomic charge of silicon is extraordinarily high, 1.35—1.36. The results of calculations on the spd basis indicate that the charges of identical atoms in the three modifications are nearly the same, there is no significant difference in the charge densities. The charges of the aromatic carbon atoms — in respect of their changes — agree well with the corresponding values obtained earlier for trimethylphenylsilane $(CH_3)_3SiC_6H_5$ by the CNDO/2 method [9], that is: *ipso*: —0.0945, *o*-: 0.0585, *m*-: —0.0132, *p*-: 0.0262. A certain correlation can be established between the net charges at the carbon atoms and the ^{13}C chemical shifts. The ^{13}C chemical shifts of the carbon atoms in phenylsilatrane are as follows [10]:

C(O)	57.62 ppm
C(N)	50.86 ppm
C(Si)	142.19 ppm
C(*ortho*)	134.00 ppm
C(*meta*)	126.92 ppm
C(*para*)	127.37 ppm

The correlation between the two quantities is only qualitative; a more exact correlation cannot be expected theoretically, either. In Table IV the modified WIBERG indices of the Si—N, Si—C and Si—O bonds are given.

Table IV

Modified WIBERG *indices of phenylsilatranes*

Base	Bond	α	β	γ
spd	Si—N	0.3497	0.3759	0.3943
	Si—C	1.0648	1.0498	1.0577
	Si—O (average)	1.1941	1.1887	1.1795
sp	Si—N	0.1533	0.1706	0.1828
	Si—C	0.8889	0.8813	0.8864
	Si—O (average)	0.7601	0.7579	0.7468

The WIBERG indices [12] express the strength of bonds developed between the atoms, that is, the bond order. The calculations confirm that in silatranes a chemical bond exists between the silicon and nitrogen atoms, its bond order being 0.35—0.39. As expected, these values change in the three modification inversely with the Si—N bond distance. The sp-based calculations gave values lower by 0.2, the **Wiberg** index was 0.15 – 0.18. This also confirms that the d-orbitals of silicon have an important role in the structures of the molecule. The values relating to the Si – C bond are about 1.05, lower than those obtained for trimethylphenylsilane (1.0866) [9]. The decrease can be explained by the fact that in phenylsilatrane the silicon can develop only a weaker bond with the aromatic carbon atom because of the formation of the Si ← N coordinative bond. The data obtained for the Si – O bond indicate that a significant π bond also developes between the silicon and oxygen atoms. Table V shows the calculated dipole moments of the phenylsilatrane modifications.

Table V

Calculated dipole moments of phenylsilatranes ($\cdot 10^{29}$ Cm)

Basis		α	β	γ
spd	from charge	1.254	1.350	1.279
	sp atomic dipole	1.286	1.301	1.340
	pd atomic dipole	0.210	0.197	0.204
	resultant	2.749	2.848	2.823
sp	from charge	0.523	0.691	0.565
	sp atomic dipole	1.560	1.583	1.649
	resultant	2.083	2.274	2.214

The calculated dipole moment data are higher than the experimental values ($1.92 \cdot 10^{-29}$ Cm [11]). The values obtained for the three modifications are near to each other. The results of calculations on the sp basis are lower by about $0.6 \cdot 10^{-29}$ Cm than those obtained in the spd-based calculations. On the basis of the latter calculations, the resultant value is obtained from three components: charge, sp atomic dipole and pd atomic dipole. All dipole components are nearly parallel to the Si – N bond and show towards the nitrogen atom. For example, in the case of the α-isomer, the dipole component resulting from the charge is 1.62°, the sp atomic dipole is 0.66°, the pd atomic dipole is 4.18°, given as angles to the Si – N bond. The value of the pd atomic dipole ($0.2 \cdot 10^{-29}$ Cm) shows the significant role of the d orbitals in the dipole moment of the molecule.

*

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SYNTHESIS AND PHOTOCHEMISTRY OF SILYLPHENYLPROPADIENES AND SILYLPHENYLPROPYNES

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The synthesis and photoisomerization of the title compounds are described. Bis (silyl)-3-phenylpropyne yields a [1,3]-photorearranged product of propadiene type, whereas tris(silyl)-3-phenylpropadiene is photochemically stable; however, a [1,3]-thermal rearrangement of the terminal silyl groups occurs.

Recently, the photolysis of pentamethyldisilanyl-phenylacetylene was found to yield 1,1-dimethyl-2-trimethylsilyl-3-phenyl-1-silacycloprop-2-ene and 1,1-dimethyl-3-trimethylsilyl-3-phenyl-1-silypropadiene [1—4]. Recent investigations on the photochemical formation of the reactive silicon species from the silyl-substituted alkynes showed evidence of the photochemical transformation of 1-silyl- and 1-disilanyl-3-trimethylsilyl-3-phenylpropynes, and the corresponding silyl-substituted phenylpropadiene derivatives were obtained [5]. We have observed a novel type of photoisomerization of 1-disilanyl-1,3-bis(trimethylsilyl)-3-phenylpropadienes involving [1,3]-shifts of both the trimethylsilyl and disilanyl groups. The title compounds having bulky and electron-withdrawing substituents, such as cyclohexyldimethylsilyl and phenyldimethylsilyl, were prepared in order to investigate the reaction mechanism of the photorearrangement. A sigmatropic mechanism was assumed and confirmed by data of photolysis and thermolysis.

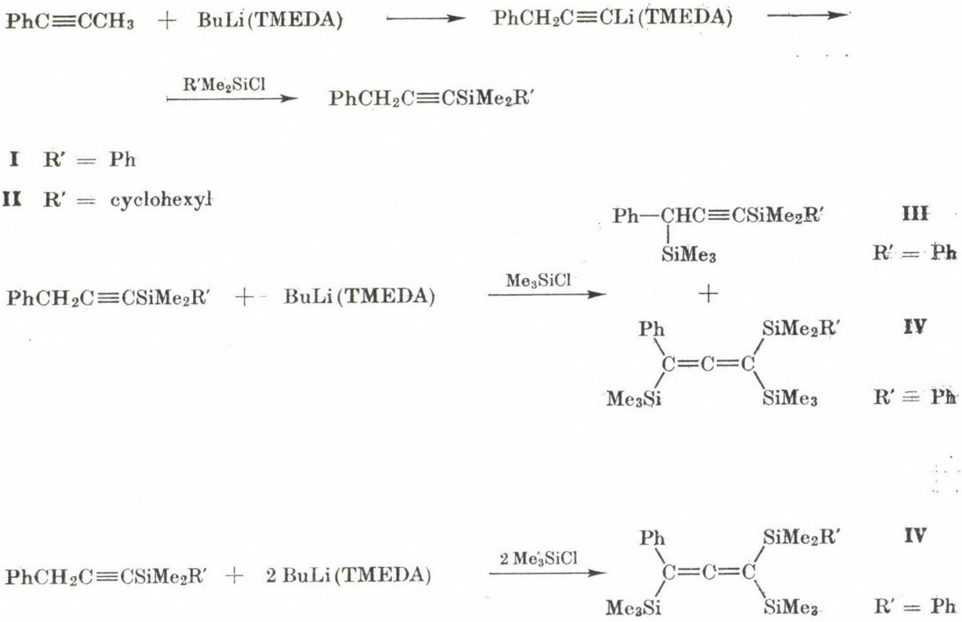
Results and Discussion

Synthesis of silyl-substituted phenylpropynes and propadienes

The compounds were synthesized by the method of WEST *et al.* used for the synthesis of analogous compounds [6]. 1-Phenyldimethylsilyl-3-phenylpropyne (**I**) was prepared in the reaction of 1-phenylpropyne with 1 molar equivalent of butyllithium-*N*,*N*,*N*',*N*'-tetramethylethylenediamine (BuLi/ /TMEDA) in hexane, followed by the coupling with chlorodimethylphenylsilane. A yield of 56% was obtained. Similar reactions of lithiated phenylpropyne with chlorodimethylcyclohexylsilane produced the corresponding cyclohexyl substituted propyne, **II**. Further lithiations and coupling reactions yielded bis- and tris-silyl-substituted **III** and **IV** (Scheme 1).

The monosilyl derivatives **I, II** could be isolated from the reaction mixture by fractional distillation. However, the fractions of the higher silylated compounds (**III, IV**) always contained 10—15% of all the respective isomers, therefore **III** and **IV** were isolated in the pure state by preparative GLC.

The structures of the new compounds **I**—**IV** were confirmed by elemental analyses and IR, MS and ^{1}H-NMR spectroscopic methods (see Table I).



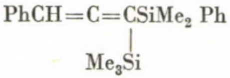
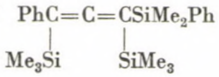
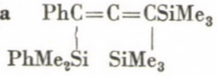
Scheme 1

Photolysis of silyl-substituted phenylpropyne

The photolysis of 1-phenyldimethylsilyl-3-trimethyl-3-phenylpropyne (**III**) with UV light yielded 1-phenyldimethylsilyl-1-trimethylsilyl-3-phenylpropadiene. Neither the expected silacyclopropenes nor silapropadiene could be detected, although both were produced in the photolysis of disilanyl-phenylacetylenes [1]. When a solution of 1-phenyldimethylsilyl-3-trimethylsilyl-3-phenylpropyne (**III**) was irradiated with a high-pressure mercury lamp for 8 hours in the presence or in the absence of methanol, the [1,3]-silyl-shift and the formation of the respective allene (**IIIa**) was observed in the equilibrium mixture having a ratio of 1 to 9 of **III**/**IIIa**. Surprisingly, the reaction

Table I

Data of silyl-substituted phenylpropynes and propadienes

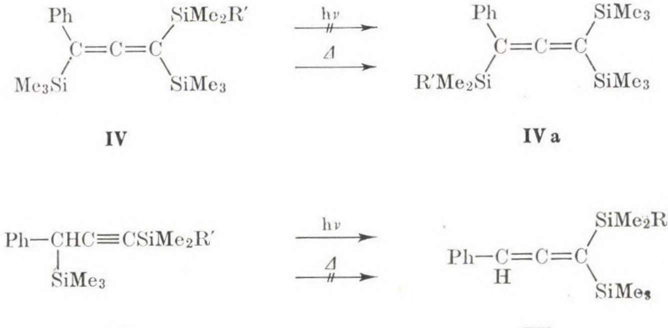
	$\nu_{C=C}$ $\nu_{C=C=C}$ [cm^{-1}]		M^+ [m/e]	^{1}H-NMR (δ [ppm], in CCl_4)	Elemental anal. calc/found [%]	n_D^{20}
	laser-Raman	IR				
I $PhCH_2C{=}CSiMe_2Ph$	2165	2170	250	0.41 $SiMe_2Ph$, s, 6H; 3.66 CH_2C, s, 2H; 7.10—7.60 aromatic, m, 10H	$C_{17}H_{18}Si$ C 81.54/81.38 H 7.25/7.13	1.5508
II $PhCH_2C{=}CSiMe_2chex$	2190	2185	256.164	0.12 $SiMe_2chex$, s, 6H; 1 18 and 1.72 chex. m, 11H; 3.66 CH_2C, s, 2H; 7.10—7.50 aromatic, m, 5H	$C_{17}H_{24}Si$	1.5183
III $PhCHC{=}CSiMe_2Ph$	2165	2160	322	0.06 $SiMe_3$, s, 9H; 0.42 $SiMe_2Ph$, s, 6H; 3.18 CHC, s, 1H; 6.95—7.55 aromatic, m, 10H	$C_{20}H_{26}Si_2$ C 74.46/74.74 H 8.12/8.30	1.5550
IIIa  $PhCH{=}C{=}C(SiMe_3)SiMe_2Ph$	1886, 1908	1910	322	0.04 $SiMe_3$, s, 9H; 0.44 $SiMe_2Ph$, d, 6H, $J = 1.9$ Hz 5.52 CHC, s, 6H; 6.95—7.55 aromatic, m, 10H	C 74.46/74.67 H 8.12/8.18	1.5713
IV  $PhC(SiMe_3){=}C{=}C(SiMe_3)SiMe_2Ph$	1908	1910	394	0.03 $SiMe_3$, s, 9H; 0.17 $SiMe_3$, s, 9H; 0.42 $SiMe_2$, s, 6H; 7.05—7.60 aromatic, m, 10H	$C_{23}H_{34}Si_3$ C 69.98/69.92 H 8.68/8.57	1.5562
IVa  $PhC(SiMe_2Ph){=}C{=}C(SiMe_3)SiMe_3$		1910	394	0.17 $SiMe_3$, s, 18H; 0.37 $SiMe_2$, s, 6H; 7.05—7.65 aromatic, m, 10H		

was found to give **IIIa** in a considerably high yield (85%), without any other by-products. The components of the reaction mixture were identified by IR and ^{1}H-NMR spectroscopy. A strong allenic peak of 1910 cm^{-1} indicated the allenic structure, and the acetylenic C≡C triple bond appeared at 2150 cm^{-1}. Furthermore, the trimethylsilyl-shift in the ^{1}H-NMR spectra provided evidence for two different trimethylsilyl groups ($\delta = 0.42$, s, for **III** and $\delta = 0.44$, d, for **IIIa**).

Thus the photoisomerization acetylen → allene shows the characteristics of a "no-mechanism" sigmatropic migration. In addition, pyrolysis experiments also support this mechanism.

Pyrolysis of silyl-substituted phenylpropyne and propadiene

The pyrolysis of the bis(silyl)phenylpropyne (**III**) did not yield rearranged products even at 400 °C. There was no sign of propadienes either in sealed tube, heated for 3 hours, or in quick-pyrolysis. However, the rearranged propadiene **IVa** and numerous by-products were obtained in the pyrolysis of tris(silyl)phenylpropadiene (**IV**) in sealed tube, heated at 400 °C for 1 hour though the yield of **IVa** did not exceed 5% (Scheme 2).



Scheme 2

Experimental

The photolysis experiments were carrried out in an atmosphere of dry nitrogen using a 100 W high-pressure mercury lamp sorrounded by a quartz cooling jacket. The pyrolysis experiments were effected partly in Pyrex tubes of 1 cm^3 volume sealed in a nitrogen atmosphere and heated for a longer period at 400 °C, and partly in a JEOL JCG 1100 chromatograph equipped with a glass pyrolysis device, in which the residence time was 2 s and the temperature range was programmed from 200 to 400 °C.

The products were identified by means of GLC using two different columns: 6% OV-1 on Chromosorb W and 10% Apiezon on Celite 545. Proton NMR spectra were recorded by a JEOL JNM-MH-100 and a Varian EM 360 A spectrometer, using carbon tetrachloride solvent and cyclohexane as internal standard. The IR spectra of thin liquid films were determined by

Zeiss Specord UR 75, while laser-Raman spectra were recorded with a Jobin Yvon Ramanor HG 2 S spectrophotometer. Mass spectra were obtained with an AEI MS 900 model, using an ionizing voltage of 24 eV. An Aerograph A 700 GLC device was used for the separation of the reaction products. The products were separated by a 9.5 mm × 4.57 m column containing 10% SE-30 on Chromosorb W. Slightly yellow liquids were obtained.

1-Dimethylphenylsilyl-3-phenylpropyne (I)

A mixture of 6.5 g (0.056 mole) of 1-phenylpropyne and 6.5 g (0.056 mole) of *N,N,N',N'*-tetramethylethylene-diamine (TMEDA) in 15 cm^3 *abs.* hexane was placed in a 200 cm^3 three-necked flask, fitted with a stirrer, dropping funnel and condenser. To this solution 43 cm^3 of 1.4 *M* butyllithium/hexane solution (1 mole-equiv.) was slowly added at −70 °C. The reaction mixture was warmed to room temperature and then gently refluxed for 15 min. Chlorodimethylphenylsilane (10.7 g; 0.063 mole) in 10 cm^3 *abs.* THF was added to the brown oily solution; the mixture was refluxed for 30 min. and then hydrolyzed with water. The organic layer was separated and washed with water. The organic content of the water layer was recovered by repeated extraction with water ether. The organic layers were then combined and dried over K_2CO_3. The solvents were evaporated and the residue was fractionally distilled at 133—135 °C at a reduced pressure of 2 mbar. A yield of 10.9 g (78%) of **I** was obtained.

1-Dimethylcyclohexylsilyl-3-phenylpropyne (II)

This compound was prepared by the same procedure as described above for **I**, however, chlorodimethylcyclohexylsilane was used as the coupling agent. 1-Phenylpropyne, TMEDA, 1.4 *M* butyllithium sloution, and the chlorosilane were allowed to react in the amounts of 2.32 g (0.02 mole), 2.32 g (0.02 mole), 15.5 cm^3 (1 mole-equiv.) and 3.6 g (0.02 mole), respectively. The product had b.p. 149—150 °C/1.3 mbar; the yield was 65%.

Chlorodimethylcyclohexylsilane (II)

This reagent was synthesized by a method similar to that of SAAM [7] and SPEIER [8]. A mixture of 16.4 g (0.2 mole) of cyclohexene, 14.1 g (0.2 mole) of chlorodimethylsilane and 4 cm^3 of 0.5 *M* hexachloroplatinate in *abs.* isopropanol was filled into 5 Pyrex-bombs of 50 cm^3 volume in 5 equal parts. The bombs were kept at 100 °C for a week; the reaction mixture was then distilled at reduced pressure; b.p. 60—61 °C/1.3 mbar, yield 22%.

1-Dimethylphenylsilyl-3-trimethylsilyl-3-phenylpropyne (III)

Compound **III** was prepared in two subsequent steps, similarly to the procedure described for **I**. The quantities used of **I**, TMEDA, 1.4 *M* butyllithium solution and chlorotrimethylsilane were 6.25 g (0.025 mole), 6.25 g (0.025 mole), 19.3 cm^3 (1 mole-equiv.) and 2.70 g (0.025 mole), respectively. The product had b.p. 148—150 °C/2 mbar, the yield was 55%; it was contaminated by small amounts of **IIIa** and **IV**, which, however, could readily be removed by means of preparative GLC.

1-Dimethylphenylsilyl-1,3-bis(trimethylsilyl)-3-phenylpropyne (IV)

Compound **IV** was prepared in two subsequent steps similarly to the procedure given for **III**. The reaction mixture had to be handled very carefully, since compound **IV** was found to be thermally unstable. The amounts of **I**, TMEDA, 1.4 *M* butyllithium solution and chlorotrimethylsilane were 2.75 g (0.011 mole), 5.50 g (0.022 mole), 17.0 cm^3 (2 mole-equiv.), and 2.70 g (0.025 mole), respectively. B.p. 155—157 °C/2 mbar, yield 41%.

Photolysis of 1-silyl-3-trimethylsilyl-3-phenylpropyne

III (1.0139 g; 3.15 mmoles) and 0.0657 g (0.3 mmole) of $C_{16}H_{34}$ internal standard were dissolved in 80 cm^3 of *abs.* cyclohexane and placed into the immersion apparatus for an 8-h irradiation. The solvent was then evaporated and the residue distilled at a reduced pressure at 200 °C/2.7 mbar. Photolysis yielded and equilibrium mixture consisting of 10% of **III** and 90% of **IIIa**, the total combined yield being 94%. The reverse reaction produced 9% of **III** and 91% of **IIIa**, in a total combined yield of 90% after irradiation in a quartz tube for 11 h. The quantities used in the small scale experiment were: 0.1240 g (0.38 mmole) of **IIIa** and 0.0067 g (0.03 mmole) of $C_{16}H_{34}$ in 10 cm^3 of *abs.* cyclohexane.

Photolysis of 1,3-bis(silyl)-3-trimethylsilyl-3-phenylpropyne

A solution of 0.5430 g (1.4 mmole) of **IV** and 0.0602 g (0.3 mmole) of $C_{16}H_{34}$ in 10 cm^3 *abs.* cyclohexane was filled in a quartz tube capped by a rubber stopper. After an irradiation for 16 h, no rearranged product could be detected by GLC. The content of **IV** in the sample was 77% of the original value.

Thermal reaction of 1-silyl-3-trimethylsilyl-3-phenylpropyne

III (0.0124 g; 0.04 mmole) was placed in a Pyrex tube of 1 cm^3 volume and sealed in a nitrogen atmosphere, then heated at 400 °C for 3 h. No evidence of acetylene/allene isomerization was found on analysis by laser-Raman spectrophotometry. Quick pyrolysis: 5 g of a 50% *n*-hexane solution of **III** was injected to a pyrolysis equipment; the mixture was then analyzed by means of GLC. No relevant change was detected in the reaction mixture by increasing the temperature from 250 to 450 °C.

Thermal reaction of 1,3-bis(silyl)-3-trimethylsilyl-3-phenylpropyne

IV (0.0156 g; 0.04 mmole) was placed in a Pyrex tube of 1 cm^3 volume and sealed in a nitrogen atmosphere, then heated at 400 °C for 1 h. The reaction mixture, which showed signs of strong carbonization was dissolved in carbon tetrachloride, filtered and analyzed by means of ^{1}H-NMR spectroscopy, using cyclohexan as internal standard. The result revealed that the shift of the 3-trimethylsilyl group disappeared ($\delta = 0.03$) and a new shift of 3-dimethylphenylsilyl ($\delta = 0.38$) was observed. The ratio of the intensity of the latter shift to that of the $\delta = 0.17$ of trimethylsilyl was found to be 1 to 3.

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REACTIONS OF AROYLPHENYLACETYLENES WITH ACTIVE METHYLENE-CONTAINING COMPOUNDS

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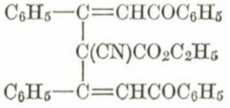
Aroylphenylacetylenes (**Ia–c**) react with ethyl cyanoacetate and ethyl acetoacetate in the presence of sodium ethoxide to give the corresponding 3-cyano-4,6-diaryl-2*H*-pyran-2-ones (**IIIa–c**) and 4,6-diaryl-2*H*-pyran-2-ones (**IVa–c**), respectively. On the other hand, malononitrile and acetylacetone gave with the same acetylenic ketones the corresponding 1-aryl-4,4-dicyano-3-phenylbut-2-en-1-ones (**Va, b**) and 1-aryl-4,4-diacetyl-3-phenylbut-2-en-1-ones (**Vc—e**), respectively. In all cases the reactions seem to take place *via* normal Michael addition.

