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V. BRUCKNER, GY. DEÁK, K. POLINSZKY,
É. PUNGOR, G. SCHAY, Z. G. SZABÓ

REDIGIT

B. LENGYEL

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PAPER AND THIN-LAYER CHROMATOGRAPHIC STUDY OF OSMIUM COMPOUNDS

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Paper and thin-layer chromatographic methods were elaborated to separate and determine higher oxidation state osmium compounds. Paper-chromatographically, OsO_4 and $KOsO_3N$ or K_2OsO_4 and $KOsO_3N$ can be separated from each other by elution in an ethanol–water–HCl mixture at room temperature, on MN 214 chromatographic paper in an ascending system. All three osmium compounds can be separated by thin-layer chromatography on Kieselgel impregnated with KOH, elution being performed in acetone–butanol–pyridine, or acetone–butanol–acetic acid. After separation, development with thiourea/HCl and washing, the osmium contents of the spots can be determined quantitatively by spectrophotometry.

In earlier investigations [1] we have encountered the problem of the detection and determination of osmium compounds, in higher oxidation states, *e.g.* osmium tetroxide (OsO_4), potassium nitridotrioxoosmate(VIII) ($KOsO_3N$) and potassium tetraoxoosmate(VI) (K_2OsO_4), in aqueous solutions containing 10—100 microgram amounts of these compounds. Paper and thin-layer chromatographic methods have now been elaborated for this purpose.

Experimental

The OsO_4 used was an analytical grade Merck product. $KOsO_3N$ and $K_2OsO_4 \cdot 2H_2O$ were prepared by the method of JOLY and CLAUS [2]. Their purities were checked by polarography and infrared spectroscopy (Radiometer PO 4 and Perkin Elmer 225 instruments). Solutions with concentrations of 6×10^{-2} mol/dm^3 were prepared from all three substances.

Macherey Nagel 214 chromatographic paper was used for the paper-chromatographic studies, elution being performed in the direction of the paper fibre.

Kieselgel G and Aloxide (Merck products) layers 0.25 mm in thickness were prepared with a Desaga apparatus on 10×20 cm glass plates for thin-layer chromatographic work. The Kieselgel and the Aloxide were suspended in water or in 0.5 or 2 *M* KOH. The bound and air-dried layers were stored in a desiccator over anhydrous $CaCl_2$.

The osmium-containing solutions were added from a micropipette, in volumes of 1, 2 or 3 microlitres. The osmium content of each spot corresponded to 12 micrograms of solution component.

Elution was in all cases performed at room temperature, in an ascending system, in closed glass baths. In the paper-chromatographic work the duration of elution was generally 2 or $2^1/_2$ hrs, and in the thin-layer chromatography 20 – 25 min. Elution was followed by drying in a current of air. and the osmium-containing spots were then developed by spraying the papers or layers with a 5% thiourea solution in 5 *N* HCl. Next came drying for 10 min at 18°C in a drying oven, when the osmium-containing spots became bright-purplish-red [3]. The R_f values were determined from the distance between the spot and the front.

Quantitative determination by thin-layer chromatography

8--10 microlitres of a solution containing an unknown quantity of osmium compound was transferred onto the layer, and the spot was run in parallel with spots of reference solutions (OsO_4, $KOsO_3N$, and K_2OsO_4). When the height of the front was about 15—18 cm, the band containing the unknown component was covered with a glass plate. A duplicate spot of the unknown and the spots of the comparative solutions were next developed with thiourea in HCl. The undeveloped spot or spots were removed from the layer at the R_f value corresponding to the unknown, and eluted separately with somewhat less than 10 ml thiourea in HCl solution in an 80°C water-bath. The purplish-red solutions were then filtered into 10 ml volumetric flasks, made up to the mark with solvent, and measured photometrically in 1 cm cells. A calibration graph was previously prepared for solutions containing 0.2—3 mg osmium, the same method being used. The osmium content of the unknown solution was determined by comparison of its extinction with the calibration graph. The error of the determination is less than 10%. In all cases the determined amount of osmium is less than that taken, as a consequence of the inefficiency of elution (Table I).

Photometric measurements were made at 485 nm on a Hilger Uvispec photometer.

Table I

Amount of osmium compound taken (mg osmium)	0.23	0.57	1.14	1.71	2.28
Extinction of thiourea complex (calibration curve)	0.105	0.234	0.476	0.711	0.946
Extinction of complex after elution	0.090	0.218	0.460	0.686	0.925
Amount of osmium determined from calibration curve (mg osmium)	0.21	0.53	1.11	1.64	2.20
Loss compared to amount taken (%)	8.6	7.1	2.8	4.1	3.5

Results

OsO_4 is fairly soluble in water, the concentration of the saturated solution at 25°C being 0.26 mol/dm^3. However, if the colourless aqueous solution was dropped onto paper or layer, the extremely volatile OsO_4 was lost as a result of the separation of OsO_4 and water. Detection is impossible even by the extremely sensitive thiourea colour reaction on either paper or layer after the dropping and drying processes. In contrast, if OsO_4 is dissolved in strong base, its non-volatile hydroxo derivative is formed:

$$\underset{\substack{\text{colourless}\\ \text{Os(VIII)}}}{OsO_4} + 2\,OH^- \rightleftharpoons \underset{\substack{\text{yellow or red}\\ \text{Os(VIII)}}}{[OsO_4(OH)_2]^{2-}}$$

Since both of these compounds contain Os(VIII) they are very powerful oxidants. They react with substances containing reducing groups, *e.g.* the alcoholic hydroxy groups of paper (cellulose), and are reduced to Os(VI).

This is confirmed by the change in colour following the dropping:

$$\underset{\text{yellow}\\\text{Os(VIII)}}{[OsO_4(OH)_2]^{2-}} + 2e + 2H_2O \longrightarrow \underset{\text{violet}\\\text{Os(VI)}}{[OsO_2(OH)_4]^{2-}} + 2OH^-$$

The reduction can also be confirmed polarographically, for the +8 step is no longer found in the polarogram of the violet spot eluted from paper after dropping.

Thus, $[OsO_4(OH)_2]^{2-}$ and $[OsO_2(OH)_4]^{2-}$ containing Os(VIII) and Os(VI) cannot be distinguished by paper chromatography, whereas $KOsO_3N$ can be readily separated from these two substances on paper too.

The pale-purple aqueous solution of $K_2OsO_4 \cdot 2H_2O$, reminiscent of $KMnO_4$ in its colour, becomes brown within a short time, and Os(VIII) can be detected in it polarographically. In alkaline solution K_2OsO_4 is present as a hydroxo complex, $K_2[OsO_2(OH)_4]$. It was observed that if the alkaline osmate solution contained traces of ethanol, the brown colour due to oxidation could be avoided. A large ethanol excess reduces K_2OsO_4 to OsO_2, and a black precipitate separates out from the violet solution. Accordingly, in the same way as for OsO_4, the K_2OsO_4 solution used for dropping was prepared with 0.5 *M* KOH.

As regards dropping of the $KOsO_3N$ solution, it was irrelevant, whether an aqueous or a KOH solution was employed. $KOsO_3N$ does not react with the paper, the polarogram of a spot eluted from paper agreeing with the original one.

A number of aspects had to be considered in the selection of the eluting mixtures. In the paper-chromatographic work there was no possibility of finding selective eluent mixtures for the three different osmium compounds. The mixtures used for osmium in the literature on paper chromatography are not suitable here [5]. The HCl mixtures mentioned in the literature are applicable in paper-chromatographic separations only with certain limitations. Depending on the HCl concentration, in ethanol–water–HCl mixtures the following reduction process takes place:

$$\underset{\text{Os(VI)}}{[OsO_4]^{2-}} \xrightarrow{EtOH-H_2O-HCl} \underset{\text{Os(IV)}}{OsO_2} + \underset{\text{Os(IV)}}{[OsCl_6]^{2-}}$$

The osmium is then present in the spot in the form of the complex acid H_2OsCl_6 or its potassium salt. These were detected partly polarographically, and in part *via* the characteristic colour reaction of $[OsCl_6]^{2-}$ [6]. $KOsO_3N$ reacts only with concentrated HCl [7], and under the conditions applied it moved in unchanged form during elution on paper.