The reaction of acetylenic ketones with malonic esters in the presence of sodium ethoxide has been reported [1] and its mechanism proposed [2—4]. The aim of the present work was to study the reactions of aroylphenylacetylenes (**Ia—c**) with other active methylene-containing compounds, such as ethyl cyanoacetate, ethyl acetoacetate, malononitrile and acetylacetone, in order to establish the structure and/or configuration of the products, as well as the mechanism of the reactions.

(a) Reaction with ethyl cyanoacetate

The reaction of benzoylphenylacetylene (**Ia**) with ethyl cyanoacetate has been reported [2] to give the trimolecular adduct (**II**). However, when the same reaction was repeated, it gave the known [5] 3-cyano-4,6-diphenyl-2*H*-pyran-2-one (**IIIa**). Similar treatment of **Ib** and **Ic** gave the hitherto unknown 3-cyano-4-phenyl-6-aryl-2*H*-pyran-2-ones, **IIIb** and **IIIc**, respectively.

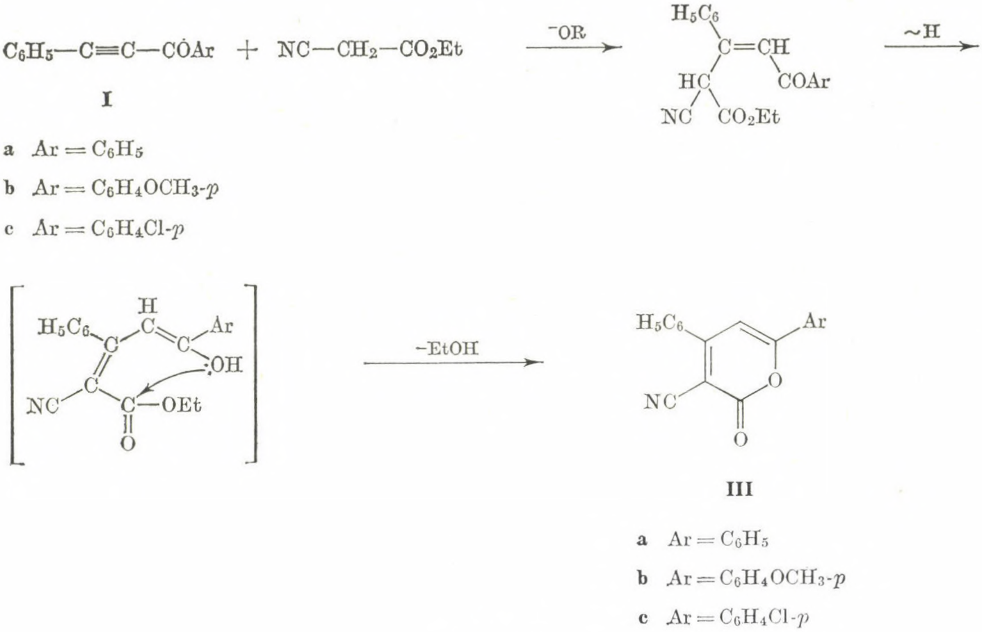
The structures of the cyanopyran-2-one derivatives were confirmed by analytical data, infrared spectroscopy (*cf.* Table I) and ^{1}H-NMR spectroscopy (see Experimental).



$$\begin{array}{ll} C_6H_5- & C=CHCOC_6H_5 \\ & | \\ & C(CN)CO_2C_2H_5 \\ & | \\ C_6H_5- & C=CHCOC_6H_5 \end{array}$$

II

The reaction seems to proceed according to Scheme 1.



Scheme 1

Table I

3-Cyano-4,6-diaryl-2H-pyran-2-ones (**IIIa—c**)

Compound	M.p., °C	Yield, %	Formula	Analysis: Calcd. Found			IR spectral data	
				C	H	N	$\nu_{C=O}$ (cm^{-1})	$\nu_{C\equiv N}$ (cm^{-1})
IIIa*	275+	75	$C_{18}H_{11}NO_2$	79.10 78.80	4.03 4.06	5.12 4.91	1724, 1720	2220
IIIb	230+	80	$C_{19}H_{13}NO_3$	75.24 74.86	4.29 4.52	4.62 4.49	1724, 1720	2220
IIIc	240+	82	$C_{18}H_{10}ClNO_2$	70.24 70.12	3.25 2.89	4.50 4.07	1724, 1720	2220

+ From ethanol
* *Cf.* Ref. [5]

(b) Reaction with ethyl acetoacetate

The reaction of ethyl acetoacetate with **Ia** gave the known [1] 4,6-diphenyl-2*H*-pyran-2-one **IVa**, prepared by a different route [1]. Similar treatment of **Ib** and **Ic** with ethyl acetoacetate yielded the hitherto unknown 4-phenyl-6-aryl-2*H*-pyran-2-ones, **IVb** and **IVc**, respectively.

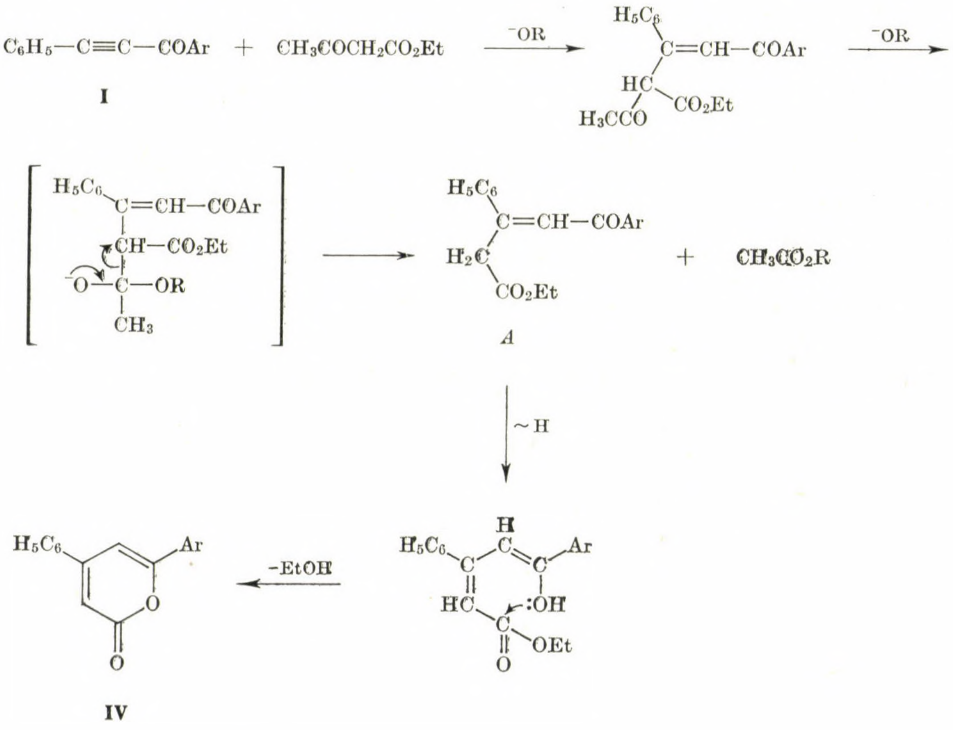
The structures of the pyran-2-ones (**IVa**—**c**) were confirmed by analytical data, infrared spectroscopy (*cf.* Table II) and ^{1}H-NMR spectroscopy (see Experimental).

Table II

4,6-Diaryl-2H-pyran-2-ones (**IVa–c**)

Compound	M.p., °C	Yield, %	Formula	Analysis: Calcd. Found C	H	Cl	IR spectral data $\nu_{C=O}$ (cm^{-1})
IVa*	143–4+	65	$C_{17}H_{12}O_2$	82.25 81.95	4.80 4.80		1720, 1700
IVb	130–1++	60	$C_{18}H_{14}O_3$	77.70 77.52	5.00 5.38		1720, 1700
IVc	180+	70	$C_{17}H_{11}ClO_2$	72.21 72.42	3.89 4.04	12.56 12.75	1720, 1700

+ From methanol
++ From benzene-light petroleum (b.p. 60–80 °C)
* *Lit.* [1] m.p. 142 °C



a Ar = C_6H_5

b Ar = $C_6H_4OCH_3$-*p*

c Ar = C_6H_4Cl-*p*

Scheme 2

Formation of the 6-aryl-4-phenyl-2*H*-pyran-2-ones (**IVa—c**) by the reaction of ethyl acetoacetate with **Ia—c** in the presence of sodium ethoxide seems to proceed by Michael addition of the ethyl acetoacetate anion to the acetylenic ketones followed by ketonic cleavage, favoured by the long time of the reaction (*cf.* Experimental), to give *A* which undergoes cyclization. The reaction may be represented as in Scheme 2.

(c) Reaction with malononitrile and acetylacetone

The reaction of malononitrile with **Ia** and **Ib** gave the hitherto unknown 1-aryl-4,4-dicyano-3-phenylbut-2-en-1-ones, **Va** and **Vb**, respectively, whose structures were confirmed by analytical data and infrared spectroscopy (*cf.* Table III). The low value in the IR spectrum of the $\nu_{C=O}$ band of the products excludes the tautomeric structure *B*.

Similarly, the reaction of acetylacetone with **Ia—c** gave the hitherto unknown 1-aryl-4,4-diacetyl-3-phenylbut-2-en-1-ones **Vc—e**, recpectively, as analytically pure substances whose infrared spectra (*cf.* Table III) further support the structure assigned to them.

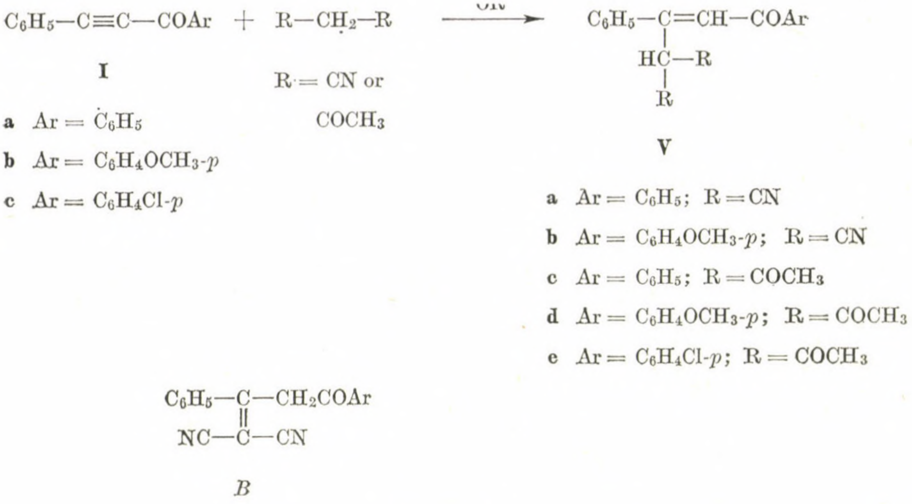
Table III

1-Aryl-4,4-dicyano-3-phenylbut-2-en-1-ones (**IV** *and* **b**)
and 1-Aryl-4,4-diacetyl-3-phenylbut-2-en-1-ones (**Vc—e**)

Compound	M.p., °C	Yield %	Formula	Analysis: Calcd. Found			IR spectral data	
				C	H	N	$\nu_{C=O}$ (cm^{-1})	$\nu_{C\equiv N}$ (cm^{-1})
Va	210^{+}	85	$C_{18}H_{12}N_2O$	79.40 79.80	4.40 4.70	10.30 10.90	1650	2215
Vb	255^{+}	80	$C_{19}H_{14}N_2O_2$	75.49 75.85	4.63 5.02	9.27 9.68	1645	2215
Vc	121^{+}	65	$C_{20}H_{18}O_3$	78.40 77.96	5.90 6.30		1640	
Vd	116^{+}	60	$C_{21}H_{20}O_4$	75.00 75.10	5.95 6.32		1645	
Ve^{++}	107^{+}	75	$C_{20}H_{17}ClO_3$	70.48 70.21	4.99 4.85		1650	

$^{+}$ From ethanol
$^{++}$ Cl Calcd. 10.42
Found 10.36

The reactions are represented in Scheme 3.



Scheme 3

Experimental

All m.p.'s are uncorrected. Infrared spectra (KBr discs) were obtained on a Unicam SP 200 spectrophotometer. ^{1}H-NMR spectra in $CDCl_3$, unless otherwise stated, were recorded on a Varian XL-100-VFT system using TMS as internal reference.

Preparation of 3-cyano-4,6-diaryl-2*H*-pyran-2-ones (IIIa—c)

Ethyl cyanoacetate (0.005 mole) and the aroylphenylacetylene (**I**) (0.005 mole) were added successively to sodium ethoxide (0.005 mole) in absolute ethanol (50 mL). The reaction mixture, which gradually acquired a red colour, was kept at room temperature until crystallization occurred (this usually took 2—3 days). The product was then filtered off and recrystallized from an appropriate solvent to give the title compounds as pale yellow to yellow crystals. Evaporation of the mother liquor followed by pouring into water and extraction with ether gave an additional amount of the product. The results are shown in Table I.

The ^{1}H-NMR spectrum of **IIIa** shows signals at δ 8.0—6.9 for the aromatic and olefinic protons and the ^{1}H-NMR spectrum (in DMSO) of **IIIb** has signals at δ8.05—6.5 (m, 10 H, aromatic and olefinic) and at δ 3.9 (s, 3 H, methyl protons).

Reaction of ethyl acetoacetate with the aroylphenylacetylenes Ia—c. Isolation of 4,6-diaryl-2*H*-pyran-2-ones (IVa—c)

Ethyl acetoacetate (0.005 mole) was added to a solution of sodium ethoxide (0.005 mole) in absolute ethanol (25 mL), followed by a solution of the aroylphenylacetylene (**I**) (0.005 mole) in absolute ethanol (20 mL). The reaction mixture, which gradually acquired a deep orange colour, was kept at room temperature for *ca.* 7 days, with occasional shaking· The precipitated solid was then filtered off and recrystallized from a suitable solvent to give the 4,6-diaryl-2*H*-pyran-2-ones (**IVa–c**). An additional amount of the product was obtained by concentration of the mother liquor. The result are given in Table II.

The ^{1}H-NMR spectrum of 4,6-diphenyl-2*H*-pyran-2-one (**IVa**) shows signals at δ 7.9—‑7.2 (m, 10 H, aromatic protons), δ 6.92 and 6.91 (d, 1 H, olefinic) and δ 6.45 and 6.43 (d, 1 H, olefinic) and that of 6-(*p*-chlorophenyl)-4-phenyl-2*H*-pyran-2-one (**IVb**) has signals at δ 7.9—‑7.1 (m, 9 H, aromatic protons), δ 6.92 and 6.91 (d, 1 H, olefinic) and δ 6.46 and 6.42 (d, 1 H, olefinic proton).

Preparation of aryl-4,4-dicyano-3-phenylbut-2-en-1-ones (Va and Vb)

Malononitrile (0.005 mole) was added to sodium ethoxide (0.005 mole) in absolute ethanol (25 mL), followed by the aroylphenylacetylene (**Ia** or **Ib**) (0.005 mole). The reaction mixture gradually acquired a deep red colour and after standing at room temperature for *ca.* 2 days it deposited colourless crystals in the case of **Ia**, and light yellow crystals in the case of **Ib**. The solid product was then filtered off and recrystallized from a suitable solvent to give the title compounds (**Va** and **Vb**). Additional amounts of the products were obtained by pouring the mother liquor into water. The results are given in Table III.

Preparation of 1-aryl-4,4-diacetyl-3-phenylbut-2-en-1-ones (Vc—e)

Acetylacetone (0.005 mole) and the aroylphenylacetylene (**Ia–c**) (0.005 mole) were added successively to sodium ethoxide (0.005 mole) in absolute ethanol (50 mL) and the reaction mixture which acquired a deep yellow colour, was kept at room temperature until crystallization occurred (this usually took 2—3 days). The precipitated solid was then filtered off. The mother liquor was evaporated, poured into water and the precipitate filtered off to give an additional amount of the product. Recrystallization of the product from a suitable solvent gave the title compounds (**Vc–e**) as yellow crystals. The results are given in Table III.

*

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SYNTHESIS OF ALKALOIDS USING REISSERT COMPOUNDS, IV*

A NEW SYNTHESIS OF (±)-MECAMBRIDINE

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A new multistep synthesis of (±)-mecambridine (**9**) has been achieved starting from 2-benzoyl-1-cyano-1,2-dihydro-8-methoxy-6,7-methylenedioxyisoquinoline (**1**) (Reissert compound) and 3-benzyloxy-4-methoxybenzyl chloride (**2**). The last two steps of this synthesis are the same as described in the literature. 11-*O*-Demethylmecambridine (**8**) has also been converted into (±)-orientalidine (**10**) using the known procedure.

Mecambridine (**9**) was isolated from *Meconopsis cambrica* by SLAVÍK [1] then from *Papaver oreophilum* by PFEIFER [2]. Its correct structure was elucidated by ŠANTAVÝ *et al.* [3—5]. Total synthesis of (±)-mecambridine was published by KAMETANI *et al.* [6] in 1974.

In the present paper a new synthesis of (±)-mecambridine, starting from a Reissert compound, will be reported.

The unknown Reissert compound (**1**) of 8-methoxy-6,7-methylenedioxyisoquinoline was synthesized as follows:

Oxidation of natural (—)-α-narcotine yielded cotarnine, which gave cotarnone on Hofmann degradation. 8-Methoxy-6,7-methylenedioxyisoquinoline was obtained by the ring closure of the cotarnone semicarbazone [7]. The isoquinoline obtained in this way was converted into 2-benzoyl-1-cyano-1,2-dihydro-8-methoxy-6,7-methylenedioxyisoquinoline (**1**) (Reissert compound) with potassium cyanide and benzoyl chloride in a mixture of dichloromethane and water [8]. 3-Benzyloxy-4-methoxybenzyl chloride (**2**), the other starting material, was prepared from isovanillin according to the known procedure [9].

The anion of the Reissert compound, formed on treatment with NaH in DMF at —20 °C, was allowed to react with 3-benzyloxy-4-methoxybenzyl chloride. The resulting Reissert compound substituted at C-1 (**3**) was hydrolyzed to 1-(3-benzyloxy-4-methoxybenzyl)-8-methoxy-6,7-methylenedioxyisoquinoline (**4**) without previous purification and identification. This compound

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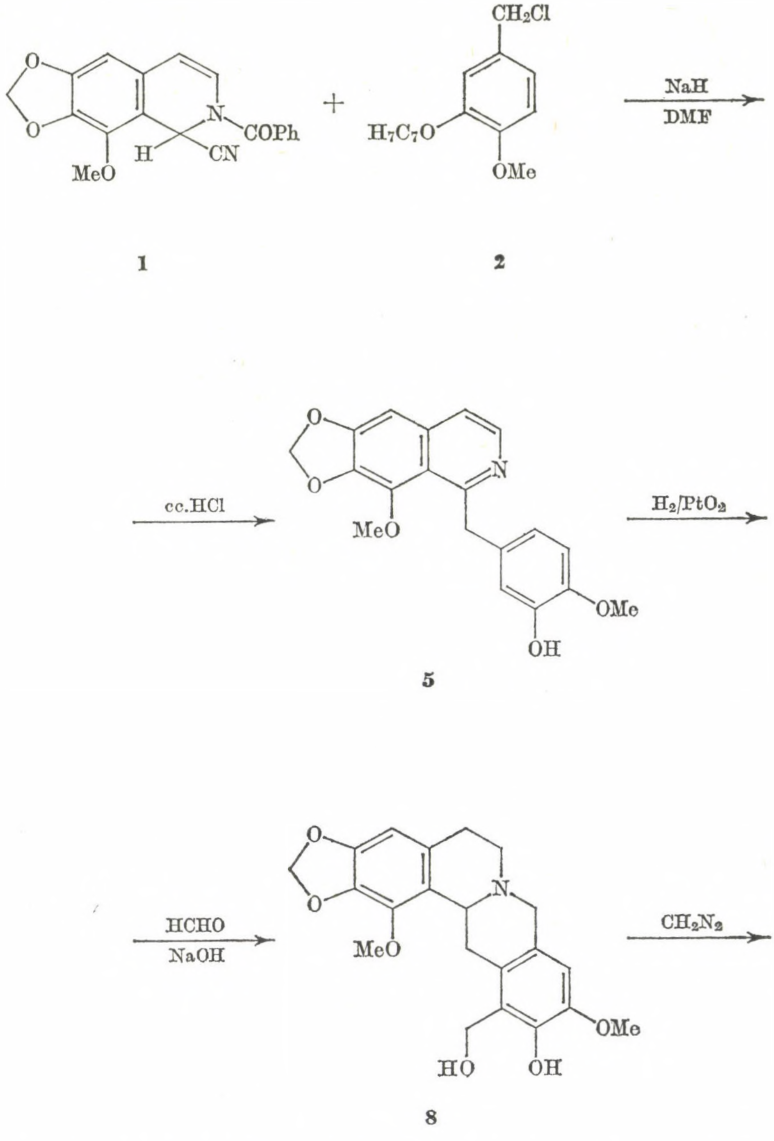
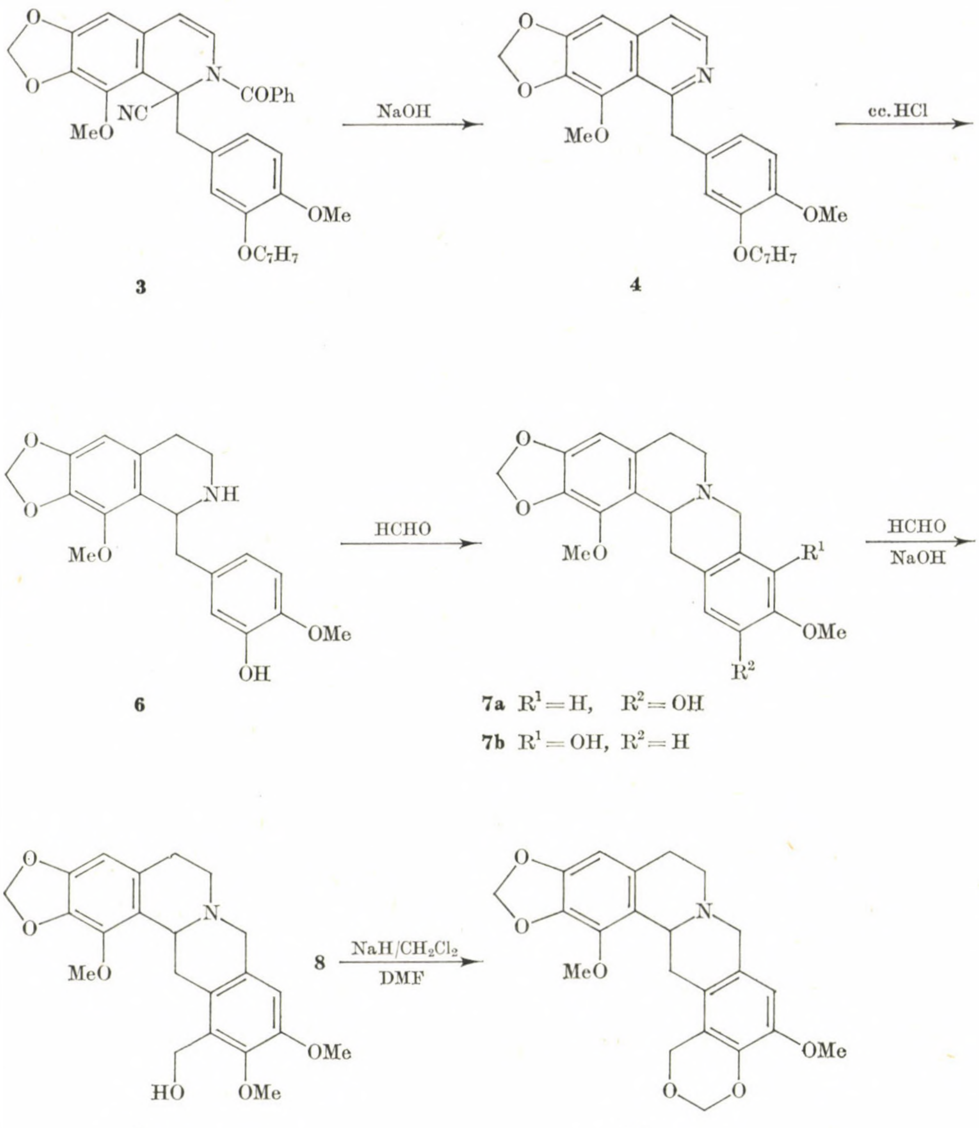
* Part III: P. KEREKES, GY. GAÁL, R. BOGNÁR, T. TÖRŐ and B. COSTISELLA: Acta Chim. Acad. Sci. Hung., **105**, 283 (1980)