Separation of the osmium compounds by paper chromatography was examined in various mixtures. The most readily evaluable chromatogram is that obtained with a 30 : 70 : 1 mixture of ethanol–water–HCl (Table II).

The aim of the thin-layer chromatographic investigations was to find a method suitable for the separation of OsO_4 and K_2OsO_4, by eliminating the paper with its reducing properties. Hitherto, similarly to paper chromatography, thin-layer chromatography had been used only to separate osmium

Table II

Elution mixture		R_f (OsO_4)	R_f (K_2OsO_4)	R_f ($KOsO_3N$)
Ethanol–water–HCl 3 : 7 : 0.1	Mn 214 paper	0.40	0.42	0.72
Butanol–acetone–acetic acid 1 : 5 : 1	2 *N* KOH Kieselgel	0.82	0.91	0.24
Butanol–acetone–pyridine 3 : 1 : 1	2 *N* KOH Kieselgel	0.00	0.70	0.40
Acetone–ethyl acetate–pyridine 1 : 1 : 0.1	2 *N* KOH Kieselgel	0.34	0.65	0.08

and other platinum metals; the separation of various osmium compounds from each other, and their determination, had not been dealt with [8]. The eluting mixtures most often mentioned in the literature included acidic components (HCl, H_2SO_4, HNO_3). For the reasons given earlier, OsO_4 cannot be determined in strongly acidic eluting mixtures, because of its volatility. In mixtures with high HCl concentrations, the otherwise fairly stable $KOsO_3N$ too gives a double spot, as a result of $[OsCl_5N]^-$ formation. The ammoniacal mixtures mentioned in the literature cannot be considered either, since OsO_4 reacts with ammonia to give $KOsO_3N$. Thus, the components of the running mixtures had to be sought among organic compounds which do not react with the above three osmium compounds at the given concentration. In the case of acetone, both OsO_4 and K_2OsO_4 have R_f values of zero, whereas a large R_f value was found for $KOsO_3N$, depending on whether the Kieselgel was suspended in water or alkali. With polar additives the R_f values of OsO_4 and K_2OsO_4 too could be varied, and a large difference was found between the R_f values of the two compounds.

The following mixtures proved to be the best for elution, the R_f values of the three osmium compounds differing by more than 10% from one another:

butanol–acetone–acetic acid 1 : 5 : 1 (vol.)

butanol–acetone–pyridine	3 : 1 : 1 „
acetone–ethyl acetate–pyridine	1 : 1 : 0.1 „

The R_f values relating to the mixtures are shown in Table II.

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MOLECULAR FORCE FIELD FOR SOME XY_6 TYPE MOLECULES

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The force field for the hexafluoride of some III B, VI A, VI B and VIII group elements was attempted through parametric representation using isotopic frequencies and observed Coriolis coupling constants. Unique force field for SF_6 has been fixed and the most probable parameter Φ was found to be 23°23′. The changes in force constants for these molecules are studied by considering SF_6 as the parent molecule and using Green's function in internal coordinate representation. The mean amplitude of vibration was calculated at 298.16°K for all these molecules.

Introduction

The unique and unambiguous determination of the molecular force field has become possible with the use of isotopic frequencies [1], Coriolis coupling constants [2], mean vibrational amplitudes [3] and rotational distortion constants [4] as additional parameters. The use of isotopic data with the help of Green's function analysis [5, 6] has been shown [7, 8] to yield a reliable force field in the case of isotopically abundant molecules of relatively high symmetry. In the parametric representation method first proposed by PULAY and TÖRÖK [9], then extended by JORDANOV and NIKOLOVA [10—12] using isotopic frequencies as additional data, the whole problem reduces to that of determining the value of the matrix A which represents the transformation between the true L and the matrix L_0 defined by the relations

$$L = L_0 A \tag{1}$$

and

$$L_0 \tilde{L}_0 = G \tag{2}$$

The matrix A can be represented in the form of a proper orthogonal matrix involving independent parameters. ANANTHAKRISHNAN and ARULDHAS [13] have attempted to evaluate the L matrix using Coriolis coupling constants of XY_3 and XY_4 type molecules, expressing them as a function of a parameter Φ characteristic of the normal coordinate transformation.

Incidentally it is possible to calculate the change in force constants due to chemical environment for the different groups of molecules using Green's function in internal coordinate representation [14].

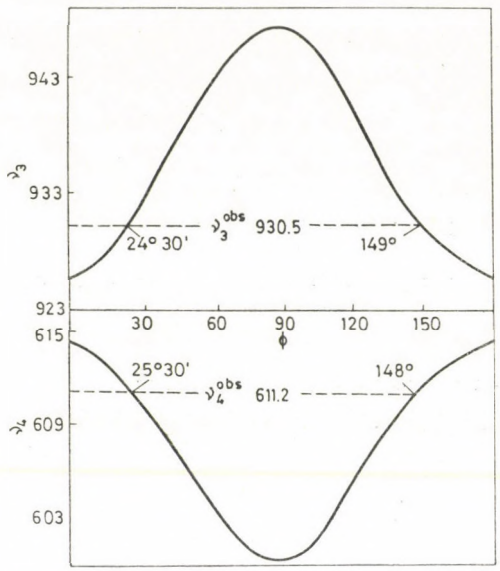

Fig. 1

Fig. 2

Fig. 1. Plot of frequency ν_3^* of SF_6 *vs.* the angle Φ for f_{1u} species of the isotopic pair $^{32}SF_6$ and $^{34}SF_6$

Fig. 2. Plot of frequency ν_4^* of SF_6 *vs.* the angle Φ for f_{1u} species of the isotopic pair $^{32}SF_6$ and $^{34}SF_6$

In the present paper an attempt has been made to fix the unique value of the parameter Φ through parametric representation of JORDANOV and NIKOLOVA [12] and ANANTHAKRISHNAN and ARULDHAS [13] for some XY_6 type molecules. The molecules chosen are hexafluorides of sulphur, selenium, tellurium, rhodium, wolfram, iridium, platinum, uranium, neptunium and plutonium belonging to VI A, VI B, VIII and III B groups of the periodic table. All these belong to the O_h point group. Of the fifteen fundamental vibrational frequencies falling under a_{1g}, e_g, f_{1u}, f_{2g}, all except f_{1u} are unidimensional and hence can be evaluated uniquely. The molecular parameters and the fundamental vibrational frequencies used in the present calculation are summarized in Table I along with the references from which they are taken.

Results and discussion

The complete isotopic data and ξ values are available for SF_6 molecule. KIM *et al.* [15] and ABRAMOWITZ and LEVIN [18] determined the force constants of some XY_6 type molecules including SF_6 using observed ξ values by drawing a graph between F_{34} *vs.* F_{44}, F_{33} and ξ_{33} or ξ_{44} and chose the correct set corresponding to the intersection of the observed ξ curve with the calculated values. KIMURA and KIMURA [19] and CLASSEN [20] have also

Table I

Vibrational frequencies (cm^{-1}), bond lengths (Å) and Coriolis coupling constants for some XY_6 type molecules

Molecule	ν_1 [a]	ν_2	ν_3	ν_4	ν_5	ν_6	Bond length, Å	Observed ξ_{33}	Constants ξ_{44}
$^{32}SF_6$	770	640	(947.9)[b]	(614.5)[b]	522	349	1.564[c]	0.83	−0.23[c]
$^{34}SF_6$	770	640	(930.5)[b]	(611.2)[b]	522	349			
SeF_6	708	661	780	437	403	262	1.688[c]		0.21
TeF_6	701	674	752	325	323	195	1.824[c]	0.18	0.28
RhF_6	634	592	724	283	269	189	1.83		0.19
WF_6	771	673	711	258	315	134	1.832[c]	0.12	
IrF_6	701	646	719	276	258	206	1.83	0.13	0.36
PtF_6	655	600	705	273	242	211	1.83		0.37
UF_6	667	535	624	186	201	140	1.999[c]	0.24	0.15
NpF_6	648	528	624	199	208	165	1.98		0.29
PuF_6	628	523	616	206	211	173	1.97		0.28

[a] All vibrational frequencies, bond lengths and Coriolis coupling constants except those marked by b and c are taken from Reference [15]; b from Reference [16], c from Reference [17]

carried out a normal coordinate treatment for XY_6 type molecules by drawing a graph between the bending force constant and the interaction constant and have shown that the most probable set is the one that corresponds to a minimum value of the interaction constant. THAKUR and RAI [21] evaluated the force constants of some XY_6 type molecules through simple and modified UBFF and interpreted them on the basis of hybridization. RAMASWAMY and MOHAN [22] determined the molecular constants of SF_6 using Green's function analysis, while CYVIN and BRUNVOLL [23] used TORKINGTON's [24] progressive rigidity method to fix the force field of XY_6 type molecules.

On the basis of Born—Oppenheimer approximation ($F = F^*$), JORDANOV and NIKOLOVA [12] obtained the relationship

$$\Lambda^* = \tilde{A}^*(\tilde{L}_0^{-1}\,\tilde{L}_0^*)A\;\Lambda\;\tilde{A}(L_0^{-1}\,L_0^*)A^* \tag{3}$$

where * stands for the isotopic molecule. The initial solution L_0 as defined by

$$L_0 = VT^{1/2} \tag{4}$$

was constructed using V, the eigenvector matrix and T, the eigenvalue matrix of G. For a 2×2 case we need a single parameter and the form of the orthogonal matrix A is given by

$$A = \begin{bmatrix} \cos\Phi & \sin\Phi \\ -\sin\Phi & \cos\Phi \end{bmatrix} \tag{5}$$

Assuming $A = A^*$, A^* was calculated for various values of Φ ranging from 0 to 180°. A graph was drawn between Φ and the calculated isotopic frequencies. That value of Φ which gives the experimentally observed isotopic frequencies was chosen to represent the A matrix. A typical graph was drawn for SF_6 between Φ and ν_3^* and ν_4^* and is shown in Figs 1 and 2. It is seen from the graph that there are two solutions for Φ corresponding to the observed value of the isotopic frequencies. The mean values of Φ for both frequencies are 25° and 148°30′. With these values, A matrix was constructed and the force constants were evaluated from the well known relation

$$F = \tilde{L}^{-1} A L^{-1} \tag{6}$$

It was found that for $\Phi = 148°30'$, the values of F obtained ($F_{33} = 3.2602$ mdyn/Å; $F_{44} = 2.1006$ mdyn/Å; $F_{34} = -1.4339$ mdyn/Å) were not consistent with the most probable values expected for the S–F bonds. Hence this solution was rejected.

Since JORDANOV and NIKOLOVA's method and Green's function procedure make use of the isotopic frequencies as the additional parameter, it is of interest to correlate the mixing parameter of Green's function with the Φ parameter. It is found that the mixing parameter a of Ref. [22] is related to Φ by

$$a = \pm \tan \Phi$$

The value obtained for the mixing parameter using tan Φ reproduces the isotopic frequencies when substituted in the isotopic rules given by RAMASWAMY and MOHAN [22].

The force field for SF_6 was also calculated using the observed Coriolis coupling constants. The procedure is essentially the same as that of ANANTHAKRISHNAN and ARULDHAS [13]. ABRAMOWITZ and LEVIN [18] reported the ξ values for SF_6 as $\xi_{33} = 0.83$ and $\xi_{44} = -0.33$ from infrared spectra. Recently BOSWORTH *et al.* [17] recalculated the ξ_{44} value using more accurate molecular parameters and reported a value of −0.23 which is comparable with the value of −0.21 observed by BRUNET and PEREZ [16] from the rotational fine structure of the band.

The value of Φ obtained using $\xi_{33} = 0.83$ is 16°21′, while with $\xi_{44} = -0.23$ is 21°47′. The fact that a low angle of $\Phi = 16°21'$ has been obtained for ξ_{33} shows that the experimentally observed ξ_{33} is not correct owing to the probable distortion of the ν_3 band by hot bands. Such a possibility has been pointed out by BOSWORTH *et al.* [17].

A mean value of Φ (25° from JORDANOV and NIKOLOVA and 21°47′ for $\xi_{44} = -0.23$) was taken as 23°23′ and the mean F matrix elements ($F_{33} = 5.29$ mdyn/Å; $F_{34} = -0.89$ mdyn/Å; $F_{44} = 1.03$ mdyn/Å), calculated as given in Table II, are in general agreement with the values ($F_{33} = 5.2616$ mdyn/Å; $F_{34} = -0.567$ mdyn/Å; $F_{44} = 1.035$ mdyn/Å) of RAMASWAMY and

Table II

Parameter Φ, symmetrized force constants (mdyn/Å), calculated frequencies (cm^{-1}), change in force constants (mdyn/Å) of f_{1u} species and computed mean vibrational amplitude (Å) for some XY_6 type molecules

Molecule	Parameter Φ (mean value)	F_{33}	F_{34}	F_{44}	ν_3	ν_4	Change in F_{33}	Change in F_{44}	Calculated mean vibrational amplitude (Å) $X-Y$
SF_6	23°23′	5.2956*	−0.8968	1.0349	947.9	614.5	0	0	0.0419
		5.2616[a]	−0.567	1.035					0.0410 [26]
									0.0420 [27]
SeF_6	32°53′	4.9438	−0.4714	0.6499	772	530	0.0600	0.3071	0.0399
									0.0390 [26]
		(4.88 ± 0.10)	(0.44 ± 0.03)	(0.64 ± 0.01)					0.0399 [27]
									0.0399 [19]
TeF_6	23°56′	5.0200	−0.2391	0.4067	752	432	0.2616	0.3369	0.0388
		(4.98 ± 0.10)	(0.24 ± 0.05)	(0.40 ± 0.05)					0.0388 [27]
		4.98 ± 0.10[b]	0.24 ± 0.05	0.40 ± 0.05					0.0388 [19]
RhF_6	23°07′	4.3067	−0.0931	0.2929	763	451	0.9999	0.4968	0.0413
		(4.30 ± 0.10)	(0.10 ± 0.10)	(0.29 ± 0.01)					0.0413 [30]
WF_6	21°43′	4.7923	−0.1904	0.2803	739	407	0.5519	0.4970	0.0384
		(4.78 ± 0.10)	(0.20 ± 0.10)	(0.28 ± 0.01)					0.0385 [27]
		5.08 ± 0.10[c]	0.188 ± 0.020	0.269 ± 0.017					0.0385 [19]
IrF_6	20°20′	4.9145	−0.1604	0.3222	738	403	0.4361	0.4525	0.0388
		(4.85 ± 0.10)	(0.16 ± 0.10)	(0.32 ± 0.10)					0.0389 [27]
									0.0390 [19]
PtF_6	20°21′	4.7368	−0.1617	0.3161	737	402	0.6153	0.4580	0.0400
		(4.72 ± 0.10)	(0.16 ± 0.10)	(0.32 ± 0.01)					0.0400 [27]
									0.0405 [19]
UF_6	7°50′	3.6754	0.1143	0.1594	736	351	1.7431	0.4657	0.0426
		(3.67 ± 0.08)	(−0.11 ± 0.10)	(0.16 ± 0.01)					0.0424 [27]
									0.0423 [19]
NpF_6	9°30′	3.7093	0.0607	0.1775	736	355	1.7079	0.4599	0.0427
									0.0426 [27]
		(3.69 ± 0.08)	(−0.06 ± 0.10)	(0.18 ± 0.01)					0.0426 [19]
PuF_6	9°04′	3.6150	0.0723	0.1919	735	356	1.7959	0.4665	0.0431
		(3.61±0.08)	(−0.06±0.10)	(0.19±0.01)					0.0430 [27]
									0.0430 [19]