afforded 1-(3-hydroxy-4-methoxybenzyl)-8-methoxy-6,7-methylenedioxyisoquinoline (**5**) on debenzylation with a mixture of ethanol, concentrated hydrochloric acid and a small amount of zinc dust. Compound **5** gave the corresponding tetrahydroisoquinoline derivative (**6**) on reduction with PtO_2 catalyst at $5 \cdot 10^5$ Pa initial pressure. The Mannich reaction of **6** was effected in neutral medium [10] to obtain the 10,11-disubstituted berbine derivative. This was, however, accompanied by about 10% of the 9,10-disubstituted berbine (**7b**) formed along with the expected **11**-hydroxy-1,10-dimethoxy-2,3-methylenedioxy-



3 **4**

6

7a R¹ = H, R² = OH

7b R¹ = OH, R² = H

9 **10**

berbine (**7a**). The two isomers were separated by crystallization and identified by means of their ^{1}H-NMR spectra. The C-11 and C-12 protons of compound **7b** displayed a characteristic AB quartet at δ 6.28 ppm.

The last two steps of the synthesis were achieved as described in the literature [6]. Compound **7a** was allowed to react with 37% formaldehyde solution and 1*M* methanolic sodium hydroxide at room temperature to obtain 11-hydroxy-12-hydroxymethyl-1,10-dimethoxy-2,3-methylenedioxyberbine (11-*O*-demethylmecambridine) (**8**) as a crystalline product. Compound **8** yielded

(±)-mecambridine (**9**) on methylation with diazomethane. The IR and ^{1}H-NMR spectra of the product were fairly identical with those of the compound synthesized by KAMETANI* and with those of natural mecambridine.

11-*O*-Demethylmecambridine (**8**) has also been converted into (±)-orientalidine (**10**) by using the procedure described by KAMETANI *et al.* [11]. The physical constants and spectral data of our substance were identical in every respect with the published ones.

Experimental

M. p.'s are uncorrected.

IR spectra were recorded with a UNICAM SP 200 G instrument in KBr pellets; ^{1}H-NMR spectra were obtained with a JEOL Minimar 100 MHz instrument in deuterochloroform solution. Chemical shifts values, referred to TMS internal standard, are given in ppm (δ) units.

2-Benzoyl-1-cyano-1,2-dihydro-8-methoxy-6,7-methylenedioxyisoquinoline (Reissert compound) (1)

Benzoyl chloride (17 mL) in CH_2Cl_2 (30 mL) was added to a vigorously stirred mixture of 8-methoxy-6,7-methylenedioxyisoquinoline (10 g; 50 mmoles) [7] in CH_2Cl_2 (100 mL) and KCN (16.25 g) in water (40 mL). After the end of the addition, the mixture was stirred for 1 h at room temperature. The two phases were separated and the CH_2Cl_2 solution was washed with water, 10% hydrochloric acid, 5% sodium hydroxide and finally again with water, then dried over $MgSO_4$ and the solvent evaporated. The residue was suspended in methanol (15 mL) and filtered off to obtain 13.5 g (81%) of solid material, m.p. 144—146 °C, which gave 10.15 g (61%) of crystalline product on crystallization from ethanol (300 mL), m.p. 146—148 °C.

Because of the decomposition of the product, the yield was considerably decreased on crystallization from ethanol and no Reissert compound could be recovered from the mother liquor. (The same behaviour was observed with the Reissert compound prepared from 6,7-dimethoxyisoquinoline [12]). The purity of the crude product was satisfactory for the further reactions.

$C_{19}H_{14}N_2O_4$ (334.32). Calcd. C 68.25; H 4.22; N 8.38. Found C 68.06; H 4.22; N 8.48%.
IR: $\nu_{C=N}$ 2230 cm^{-1} (very weak).

1-(3-Benzyloxy-4-methoxybenzyl)-8-methoxy-6,7-methylenedioxyisoquinoline (4)

A solution of the Reissert compound (**1**) (3.34 g; 10 mmoles) in dry DMF (15 mL) was added to a stirred suspension of sodium hydride (0.3 g) in dry DMF (20 mL) under nitrogen atmosphere at −20 °C. Stirring was continued for 5 min, then 3-benzyloxy-4-methoxybenzyl chloride (2.7 g; 11 mmoles) (**2**) [9] dissolved in dry DMF (10 mL) was added dropwise. The reaction mixture was stirred for 2 h at −20 °C, then for 3 h at room temperature. The excess of sodium hydride was decomposed with ethanol and the solvent evaporated under reduced pressure. The residue was dissolved in benzene (100 mL) washed twice with water (50 mL each) and the aqueous phase was extracted with benzene (50 mL). The combined benzene solution was washed with two 50-mL portions of water, dried over Na_2SO_4, then the solvent was evaporated to obtain a yellow oil (5.25 g) which was subjected to hydrolysis without purification.

Sodium hydroxide (50 g) in water (50 mL) was added to the ethanolic solution (100 mL) of the oil, and the reaction mixture was refluxed for 2.5 h on a steam bath; the ethanol was

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* We are indebted to Professor KAMETANI (Sendai Japan) for the comparison of the IR and ^{1}H-NMR spectra of our substance with those of the compound synthesized by them and with those of natural mecambridine.

then removed in vacuum. The residue was triturated with water (50 mL) and extracted with benzene (3×50 mL), then washed with water (4×50 mL). 10% hydrochloric acid (50 mL) was added to the benzene solution and the insoluble hydrochloride filtered off. The benzene solution was extracted with 5% hydrochloric acid (2×25 mL). The hydrochloride was combined with the acidic extract, made alkaline with NH_4OH and the base was extracted with $CHCl_3$ (3×50 mL). The $CHCl_3$ solution was washed with water (3×50 mL), dried over Na_2SO_4 and the solvent removed. The residue was converted into the hydrochloride (3 g), m.p. 190—192 °C, with abs. ethanolic hydrochloric acid. The salt was then transformed back to the base to yield 2.5 g (58%) of the product, m.p. 128—130 °C, on crystallization from ethanol (26 mL).

$C_{26}H_{23}NO_5$ (429.45). Calcd. C 72.71; H 5.40; N 3.26. Found C 73.08; H 5.33; N 3.16%.

1-(3-Hydroxy-4-methoxybenzyl)-8-methoxy-6,7-methylenedioxyisoquinoline (5)

A mixture of compound **4** (2.6 g; 6 mmoles), zinc dust (0.3 g), ethanol (300 mL) and *conc.* hydrochloric acid (300 mL) was refluxed for 3 h. The solvent was evaporated, the residue diluted with water (10 mL) and made alkaline with conc. NH_4OH. The reaction product was extracted with $CHCl_3$ (3×75 mL), washed with water (4×50 mL), dried over Na_2SO_4 and the solvent evaporated. The residue was crystallized from ethanol (24 mL) to afford 1.6 g (79%) of the product, m.p. 163—165 °C.

$C_{19}H_{17}NO_5$ (339.34). Calcd. C 67.25; H 5.05; N 4.13. Found C 67.24; H 4.98; N 4.13%.

^{1}H-NMR: 3.72 (3H, s, OCH_3), 3.84 (3H, s, OCH_3), 4.58 (2H, s, $ArCH_2$), 6.06 (2H, s, OCH_2O), 6.4—6.9 (4H, m, ArH's), 7.39 and 8.20 (2H, 2d, J = 6 Hz, C-3 and C-4 H's).

1-(3-Hydroxy-4-methoxybenzyl)-8-methoxy-6,7-methylenedioxy-1,2,3,4-tetrahydroisoquinoline (6)

Compound **5** (1.36 g; 4 mmoles) dissolved in ethanol (250 mL) was hydrogenated in the presence of PtO_2 (0.2 g) under $5 \cdot 10^5$ Pa initial pressure for 24 h at room temperature. The catalyst was filtered off, the solvent evaporated and the residue crystallized from ethanol (10 mL) to obtain 1.02 g (74%) of crystalline material, m.p. 144—146 °C.

$C_{19}H_{21}NO_5$ (343.37). Calcd. C 66.46; H 6.17; N 4.08. Found C 65.70; H 5.88; N 4.08%.

^{1}H-NMR: 3.77 (3H, s, OCH_3), 4.04 (3H, s, OCH_3), 5.84 (2H, s, OCH_2O), 6.30 (1H, s, C-5 H), 6.6—6.8 (3H, m, ArH's).

Mannich reaction of 6

A mixture of tetrahydroisoquinoline (**6**) (1 g; 3 mmoles), ethanol (30 mL) and 37% formalin (5 mL) was refluxed for 1 h under nitrogen atmosphere, then the solvent was evaporated in vacuum. The residue was crystallized from ethanol (23 mL) to afford 0.6 g (56%) of 11-hydroxy-1,10-dimethoxy-2,3-methylenedioxyberbine (**7a**) as needles, m.p. 186—188 °C (*lit.* [6] m.p. 192—194 °C and 204—206 °C, respectively).

$C_{20}H_{21}NO_5$ (355.38). Calcd. C 67.59; H 5.96; N 3.94. Found C 67.91; H 5.95; N 4.14%.
IR: ν_{OH} 3460 cm^{-1}.

^{1}H-NMR: 3.82 (3H s, OCH_3), 3.97 (3H, s, OCH_3), 5.86 (2H, s, OCH_2O), 6.32 (1H, s, C-4 H), 6.56 (2H, broad s, C-9 and C-12 H's).

On standing, 0.19 g of prismatic crystals, m.p. 196—200 °C, separated from the mother liquor, which on crystallization from ethanol (22 mL) gave 0.12 g (11%) of 9-hydroxy-1,10-dimethoxy-2,3-methylenedioxyberbine (**7b**), m.p. 198—200 °C.

$C_{20}H_{21}NO_5$ (355.38). Calcd. C 67.59; H 5.96; N 3.94. Found C 67.01; H 5.93; N.3.88%.
IR: ν_{OH} 3460 cm^{-1}.

^{1}H-NMR: 3.68 (3H, s, OCH_3), 3.84 (3H, s, OCH_3), 5.6 (2H, s, OCH_2O), 6.0 (1H, s, C-4 H), 6.28 (2H, ABq, J = 8 Hz, C-11 and C-12 H's).

11-Hydroxy-12-hydroxymethyl-1,10-dimethoxy-2,3-methylenedioxyberbine (8)

The berbine derivative (**7a**) (0.35 g; 1 mmole) was allowed to react with 37% formalin as described in the literature [6], and the reaction product was purified by means of preparative layer chromatography (developing mixture: chloroform: methanol 9 : 1) to yield a yellow gum (0.38 g) which was crystallized from a mixture of methanol and ether to give 0.24 g (63%) of yellow needles, m.p. 131—132 °C.

$C_{21}H_{23}NO_6$ (385.40). Calcd. C 65.44; H 6.01; N 3.64. Found C 65.39; H 6.29; N 3.40%.

IR: ν_{OH} 2300—3500 cm^{-1} (associated).

^{1}H-NMR: 3.76 (3H, s, OCH_3), 3.94 (3H, s, OCH_3), 4.61 (2H, s, CH_2OH), 5.82 (2H, s, OCH_2O), 6.29 (1H, s, C-4 H), 6.42 (1H, s, C-9 H).

(±)-Mecambridine (9)

Compound **8** (0.47 g; 1.2 mmole) was methylated with diazomethane dissolved in ether to afford 0.369 g of a substance; after purification by means of preparative layer chromatography (developing mixture: chloroform : methanol, 9 : 1), this was crystallized from a mixture of methanol and ether, then from ethyl acetate to obtain 0.129 g of **9**, m.p. 148—150 °C (*lit.* [6] m.p. 158—160 °C).

$C_{22}H_{25}NO_6$ (399.43). Calcd. C 66.15; H 6.31; N 3.51. Found C 66.39; H 6.47; N 3.13%.

^{1}H-NMR: 3.84 (6H, s, $2OCH_3$), 3.98 (3H, s, OCH_3), 4.66 (2H, s, CH_2OH), 5.87 (2H, s, OCH_2O), 6.33 (1H, s, C-4 H), 6.59 (1H, s, C-9 H).

MS: *m/e* 399 (M^+), 206, 204, 194, 179.

(±)-Orientalidine (10)

Compound **8** (0.19 g; 0.5 mmole) was converted into orientalidine as described in the literature [11]. The crude product was crystallized from ethyl acetate to afford 0.075 g of crystalline substance, m.p. 190—192 °C (*lit.* [11] m.p. 190—192 °C).

$C_{22}H_{23}NO_6$ (397.41). Calcd. 66.48; H 5.83; N 3.52, Found C 66.67; H 5.88; N 3.46%.

^{1}H-NMR: 3.84 (3H, s, OCH_3), 3.94 (3H, s, OCH_3), 4.60 and 4.84 (2H, 2d, $J = 16$ Hz, $ArCH_2O$), 5.21 (2H, s, $ArOCH_2OCH_2$), 5.87 (2H, s, OCH_2O), 6.34 (1H, s, C-4 H), 6.51 (1H, s, C-9 H).

MS: *m/e* 397 (M^+), 204, 192, 162.

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REACTION OF PHENYLDIAZOMETHANE WITH AROMATIC ALDEHYDES IN THE PRESENCE OF ZINC IODIDE

(*SHORT COMMUNICATION*)

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The catalytic action of zinc iodide in reactions of phenyldiazomethane with aromatic aldehydes is described. It was found that the formation of desoxybenzoins **3** occurs without participation of a carbenoid intermediate PhCHIZnI (**4**).

The reactions between olefins and carbenes generated from diazoalkanes have been intensively studied. It is known that in the reactions catalyzed by metal salts (reactions of the Simmons—Smith type) carbenoids of organometallic character are involved as intermediates. Thus, the decomposition of phenyldiazomethane in the presence of ZnX_2 (X = halogen) leads to the formation of α-halobenzyl zinc halide $C_6H_5CHXZnX$ [1], which then reacts with the olefin giving a cyclopropane derivative [2]. However, the reactions of phenylmethylene with a C=Y double bond (Y = heteroatom) have not been studies as yet.

We have found recently that in the course of the decomposition of phenyldiazomethane by zinc iodide in the presence of some *N*-substituted benzaldimines, tertiary aziridines were formed [3] as well as desoxybenzoin, which have been isolated as side-products. In our opinion, desoxybenzoin formation is due to the benzaldehyde present as an admixture in easily hydrolyzable aldimines. In order to verify this hypothesis, we have studied the reaction of aromatic aldehydes with phenyldiazomethane in detail.

In the literature, the reactions of some aliphatic diazocompounds of the $RCHN_2$ type with aldehydes in the presence of aluminium chloride or boron trifluoride were described. Depending on the reaction conditions and the type of catalytic agent, the product was a ketone, or oxirane derivative, or both [4—6]. Zinc halides were not used in this type of reactions.

Upon addition of phenyldiazomethane (1) to a solution of an aromatic aldehyde **2a—d** and ZnI_2 in ether, we observed the evolution of nitrogen and immediate disappearance of the red colour of diazocompound. ^{1}H-NMR spectra of the reaction mixtures showed the presence of desoxybenzoin derivatives **3a—d** besides the usual products of the decomposition of phenyldiazomethane (benzalazine and trans-stilbene). The yields of desoxybenzoins have been determined from ^{1}H-NMR spectra by comparing the signal intensities of desoxybenzoin and the starting aldehyde. The results are presented in Table I.

$$\underset{(\mathbf{1})}{C_6H_5CHN_2} + \underset{(\mathbf{2a-d})}{Ar{-}CHO} \xrightarrow[\text{ether, }20\,^\circ C]{ZnI_2} \underset{(\mathbf{3a-d})}{Ar{-}CO{-}CH_2{-}C_6H_5} + N_2$$

Scheme 1

Table I

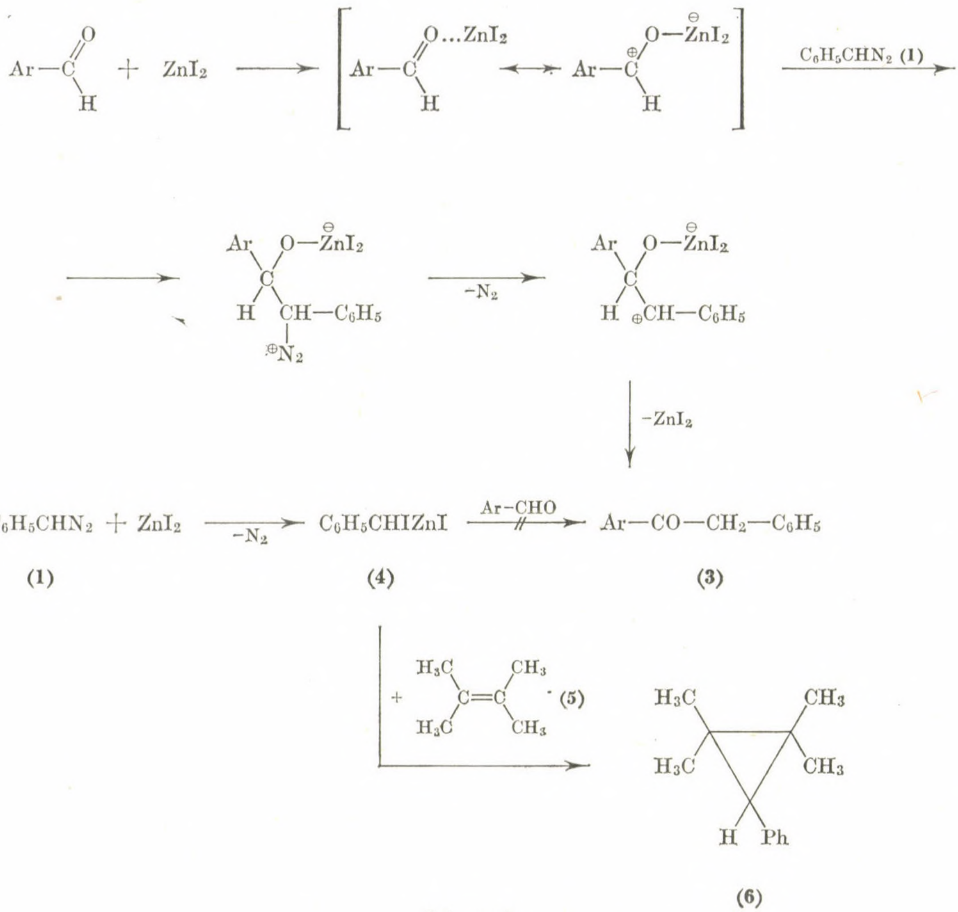
Desoxybenzoin derivatives **3a—d**

3	Ar	Yield, (%)	M.p., (°C)	^{1}H-NMR δ ppm ($CDCl_3$, TMS = 0)
a	C_6H_5	40	56—57 (58—59 [8])	4.15 (2H, CH_2, s); 7.0—8.0 (10H, Ar, m)
b	4-$CH_3C_6H_4$	38	108—110 (110—110.5 [9])	2.30 (3H, CH_3, s); 4.20 (2H, CH_2, s); 7.0—8.0 (9H, Ar, m)
c	4-$CH_3OC_6H_4$	41	73—75 (77 [10])	3.65 (3H, OCH_3, s); 4.10 (2H, CH_2, s); 6.70—8.00 (9H, Ar, m)
d	4-$O_2NC_6H_4$	70	156—158 (156—157.5 [11])	4.30 (2H, CH_2, s); 7.00—8.50 (9H, Ar, m)

It is assumed in the literature that the mechanism of the reaction of diazocompounds with aldehydes in the presence of Lewis acids involves nucleophilic attack of the diazocompound on the carbonyl group and subsequent elimination of nitrogen.