* This number of significant figures is retained to secure internal consistency in calculations
Values in parentheses refer to the work of KIM *et al.* [15]
a: Ref. [22]; b: Ref. [18]; c: Ref. [29]

MOHAN [22] obtained from Green's function analysis. The mean vibrational amplitude calculated from the well known relations of CYVIN [25] for the S—F bond 0.0419 Å is in agreement with the values 0.0410 Å and 0.0420 Å reported by EWING and SUTTON [26] and CYVIN [27], respectively. This is also in agreement with the value of 0.0419 Å reported by MULLER and MOHAN [28]. With $\Phi = 23°23'$, ξ_{33} and ξ_{44} calculated from the Meal and Polo relation are found to be 0.70 and —0.20 respectively.

The force constants of SeF_6, TeF_6, RhF_6, WF_6, IrF_6, PtF_6, UF_6, NpF_6 and PuF_6 were calculated for the values of Φ obtained using the available ξ values as additional parameters. The results are summarized in Table II. It is seen that these values are in good agreement with the values reported by KIM *et al.* [15] and ABRAMOWITZ *et al.* [18].

It is possible to calculate the change in force constants as one goes from SF_6 to any other molecule by treating sulphur as the parent atom and utilizing the Green's function in internal coordinate representation. This has been done for the molecules under consideration and the results are tabulated in Table II. Frequencies of f_{1u} species for SeF_6, TeF_6, RhF_6, WF_6, IrF_6, PtF_6, UF_6, NpF_6 and PuF_6 were predicted by treating SF_6 as the parent molecule with $\Phi = 25°$ and the calculated frequencies are summarized in Table II. It is seen from Table II that the change in stretching force constant increases as the difference in electronegativity increases in the series of SF_6 to TeF_6. RAMASWAMY and MOHAN [22] calculated the change in force constant for SF_6, SeF_6 and TeF_6 and the trend observed is essentially the same as in the present case.

As seen from Table II the calculated mean vibrational amplitudes for these molecules are in agreement with the values of KIMURA and KIMURA [19] and CYVIN [27]. The Coriolis coupling constant ξ_{55} for the f_{2g} species was also calculated using the Meal and Polo relation and a value of —0.50 was obtained for all these molecules. This value is in agreement with the work of BOSWORTH *et al.* [17].

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A CRITICAL SURVEY ON THE TRANSITION STATE THEORY*

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The kinetic schemes involving classical and 'quasi' equilibria are compared for bimolecular, second order processes. The usual treatment applied by transition state theory (TST) involves the results of two opposite limiting cases of the kinetic formalism. Some characteristic features of TST are discussed. The main disadvantage of the theory is shown to be the unjustified application of Boltzmann's distribution law and of partition functions to the 'activated complex'. Characteristic errors in some individual derivations used to obtain the TST formula from different models are pointed out. By reversing the usual procedure and by a more careful application of the partition functions, the model implied in the TST rate expression itself is obtained and shown to be far from reality.

TST can properly be regarded as a heuristic approximate method without theoretical justification. Conclusions drawn from TST may be reasonable mainly as a consequence of adjustable parameters introduced. The concepts of 'activation entropy' and 'activation enthalpy' have no thermodynamic meaning.

I. Introduction

The transition state theory (TST)** [1] is practically the only kinetic theory which is regarded to be applicable to reactions of complex reactants. The introduction of the concept of potential energy surfaces [2] and TST [3] was so highly suggestive in the 1930's that generations of chemists adopted the visualization of geographical analogues for chemical transformations. As a matter of fact, in most cases, we are able to think only in those terms created by kineticists forty years ago. It is, therefore, somehow awkward to approach our basic ideas with scepticism. On the other hand, the ever-growing kinetic practice has already produced ample evidence that our "theoretical knowledge" has very slight, if any, predictive power. In such a situation, it is inevitably necessary to reconsider the validity of TST and recognize its limits.

This analysis is desirable for another reason, too. Recent literature bears witness to the very wide application of TST to different kinetic phenomena.

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** TST is also referred to in the literature as activated complex theory or absolute rate theory. Analogously, the terms transition state and activated complex are used in the same sense for bimolecular reactions.

Many of the appliers believe that TST is a well-founded theory [4], as good as, say, the laws of perfect gases. This problem is connected with the unbalanced presentation of TST in some textbooks on reaction kinetics [1, 5—9]. Although critical sources [10—13] are also available, they are not quite familiar to many kineticists interested mainly in liquid phase experiments.

The aim of this paper is to focus attention on TST itself rather than on its individual applications, and to demonstrate explicitly the implications accepted when TST is applied to individual problems.

II. Historical

The earliest root of TST dates back to 1889. ARRHENIUS [14, 15] interpreted the temperature dependence of the rate constant by assuming an equilibrium between 'active' and 'inactive' cane sugar during chemical transformation. The next step forward was taken by MARCELIN [16] who gave a sophisticated definition of the reaction rate in phase space.

TST was actually founded by EYRING [3], who introduced the concept of reaction coordinate attached to an internal translation of the activated complex and described the properties of transition state in terms of partition functions. The theory was thoroughly debated at the 1937 Faraday Society Discussion [17]. The basic textbook [1] representing the theory with the claim of being universal became the main source of knowledge in post-war years. TST gained predominance over collisional treatments for about two decades. In this period, the application of TST to isotope effects gave considerable support for the theory. The treatment of kinetic isotope effects [18—23], *i.e.* of the ratio of isotopic rate constants, was probably the most successful application of TST ever made.

ELIASON and HIRSCHFELDER were the first to call attention to the important fact that the TST rate expression can be derived from a careful collisional treatment only if drastic approximations are introduced [24].

The 1960's saw a significant development in both collisional experimental techniques and theoretical model calculations. These led to gradually increasing doubts [25, 26] in TST.

In response, theoretical activities were aimed at setting up numerous variations of TST in order to avoid some of the defects, and at giving confirmation to TST derivations.

III. The structure of TST

The complex structure is very characteristic of TST. It involves a number of *ad hoc* ideas taken from different fields of physics and chemistry.

Potential energy surfaces and the consideration of quantized vibrations come from quantum mechanics. The motion along the reaction coordinate,

i.e. the internal translation of the activated complex, is treated essentially in a classical way. The use of activation parameters (enthalpy and entropy of activation) resembling thermodynamic quantities [27] is a consequence of the partition function formalism. Partition functions, in turn, imply the realization of the Boltzmann distribution of energy for each degree of freedom, as usual in equilibrium statistical physics. As a basic concept, TST assumes that the reaction coordinate can be attributed to a single degree of freedom which is separable from the other (normal) degrees.

The choice of suitable kinetic models, the performing of the chemical reaction with measurable rate, the best possible exclusion of experimental errors and evaluation of elementary rate constants are the concern of the experimental kineticist. It is understandable if, after completing the experimental task, the kineticist is inclined to accept TST and all its implications without further considerations. He will then transform experimental Arrhenius parameters into enthalpy and entropy of activation in order to obtain information on the structure of the transition state and to interpret the reaction mechanism.