Neither aluminium chloride nor boron trifluoride, used as catalysts in the above reactions of diazocompounds with aldehydes [4—6], yields carbenoids [7], hence such a mechanism cannot be doubted. Our studies aimed at establishing whether zinc iodide reacts similarly to other Lewis acids or if the reaction runs with the participation of the carbenoid $C_6H_5CHIZnI$ (**4**). In order to find an answer to this problem, we prepared a solution of organometallic compound **4** by decomposing **1** with ZnI_2 at a low temperature, to which benzaldehyde (**2a**) or an olefine **5** was added. Such a procedure with the use of **5** affords cyclopropane derivative **6**, which indicates a carbenoid character of the reaction. During the experiment with benzaldehyde we did not observe the formation of desoxybenzoin (**3a**).

The above evidence indicates that the catalytic action of ZnI_2 is not based on the formation of carbenoid **4** but, like other Lewis acids, it polarizes



Scheme 2

the carbonyl group and this complex reacts next with phenyldiazomethane. Subsequent elimination of nitrogen and the migration of a proton gives product **3**. This supports the results published by SEYFERT [12], who found that carbenoids do not react with the carbonyl group of common oxo-compounds (except Cl_3C-CHO, F_3CCOCF_3, *etc.*).

Experimental

Melting points were determined in a capillary using a Dr. Tottoli apparatus, and are uncorrected. ^1H-NMR spectra were recorded on a Tesla BS 487 (80 MHz) spectrometer, using TMS as an internal standard. Mass spectra were obtained on a LKB GCMS 2091 spectrometer with 70 eV ionization potential. IR spectra were measured on a Perkin-Elmer 325 spectrophotometer.

Phenyldiazomethane (**1**) was prepared according to FARNUM [13].

Reaction of phenyldiazomethane with aromatic aldehydes in the presence of ZnI_2

An ethereal solution (10 mL) of phenyldiazomethane (1.35 g; 11 mmol) was added dropwise, with stirring under nitrogen, over a period of 1 hour at room temperature to a solution of 3.2 g (10 mmol) ZnI_2 and 10 mmol of aromatic aldehyde in 40 mL of diethyl ether. The reaction mixture was stirred for the next hour and 100 mL of chloroform was added. Zinc iodide was extracted with a 5% ammonia solution, the organic layer was dried over $MgSO_4$ and chloroform was evaporated. Absolute ethanol (5 mL) was added to the residue and the mixture was kept in a refrigerator. After several days, crude ketones **3** were filtered and purified by crystallization from ethanol. The results are presented in Table 1.

Attempts of the reactions of $C_6H_5CHIZnI$ (4)

a) with benzaldehyde (**2a**)

A solution of phenyldiazomethane (1.2 g, 10 mmol) in 10 mL ethyl ether was added slowly, under nitrogen, to an ethereal solution (20 mL) of ZnI_2 (3.2 g, 10 mmol) cooled to −45 °C. Each portion of phenyldiazomethane solution was added when the red colour of the diazo compound disappeared. The addition took about 1 hour. Benzaldehyde (1.09 g, 10 mmol) was then added at −40 °C and the mixture was allowed to warm up to room temperature. The reaction mixture was worked up as previously. ^{1}H-NMR spectrum showed the absence of desoxybenzoin.

b) with 1,1,2,2-tetramethylethylene (**5**)

To an α-iodobenzylzinc iodide solution prepared identically as in procedure *a*, 1,1,2,2-tetramethylethylene (15 mL) was added at −40 °C and stirring under nitrogen was continued at a room temperature for 12 h. After this time the catalyst was removed and the mixture was worked up as previously. 1-Phenyl-2,2,3,3-tetramethylcyclopropane (**6**) was distilled from the reaction mixture in vacuum. It was additionally purified on a column (neutral alumina, hexane). Yield: 520 mg (15% on crude **1**). Oil. B.p. 130−135°/4 Torr.

$C_{13}H_{18}$ (174.27). Calcd. C 89.59; H 10.40. Found C 89.75; H 10.21%.

IR (neat): ν_{ring} 1020 cm^{-1}; $\nu_{\text{C-H}}$ 3101 cm^{-1}.

^{1}H-NMR (CCl_4, TMS = O): 0.90 (6H, s, CH_3), 1.25 (6H, s, CH_3), 1.50 (1H, s, CH−Ph), 7.10 (5H, m, aromatic).

MS: 174 (M^+, 67%), 160, 159 (100%), 131, 117, 105, 57, 28.

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A STUDY OF THE VISCOSITY OF MIXTURES OF CARBOXYLIC ACIDS AND AMINES

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The dynamic viscosities of mixtures of aliphatic (mainly propionic) acids with primary or secondary or tertiary amines have been measured between 293.15 and 333.15 K. The study of the viscosity coefficient and of the activation enthalpy of viscous flow in function of concentration yields qualitative information on the association processes. Results allow to conclude that associates with compositions of AB, and AB_3, form in mixtures of propionic acid and a tertiary alkyl amine (A stands for the amine, B for the acid molecule). AB, further AB_3 associates form also in mixtures of secondary alkyl amine and propionic acid, but these associates combine with each other. Consequently, generally AB_3 associates will form in equimolar mixtures, and generally $(AB_3)_2$ associates when the mole fraction of the acid is 0.75. Due to similar processes, $(AB)_4$ or $(AB)_5$ are the characteristic associates in equimolar mixtures of primary alkylamine and carboxylic acid, in such mixtures further combinations of AB_3-associates is very unlikely.

The study of viscosity supplies additional information on the structure of, and on associations in, a mixture of liquids. Unfortunately this information allows but qualitative deductions, since the theories on the viscosity of mixtures can not serve us a solid basis for quantitative evaluations. Neither are the theories in respect to viscosity of solutions of polymers [1] applicable to mixtures which contain association polymers; also the calculation of the degree of association based upon a determination of the activation enthalpy of viscous flow [2] is to be considered a semi-qualitative method only. After all this it seems justified to ask whether or not a study of viscosities is energy well spent? We think that a reply in the affirmative is fully appropriate because such studies are justified not only in view of the lack of methods of calculation relevant to the viscosity of mixtures but also in view of the fact that, in some cases, viscosity data help to evolve an acceptable physical notion of the structure of liquids.

In that follows, we propose to discuss studies carried out with mixtures of a few carboxylic acids with primary-, secondary- or tertiary alkylamines.

Experimental

A rotational viscosimeter, type Rheotest 2—50 Hz RV2, was used for the recording of viscosity data. The substances were purified by rectification on a column of about 30 theoretical plates: the middle fraction recovered at a reflux ratio of 1 : 10 was used in the experiments. No contaminants were detectable in these substances by gas chromatography.

Temperatures were kept constant within ±0.05 K limits with the help of an ultrathermostat. Mixtures were prepared by dosage of the pure substances, from burettes. Overall volumes of the mixtures were kept between 30 and 40 mL. The experimental results are collected in the Tables which follow, and are presented as functions of molar fractions, x, and of temperature. Dynamic viscosities are noted in 1 mPa.s = 10^{-3} Pa.s = 1 cP units.

Evaluation of experimental data

Viscosity itself is a good indication of association processes occurring in a mixture since the increase in size of hydrodynamical units dislocated during viscous flow, *i.e.* of molecules and their associates, generally causes the increase of the viscosity coefficient [3]. Of course, this statement is valid only if no significant change occurs in the structure of the liquid.

Besides the viscosity coefficient the activation enthalpy of viscous flow gives some information on the size of the hydrodynamical units in common movement. On the basis of the hole theory of liquids, this magnitude is easily interpretable for chain molecules and their associates [2]; also, according to experience, it enables an estimation to be made of the relative molecular masses of *e.g.* tertiary amines, carbonic acids, and their accociates [4]. In the course of evaluations also the activation enthalpies of viscous flow of the mixtures studied were calculated from the slopes of $\ln \eta$ *vs.* $-\frac{1}{T}$ diagrams. This way of plotting had not always produced correctly straight lines, but this was not expected since association processes are sensitive to temperature, thus it can be foreseen that from data recorded at lower temperatures a sharper rise of the curve, *i.e.* higher activation enthalpy will be deduced, consequently higher figures for the average relative molecular mass will be calculated than from data recorded at higher temperatures. Nevertheless, the apparent relative

Table 1

Dynamic viscostiy of mixtures of propionic acid x_1, with tri-n-propylamine

T K	x_1=0.000	0.100	0.400	0.500	0.600	0.700	0.750	0.775	0.800	0.900	1.000
	Dynamic viscosity, mPas										
293.15	0.670	0.734	4.43	5.62	5.97	13.95	20.55	23.47	23.75	8.57	1.10
298.15	0.523	0.664	3.85	5.12	5.22	11.20	16.25	18.67	18.96	7.50	—
303.15	0.495	0.589	3.50	4.35	4.50	9.20	13.02	15.00	15.59	6.47	0.96
308.15	0.459	0.543	3.10	3.75	3.80	7.70	10.85	12.22	12.77	5.81	—
313.15	0.445	0.511	2.80	3.62	3.35	6.52	9.00	10.32	10.76	5.04	0.84
318.15	0.412	0.499	2.45	3.03	3.00	5.57	7.62	8.68	8.96	4.40	—
323.15	0.380	0.464	2.22	2.75	2.67	4.82	6.46	7.44	7.72	4.05	0.75

molecular mass, and the activation enthalpy were calculated from all the experimental data available, by means of the least-squares method, because owing to the semi-quantitative character of this calculation, we thought it was not worthy to perform calculations for narrower temperature intervals.

Table II

Dynamic viscosity of mixtures of propionic acid, x_1, and tri-n-butylamine

T K	$x_1=0.000$	0.100	0.200	0.300	0.400	0.500	0.600	0.700	0.800	0.900
	Dynamic viscosity, mPa.s									
293.15	1.450	1.867	2.526	4.226	6.422	6.442	12.71	26.10	23.66	6.57
298.15	1.280	1.389	1.676	2.303	3.571	5.447	10.24	20.63	19.13	5.91
303.15	1.170	1.228	1.495	1.923	3.107	4.591	8.37	16.90	15.79	4.93
308.15	1.070	1.112	1.342	1.728	2.693	3.887	7.04	13.12	13.19	4.33
313.15	0.990	1.015	1.212	1.523	2.359	3.372	5.67	10.81	10.94	3.79
318.15	—	0.938	1.096	1.361	2.071	2.954	5.03	8.92	9.32	3.39
323.15	0.863	0.878	0.994	1.245	1.839	2.557	4.35	7.55	8.06	3.04
328.15	—	0.806	0.920	1.138	1.627	2.243	3.81	6.41	6.95	2.69
333.15	0.740	0.738	0.850	1.036	1.458	2.013	3.29	5.38	6.05	2.46
338.15	—	0.694	0.771	0.943	1.291	1.797	2.88	4.71	5.29	—
343.15	0.632	0.646	0.734	0.864	1.189	1.603	2.52	4.08	4.60	—

Table III

Dynamic viscosity of mixtures of pivalinic (trimethyl-acetic-)acid, x_1, and tri-n-propylamine

T K	$x_1=0.100$	0.200	0.300	0.400	0.500	0.600	0.700	0.725	0.750	0.800	0.900	1.000
	Dynamic viscosity, mPa.s											
293.15	1.239	1.593	1.998	3.304	5.525	14.34	41.75	62.84	69.20	54.33	15.35	solid
298.15	1.113	1.416	1.897	2.795	4.857	11.43	29.64	43.60	52.11	40.03	11.96	solid
303.15	1.090	1.371	1.631	2.479	3.946	9.15	21.72	31.12	39.98	28.38	9.46	solid
308.15	1.007	1.265	1.619	2.325	3.560	7.47	16.62	22.68	28.77	21.17	7.88	solid
313.15	0.961	1.163	1.474	2.14	3.069	6.17	12.77	17.62	21.17	16.84	6.57	2.45
318.15	—	1.088	1.375	1.94	2.62	5.00	10.24	14.04	17.53	13.12	5.51	2.23
323.15	—	1.017	1.285	1.79	2.72	4.15	8.33	11.21	13.24	10.81	4.73	2.06
328.15	—	—	—	—	—	3.421	6.92	9.44	10.09	8.72	4.06	1.86
333.15	—	—	—	—	—	2.81	5.78	6.77	8.86	7.21	3.62	1.64
338.15												1.49
343.15												1.35

Table IV

Dynamic viscosity of mixtures of propionic acid, x_1, and di-n-butylamine

T	$x_1 = 0.000$	0.200	0.400	0.500	0.600	0.700	0.750	0.800
K	Dynamic viscosity, mPa.s							
293.15	0.850	2.45	20.21	—	109.28	125.94	139.33	16.74
298.15	—	2.21	15.81	—	80.86	94.32	102.52	14.24
303.15	0.730	2.05	12.24	48.04	64.20	72.81	74.31	11.85
308.15	—	1.87	9.94	35.66	49.41	54.50	58.19	10.22
313.15	0.640	1.69	7.97	27.31	39.46	42.04	44.26	8.75
318.15	—	1.54	6.42	21.32	31.87	34.15	35.31	7.62
323.15	0.560	1.44	5.61	17.49	25.80	27.70	27.67	6.98
328.15	—	1.34	4.66	13.81	21.24	22.53	22.14	6.22
333.15	0.500	1.24	3.99	11.45	17.99	18.98	18.63	5.42

Table V

Dynamic viscosity of mixtures of propionic acid, x_1, and n-butylamine

T	$x_1 = 0.000$	0.200	0.300	0.400	0.500	0.600	0.700	0.750	0.800	0.875
K	Dynamic viscosity, mPa.s									
293.15	0.523	1.82	15.13	63.74	566.2	178.0	54.56	30.14	18.72	5.08
298.15	0.480	1.75	12.72	51.68	400.2	137.5	43.20	25.03	15.68	4.48
303.15	0.444	1.63	10.92	41.89	300.9	107.7	35.21	20.17	13.00	4.05
308.15	0.421	1.56	9.48	34.98	230.9	85.1	29.21	17.49	11.15	3.57
313.15	0.401	1.44	8.34	29.06	176.5	71.2	24.51	15.02	9.51	3.09
318.15	—	1.41	7.31	24.58	136.6	57.9	20.64	12.59	8.34	2.86
323.15	—	—	6.66	21.02	112.7	47.7	17.83	11.15	7.33	2.73
328.15	—	—	6.08	18.51	85.4	41.4	15.10	9.98	6.47	2.52
333.15	—	—	5.43	15.40	70.3	35.3	13.58	7.97	5.81	2.43

$M_r = 16.7\ \Delta H - 34.3$ is the correlation found for hydrocarbons but applicable also for alcohols, amines, and carboxylic acids, as shown in previous communications. This is used also here for the estimation of molecular mass; ΔH is in kJ · mole^{-1} unit. The results of such calculations are shown in Tables VII.1.—VII.6.

Let the carboxylic acid + tertiary amine mixtures be first considered to interpret the association phenomena. Viscosities recorded at 293.15 K are shown in Figure 1, activation enthalpies of viscous flow are shown in Figure 2. The best appreciation of the behaviour, respectively, of a primary, a secondary or a tertiary amine is possible by a comparison of that of the systems propionic

Table VI

Dynamic viscosity, η, of the mixtures of propionic acid, x_1, and n-pentylamine

T	$x_1 = 0.000$	0.100	0.200	0.300	0.400	0.500	0.600	0.700
K	Dynamic viscosity, mPa.s							
293.15	0.656	1.62	1.97	13.70	85.81	707.80	368.13	75.40
298.15	0.609	1.53	1.86	11.78	71.98	510.19	274.56	60.40
303.15	0.563	1.42	1.74	10.12	56.82	386.03	209.99	48.75
308.15	0.523	1.40	1.69	8.82	46.99	296.28	164.60	40.40
313.15	0.484	1.32	1.60	7.77	39.47	226.21	130.79	33.80
318.15	0.457	1.24	1.51	6.87	33.60	178.26	103.82	28.40
323.15	0.441	1.20	1.43	6.62	28.82	137.64	80.59	24.80
328.15	0.421	1.16	1.39	5.75	25.65	105.73	70.35	21.20
333.15	0.404	1.10	1.34	5.25	21.92	74.57	57.37	18.45

acid + tri-*n*-butylamine, + di-*n*-butylamine, and + *n*-butylamine; this is illustrated on Figures 3 and 4.

Suitably, the data for the propionic acid + *n*-butylamine system are compared with those for the propionic acid + *n*-pentylamine system. This is illustrated on Figures 5 and 6.

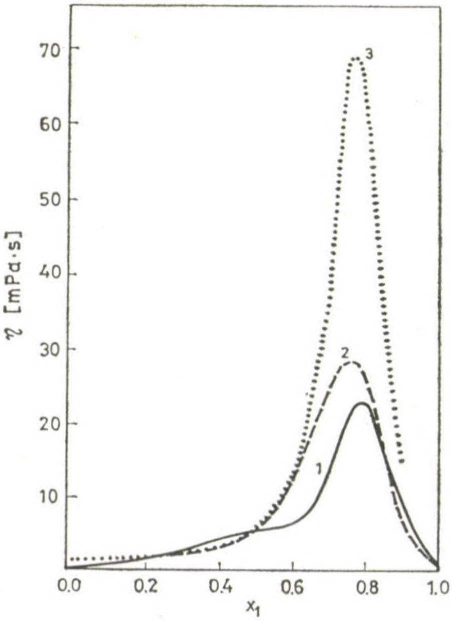


Fig. 1. Dynamic viscosity at 293.15 K, of the mixtures propionic acid, x_1 + tri-*n*-propylamine (1), + tri-*n*-butylamine (2), and pivalinic acid, x_1 + tri-*n*-propylamine (3)

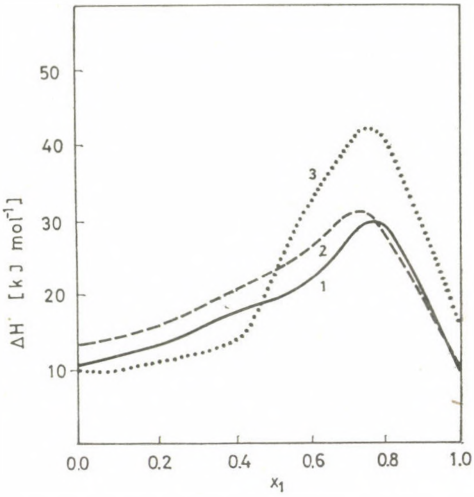


Fig. 2. Activation enthalpy of viscous flow, between 293.15 K and 333.15 K, of the mixtures propionic acid, x_1 + tri-*n*-propylamine (1), + tri-*n*-butylamine (2), and pivalinic acid, x_1 + tri-*n*-propylamine (3)

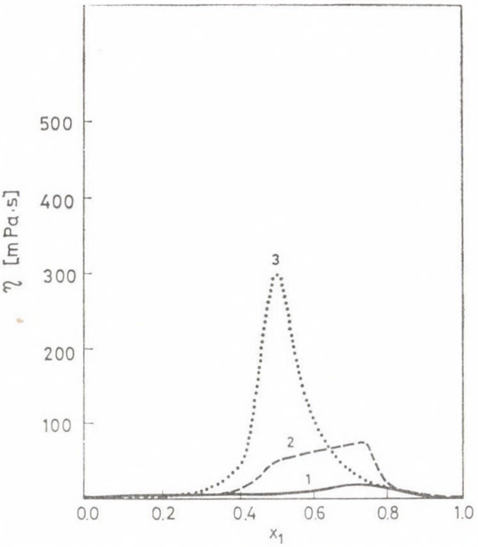


Fig. 3. Dynamic viscosity at 303.15 K of the mixtures propionic acid, x_1 + tri-*n*-butylamine (1), + di-*n*-butyalmine (2), and + *n*-butylamine (3)

Based upon the data of the Figures and of Table VII concerning the liquid structures of these mixtures the following can be stated.

The extreme increase in viscosity, as well as the maximum, at the composition $x_1 = 0.75$, of the activation enthalpy of viscous flow indicate that considerable association occurs at the mole ratio 3 : 1 of acid: tertiary amine.

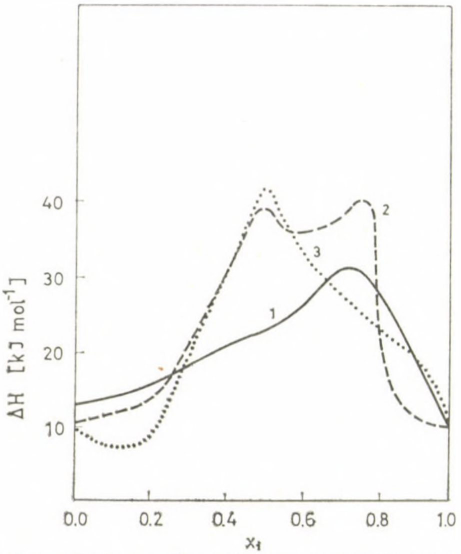


Fig. 4. Activation enthalpy of viscous flow, between 293.15 and 333.15 K, of the mixtures propionic acid, x_1 + tri-*n*-butylamine (1), + di-*n*-butylamine (2), and + *n*-butylamine (3)

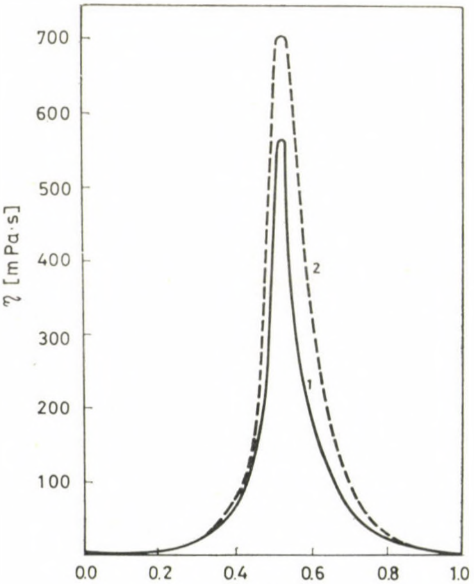


Fig. 5. Dynamic viscosity at 293.15 K, of the mixtures propionic acid, x_1 + *n*-butylamine (1), and + *n*-pentylamine (2)

This can be interpreted as the formation of an AB type mixed associate between propionic acid and tertiary amine, *viz.* of tertiary alkyl-ammonium propionate; then this species and the dimerized molecules of excess propionic acid interact and an AB_3-type associate is formed, where A stands for the

Table

Activation enthalpy of viscous flow, ΔH, ($kJ \cdot mole^{-1}$) and the estimated relative

1			2			3		
Propionic acid, x_1, + tri-*n*-propylamine			Propionic acid, x_1, + tri-*n*-butylamine			Pivalinic acid, x_1, + tri-*n*-propylamine		
x_1	H	M_r	x_1	H	M_r	x_1	H	M_r
0.100	10.54	142	0.000	13.34	189	0.100	9.89	131
0.100	11.76	162	0.100	13.98	199	0.200	11.28	154
0.400	17.44	257	0.200	15.82	230	0.300	11.71	161
0.500	18.92	281	0.300	17.97	266	0.400	14.02	200
0.600	21.81	330	0.400	20.84	314	0.500	22.58	377
0.700	27.65	428	0.500	23.12	352	0.600	32.59	510
0.750	30.02	467	0.600	24.46	408	0.700	39.69	628
0.775	30.03	467	0.700	31.01	484	0.750	42.80	680
0.800	29.39	457	0.800	27.02	417	0.800	40.71	646
0.900	19.98	299	0.900	20.26	304	0.900	29.11	452
1.000	10.06	134				1.000	15.68	227

amine and B for the acid molecules. The AB-type associate at a mole ratio of 1 : 1 causes a well-observable distortion on the viscosity curve and also on the curve for the activation enthalpy of viscous flow. This phenomenon is much less conspicuous with pivalinic acid because its acidic character is considerably weaker than that of propionic acid. The estimated relative molecular masses are in qualitative agreement with this physical picture. The comparison is given in Table VIII.

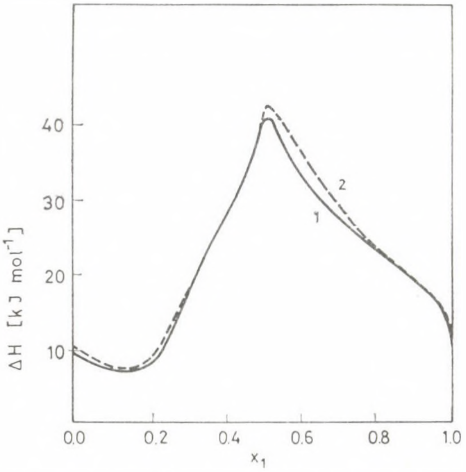


Fig. 6. Activation enthalpy iof viscous flow, between 293.15 and 333.15 K, of the mixtures propionic acid x_1 + *n*-butylamine (1), and + *n*-pentylamine (2)

VII

molecular mass, M_r, for mixtures of carboxylic acids and amines

4			5			6		
Propionic acid, x_1, + di-*n*-butylamine			Propionic acid, x_1, + *n*-butylamine			Propionic acid, x_1, + *n*-pentylamine		
x_1	H	M_r	x_1	H	M_r	x_1	H	M_r
0.000	10.78	146	0.000	10.08	134	0.000	11.55	158
0.200	13.57	192	0.200	7.97	99	0.100	7.68	94
0.400	32.82	514	0.300	20.44	307	0.200	7.97	99
0.500	39.74	629	0.400	28.33	439	0.300	19.16	286
0.600	36.42	574	0.500	41.76	663	0.400	27.65	427
0.700	38.54	609	0.600	32.66	511	0.500	43.10	685
0.750	40.84	648	0.700	28.17	436	0.600	35.99	567
			0.800	23.70	361			
			0.975	15.40	223			

The data of this Table show that theoretical and estimated figures for the molecular masses of pure components tally acceptably well and that estimated figures for associations are higher than theoretical ones in every instant. This seems to be quite reasonable if we regard the associates as more rigid structures than are the chain molecules. Thus much higher activation energies are needed to dislocate the former than to dislocate a chain molecule of the

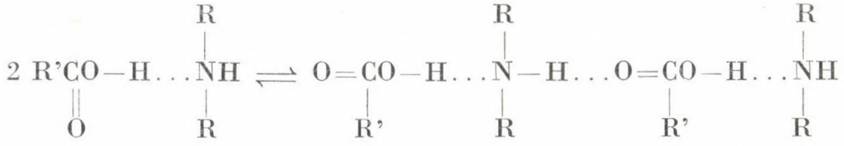
Table VIII

Theoretical, and estimated, relative molecular mass of the components, and of the associates, in mixtures of carboxylic acid and tertiary alkylamine

Component	Mark	M_r, theoretical	M_r, estimated	Deviation, %
Propionic acid dimer	B_{pr_2}	148.16	134	− 9.6
Pivalinic acid dimer	B_{pi_2}	204.28	227	+11.3
tri-*n*-Propylamine	A_p	143.27	142	− 0.9
tri-*n*-Butylamine	A_b	185.36	189	+ 2.0
Association 1 : 1	A_pB	217.35	281	+29.5
Association 1 : 1	A_pB_{pi}	245.41	377	+53.9
Association 1 : 1	A_bB_{pi}	259.44	352	+35.9
Association 1 : 3	$A_pB_{pr_3}$	365.51	467	+27.8
Association 1 : 3	$A_pB_{pi_3}$	449.69	680	+51.1
Association 1 : 3	$A_bB_{pr_3}$	407.60	490	+20.1

same mass. This conclusion seems to be supported by the results obtained for pivalinic acid: here a deviation amounting to +11.3 per cent is observable already with the dimerized acid, also in the case of mixed associates this deviation increases, to about 50 per cent, only for associates with pivalinic acid, presumably owing to its branched chain structure. In the other instances this deviation is between 20 and 30 per cent.

The primary-, secondary- and tertiary amines, respectively, show an essentially different behaviour. Regarding only viscosity data (Fig. 3) it might be thought that the primary amines form only 1 : 1 associates, that the secondary amines form mainly 1 : 1 and 1 : 3 associates and the tertiary amine form preferably 1 : 3 associates with the acid. As shown before, at equimolar composition also the tertiary amine is present practically entirely in 1 : 1 associates, thus we are promoted to think that the 1 : 1 associates of secondary and of primary amines will combine, else no explanation seems to be forthcoming of the fact that viscosity as well as activation enthalpy of viscous flow are conspicuously high at equimolar compositions. It seems that the secondary amine — in itself a weakly associated system — first forms an 1 : 1 associate with the acid, $M_r(\mathrm{AB}) = 203$; this brings about a slight increase of the average relative molecular mass the $x_1 = 0.0 - 0.2$ mole fraction range. When acid concentration is higher than this, a further association occurs, *e.g.*



$$2\,\mathrm{R'}\underset{\substack{\| \\ \mathrm{O}}}{\mathrm{C}}\mathrm{O{-}H\ldots}\overset{\substack{\mathrm{R} \\ |}}{\underset{\substack{| \\ \mathrm{R}}}{\mathrm{N}}}\mathrm{H} \rightleftharpoons \mathrm{O{=}}\underset{\substack{| \\ \mathrm{R'}}}{\mathrm{C}}\mathrm{O{-}H\ldots}\overset{\substack{\mathrm{R} \\ |}}{\underset{\substack{| \\ \mathrm{R}}}{\mathrm{N}}}\mathrm{{-}H\ldots O{=}}\underset{\substack{| \\ \mathrm{R'}}}{\mathrm{C}}\mathrm{O{-}H\ldots}\overset{\substack{\mathrm{R} \\ |}}{\underset{\substack{| \\ \mathrm{R}}}{\mathrm{N}}}\mathrm{H}$$

By analogy to the dimerization written as an example, chain-polymers are formed. This polymerization may serve as an explanation why the activation enthalpy of viscous flow of a system composed of an 1 : 1 mixture of secondary amine + acid is twice that of a system similarly composed of the tertiary amine and the acid. The calculated relative molecular mass of the AB associate, $M_r(\mathrm{AB}) = 203.33$, the estimated figure at equimolar composition is 629. This deviation (about 300 per cent) cannot, perhaps, be explained but by supposing that the polymerization of the mixed associates indeed takes place and that, on the average, about three associates combine. The increase of the mass of hydrodynamic units, *i.e.* of particles moving together, causes a substantial increase in the viscosity coefficient, therefore the viscosity of the secondary amine + acid mixture is substantially greater than that of the tertiary amine + acid mixture. This phenomenon, *i.e.* the further association occurs also when the mole ratio is 1 : 3 and its effect is evident in the figures of the viscosity coefficient as well as in those of the activation enthalpy of viscous flow.

However, the agregation of AB_3-type associates does not proceed up to the formation of trimers. Most probably the spatial arrangement of the 1 : 3 complex hinders polymerization.

The relative molecular mass $M_r(AB_3)$ is 277.41, that of a supposed dimer, $M_r(AB_3)_2$ is 544.82, the estimated figure is 648. The deviation in the case of tertiary amine: this estimate does not contradict the assumed association process. Seemingly, the dimerization of AB_3 associates takes place here.

At a composition of $x_1 = 0.5$ the viscosity of the primary amine + acid system is roughly three hundred times higher than that of the pure substances. This suggests that 1 : 1 association is decisive also in this instance. Also AB-type associates undergo polymerization as indicated by activation enthalpy data.

The estimated relative molecular mass, 633, represents an about 450 per cent positive deviation from the calculated relative molecular mass $M_r(AB) = 147.22$, of the AB associate, thus it seems to be justified to suppose that, on the average, about 4 or 5 AB-associates combine. The two hydrogens of the primary amine allow the formation of branched chains or of ring structures so it is in this case that estimation of relative molecular masses is the most uncertain.

The AB_3-type association seems to be present also in the primary amine+acid system. At a composition of $x_1 = 0.75$ the calculated relative molecular mass $M_r(AB_3)$ is 295.38, the estimated figure is 398, the deviation is +35 per cent: hardly greater than the positive deviations found with tertiary amines, thus it is quite probable that here only the formation of 1 : 3 associates should be considered. This seems to be supported by practically the same conclusion to be drawn from the study of the *n*-pentyl-amine + propionic acid system.

It should be noted that in the mole fraction range of $x_1 = 0.0-0.2$ of the two primary amines and relative molecular masses show figures lower than those found for the pure substances. The likely reason is, that the primary amine in itself is a strongly associated system and that also in propionic acid practically dimeric molecules are present, therefore formation of AB associates does not increase the average relative molecular mass, but these, as a new component, dilute the system and promotes the dissociation of the associates.

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ACTIVITY COEFFICIENT OF STRONG ELECTROLYTES IN CONCENTRATED SOLUTIONS*

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The RUFF's theory based on a lattice-like model of concentrated strong electrolytes is used *via* experimental static relative permittivities. It is found that the theory is suitable for prediction of the activity coefficients of strong electrolytes in concentrated solutions. The results indicate that a concentrated solution has a crystal structure similar to that of the corresponding solid phase. Using empirical lattice parameters (r° and M) the theory gives an extrapolation method with high accuracy.

1. Introduction

In 1977 RUFF published [1] a new model for concentrated solution of strong electrolytes. The model has the following characteristic features:

a) the ions of the strong binary electrolyte are distributed in a lattice-like arrangement,

b) the ions are immersed in an incompressible, structure-less, continuous dielectric, but this medium has a dielectric gradient in the vicinity of ions due to the polarizing effect of their electric field,

c) the coulombic forces are taken into account *via* an average relative permittivity which is a function of the interionic distances,

d) the dielectric gradient around the ions creates a repulsive energy among them. The repulsive energy equal to the work needed by the removal of solvent molecules from the medium with dielectric gradient then the interionic distances decrease.

According to this physical picture the excess Gibbs free energy of the electrolyte solutions, is

$$\varDelta G_e = \nu RT \ln \gamma = -\frac{2 N_A M z^2 e^2}{\varepsilon_0 r^0} \left[c^{1/3} + \frac{1}{h f_a r^0} \left(\ln \frac{\varepsilon_0}{\hat{\varepsilon}_d} \right) c^{2/3} - \right.$$

$$\left. - \frac{2}{3\pi \sqrt{3}\, z^2 h f_a r^0} \left(\frac{\varepsilon_0}{\hat{\varepsilon}_d} - 1 \right) c^{2/3} + \frac{2}{3\pi\sqrt{3}\, z^2 h^2 f_a^6 r^{02}} \left(\ln \frac{\varepsilon_0}{\hat{\varepsilon}_d} \right) c \right] \qquad (1)$$

---

*Magyar Kémiai Folyóirat (in Press)

where: γ — **mean ionic activity coefficient,** R**-gas constant,** T — **temperature,** ν – **number of ions in one mole electrolyte,** N_A – **Avogadro constant,** M — **Madelung constant,** z — **highest common factor of the charge numbers of the cation and the anion,** e — **charge of the electron,** ε_0 — static relative permittivity of the solution in a weak field, r° — the shortest distance **between a cation and an anion in a lattice-like arrangement if the solution has a concentration of 1 mol** dm^{-3}, c — **concentration in mol** dm^{-3}, h — **a constant characteristic for the nonlinear dielectric behaviour,** f_a **is given by Eq (2):**

$$f_a = \frac{\frac{2}{9}\left(1 - \pi\left(a_c^3 + a_a^3\right) c / r^{03}\right)}{\left[\frac{\pi}{2\sqrt{2}} \ln \frac{2+\sqrt{2}}{2-\sqrt{2}} + \frac{3\sqrt{2}}{16}\left(1 - \frac{\sqrt{2}}{2}\right) - \frac{\pi\sqrt{2}\left(a_a + a_c\right)}{2 r^0} c^{1/3}\right] z} \tag{2}$$

where: a_a and a_c are the radii of the anion and the cation, respectively, and $\hat{\varepsilon}_d$ is the average differential relative permittivity, which is calculated by RUFF *via* the following equation:

$$\varepsilon_d = \varepsilon_0 \left[1 - g / \exp\left(h f_a r_0\right)\right] \tag{3}$$

where g is a constant and

$$r_0 = r^{\circ} / c^{1/3} \tag{4}$$

Equation (3) is an approximative formula based on the BOOTH's theory [2a]. The aim of the present paper is such a check and application of RUFF's theory in which experimental static relative permittivities are used instead of the approximative values given by Eq. (3).

2. Static relative permittivity in concentrated solutions of strong electrolytes

On account of the ohmic conductivity the static relative permittivity of concentrated solutions of the strong electrolytes cannot be determined by direct measurements. However, it can be calculated from high frequency data using a suitable method of extrapolation. BARTHEL, SCHMITHALS and BEHRET [2] experimentally determined the complex relative permittivity as a function of the concentration for alkali chlorides and nitrates at wavelengths: 2.5 cm, 3.0 cm and 3.6 cm. Our treatment on dielectric data is based on these results belonging to 298 K.

The frequency dependent complex relative permittivity is

$$\varepsilon^* = \varepsilon'(\omega) + j\varepsilon''(\omega) \tag{5}$$

where $\varepsilon'(\omega)$ is the real part, $\varepsilon''(\omega)$ is the imaginary part of the relative permittivity, ω is the circular frequency and j is the imaginary unit. For conducting dielectric $\varepsilon''(\omega)$ originates from both the ohmic and the displacement current [3]. Discussing the dielectric data one has to separate the ohmic part of $\varepsilon''(\omega)$ and consider only the displacement current. In the following ε'' denotes the part of complex relative permittivity from the displacement current and the real part is ε'.

The Debye equation for a dielectric with one relaxation frequency [4] is

$$\varepsilon^* - n^2 = \frac{\varepsilon - n^2}{1 + j\omega\tau} \tag{6}$$

where: n — internal refractivity, ω — static relative permittivity, τ — relaxation time. Separating the real part from the imaginary one, equations for straight line or semicircle can be obtained [4]. In the literature the COLE—COLE plot [5] is generally used. The end point of the semicircle in the low frequency region points out the static relative permittivity (ε) while the high frequency end point gives the square of the internal refractivity (n^2). Discussing the data of BARTHEL and coworkers [2] it was found that the investigated electrolytes had only one relaxation frequency, consequently the static relative permittivity could be determined *via* Eq. (6). The COLE—COLE plot for NaCl as an example is given in Fig. 1. It can be seen that by increasing the concentration the static relative permittivity of the solution decreases, but even at a concentration of 4 mol dm^{-3} it is higher than $\varepsilon \sim 29$, the value corresponding to the ONSAGER equation [6] (that is to unity KIRKWOOD's g [7]). On the other side, the presence of the ions (that is the strong local electric field) has no effect on the displacement polarization, all the semicircles have common end point in the high frequency region $\varepsilon' = n^2$.

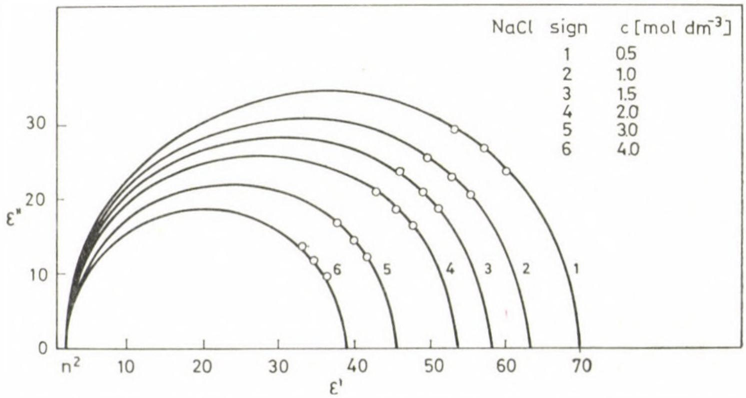

Fig. 1. Cole—Cole plot of NaCl solutions as a function of concentration

On the basis of Eq. (6) the static relative permittivity of alkali chlorides and nitrates are calculated as a function of the concentration. The results are given in Table I and II. The Tables also contain the relative permittivities calculated by Eq. (3).

The constants of Eq. (3) for water at 298 K are: $h = 0.939$, $g = 6.52$ [1]. In the Tables ε is also differential relative permittivity like ε_d, however, in electrolyte solutions the strong static electric field is caused by the ions, and the electric field of the ions is inhomogeneous, while the nonlinear dielectric behaviour is usually measured by homogeneous field (see *e.g.* [8]). At present, the difference between the effects of homogeneous and inhomogeneous fields is not known and it was supposed that this difference could be neglected considering the relative permittivities were macroscopic properties.

Table I

Static relative permittivities of alkali chloride solutions as a function of concentration

Electrolyte	C (mol dm^{-3})	ε (extrapolated)	$\hat{\varepsilon}_d$ [Eq. (3)]
NaCl	0.5	69.98	73.67
	1.0	63.38	67.15
	1.5	58.42	61.59
	2.0	53.91	56.87
	3.0	45.40	49.25
	4.0	39.28	43.31
KCl	0.5	71.09	74.03
	1.0	66.01	68.02
	1.5	61.45	62.98
	2.0	57.26	58.75
	3.0	48.92	52.06
	4.0	43.24	47.02
RbCl	0.5	70.85	74.15
	1.0	65.70	68.32
	1.5	62.30	63.45
	2.0	57.80	59.39
	3.0	50.40	53.03
CsCl	0.5	71.60	74.42
	1.0	67.0	68.99
	1.5	63.3	64.51
	2.0	59.2	60.82
	3.0	52.0	55.18

The static relative permittivity of the pure water at 298 K is 78.36. The relative permittivity of the water is decreased by the electrolytes *via* the strong local field of the ions; the concentration is higher the decrease is stronger.

Eq. (3) predicts this decrease, moreover, for alkali nitrates nearly exactly reproduces the experimental data. The effect of the difference between ε and ε_d on the activity coefficients is studied in the next section.

Table II

Static relative permittivities of alkali nitrate solutions as a function of concentration

Electrolyte	C (mol dm^{-3})	ε (extrapolated)	$\hat{\varepsilon}_d$ [Eq. (3)]
$NaNO_3$	0.5	69.77	73.10
	1.0	64.36	66.75
	1.5	60.02	61.61
	2.0	55.95	57.38
	3.0	49.84	50.76
	4.0	44.50	45.78
KNO_3	0.5	71.05	73.57
	1.0	67.70	67.91
	1.5	64.53	63.50
	2.0	61.75	60.02
$RbNO_3$	0.5	72.00	73.73
	1.0	68.25	68.31
	1.5	65.50	64.15
$CsNO_3$	0.5	72.10	74.09
	1.0	68.75	69.20

3. Activity coefficients of strong electrolytes in concentrated solutions

The mean activity coefficients can be calculated by Eq. (1). In this equation r° and M are parameters characteristic for the lattice type. For alkali chlorides the data given by RUFF were adopted, namely: $r^\circ = 10.24$ Å, $M = 1.763$. f_a can be calculated by Eq. (2) using the radii given by GOURARY and ADRIAN [9]. However, in the present calculations another method is applied, namely, f_a is calculated by Eq. (3) using the experimental static relative permittivities. The two methods give similar f_a values. The results for alkali chlorides are given in Table III. In the Table the experimental activity coeffi-

Table III

Mean activity coefficients of alkali chlorides as a function of concentration, at 298 K

Electrolyte	C (mol dm^{-3})	γ (obs.)	γ (calc.)	γ (RUFF)
NaCl	0.5	0.680	0.682	0.634
	1.0	0.658	0.654	0.592
	1.5	0.660	0.641	0.577
	2.0	0.675	0.647	0.575
	3.0	0.730	0.740	0.589
	4.0	0.815	0.851	0.620
KCl	0.5	0.648	0.663	0.631
	1.0	0.600	0.607	0.582
	1.5	0.583	0.579	0.558
	2.0	0.572	0.568	0.543
	3.0	0.570	0.599	0.525
	4.0	0.584	0.623	0.510
RbCl	0.5	0.600	0.667	0.631
	1.0	0.545	0.611	0.579
	1.5	0.510	0.567	0.552
	2.0	0.480	0.558	0.534
	3.0	0.475	0.559	0.508
CsCl	0.5	0.600	0.656	0.629
	1.0	0.536	0.593	0.573
	1.5	0.510	0.554	0.541
	2.0	0.483	0.537	0.517
	3.0	0.475	0.526	0.478

cients and the data calculated by Eqs (1)—(3) can also be seen. The agreement with the experiments for NaCl and KCl is better if experimental relative permittivities are used, while for RbCl and CsCl Eq. (3) gives better results. However, it must be emphasized that the agreement with experiments is satisfactory in both of the cases which clearly shows the applicability of the lattice model.