IV. A simple kinetic representation

At first let us consider a usual two-step mechanism for the reaction of reactant molecules A and B. In the reversible first step the intermediate AB is formed which reacts further in the second step to give C and D as products:

$$A + B \underset{-1}{\overset{1}{\rightleftharpoons}} AB \xrightarrow{2} C + D \tag{1}$$

The rate of formation of C

$$\frac{d[C]}{dt} = k_2 [AB] = \frac{k_2}{k_{-1} + k_2} \left\{ k_1 [A] [B] - \frac{d[AB]}{dt} \right\} \tag{2}$$

is of second order in terms of concentrations (or activities) of reactants A and B, if the second term in brackets is negligibly small compared with the first. Then the overall rate constant is given by:

$$k = k_1 \frac{k_2}{k_{-1} + k_2} = k_1 \varkappa \tag{3}$$

where $\varkappa = k_2/(k_1 + k_2)$ denotes the relative probability of decomposition of AB into products (similarly to the transmission coefficient of TST).

If AB decomposes mainly into reactants, *i.e.* $k_1 \gg k_2$, then we can write with a high degree of accuracy

$$k = \frac{k_1 k_2}{k_{-1}} = Kk_2 = k_2 \frac{Q_{AB}}{Q_A Q_B} \exp\left(-\frac{E_0}{\mathbf{k}T}\right) \tag{4}$$

hence, the classical equilibrium constant K of the pre-equilibrium becomes a factor of the rate constant. Since AB is a true intermediate (as opposed to the activated complex of TST), one can use partition functions Q_i to calculate the equilibrium constant. E_0 is the energy difference between the ground levels of the intermediate and the reactants. This limiting case is characterized by the inequality

$$\varkappa \ll 1 \tag{5}$$

If, however, AB decomposes mainly into products, *i.e.* $k_2 \gg k_1$, this second limiting case is characterized by

$$\varkappa \approx 1 \tag{6}$$

and the overall rate constant, k, tends to k_1. In this case (as opposed to (4)) the equilibrium constant $K = k_1/k_{-1}$ is not an essential factor in the expression of k. The concentration of the intermediate $[AB] = K(1 - \varkappa)[A][B] \approx \approx k_{-1}/k_2\, K[A][B]$, though in the steady state, would remain far below the equilibrium value of $K[A][B]$. Therefore, the quantity $[AB]/[A][B]$, necessary to calculate k according to (2) as $k = k_2\, [AB]/[A][B]$, cannot be expressed as a ratio of the partition functions Q_i.

The activated complex of TST is not a true chemical intermediate, and it is postulated to be in 'quasi-equilibrium' with the reactants. The formal kinetic scheme of TST may be given as

$$A + B \rightleftharpoons AB^{\ddagger} \longrightarrow C + D \tag{7}$$

were the dotted line indicates that TST does not insist on the re-decomposition of the activated complex into reactants [28—30] in order to maintain equilibrium. On the contrary, the activated complex is to decompose mostly into products, according to TST ($k_{-1}/k_2 \approx 0$), and the transmission coefficient does not considerably differ from unity [31, 32]. Nevertheless, one might apply the whole of the above algebra to the TST complex as well and conclude that the quasi-equilibrium treatment of TST involves Eqs (4) and (6), *i.e.* the results of two different limiting cases of the simple scheme corresponding to a classical pre-equilibrium. This is connected with a different (rather arbitrary) treatment of the equilibrium constant in TST. In fact, TST starts by considering the rate of formation of C or D as the product of the concentra-

tion of the activated complex, $[AB^{\ddagger}]$, and the rate of its decomposition into the products. In order to calculate the rate constant, TST goes, however, further and *postulates* that the ratio of the concentrations $[AB^{\ddagger}]/[A][B]$ has the equilibrium value irrespective of the ratio of k_2 and k_{-1} and can be expressed (as if it were a usual equilibrium constant) by means of the partition functions of the complex and of the reactants, similarly to the right-hand side of (4). (The height of the potential barrier is considered as zero point energy difference.) A characteristic feature is that this equilibrium constant is not identified with k_1/k_{-1} and is not related to the latter quantity which may even be infinitely high according to TST. This is just the difference between a usual equilibrium and the quasi-equilibrium of TST.

This discussion shows that there is no clear distinction in the usual TST treatment between the concepts of steady state and equilibrium concentrations. The even more important and crucial problem of the inapplicability of the partition function formalism to the activated complex of TST will be discussed later on in detail.

V. Some characteristic features

The main idea of TST is to determine the flux of systems moving in the forward direction (*i.e.* from reactants to products) at the saddle-point region of the appropriate potential energy surface. It is assumed that most of the systems surmounting this critical point will attain the product region. By introduction of the reaction coordinate normal to the barrier [1, 3, 33—35], the dynamics of the chemical reaction is apparently reduced to an essentially one-dimensional problem. The motion along the reaction coordinate is, however, not entirely independent of the motion in other degrees of freedom (*i.e.* the reaction coordinate is not fully separable). Therefore, the transmission coefficient, $\varkappa$, was introduced. TST does not give detailed information on the value of $\varkappa$ (the ratio of the flux of systems which actually undergo reaction, to the overall flux over the saddle point region). This would only be possible by means of a complete solution of the many-dimensional dynamic problem, and the very aim of TST is to avoid such a tedious dynamic consideration. It is assumed that the coupling between different degrees of freedom is small, the separation of the motion along the reaction coordinate does not introduce serious errors and the value of $\varkappa$ can be taken in most cases as close to unity.

The motion along the reaction coordinate is treated, in fact, in a classical manner. Accordingly, the condition of surmounting the barrier is that the energy corresponding to the motion along the reaction coordinate should not be less than the height of the barrier.*

* Allowance for quantum mechanical tunneling in TST can only be made by introducing an additional correction factor [36, 37].

Classical description is also applied for calculating the flux of systems crossing the barrier. In the vicinity of the saddle-point, the potential energy surface is regarded sufficiently flat in order to reduce the importance of quantum effects. This is not the case, however, especially if light atoms are involved [38]. The potential energy changes considerably within distances less than or comparable with typical bond lengths. The introduction of a factor into the rate formula [39—41] which corrects for the one-dimensional penetration of the barrier is not identical with a quantum mechanical description. In a quantum mechanical approach, the whole potential energy surface* becomes significant, therefore, consideration of either a one-dimensional problem, or only the vicinity of the saddle-point is not sufficient. The transition probability is strongly influenced by quantum mechanical 'resonances' or 'quasi-bound states'** [42, 43]. Thus, quantum effects can change the picture not only quantitatively but also qualitatively with respect to the one-dimensional or classical cases.

No doubt, a careful quantum mechanical treatment of chemical reactions is still very difficult. A description in which some problems are treated in a classical way may possibly be a useful zeroth order approximation if one bears in mind that the problem treated is essentially quantum mechanical and not classical.

VI. The central problem

Though the somewhat arbitrary mixture of classical and quantum mechanical ideas is characteristic of TST, the central problem of the theory is the way in which the flux through the saddle-point is calculated. TST applies partition functions (*i.e.* the combination of Boltzmann factors) in order to calculate the number of systems atop the barrier. In some versions of deriving the rate expression, the Maxwell—Boltzmann distribution of velocities is used for determining the mean velocity normal to the barrier. The treatment is identical with assuming the validity of the Boltzmann distribution of energy in any degree of freedom of the activated complex. The assumption is called the 'quasi-equilibrium hypothesis' stating that "the activated complex is in equilibrium with the reactants".

The problem, whether or not the application of Boltzmann distribution for activated complexes is correct, seems to be the crucial point. The original derivation of the TST expression was introduced by stating [3] that "the proba-

* It is generally disregarded that the internal motions and overall rotations are always coupled. Hence, the effective potential energy depends not only on internal coordinates (distances and angles between atoms) but also on a centrifugal barrier. Moreover, the potential energy surface itself is sometimes insufficient for kinetic considerations (non-adiabatic reactions).

** The classical analogues of these are closed trajectories in the transition region of the potential energy surface.

bility of the activated state is calculated using ordinary statistical mechanics", although this would have required specific justification, since the activated state differs from an ordinary molecule.

The usual arguments to justify TST treatment are:

1. The Boltzmann distribution is, by all means, valid for all species (hence, also for the activated complex) in complete equilibrium between reactants and products [6, 29, 44].

2. In such cases, the rate of reaction in the forward and reverse directions can be calculated reliably by applying an equilibrium expression to the activated complex [6].

3. For not too fast reactions (*i.e.* in case the chemical reaction is slow compared with thermal relaxation) which obey the kinetic mass action law, the rate of the forward reaction would be unaffected if the products were removed and the reverse reaction ceased to proceed [29, 44].

Although the correctness of neglecting the reverse reaction is also questionable [45], the common weakness of the above arguments is the fact that the activated complex is not an ordinary chemical species. The activated complex, as a system, is only formed in the instant of the collision leading to reaction and, according to its definition, exists only for the very short time of passing over the top of the barrier.

This means that the activated complex does not fulfil the conditions of forming a canonical ensemble for which the Boltzmann distribution is derived [46, 47].

A canonical ensemble can be constructed for 'quasi-closed subsystems' interacting with the thermostat in which they are placed. The interaction should (a) be weak enough so that its energy might be negligible, at least in time average, compared with the internal energy of the subsystem and the rest of the thermostat (thus the total energy of the whole system is to be taken as the sum of the energies of these two parts); (b) exist, and allow a change in energy and state of the subsystem.

During its very short lifetime, the activated complex is a fully closed system not interacting with the environment. (The role of ternary collisions in a bimolecular reaction is quite negligible.) Thus, the activated complex has a strictly constant energy and condition (b) (formation of a canonical ensemble) is not fulfilled. In other words, there is no relaxation mechanism allowing the complex to attain the equilibrium Boltzmann energy distribution in all degrees of freedom. In the course of the reaction, a number of degrees of freedom undergo drastic changes. *E.g.*, the reactants have altogether six translational degrees of freedom and this number reduces to three in the activated complex. The redistribution of energy between the different degrees of freedom during the collision is governed by some hardly known factors of collision dynamics. In steady state conditions when reactants can be re-

garded as Boltzmann-distributed, there is, of course, a distribution of activated complexes which is *stationary* but cannot be identified with a Boltzmann distribution.

One may give another possible example of applying 'ordinary' statistical mechanics to the problem. Let us consider a system containing N_A molecules of type A and N_B molecules of type B. Then try to consider any pair of different molecules A and B as an element of the ensemble. In this case, there are $N_A N_B$ such 'subsystems', much more than the overall number of individual molecules in the vessel $(N_A + N_B)$. Since each molecule A is simultaneously 'contained' in N_B different 'subsystems', one cannot perform the separation of energy into the internal energy of the subsystem and the energy of the rest of the thermostat. In other words, we cannot present the energy of the whole gas as the sum of energies of all $(N_A N_B)$ pairs of molecules A and B; an analogous consideration is possible if one takes the individual molecules as elements of the ensemble. Thus, pairs of molecules at arbitrary distances from each other do not form a canonical ensemble (condition (a) is not fulfilled). Consequently, without further specific justification, one cannot use the simple Boltzmann distribution in order to determine the proportion of the particles being atop the barrier.

The Boltzmann distribution for the activated complex is sometimes assumed to be a consequence of the Boltzmann distribution of reactants [6, 48]: the Liouville theorem of classical mechanics prescribes really constant probability density in the phase space for the motion along phase-space trajectories. According to this argument, the Boltzmann distribution for reactants leads automatically to that of the activated complex.

This is not the case, however [49] and even the Liouville theorem cannot verify the TST equilibrium treatment. Owing to the many-dimensional character of the potential energy hypersurface, there are, in general, phase space trajectories with both ends in the product region. Along those, no reaction is considered and even the Liouville theorem cannot guarantee the Boltzmann distribution for the whole activation hyperplane.* The problem is connected with the reflexion of systems which have surmounted the barrier in the reverse direction. The introduction of the 'conversion coefficient' [48] intended also for the proper consideration of this effect is in fact the replacement of one undetermined parameter (transmission coefficient) by another. It may be noted that $\varkappa$ was used in the function of the conversion coefficient as early as 1939 by HIRSCHFELDER and WIGNER [50].

The greatest difficulty of applying the Liouville theorem to chemical reactions is that the reactant vibrations (and rotations) are quantized, a fact that must not be disregarded [78].

* *I.e.*, for the hyperplane, which is orthogonal to the reaction coordinate at the transition state and corresponds to the forward motion.

Classical mechanics may be applied for free translation, *i.e.* for the motion along the reaction coordinate, only when the reactants do not yet interact. For short distances, however, the reaction coordinate is not identical with free translation and classical mechanics is inapplicable to internal degrees of freedom.

Hence, any reference to this classical theorem should be dropped as inadequate for the problem of reactions.

MARCUS gave the most general formulation of the quasi-equilibrium hypothesis [51], as follows:

"When all quantum states of a reacting pair having a given J, M (angular momentum quantum numbers)* and a total energy within $(E, E + dE)$ are made equally likely, all quantum states in the activated-complex region having this J, M and $(E, E + dE)$ are also equally likely, each occurring with the same probability as those of the pair." He clearly realized, however, that the quasi-equilibrium hypothesis is not more than an approximation and the degree of its accuracy can be checked only by *a posteriori* tests.

In summary, we conclude that the quasi-equilibrium assumption of TST is not a well founded hypothesis but is rather a postulate. It may be hoped, at best, that it will lead to no serious errors.

A sufficient general basis for the 'absolute' theory of 'rate processes' is, contrary to enthusiastic views, still lacking and will probably never be found.

VII. Some individual derivations

Since the first formulation of TST, a number of different derivations have appeared. Their common aim has been to improve the presentation of the rate expression. Considerable efforts were made to obtain the *same expression* from significantly *different models.*

The common procedure of deriving the rate constant is to multiply the equilibrium constant of the activation process (K) by a frequency (ω)

$$k = \omega K \tag{8}$$

thus connecting reaction kinetics with thermodynamics. The equilibrium constant is to be written as a product of the single partition function attributed to the reaction coordinate (q_{rc}) and the remaining part of the equilibrium constant ($K^{\ddagger}$), which is to be expressed in terms of partition functions of the other degrees of freedom. The complete expression also includes $\varkappa$, the transmission coefficient:

$$k = \varkappa \omega q_{rc} K^{\ddagger} \tag{9}$$

* Explanation added by the authors.

Individual derivations differ in the way they define the quantities ω and q_{rc}, but are similar in yielding the 'universal frequency factor' for the product

$$\omega q_{rc} = \frac{\mathbf{k}T}{h} \tag{10}$$

The most usual derivation applies a 'δ-box model' [1, 5]. q_{rc} is expressed by the high temperature partition function of a particle trapped in a potential box of length δ in the flat region atop the barrier. ω is given by the frequency at which reacting systems with the classical mean translation velocity pass the δ region of the barrier.