The alkali nitrates have a lattice type different from that of alkali chlorides. For alkali nitrates $r^\circ = 9.5$ Å and $M = 2.2$ are used following the results of JENKINS and WADDINGTON [11] for solid state nitrates. The results of the calculations together with the experimental data [10] are given in Table IV. The agreement with the experiments is satisfactory. The average difference

Table IV

Mean activity coefficients of alkali nitrates as a function of concentration, at 293 K

Electrolyte	C (mol dm^{-3})	γ (obs.)	γ (calc.)
$NaNO_3$	0.5	0.615	0.577
	1.0	0.540	0.506
	1.5	0.505	0.464
	2.0	0.480	0.440
	3.0	0.440	0.401
	4.0	0.415	0.382
KNO_3	0.5	0.540	0.559
	1.0	0.435	0.471
	1.5	0.365	0.418
	2.0	0.315	0.381
$RbNO_3$	0.5	0.530	0.548
	1.0	0.420	0.465
	1.5	0.350	0.412
$CsNO_3$	0.5	0.521	0.547
	1.0	0.410	0.462

between the measured and calculated data is 8% (smallest for 0.5 mol dm^{-3} KNO_3: −3.4% largest for 2 mol dm^{-3} KNO_3: −20.9%).

The agreement with the experiments as well as the fact that the alkali chlorides and nitrates have lattice parameters (r° and M) different from each other but these parameters in both cases are near to those of the corresponding solid crystals indicate that the concentrated electrolyte solution has a lattice structure similar to that of the solid phase. (The ions in the solution "remember" the lattice structure of the crystal.) Of course the lattice structure of an electrolyte solution cannot be exactly the same as that of the corresponding crystal. The thermal motion has perturbation effects, an electrolyte solution cannot be considered as a "regularly expanded lattice", however, the similarity of lattices is a remarkable experience.

If an electrolyte solution really has a lattice-like structure and its structure (because of the thermal motion or on the account of other effects) is different from the structure of the corresponding solid crystal, then r° and M can be determined from experimental activity coefficients and the lattice model can be the basis of an extrapolation method. From experimental activity coeffficients (using experimental static relative permittivities) r° and M

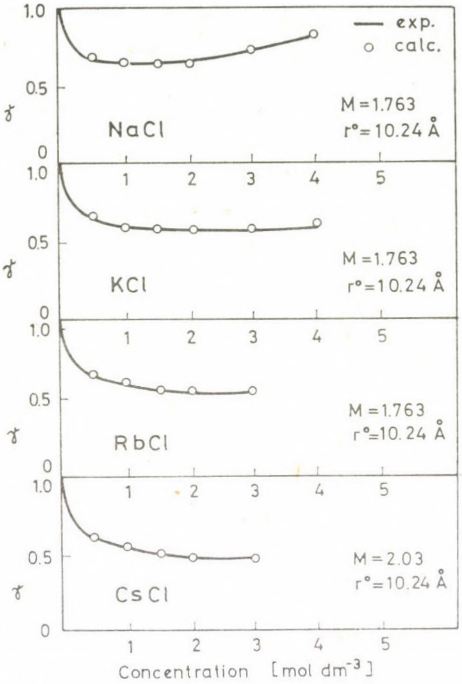

Fig. 2. Mean activity coefficients of alkali chlorides as a function of concentration

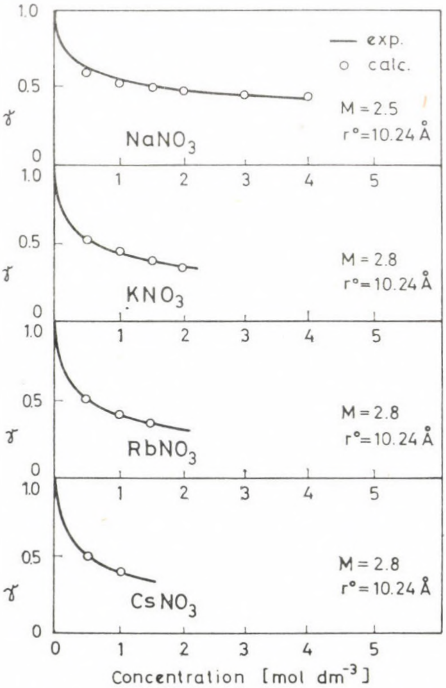

Fig. 3. Mean activity coefficients of alkali nitrates as a function of concentration

were determined for the investigated electrolytes and these data were inserted into Eq. (1) to calculate activity coefficients. The results are given in Figs 2 and 3. The experimental and calculated activity coefficients practically are the same (the average deviation is -2%). Consequently, the lattice model and the RUFF's equation based on this model can be used as a precise extrapolation method for the calculations of the activity coefficients of strong electrolytes in concentrated solutions.

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INVESTIGATION OF THE ADSORPTION AND ELECTROREDUCTION OF ACETONITRILE BY TRACER METHOD ON PLATINIZED PLATINUM ELECTRODE

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The adsorption and reactivity of acetonitrile have been studied in dilute aqueous solutions ($c < 10^{-2}$ M), in 1 M H_2SO_4 supporting electrolyte, on a platinized platinum electrode by a tracer technique and polarization methods. It has been found that at the low concentrations studied acetonitrile is reduced primarily to acetaldehyde through acetimine as intermediate in a relatively wide potential range (0—200 mV *vs.* HE). Under certain conditions ethane may also be formed from acetaldehyde. As these phenomena prevent, in part, the application of direct adsorption techniques, the adsorption of acetonitrile was measured by indirect technique by investigating the adsorption of labelled Cl^- ions. It has been found that in the system investigated the adsorption of acetonitrile cannot be regarded unambiguously as irreversible, and there are presumably two adsorption processes, one reversible and one irreversible.

The electrosorption of acetonitrile and other simple nitriles on bright platinum electrodes in acidic, aqueous medium was investigated in detail by ANGERSTEIN—KOZLOWSKA, MACDOUGALL and CONWAY [1—3]. It has been found that —

a) Acetonitrile and some simple nitriles are chemisorbed on platinum electrodes, and the adsorbed molecules form a reversible redox system on the surface of the electrode.

b) The adsorbed nitriles suppress the chemisorption of hydrogen to a certain extent, but even in the case of complete coverage with nitriles the chemisorption of hydrogen is possible.

c) If the adsorption of nitriles takes place in the potential range corresponding to the adsorption of hydrogen, not too far from the equilibrium hydrogen potential, a replacement of adsorbed hydrogen can be observed together with a corresponding transient anodic electrosorption process.

The observations may play an important role in the interpretation of the electrosorption properties of organic compounds. It appears therefore justified to gain information on the electrosorption of nitriles, primarily acetonitrile, on platinized platinum electrode as well, with the application of tracer techniques.

On the basis of previous experience [4—8], there are two ways of the application of tracer techniques in adsorption studies:

1) The compound to be investigated is labelled, *e.g.* acetonitrile with ^{14}C, and its adsorption is followed directly (direct adsorption method). This method has been applied to several organic compounds [4–8].

2) The changes in the adsorption of a reversibly adsorbed labelled compound or ion are monitored in the presence of the compound to be investigated, and from these changes conclusions are drawn on the adsorption processes studied. This way appears to be particularly advantageous in the case of irreversibly adsorbed compounds, since then *e.g.* from the decrease in the adsorption of reversibly adsorbed labelled component — as discussed in one of our previous papers [8] — the extent of chemisorption can be derived relatively easily. It is a doubtless advantage of this method, which compensates to a certain extent for the disadvantages of indirect measurements, that the compound to be studied can be applied in any concentration, in contrast with the direct methods in which the concentration of the labelled compound may not exceed a certain limit because of technical difficulties.

For the investigation of the adsorption of acetonitrile both techniques were applied. In the indirect method, the adsorption of Cl^- ions was investigated in the presence of non-labelled acetonitrile. Besides the investigation of adsorption, it also proved to be necessary to study some problems connected with the reduction of acetonitrile.

Experimental

The methods of measurement and the application of the tracer technique were described in our previous papers [4–9]. For the measurements ^{14}C labelled acetonitrile of $7-11\times10^6$ Bq/mmol specific activity and ^{36}Cl labelled HCl of 3.7×10^6 Bq/mmol activity were used. The supporting electrolyte was 1 *M* $HClO_4$. The electrode potentials were measured against a 1 atm hydrogen electrode immersed into the supporting electrolyte. The method of polarization studies connected with the investigation of the reduction of non-labelled acetonitrile was the same as applied in the reduction of oxo compounds [10–12].

Results

A) *Investigations with ^{14}C labelled acetonitrile*

At the relatively low concentrations permitted by the tracer technique the adsorption of acetonitrile proved to be very slow, and it was hard to determine when the adsorption process terminated. This is illustrated by Fig. 1 for various concentrations of labelled acetonitrile.

On investigating the potential dependence of adsorption at constant concentration the curves shown in Fig. 2 were obtained. Labelled acetonitrile was introduced into the system at 300 mV, and after a long settling time the potentials were held for 20–40 min (curve 1). After reaching 1200 mV, the

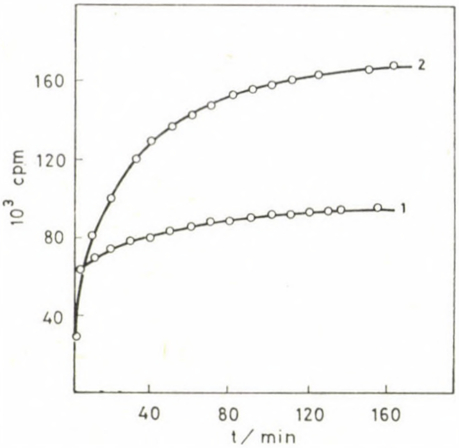


Fig. 1. Activity (cpm) as a function of time in the adsorption of labelled acetonitrile at 600 mV at concentrations of 2.5×10^{-4} mol/dm³ (1) and 1.5×10^{-3} mol/dm³ (2)

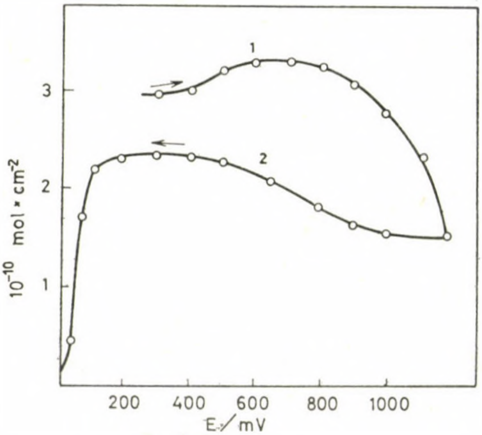


Fig. 2. The potential dependence of adsorbed amount when proceeding in the direction of increasing (1) and descreasing (2) potentials. $c_{AN} = 8 \times 10^{-4}$ mol/dm³

potential dependence was also measured in the direction of decreasing potentials (curve 2).

As can be seen from the curves, there is a substantial hysteresis, which can be explained at least in part (in the 700—1200 mV potential range) by the gradual formation of an oxide layer above 800 mV, and by the irreversibility of the reduction of this layer. It is, however, not completely clear why the two curves do not coincide in the 300—500 mV range. Above 1000 mV the possible oxidative desorption of chemisorbed acetonitrile may also play a role. However, a steady oxidation process could not be observed at these potentials even for high acetonitrile concentrations, and thus this hysteresis

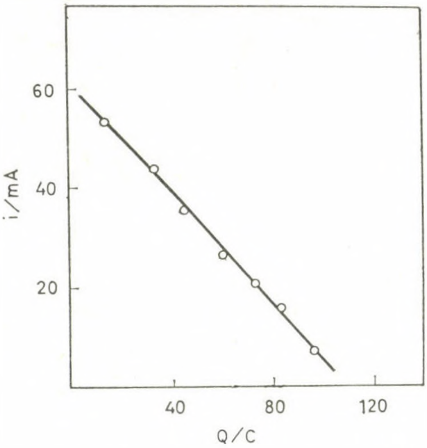


Fig. 3. Current measured in the reduction of 6×10^{-4} mol of acetonitrile at constant potential (50 mV) as a function of the charge passing through the system

cannot be interpreted by a decrease in the concentration of acetonitrile. At potentials lower than 200 mV the decrease in adsorption can be traced back to the reduction of acetonitrile. Therefore, in order to determine the potential region in which the reduction of acetonitrile on platinized platinum electrodes should be taken into account, separate experiments were carried out. As known, in the aqueous solutions of nitriles it is difficult to prepare the corresponding primary amines, since the imines formed as intermediates relatively easily undergo hydrolysis, and the resulting aldehyde forms a Schiff base with the amine formed in the further reduction of the imine. Furthermore, the reduction of Schiff bases yields secondary amines. Therefore, our main concern was to find the reactions that may be relevant at very low, 10^{-3}—10^{-4} mol/l acetonitrile concentrations. First we investigated the charge required for the complete transformation of a given amount of acetonitrile at the given potential, of course with the provision that the initial acetonitrile concentration is small as given above. A plot of the reduction current observed at a given potential against the charge passing the system produces the straight line shown in Fig. 3. Owing to the low concentration, there is, evidently, a diffusion limit and therefore the decrease in the charge passing through the system, *i.e.* the decreasing amount or concentration of acetonitrile, involves a linear decrease in current. On the other hand, it was surprising that the reaction practically terminated after a reduction corresponding to the uptake of 2 electrons. This means that the reduction proceeded to the imine stage only. It was found by analyzing the solution and the argon gas passed through the solution that a noticeable amount of acetaldehyde had formed. This observation is in harmony with the above mentioned experimental fact which suggests that imine is formed exclusively.

Accordingly, the formation of acetaldehyde is due to the reaction

$$CH_3-CN + 2\,H^+ + 2e \rightarrow CH_3-CH{=}NH \tag{1}$$

$$CH_3-CH{=}NH + H_3O^+ \rightarrow CH_3CHO + NH_4^+ \tag{2}$$

The fact that the overall reaction, under these conditions, corresponds to the uptake of two electrons only, can be explained by assuming that the rate of the reaction

$$CH_3-CH{=}NH + 2\,H^+ + 2e \rightarrow CH_3-CH_2-NH_2 \tag{3}$$

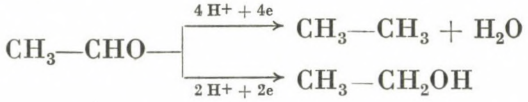
competing with reaction (2) is small in comparison with reaction (2).

Therefore the reactions

$$CH_3-CH_2-NH_2 + OHC-CH_3 \rightarrow CH_3-CH_2-N{=}CH-CH_3 \tag{4}$$

$$CH_3-CH_2-N{=}CH-CH_3 + 2\,H^+ + 2e \rightarrow CH_3-CH_2-NH-CH_2-CH_3 \tag{5}$$

which would yield secondary amine, are also suppressed. Of course, it must be stressed that the electrode potential has a significant role in determining the product distribution, since, whereas reaction (2) is independent of the electrode potential, the rates of reactions (3) and (1) depend on it, and thus the relative rates of partial processes and therefore the product distribution can be influenced through the electrode potential. This point was not studied in detail, since our concern was to point out that the investigation of acetonitrile adsorption on platinized platinum electrodes is disturbed in a wide potential region by reduction processes, and that acetaldehyde appears among the reaction products. In the application of a tracer technique the presence of acetaldehyde causes several complications, since ^{14}C labelled acetonitrile is transformed into ^{14}C labelled acetaldehyde. The chemisorption of acetaldehyde is by no means negligible, and thus the results obtained by the tracer technique will be ambiguous, since they refer only to the total amount of ^{14}C labelled adsorbed molecules. The formation of labelled amines, alone, would not cause difficulties, since under the given experimental conditions the adsorption of amines is insignificant over a broad potential range. This was proved separately by investigating the adsorption of labelled ethylamine. In addition, further electrochemical reactions of acetaldehyde must also be taken into consideration, although the rates of these reactions may evidently be not too high, since otherwise they should have significantly modified the experimentally determined number of electrons, about two, required for the reduction of one mole of acetonitrile. As we have shown in our previous papers [11, 13], the following reactions may take place:

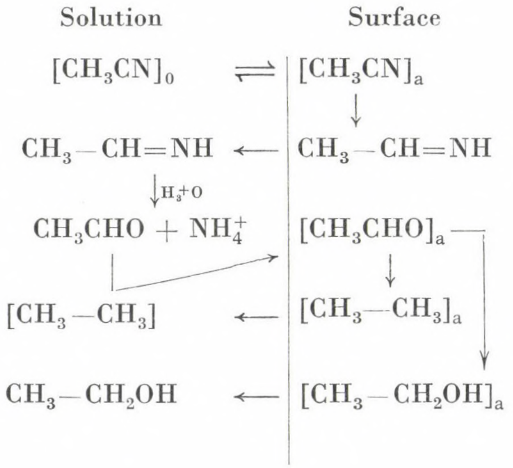


$$CH_3{-}CHO \begin{cases} \xrightarrow{4\,H^+ + 4e} CH_3{-}CH_3 + H_2O \\ \xrightarrow[2\,H^+ + 2e]{} CH_3{-}CH_2OH \end{cases}$$

The formation of ethane can, indeed, be detected during reduction in a closed system at relatively high acetonitrile concentrations, and therefore there may be no doubt concerning the reality of the overall process

$$CH_3CN + 7\,H^+ + 6e \rightarrow CH_3{-}CH_3 + NH_4^+$$

The result of such experiments are shown in Fig. 4. On applying much higher initial acetonitrile concentrations then above, intense gas evolution can be observed in the final stage of the complete reduction. According to the gas chromatographic analysis of the product, the gas consists predominantly of ethane, *i.e.* acetonitrile is really transformed into ethane. It is obvious from the above that the acetaldehyde intermediate, enriched in the reaction medium, was reduced. Of course, in addition to ethane, ethanol may also be expected to form. The complete process can be characterized by the following scheme:



Finally, on the basis of the polarization curve of acetonitrile one can estimate the potential range over which the adsorption of acetonitrile cannot be studied owing to the formation and interference of reduction products. A polarization curve measured at not too low concentrations can be seen in Fig. 5. In a log *i* *vs.* *E* plot a straight line is obtained with a slope of *ca.* 1/60 mV^{-1}. The slope

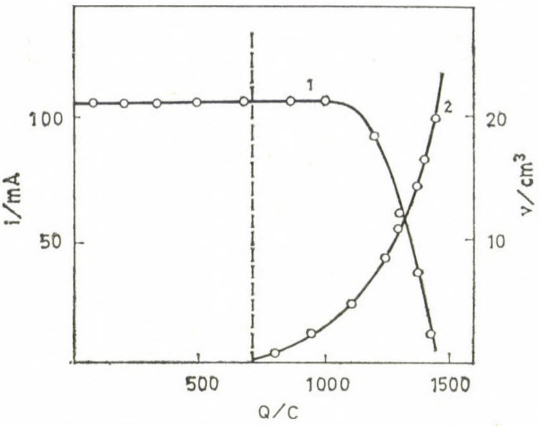


Fig. 4. Reduction current (1) and the volume of gas evolved (2) as a function of the charge passing through the system, in the reduction of 3.8×10^{-3} mol of acetonitrile in a closed system at 50 mV (the dashed line denotes the charge corresponding to the reaction $CH_3-CN \rightarrow CH_3CH=NH$)

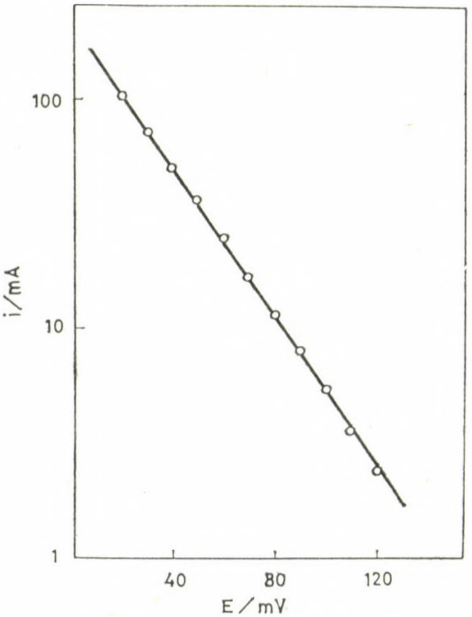


Fig. 5. The polarization curve of acetonitrile ($c = 5 \times 10^{-2}$ mol/dm^3)

of the polarization curve suggests that the rate-determining step of reduction is presumably a reaction between adsorbed acetonitrile and adsorbed hydrogen atoms.

The polarization measurements show that in the investigation of adsorption the interference of the reduction products of acetonitrile becomes negligible only above 200 mV.

At this point it was a fundamental question whether there is, indeed, a reversible adsorption of acetonitrile at the potentials corresponding to the double-layer section of the charge curves, as suggested by the references cited above.

By investigating the mobility of adsorbed molecules we have concluded that the adsorption of acetonitrile cannot be regarded unambiguously as irreversible process. This is supported by the experimental results on the exchange between adsorbed, labelled and dissolved, non-labelled acetonitrile molecules. After the adsorption of labelled acetonitrile, we added a large excess of non-labelled acetonitrile to the system, and observed a decrease in the radioactivity of the adsorption layer, indicating that a part of labelled, adsorbed acetonitrile was replaced on the electrode surface (Fig. 6). However, depending on the conditions, only some fraction of the adsorbed substance was observed to leave the surface at an appreciable rate.