Unfortunately, there is no box of infinitely high wall atop the barrier and the use of the partition function corresponding to such a situation is arbitrary. Moreover, it has been shown by MACOMBER and COLVIN [52] that such a δ-box requires the low- rather than the high-temperature limit of the partition function and if one takes the limit $\delta \to 0$ (since the barrier is strictly flat only at a single point) then "the particle-in-a-δ-box model predicts that no chemical reaction can ever occur" [52].

In order to improve the treatment, MACOMBER and COLVIN replaced the δ-box by an 'L-box', L being the mean free path. They regarded the motion along the reaction coordinate as free translation of molecules between the collisions preceding and following the reaction. They applied the eigenvalues of the particle-in-a-box of length $2L$ and the factor δ/L to give the probability of the particle being in the transition region [52].

Unfortunately, there is no L-box either in which the motion would be stationary (periodic in the classical limiting case) and the energy values applied by MACOMBER and COLVIN correspond only to stationary states. Even in a stationary box, the presence of a barrier would strongly influence both the energy values and the wave functions. Thus neither the energy levels applied are appropriate, nor can the probability of finding the particle in the interval atop the barrier be given by the simple ratio of δ/L.

In another usual derivation, motion along the reaction coordinate is treated as vibration [6]. It is assumed that a harmonic vibration with a frequency of $\nu^{\ddagger} \ll \mathbf{k}T/h$ leads in each period to the decomposition of the activated complex. Thus $\omega = \nu^{\ddagger}$ and $q_{rc} = \mathbf{k}T/h\nu^{\ddagger}$.

Besides the obvious arbitrariness of regarding the decomposing chemical bond as a harmonic oscillator,* the reaction coordinate does not allow any *real* vibration. The top of the barrier represents a maximum along the reaction coordinate which implies a negative force constant and an imaginary frequency

* Harmonic vibration is a bonded motion while the reaction corresponds to an unbonded one.

for the critical vibration. (This fact has been realized by many authors and the idea of imaginary frequency has spread throughout the literature [25, 53]. Generally, it is not regarded as a serious defect since this frequency disappears in the final expression.) Then not only $\nu^{\ddagger}$, but also q_{rc} is imaginary. Unfortunately this is absurd. As the probability of finding a species in its lowest energy state equals Q^{-1}, the activated complex has an imaginary probability and should decompose with imaginary velocity to give a real rate. It was stated that not the phenomena but only the quantities would be imaginary [54].

One cannot have any idea about the meaning of these imaginary quantities.

In some cases the TST rate formula was obtained [55] formally. A complicated rate expression was multiplied and divided by the partition function of the activated complex. Simultaneously, an 'average' was defined so as to include all those terms which did not appear in Eq. (9). The meaning of such a procedure is rather questionable.

Occasionally the activated complex is defined not on the potential energy surface but with respect to the so called 'free energy surface' [6, 56]. Such a surface could be determined by calculating the partition functions for each point of the configuration space. The minimum state density and related principles are connected with this approach [57].

Unfortunately, partition functions and the free energy depend on the temperature. Therefore, such a definition of the transition state is, in general, also temperature dependent. In addition, the application of free energy surfaces is not compatible with TST [58].

In the case of reactants without internal structure (hard spheres) TST reduces to simple collision theory with a particular specification of the effective cross section related to the size of the activated complex [59]. Recent investigations, making use of Laplace transform techniques, determined the average reaction cross section corresponding to the TST rate formula [60]. For the standard 'rigid rotator — harmonic oscillator' TST treatment an improper high-energy limit was found: the effective cross section diverges with increasing energy. This meaningless result was 'corrected' by introducing a 'truncated rotator oscillator model' which excluded certain 'disallowed states' for the complex [61, 62].

The result is a new adjustable parameter (the dissociation energy of the complex) which we have in abundance, anyway.

We may conclude that there is no acceptable derivation of the TST rate expression. The TST formula is to be regarded, therefore, as a *postulate* rather than a result of deduction.

VIII. The model implied in the TST expression

Since there is no adequate connection between the models proposed so far and the TST expression, we shall now follow an unusual approach. Let us try to find a model which is consistent with the rate expression:

$$k = \varkappa \frac{\mathbf{k}T}{h} \frac{Q^{\ddagger}}{Q_A Q_B} e^{-\frac{E}{\mathbf{k}T}} \tag{11}$$

The procedure is a stepwise consideration of the different terms in Eq. (11) and the subsequent definition of the properties of the model according to the requirements necessary to obtain these terms.

1. The proper application of partition functions indicates that the elementary reaction involves a long-lived complex.

In order to avoid ambiguity, we must not confuse this complex with an intermediate of consecutive reactions. Though long-lived, the complex considered is metastable (internally unstable) and capable of decomposing spontaneously without any further energy requirement even in its lowest possible energy state.

Consequences:

(a) The long lifetime allows relaxation and the attainment of equilibrium Boltzmann energy distribution.

(b) Any internal degree of freedom of the complex should be of vibrational or rotational character; translation over a barrier would require such a short lifetime within which no relaxation could be realized.

(c) Since $Q^{\ddagger}$ involves all but one partition function, the reaction coordinate has to be separable with a sufficient accuracy. Hence the reaction coordinate also must be associated with a real vibration, *i.e.* we must assume that there is a local minimum atop the barrier the complex is trapped in.

2. Eq. (10) must be fulfilled: $\omega q_{rc} = \mathbf{k}T/h$.

Consequences:

(a) The shape of the local minimum is nearly parabolic allowing a harmonic vibration for the reaction coordinate.

(b) $\mathbf{k}T \gg h\nu^{\ddagger}$, *i.e.* the high temperature limit of the partition function may be used:

$$q_{rc} = \frac{\mathbf{k}T}{h\nu^{\ddagger}} \gtrsim 10 \tag{12}$$

which, in turn, can be satisfied only if the number of energy levels in the local minimum is sufficiently large (say not less than 20).

(c) Since $\nu^{\ddagger}$ must cancel out, the frequency of decomposition of the complex into products is proportional to the frequency of vibration along

the reaction coordinate:

$$\omega = p\nu^{\ddagger} \tag{13}$$

(d) Since the lifetime of the complex is much longer than the vibrational period, Eq. (13) can be fulfilled if the complex decomposes into products by tunnelling* through the potential barrier bordering the local minimum. The factor p is then the probability of tunnelling and is much smaller than unity.** Collisions of the complex with other molecules should not lead to the formation of products, which would contradict Eq. (13). Instead, they lead to energy transfer (relaxation of the complex) and, possibly, to decomposition into reactants (equilibrium between complex and reactants).

(e) As the attainment of the equilibrium is much faster than its disturbance due to the formation of products, it is unnecessary to consider the rate of formation of the activated complex. Owing to tunnelling, decomposition into products does not involve passing over a second barrier (which would be the case for a true chemical intermediate). Therefore, we need not consider two activated states atop the two barriers bordering the local minimum; the activated state, in the given case, corresponds to the system trapped in this well.

(f) If the complex decomposes, on the average, in each α-th vibrational period into reactants and in each β-th period into products, the probability factor, p, equals β^{-1}. Moreover, $\alpha \ll \beta$ is a condition of the equilibrium assumption. The usual factor, $\varkappa$, can be expressed in these terms as

$$\varkappa = \frac{\beta^{-1}}{\alpha^{-1} + \beta^{-1}} = \frac{\alpha}{\alpha + \beta} \cong \alpha p \tag{14}$$

which is also much smaller than unity.

As a result of the above considerations, the model described permits to derive expression (15) much more correctly than is usually done

$$k = p \frac{\mathbf{k}T}{h} \frac{Q^{\ddagger}}{Q_A Q_B} e^{-\frac{E_0}{\mathbf{k}T}} \tag{15}$$

This expression differs from Eq. (11) only in the replacement of the transmission coefficient by a related quantity, the average local tunnelling probability.

The shape of the potential barrier representing the model is given in Fig. 1.