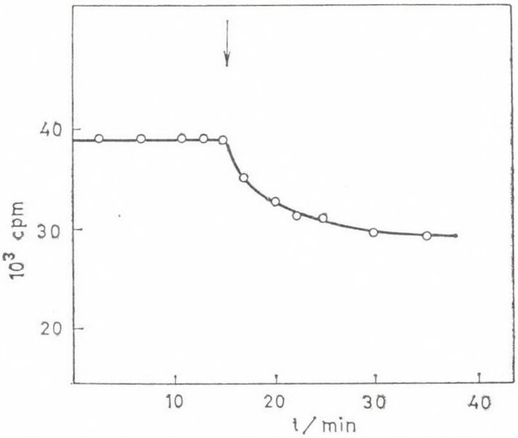


Fig. 6. Exchange of labelled adsorbed acetonitrile with non-labelled acetonitrile added to the solution at the point marked with the arrow. $E = 400$ mV. (Initial concentration 4×10^{-3}, final concentration 1×10^{-1} mol/dm^3)

The above results show that —

1) The adsorption process is not completely irreversible.

2) In a relatively wide potential range a steady reduction process occurs, which restricts the possibilities for studying the behaviour of chemisorbed molecules, and the comparison of the results to those obtained with a bright platinum electrode.

One must also take into account that at the concentrations applied in direct tracer methods the adsorption rate of acetonitrile is low, and it cannot be determined safely whether equilibrium or a steady state has been reached.

With the indirect adsorption technique this difficulty can be eliminated to a certain extent owing to the higher acetonitrile concentrations applicable.

B) *Indirect tracer measurements*

In the indirect tracer method, labelled Cl^- ions were used, and the adsorption of these ions was investigated after the adsorption of non-labelled acetonitrile. In the first stage of the experiment the electrode was contacted with an acetonitrile solution of given concentration (10^{-3} to 10^{-1} mol/dm^3) at a constant potential (*e.g.* 400 mV) for 2—2.5 hours. Then, a very dilute solution (10^{-4} mol/dm^3) of labelled chloride ions was added to the system, and the activity of adsorbed chloride ions was measured (in cpm) as a function of time. After reaching the equilibrium or steady state the potential of the electrode was reset to another value, and the changes in the adsorption of chloride ions were measured again. The results of these experiments are shown in Fig. 7.

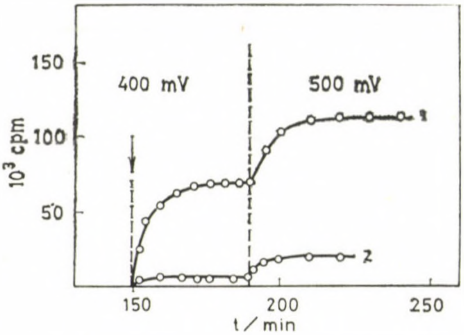


Fig. 7. The adsorption of Cl^- ions in the presence of acetonitrile. Labelled chloride ions were added to the system at the point marked with the arrow. $c_{Cl^-} = 10^{-4}$; $c_{AN} = 6 \times 10^{-3}$ (1) and 3×10^{-2} (2) mol/dm^3

The potential dependence of the adsorption of chloride ions for various acetonitrile concentrations is shown in Fig. 8.

The first important conclusion drawn from these results is that the adsorption of chloride ions at constant potential depends on the concentration of acetonitrile. It the adsorption of acetonitrile were irreversible, as suggested by the results pertaining to a bright platinum electrode [1—3], this phenomenon would obviously not occur.

It is also important that the adsorption of Cl^- ions increases monotonically with the potential at all acetonitrile concentrations, which is also in contradiction with the assumption that there is only a chemisorbed aceto-

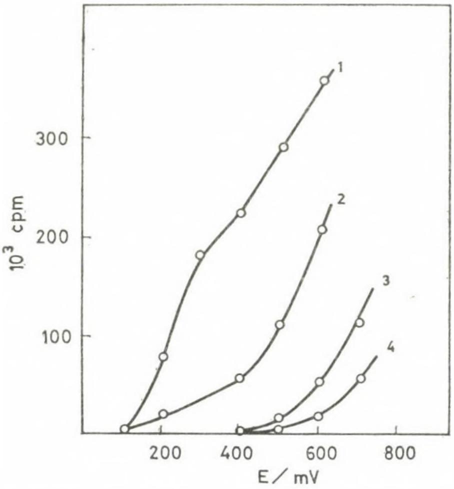


Fig. 8. **The potential dependence of the adsorption of Cl$^-$ ions at various concentrations of acetonitrile. $c_{Cl^-} = 10^{-4}$; $c_{AN} = 0$ (1); 6×10^{-3} (2); 3×10^{-2} (3); 3×10^{-1} (4) mol/dm^3**

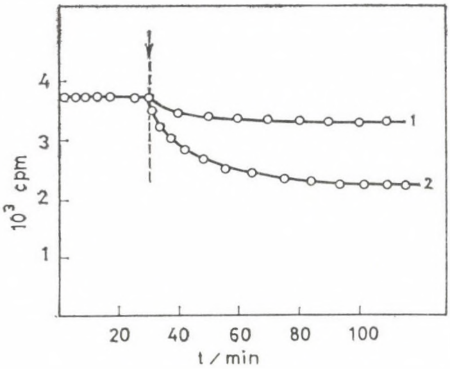


Fig. 9. The effect of acetonitrile on the adsorption of labelled Cl$^-$ ions at 500 mV. $c_{Cl^-} = 10^{-4}$ $c_{AN} = 3\times10^{-4}$ (1) and 2×10^{-3} (2) mol/dm^3

nitrile layer on the surface of the electrode which remains there in a broad potential range. Although in the cases investigated the concentration of acetonitrile was higher, sometimes by several orders, than that of the Cl$^-$ ions, remarkable anion adsorption could be observed, particularly at potentials higher than 500 mV.

When Cl$^-$ ions were adsorbed first at the given potential and then acetonitrile was added to the system in a concentration commensurable with that of Cl$^-$ ions, the adsorption replacement of adsorbed Cl$^-$ ions was very small, as illustrated in Fig. 9.

Conclusions

The experimental results obtained for platinized platinum electrode can be brought into harmony with the relationships concerning bright platinum electrode, published in the literature, only if it is assumed that acetonitrile has at least two independent adsorption states. This assumption is not far-fetched at all, if one takes into account that the oxidation mechanism of simple organic compounds (*e.g.* alcohols) can be interpreted only by assuming different adsorption states. The formation of the two species may be illustrated by the following simple scheme:

$$\begin{tikzcd} {[\mathrm{CH_3CN}]_0} \arrow[r, shift left] \arrow[dr] & {[\mathrm{CH_3CN}]^1_a} \arrow[l, shift left] \\ & {[\mathrm{CH_3CN}]^2_a} \end{tikzcd}$$

The adsorbed species denoted with superscript 2 is assumed to adsorb irreversibly and to remain on the surface in a wide potential range. Its behaviour corresponds to the relationships found with bright platinum electrodes.

The adsorbed species denoted with superscript 1 can be regarded as mobile, and it is probably this species that plays a role in the stationary reduction reaction characterized by the equation

$$[\mathrm{CH_3CN}]^1_a + \mathrm{H_a} \rightarrow [\mathrm{CH_3CH{=}N}\cdot]_a \xrightarrow{\mathrm{H_a}} [\mathrm{CH_3{-}CH{=}NH}]_a$$

Furthermore, it must be assumed that the two types of adsorption take place at different adsorption sites, and they are probably independent of one another.

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ON THE ROLE OF BROMIDE IONS IN THE BELOUSOV-ZHABOTINSKII REACTION OF MALONIC ACID

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It is shown experimentally that in strongly acidic media the bromide sensitive electrode gives a response to hypobromous acid (or to Br^+ ions) as well. It is rather probable that the potential oscillations of the same electrode in the BZ reaction can be explained in this way. Theoretical difficulties in the current theories of the BZ reaction caused by the different "jump down" and "jump up" critical concentrations of bromide ions are also discussed.

Introduction

Theory of Bromide Controlled Oscillations

In the current theories of the well known Belousov—Zhabotinskii (BZ) reaction of malonic acid the bromide ion plays a rather important role [1, 2]. The usual explanation of the observed oscillations is based on the following system of chemical processes:

A) Inorganic reactions [3]

$$HOBr + Br^- + H^+ \xrightarrow{k_1} Br_2 + H_2O \quad (R1)$$

$$HBrO_2 + Br^- + H^+ \xrightarrow{k_2} 2\,HOBr \quad (R2)$$

$$BrO_3^- + Br^- + 2\,H^+ \xrightarrow{k_3} HBrO_2 + HOBr \quad (R3)$$

$$2\,HBrO_2 \xrightarrow{k_4} BrO_3^- + HOBr + H^+ \quad (R4)$$

$$BrO_3^- + HBrO_2 + H^+ \xrightarrow{k_5} 2\,BrO_2\cdot + H_2O \quad (R5)$$

$$BrO_2\cdot + Ce^{3+} + H^+ \underset{k_{-6}}{\overset{k_6}{\rightleftharpoons}} HBrO_2 + Ce^{4+} \quad (R6)$$

$$BrO_2\cdot + Ce^{4+} + H_2O \xrightarrow{k_7} BrO_3^- + Ce^{3+} + 2\,H^+ \quad (R7)$$

B) Bromination of malonic acid by Br_2 or by HOBr [3]

$$Br_2 + MA \longrightarrow BrMA + Br^- + H^+ \qquad (R8)$$

$$HOBr + MA \longrightarrow BrMA + H_2O \qquad (R8a)$$

Here MA and BrMA stand for malonic and bromomalonic acid, respectively.

C) Bromide production by Ce^{4+} and other reactions involving organic substrates [4]

$$Ce^{4+} + MA + BrMA + H_2O \rightarrow Ce^{3+} + FBr^- + \text{other products} \qquad (C)$$

Process "C" and the so called "organic reaction subset" [5] is not known in all details [4, 6], but here we are going to deal mainly with the inorganic reaction subset of "A".

According to detailed calculations [2], the autocatalytic oxidation of Ce^{3+} by acidic bromate — (R5) and (R6) — can begin exclusively when the bromide concentration decreases below a critical value

$$[Br^-]_{\text{crit}}^{\text{jump down}} = \frac{k_5}{k_2}[BrO_3^-] \qquad (1.1)$$

At that moment, the start of the autocatalytic accumulation of $HBrO_2$ causes a sudden fall of the bromide concentration because of reaction (R2) ("jump down" [7] or "rapid bromide consumption period" [3]). In the next phase the bromide concentration is increasing slowly ("slow bromide production period" [3]) because of process "C" and reaching another critical value [3]:

$$[Br^-]_{\text{crit}}^{\text{jump up}} = \frac{k_5[BrO_3^-][H^+]\{k_6[Ce^{3+}][H^+] - k_7[Ce^{4+}]\} - k_{-6}k_7[Ce^{4+}]^2}{k_2[H^+]\{k_6[Ce^{3+}][H^+] + k_7[Ce^{4+}]\}} \qquad (1.2)$$

it stops the Ce^{4+} production. (Actually (1.1) is a special case of (1.2): if $Ce^{4+} \ll Ce^{3+}$, then Eq. 1.2 simplifies to (1.1).)

At this point a sudden rise of the bromide concentration appears ("jump up" [7] or "rapid bromide production period" [3]) and a new cycle begins.

That is, in the classical theories the bromide ion is a control intermediate, the concentration variations of which can "turn on" and "turn off" the autocatalytic Ce^{4+} production. However, recently some new BZ systems were discovered which are difficult [8, 9] or impossible [10] to regard as bromide controlled oscillators. Thus it seemed reasonable to reexamine the experimental facts and their theoretical interpretation suggesting a decisive role for the bromide ion in the BZ reaction of malonic acid.

Formulation of the Problem: the Bromide Sensitive Electrode in the BZ Reaction

It was ZHABOTINSKII [1] who first observed that the presence of bromide ions could inhibit the autocatalytic oxidation of Ce^{3+} by acidic bromate but he had not proved experimentally the presence of bromide ions in the BZ reaction. Later on FIELD, KŐRÖS and NOYES (FKN) [2] have found that the potential of a bromide sensitive electrode oscillates synchronously with the redox potential of the BZ system. Their results were in rather good agreement with ZHABOTINSKII's theoretical predictions: when the bromide concentration was high, the Ce^{4+} concentration was decreasing (the autocatalytic process was "switched off") and when the bromide concentration was low, the Ce^{4+} concentration was increasing (the autocatalytic process was "switched on"). However, one problem appeared concerning the experimental data: all the measured bromide concentrations were curiously low. Even the maximal values were around $\sim 10^{-6}$ M, not to mention the minimal values of 10^{-7} M. GEISELER and FÖLLNER [11] followed the reaction of Ce^{3+} with acidic bromate by a bromide sensitive electrode and they could measure still smaller bromide concentrations: between 10^{-7} and 10^{-8} M when the reaction was over. Before the start of the reaction, they recorded a bromide concentration of $\sim 10^{-6}$ M. It is known [12] that a bromide concentration of 10^{-6} M can be measured by a bromide sensitive electrode in an originally bromide-free solution due to the solubility product of AgBr $K_s = 7 \times 10^{-13}$ M^2 at 25 °C [13]. FKN [2] report that "In static systems the electrode did not respond linearly to still lower bromide concentrations (that is below 10^{-6} M); however, it did appear to behave ideally during short periods of depleted bromide ion". In other words, they think that even if the bromide sensitive electrode does not behave ideally, its potential variations are mainly due to the bromide concentration variations of the oscillating solution. Nevertheless, the steady bromide concentration of nearly two orders of magnitude below 10^{-6} M measured by GEISELER and FÖLLNER [11] suggests that a stable "depletive" agent has to be present which removes the bromide ions coming from the electrode continuously. At this point two problems arise:

1) Which chemical component is the depletive agent?

2) If such an agent exists, how can it exert its influence on the electrode potential?

In the following we wish to propose a possible answer to the above questions based on some experiments with a bromide sensitive electrode.

Experimental

Materials and Methods

The chemicals used were of reagent grade and the hypobromous acid was prepare feshly according to the literature [14]: Ag_2SO_4 was added inexcpess to bromine and the hypobromous acid was distilled in vacuum. The product was diluted: one part of it was added to four parts of 0.1 *M* sulfuric acid. The stock solution of HOBr produced in this way was stored for some hours before the experiments at 0 C°. According to titrations by 0.01 *M* KBr in the presence of a bromide selective electrode as an indicator, some hours after the preparation it was a 0.053 *M* solution of HOBr (in ~0.02 *M* solution of sulfuric acid). All the other reagent solutions contained sulfuric acid in 1.5 *M* concentration.

We used a "home made" bromide sensitive electrode based on a disc of pure AgBr. The electrode was prepared according to a method described by PUNGOR *et al.* [15] and it was filled with an inner reference solution of 0.01 *M* $AgNO_3$ contacting a silver wire inner electrode and the AgBr disc as well. (The widely used "Orion" bromide sensitive electrode is slightly different: it contains a pellet made of a $AgBr-Ag_2S$ mixture [12]).

The reference electrode was a satured calomel electrode (Radelkis OP-830) connected via a "salt" bridge containing 1.5 *M* sulfuric acid solution.

The electromotive force of the galvanic cell described above was measured by a millivoltmeter (Radelkis TR-1456) connected to a recorder (Radelkis OH-814) to display the potentiometric traces.

The experiments were carried out in continuously stirred solutions (~60 rpm).

Effect of Hypobromous Acid on the Bromide Sensitive Electrode

As a first step we repeated GEISELER's experiments in a modified form (without bromide ion). The results of the experiment depicted in Figure 1a show clearly that some depletive agent must be present, causing a permanently low level of the measured bromide concentration. (The "bromide concentration" was calculated assuming an ideal Nernstian response of the electrode as usual [2, 3, 11].) It can be seen as well (Figures 1a and 1b) that neither Ce^{3+} nor Ce^{4+} nor bromate can produce alone the measured change of electrode potential, only a reaction between Ce^{3+} and bromate yields the observed effect.

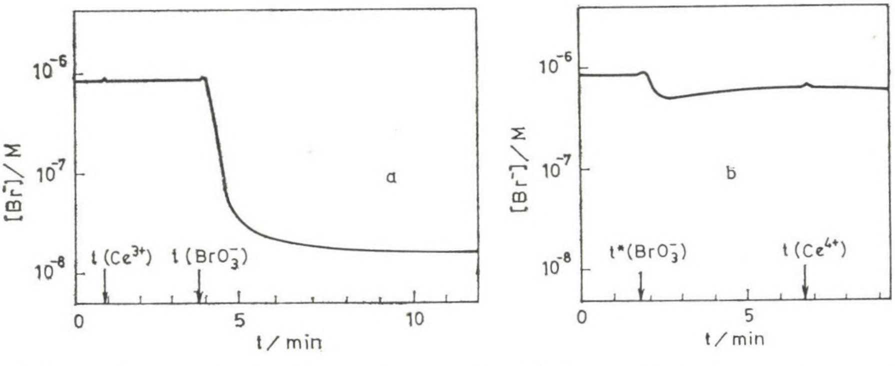

Fig. 1. "Bromide concentration changes" measured by the bromide selective electrode in two experiments

Experiment a): At the moment $t(Ce^{3+})$, 8 cm^3 of 10^{-3} *M* $Ce(NO_3)_3$ solution was added to 40 cm^3 of 1.5 *M* H_2SO_4 solution. No change of the electrode potential was observed. At the momen $t(BrO^-)$, 2 cm^3 potassium bromate solution ($[KBrO_3] = 8\times10^{-2}$ *M*) was added to the mixture establishing the following initial concentrations: $[Ce^{3+}] = 1.6\times10^{-4}$ *M* $[KBrO_3] = 3.2\times10^{-3}$ *M*, $[H_2SO_4] = 1.5$ *M*

Experiment b): At the moment $t^*(BrO_3^-)$, 2 cm^3 potassium bromate solution ($[KBrO_3] = 8\times10^{-2}$ *M*) was added to 48 cm^3 1.5 *M* H_2SO_4 solution (no Ce^{3+} was present). At the moment $t(Ce^{4+})$, 2 cm^3 Ce^{4+} solution ($[Ce(SO_4)_2] = 4\times10^{-2}$ *M*) was added to the mixture. No measurable change of the electrode potential was detected

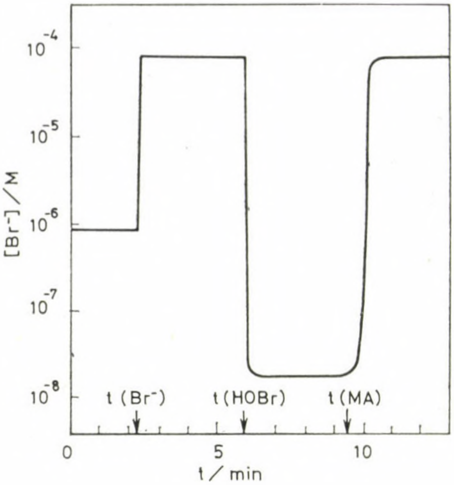

Fig. 2. Bromide concentration changes due to bromide ions and hypobromous acid. At the moment $t(\mathrm{Br}^-)$, 0.4 cm^3 potassium bromide solution ($[\mathrm{KBr}] = 10^{-2}$ *M*) was added to 40 cm^3 of 1.5 *M* H_2SO_4. At the moment $t(\mathrm{HOBr})$, 0.2 cm^3 hypobromous acid solution ($[\mathrm{HOBr}] = 5.3 \times 10^{-2}$ *M*) was introduced. At the moment $t(\mathrm{MA})$, 0.7 cm^3 malonic acid solution ($[\mathrm{CH_2(COOH)_2}] = 0.2$ *M*) was added

It is straightforward to assume that the depletive agent is an end product of the Ce^{3+}—bromate reaction. The stoichiometry of this reaction was reported by THOMPSON [16], who claims that hypobromous acid appears in the mixture according to (2.1)

$$5\,\mathrm{H}^+ + 4\,\mathrm{Ce}^{3+} + \mathrm{BrO}_3^- \rightarrow 4\,\mathrm{Ce}^{4+} + \mathrm{HOBr} + 2\,\mathrm{H_2O} \tag{2.1}$$

Thus hypobromous acid is a rather plausible candidate for the unknown depletive agent especially because of its very fast reaction (R1) [17]. To check this hypothesis, we recorded the response of our bromide sensitive electrode for hypobromous acid. The results of the experiment depicted in Figure 2 show that

1) Hypobromous acid can really change the potential of the bromide sensitive electrode in the expected way: it establishes apparent bromide concentrations much below 10^{-6} *M*.

2) The hypobromous acid used in our experiments was free of contaminating silver ions, that is the detected change of the electrode potential is due solely to hypobromous acid. To prove this malonic acid was added to a reaction mixture of bromide and hypobromous acid and in this way the same bromide level could be restored which was measured before the addition of hypobromous acid to the bromide solution.

We made a systematic calibration of the bromide sensitive electrode with hypobromous acid and with bromide and silver ions. The results can be seen in Figure 3. $\Delta\varepsilon^{\mathrm{M}}$ is the measured electrode potential change due to the species mentioned above. The theoretical values for $\Delta\varepsilon^{\mathrm{T}}$ were calculated according to the following expressions [18]

$$\Delta\varepsilon^{\mathrm{T}}_{\mathrm{Br}} = 59 \lg \frac{[\mathrm{Br}^-]_{\mathrm{c}} + \sqrt{[\mathrm{Br}^-]^2_{\mathrm{c}} + 4\,K_{\mathrm{s}}}}{2\sqrt{K_{\mathrm{s}}}} \ \mathrm{mV} \tag{2.2}$$

$$\Delta\varepsilon^{\mathrm{T}}_{\mathrm{Ag}} = -59 \lg \frac{[\mathrm{Ag}^+]_{\mathrm{c}} + \sqrt{[\mathrm{Ag}^+]^2_{\mathrm{c}} + 4\,K_{\mathrm{s}}}}{2\sqrt{K_{\mathrm{s}}}} \ \mathrm{mV} \tag{2.3}$$

where $[\mathrm{Br}^-]_{\mathrm{c}}$ and $[\mathrm{Ag}^+]_{\mathrm{c}}$ are the concentrations of the bromide and silver ions introduced into the solution for calibration. (The actual concentrations are higher because of the solubility of the silver bromide precipitate.) $\Delta\varepsilon^{\mathrm{T}}_{\mathrm{Br}}$ and $\Delta\varepsilon^{\mathrm{T}}_{\mathrm{Ag}}$ are the theoretical electrode potential changes caused by the introduction of bromide and silver ions respectively. ($\Delta\varepsilon^{\mathrm{M}}$ and $\Delta\varepsilon^{\mathrm{T}}$ were regarded

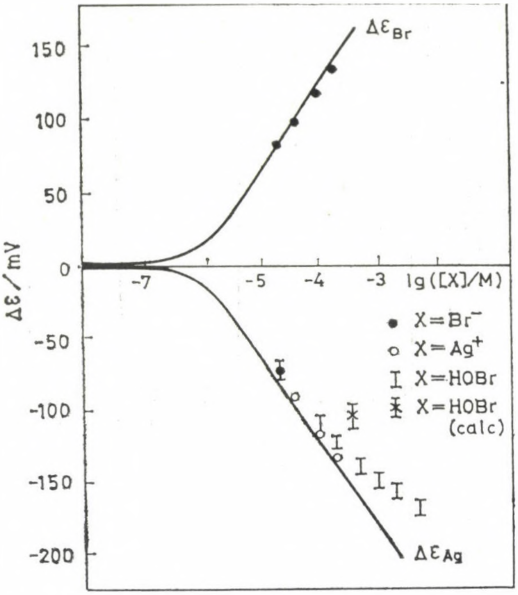

Fig. 3. Calibration of the bromide selective electrode by bromide and silver ions and by hypobromous acid. The solid curves are theoretical ones calculated according to Eqs (2.2) and (2.3). The points are measured values. The point X = HOBr (calc) is calculated from the experiment depicted in Figure 1a. It was assumed that the hypobromous acid concentration can be calculated according to the stoichiometry of (1.1)

as positive if the bromide concentration was increasing.) The reproducibility of the calibration points for hypobromous acid below 10^{-5} *M* was not as good as between 10^{-5} *M* and 10^{-4} *M*. It is rather probable that some trace amount of an unknown material reducing hypobromous acid disturbed our measurements in the low concentrations region.

In Figure 4 the electrode potential changes and the apparent bromide concentration changes observed with the bromide selective electrode are depicted in the induction period

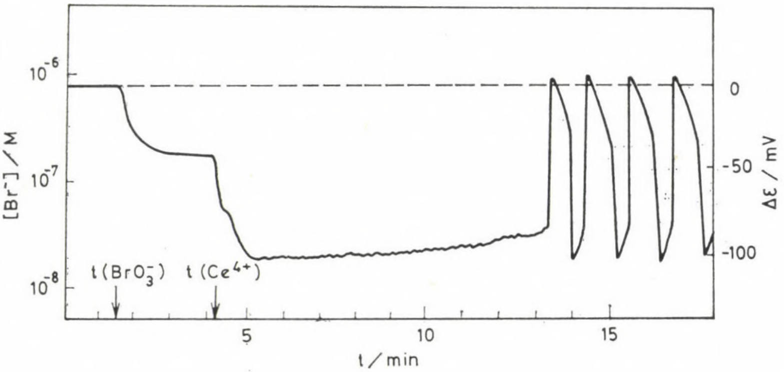

Fig. 4. Potential changes of the bromide sensitive electrode in the BZ reaction of malonic acid. At the moment $t(BrO_3^-)$, 40 cm³ potassium bromate solution ($[KBrO_3) = 8\times10^{-2}$ *M*) was added to 40 cm³ malonic acid solution $[CH_2(COOH)_2] = 0.2$ *M*. At the moment $t(Ce^{4+})$, 2 cm³ Ce^{4+} solution ($[Ce(SO_4)_2] = 4\times10^{-2}$ *M*) was added to the mixture. The concentration of H_2SO_4 was 1.5 *M* in all of the solutions

and during oscillations in the BZ reaction of malonic acid. It is interesting to observe that all the changes in the electrode potential (within the experimental error) are in the "silver ion (or hypobromous acid) region", that is $\Delta\varepsilon < 0$.

Discussion

An Explanation for the Hypobromous Acid Response of the Bromide Selective Electrode

The comparison of the calibration points for hypobromous acid and for the silver ions show that their effects are nearly the same. This fact suggests that hypobromous acid produces silver ions on the surface of the electrode. In a rather usual and simple picture [19] we can imagine this process as it is shown in Figure 5.

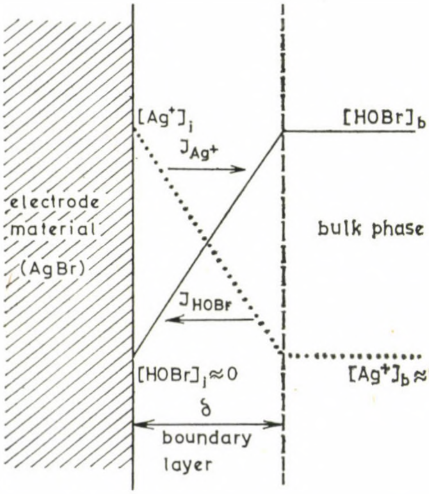

Fig. 5. Concentration profiles of silver ions (dotted line) and of hypobromous acid (solid line) near the surface of the bromide sensitive electrode in the steady state. See text for the explanation of notation

Due to the dissolution of the electrode material, silver and bromide ions appear at the electrode-electrolyte interface. The silver ions diffuse through the adhering boundary layer to the bulk solution, where their concentration is practically zero. The bromide ions however react with hypobromous acid in the rapid reaction of (R1) at the electrode-electrolyte interface. (It is possible that the active species in (R1) is not hypobromous acid but Br^+ ions [20] but this does not change the following theoretical considerations, only the notation alters.) Due to this reaction, the concentration of hypobromous acid at the electrode-electrolyte interface is much lower than its concentration in the bulk phase. Thus hypobromous acid will diffuse continuously from the bulk phase to the interface through the boundary layer.

In steady state the molar current densities of silver ($\mathbf{J}_{Ag^+}$) and of hypobromous acid ($\mathbf{J}_{HOBr}$) are equal but they flow in opposite directions, that is

$$\mathbf{J}_{Ag^+} = -\mathbf{J}_{HOBr} \tag{3.1}$$

Applying Fick's law, we get the following expressions

$$\mathbf{J}_{Ag^+} = -D_{Ag^+}\frac{[Ag^+]_b - [Ag^+]_i}{\delta} \approx D_{Ag^+}\frac{[Ag^+]_i}{\delta} \tag{3.2}$$

provided that

$$[Ag^+]_b \ll [Ag^+]_i \tag{3.3}$$

similarly

$$\mathbf{J}_{HOBr} = -D_{HOBr}\frac{[HOBr]_b - [HOBr]_i}{\delta} \approx -D_{HOBr}\frac{[HOBr]_b}{\delta} \tag{3.4}$$

provided that

$$[HOBr]_i \ll [HOBr]_b \tag{3.5}$$

In Eqs (3.1)—(3.5) the following notation was used

D_{Ag^+}, D_{HOBr}	are the diffusion coefficients of silver ion and of hypobromous acid,
δ	is the thickness of the boundary layer,
$[Ag^+]_i$, $[Ag^+]_b$	are silver ion concentrations at the electrode-electrolyte interface and in the bulk of the solution,
$[HOBr]_i$, $[HOBr]_b$	are hypobromous acid concentrations at the interface and in the bulk phase.

On the basis of Eqs (3.1)—(3.5) we can write

$$[Ag^+]_i = [HOBr]_b\frac{D_{HOBr}}{D_{Ag^+}} \tag{3.6}$$

The electrode potential ε of the bromide sensitive electrode in the presence of silver ions can be given in the following form [12]

$$\varepsilon = \varepsilon_0 + \frac{RT}{F}\ln[Ag^+]_i \tag{3.7}$$

Expression (3.6) can be substituted into (3.7) giving (3.8):

$$\varepsilon = \varepsilon_0 + \frac{RT}{F}\ln[HOBr]_b + \frac{RT}{F}\ln\frac{D_{HOBr}}{D_{Ag_+}} \tag{3.8}$$

If the two diffusion coefficients are not too different, that is

$$D_{\mathrm{HOBr}} \approx D_{\mathrm{Ag^+}} \tag{3.9}$$

then

$$\varepsilon \approx \varepsilon_0 + \frac{RT}{F} \ln [\mathrm{HOBr}]_\mathrm{b} \tag{3.10}$$

which expression describes rather well the experimental findings in the concentration range of 10^{-6}—10^{-4} M HOBr.

Possible Interpretations of the Potential Oscillations of the Bromide Sensitive Electrode in the BZ Reaction

If we look at the potential range of the oscillations measured in the BZ reaction by the bromide selective electrode (Figure 4), we can see that it falls into a region where the electrode potential is controlled by silver ions or by hypobromous acid.

Thus it is rather probable that the measured changes in the "bromide level" of the oscillating solution are due to variations of the hypobromous acid concentration.

We have to mention that this idea is not entirely new: TOCKSTEIN and HANDLIŘOVA [21] and ZHABOTINSKII [22] were suspecting such effects. TOCKSTEIN and HANDLIŘOVA [21] investigated the uncatalyzed oscillatory reaction of bromate ion with phenols and they state that in their system "the ion-selective electrode does not indicate oscillations of concentration of bromide ion but that ions in which bromine is in higher oxidation state". According to a recent remark of ZHABOTINSKII [22]: "it is likely that compounds similar to $HBrO_2$ and HOBr reacting rapidly with Br^- in solution can also react with Br^- on the electrode surface and thus strongly affect its potential".

Now we have two extreme possibilities to interpret the potential variations of the bromide sensitive electrode in the BZ reaction.

1) There is no connection at all between the measured electrode potential and the actual bromide concentration of the bulk phase

2) Some complicated and unknown but definite connection exists. Some rapid processes could establish such a connection. For example if the bromine concentration were constant, the bromide concentration could be expressed by the potential determining hypobromous acid concentration

$$[\mathrm{Br^-}] = \frac{[\mathrm{Br_2}]}{K[\mathrm{H^+}][\mathrm{HOBr}]} \tag{3.11}$$

where

$$K = \frac{k_1}{k_{-1}} \tag{3.12}$$

k_1 and k_{-1} are rate constants of the reaction (R1). (This is only a hypothetical example because it is proved experimentally [23, 24] that the concentration of bromine is not constant in the BZ reaction.) Thus it is not impossible that somehow a complicated — perhaps non Nernstian — relation can be found, according to which, the electrode potential can be expressed as a function of the bromide concentration of the bulk phase:

$$\varepsilon = f\{[\mathrm{Br}^-]_\mathrm{b}\} \tag{3.13}$$

In the following we shall examine the theoretical consequences of the second interpretation.

On the Two Critical Bromide Concentrations

We have seen in the introduction that there are two critical bromide concentrations: $[\mathrm{Br}^-]_\mathrm{crit}^\text{jump down}$ and $[\mathrm{Br}^-]_\mathrm{crit}^\text{jump up}$. Using expressions (1.1) and (1.2), we can write

$$[\mathrm{Br}^-]_\mathrm{crit}^\text{jump up} = [\mathrm{Br}^-]_\mathrm{crit}^\text{jump down} \frac{1 + \dfrac{k_7}{k_6[\mathrm{H}^+]}\dfrac{[\mathrm{Ce}^{4+}]}{[\mathrm{Ce}^{3+}]} - \dfrac{k_{-6}k_7[\mathrm{Ce}^{4+}]^2}{k_6k_5[\mathrm{BrO}_3^-][\mathrm{H}^+]^2[\mathrm{Ce}^{3+}]}}{1 + \dfrac{k_7}{k_6[\mathrm{H}^+]}\dfrac{[\mathrm{Ce}^{4+}]}{[\mathrm{Ce}^{3+}]}} \tag{3.14}$$

On the basis of Eq. (3.14), we can calculate the ratio of the two critical concentrations collecting the required numerical data. It was assumed [5, 26, 27] that $k_{-6} = 2.4 \times 10^7\ M^{-1}\,\mathrm{s}^{-1}$. However, recently SULLIVAN and THOMPSON [25] have proved experimentally that $k_{-6} \approx 0$. According to measurements [24],

$$\frac{[\mathrm{Ce}^{4+}]}{[\mathrm{Ce}^{3+}]} \leq 0.3 \tag{3.15}$$

Several authors [5, 26, 27] claim that $k_6 = 6.5 \times 10^5\ M^{-2}\,\mathrm{s}^{-1}$. The value of k_7 is not so well defined, it is "decreasing". Its "oldest" value is $9.4 \times 10^4\ M^{-1}\,\mathrm{s}^{-1}$ [26] (1975) the "newest" one is $1.7 \times 10^{-1}\ M^{-1}\,\mathrm{s}^{-1}$ [5] (1979). The hydrogen ion concentration $[\mathrm{H}^+] \approx 1$. Using all these data

$$\frac{[\mathrm{Br}^-]_\mathrm{crit}^\text{jump down}}{[\mathrm{Br}^-]_\mathrm{crit}^\text{jump up}} \equiv R \tag{3.16}$$

$$1.0000002 \leq R \leq 1.1 \tag{3.17}$$

Now we can see that the ratio "R" must be rather near to 1, especially if we see the latest data. Thus the two critical bromide concentrations should have been the same in theory. However, according to measurements [2, 24] $R \approx 3$, which is very much larger than the expected value.

Conclusion

If we regard bromide ion as a control intermediate of the BZ reaction of malonic acid, we have to face a serious dilemma. Provided there is some definite relation between the potential of the bromide selective electrode and the concentration of bromide ion we cannot explain the two different critical concentrations ("up" and "down"). We may say that there is no definite relation between those variables. Our experiments show that the response of the bromide selective electrode is probably due to hypobromous acid and gives no information about the bromide concentration of the bulk phase. However, in this way we lose the only direct experimental evidence for the decisive role of bromide ions in the BZ reaction.

*

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STEREOSELECTIVE REDUCTION OF A HYDROXY-METHYLENE KETO STEROID

(PRELIMINARY COMMUNICATION)

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15-Formyl-16-keto-3β,17β-di-(2'-tetrahydropyranyloxy)-5-androstene was reduced stereoselectively to the 15α-hydroxymethyl-16β-hydroxy derivative; chemical and ^{1}H—NMR evidence for the steric structures of the compounds are given.

15-Formyl-16-keto-3β,-17β-di-(2'-tetrahydropyranyloxy)-5-androstene (**1**) was prepared from 3β,17β-di-(2'-tetrahydropyranyloxy)-16-keto-5-androstene by the formylation process generally applied [1]. The brown oily formyl derivative (**1**) was reduced without further purification with sodium borohydride in methanol, giving rise to two isomeric diols (**2a**) which were separated on alumina. The less polar compound had a melting point of 172—175°C and $[\alpha]_D$ $-36° \pm 2°$ (*c* 1, *abs.* methanol) the more polar one 184—187°C and $[\alpha]_D$ $+44° \pm 2°$ (*c* 1, *abs.* methanol). The **2a** mixture of diols gave the diacetates **2b** with m. p. 123—126°C, $[\alpha]_D$ $-30° \pm 2°$ (*c* 1, chloroform) and m. p. 128—131°C, $[\alpha]_D$ $-48° \pm 8°$ (*c* 0.25, chloroform), and the acetonides **2c**: m. p. 123—126°C, $[\alpha]_D$ $-64° \pm 2°$ (*c* 1, *abs.* methanol) and m. p. 124.5—127°C, $[\alpha]_D$ $+32° \pm 2°$ (*c* 1, *abs.* methanol). On acid-catalyzed hydrolysis the **2a** pair of diols, their acetates (**2b**) and acetonides (**2c**) all gave the same single tetraol isomer **2d**, m. p. 232—234°C, $[\alpha]_D$ $-28° \pm 4°$ (*c* 0.5, ethanol); thus, the pairs of compounds were isomeric on the chiral carbon atom of the tetrahydropyranyl ether moiety, and the reduction concerning the carbon atoms 15 and 16 was stereoselective.

^{1}H—NMR evidence for the configurations of the new asymmetric centres in the above compounds and the tetraacetate derivative **2e**, m. p. 176—178.5°C, $[\alpha]_D$ $-46° \pm 2°$, (*c* 1, chloroform), was not conclusive (H C—16 5.2 ppm, dd: $J_{16,17}$ 7.5 Hz, $J_{15,16}$ 4 Hz). Hence, we tried to determine the configurations by our chemical methods developed earlier in the case of 16-hydroxymethyl-17-hydroxysteroid derivatives.

Deacetylation of the diacetate **2b** on basic alumina did not show the selectivity expected [2]; besides the monoacetate **2f** (m. p. 158—161°C, $[\alpha]_D$ $+68° \pm 4°$, (*c* 0.5, chloroform) also the diol **2a** was obtained. The latter com-

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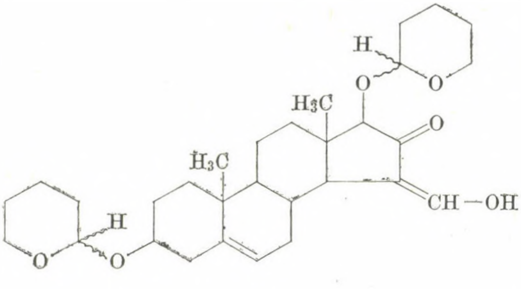

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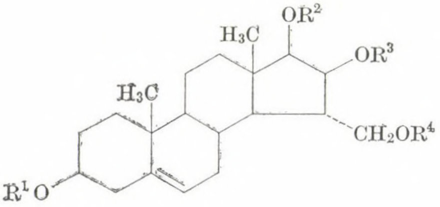

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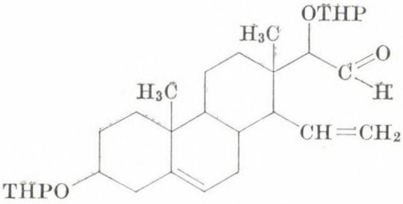

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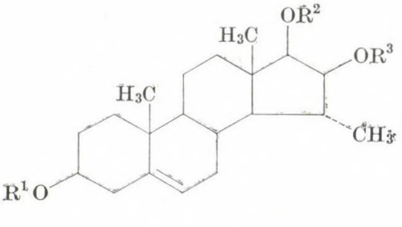

(4)

2	R^1	R^2	R^3	R^4
a	THP	THP	H	H
b	THP	THP	Ac	Ac
c	THP	THP	$H_3C{-}C{-}CH_3$	
d	H	H	H	H
e	Ac	Ac	Ac	Ac
f	THP	THP	Ac	H
g	H	$H_3C{-}C{-}CH_3$		H
h	H	H	$H_3C{-}C{-}CH_3$	
i	Ac	$H_3C{-}C{-}CH_3$		Ac
j	Ac	Ac	$H_3C{-}C{-}CH_3$	
k	Ac	$H_3C{-}C{-}CH_3$		H
l	THP	THP	Ac	Ts
m	THP	THP	H	CH_3
n	H	$H_3C{-}C{-}CH_3$		Ts
o	THP	THP	H	Ts

4	R^1	R^2	R^3
a	THP	THP	H
b	H	$H_3C{-}C{-}CH_3$	
c	H	H	H
d	Ac	Ac	Ac

pound may form through a deacetylation — acetyl-migration — deacetylation process. This involves the formation of a six-membered orthoester ring, which is possible here in the case of either *cis* or *trans* substituents.

The tetraol **2d** gave two different acetonide derivatives: **2g** (m. p. 251 — 254°C, $[\alpha]_D$ $-32° \pm 4°$, *c* 0.5, chloroform) and **2h** (m. p. 254—257°C, $]\alpha]_D$

—10° ± 2°, *c* 1, chloroform). Chemical evidence for their structures was provided by the treatment of the **2i** (m. p. 151.5—152.5°C, $[\alpha]_D$ —24° ± 2°, *c* 1, chloroform), and **2j** (m. p. 146—148°C, $[\alpha]_D$ —2° ± 2°, *c* 1, chloroform) acetonide diacetates with basic alumina, whereupon **2i**, containing a primary acetoxy group, was deacetylated to **2k** (m. p. 194—198°C, $[\alpha]_D$ —32° ± 4°, *c* 0.5, chloroform), while **2j** having secondary acetoxy groups, remained unaltered. The formation of the acetonide **2g** is possible only when the 16-hydroxy group is of β steric orientation.

Refluxing of the tosylate acetate **2l** (non-crystallizable oil, $[\alpha]_D$ —50° ± 5°, *c* 0.4, chloroform) in methanolic sodium hydroxide solution resulted in two products: **2m** (m. p. 62—65°C, $[\alpha]_D$ —58° ± 2°, *c* 1, chloroform) and **3** (oil, ^{1}H—NMR, 60 MHz: vinyl protons 5.2; H C-6 5.3; H-aldehyde 9.85 ppm) in equal amounts. Thus the reaction took place without neighbouring group participation, which would be expected if the 15-tosyloxymethyl and 16-acetoxy groups were in *cis*-position, and resulted in carbon-carbon bond fission, characteristic of *trans*-oriented substituents [3].

^{1}H—NMR evidence for the α-position of the 15-hydroxymethyl group was given by the investigation of **4d** (m. p. 182—185°C, $[\alpha]_D$ —56° ± 4°, *c* 0.5, chloroform), obtained from **2n** (oil) and **2o** (oil) by lithium aluminium hydride reduction [**4a** not isolated and **4b** (m. p. 156—160°C, $[\alpha]_D$ —24° ± 2°, *c* 1, chloroform)], then through acid-catalyzed hydrolysis **4c** and acetylation. The signal of the proton at C-16 is split to a double doublet with the coupling constants 7.5 ($J_{16,17}$) and 3.5 Hz ($J_{15,16}$), which are characteristic of 15 α, 16β, 17β-substitution [4].

*

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