* Hence, the reduced mass of the system should be small.

** The value of p is an average weighted by the population of complex energy levels; consequently, p is temperature dependent.

As for a representative example, the following estimates are given:

$$T = 500\ K\,; \qquad \mu = m_H\,; \qquad \frac{\mathbf{k}T}{h\nu^{\ddagger}} = 10\,;$$

the number of energy levels in the local minimum is 20.

As a result, we obtain 2.0 kcal/mol for the depth of the dip (y), and 35 Å for the diameter of the potential well at the edge (x).

The results are totally unrealistic.

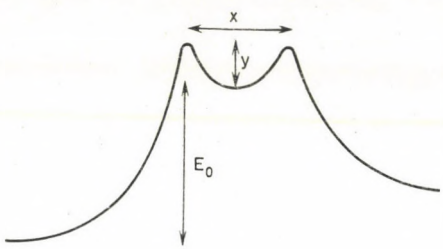

Fig. 1

IX. Concluding remarks

The role of theories in science has been marvellously characterized by ALLEN [63], as follows:

" . . any scientific study begins with facts on which observers can agree. Facts give rise to hypotheses which suggest controlled experiments designed to yield further facts, and in turn to generate new hypotheses. From data established progressively in this cyclic way generalizations are induced and subjected to further critical experimental test. The useful generalizations, the principles, the theories of science, are those which emerge temporarily triumphant from these never-ending attempts to disprove them. In seeking these generalizations, the aim is to be able to predict the behaviour of a particular system, be it a mechanism, a chemical reaction, or a physical transformation, which has not itself been studied experimentally."

Besides this principal task, theories are often used as patterns of elaborating experimental data. This secondary role is generally considered useful as helping the storage of facts and their understanding. The pattern of elaboration has not necessarily to be a well founded theory. A useful treatment can be entirely empirical. Inconsistencies of a method may, however, cause confusion.

TST has obtained a great popularity mainly because of its relatively simple, familiar and intuitive concepts and because it created a hope that

'absolute' (*i.e. a priori*) calculations of reaction rates would be possible if one obtained sufficiently precise potential energy surfaces. Despite the progress in quantum chemistry, we are still not able to obtain potential energy surfaces for most cases of chemical interest. This fact strongly hinders any straightforward test of TST.

TST was clearly useful in predicting maximum values for the kinetic isotope effect as far as the experimental values were smaller than the predicted ones [22]. Since 1964, we know of some extremely large effects [64—68]. Such cases are regarded as evidence for the appearance of the tunnel effect.* The relative success of TST in treating kinetic isotope effects is obviously due to cancellation of errors in the rate constant ratio. *E.g.*, good agreement with the experiment was found for k_H/k_D in cases when the Arrhenius preexponent was calculated only within a factor of 10 although the *experimental* activation energy served for adjusting a parameter in the LEPS potential energy surface [69].

TST was harmful in causing considerable confusion of some concepts. Owing to the quasi-thermodynamic activation parameters, there is no clear distinction (for many people applying TST formalism) among three, fully different things.

1. Although a highly reactive species undergoing decomposition under given experimental conditions, the *true chemical intermediate* is a stable particle in its ground state and can be, at least in principle, isolated (*e.g.* carbonium ions, free radicals [70], organic tetroxides in oxidation processes [71], etc.).

2. *Internally unstable complexes with lifetimes longer than the vibrational or rotational periods*** have been experimentally found by molecular beam techniques [73].

3. The *activated complex* defined atop the barrier is only the means of calculation in TST and should be distinguished from the above two types.

While one can attribute quantum mechanical meaning to the first two types, this would be hardly possible for the third one; it is difficult to treat by wave mechanics a particle at the moment of passing over the saddle-point. (The problem connected with the uncertainty principle was early noted [36, 50].) When the properties of the transition state are discussed (*e.g.* its vibrations are characterized), this transitory formation is attributed a serious reality and one often does not know which of the above three types should be understood.

* New limiting values can be predicted [79] by calculating kinetic isotope effects as a function of barrier width.

** Some kinetic consequences of a model in which the reaction proceeds only *via* such complexes with non-overlapping energy levels [72] have been discussed.

Another confusion is connected with the quasi-equilibrium assumption. According to the classical considerations of ARRHENIUS [14, 15]:

(a) the rate is proportional to the number of active particles;

(b) the rate is found to be proportional to the number of all (inactive) reactant particles;

(c) consequently, there is a proportionality between active and inactive particles (equilibrium). Following these lines, the kinetic mass action law was regarded as an indication of the equilibrium [44].

In fact, an elementrary reaction proceeds via a great number of different channels, each with its own restrictions for the initial state of reactants and with its own probability [24, 74]. The population of each channel is, of course, proportional to the number of encounters of reactants, *i.e.* to the product of reactant concentrations. The coexistence of the parallel channels results in a stationary distribution with an effective (average) activation energy. The population of the channels also depends, however, on a number of probability factors and not only on the energy. This is why the stationary distribution is not identical and must not be confused with the equilibrium distribution.

The complexity of microscopic processes involved in the elementary reaction causes such a complication that it is hardly possible to construct a theory which would be neither purely abstract and sterile nor oversimplified by using arbitrary assumptions.

In summary, TST and collision theory give identical results for the 'hard sphere' model of reaction. One may regard, therefore, TST as an extrapolation method for considering the role of internal degrees of freedom. In lack of other theories, one may apply TST with the clear realization of its approximate, incomplete and theoretically unfounded character [75—77].

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FORMATION OF ETHYLENE GLYCOL–BORATES IN AQUEOUS MEDIUM, II

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Equilibria set up in solutions containing 0.050—0.200 *M* boric acid, 0.1000—2.000 *M* ethylene glycol and 1.000 *M* $Na(ClO_4)$ were studied at 25°C by potentiometric method in the pH range from 6.5 to 9.5. Denoting boric acid $[B(OH)_3]$ as HB, and ethylene glycol ($C_2H_6O_2$) as D, the system can be well described by the formation of $H_2B_3^-$, HB_3^{2-} and $H_2B_4^{2-}$ polyanions and BD^-, BD_2^-, $H_2B_3D^-$ glycol complexes. $-\log K_{231} = 7.35 \pm 0.20$.

From the aqua-hydroxo complexes of elements of medium electronegativity (1.6—2.2 on the Pauling-scale), polynuclear cationic or anionic complexes are formed in aqueous medium [1].

B, Ge, Sn, As, Te, I, Mo, W, forming polyanions in their highest oxidation state, form also complexes with *cis*-vicinal glycols [2—6]. The electronegativity of all the elements mentioned is between 1.8 and 2.2, which is indicative of the analogy between the two phenomena.

In our previous communication [7] we have dealt with the formation of the mononuclear ethylene glycol–borate complexes, the most simple representatives of glycol–borate systems, best known among the above compounds, and pointed out the inconsistencies in the relevant literature. It should be mentioned that contradictory results may arise partly from the fact that the authors carried out measurements also in solutions more concentrated than 0.025 *M*, but took into consideration different equilibria for the formation of borate polyions. For example, SVARCS *et al.* [8] calculated with pentaborate ions of charge —1 and hexaborate ions of charge —2, ANTIKAINEN and his group [9] with triborate and tetraborate polyions of charge —1 as the predominant forms, while according to MAZUREK and PERLIN [10] the concentrated solutions are to be considered as the equimolecular mixture of H_3BO_3 and alkali borate.

From diborate up to hexaborate the existence of several forms has been assumed in aqueous medium [2]. After INGRI [1] the borate equilibrium measured potentiometrically can be characterized with any of three variations of the polyion species (Table I). The picture given by him has been supported later by physical methods [11—13].

The 3 : 1 compound of boron–curcumin is known from the analytical literature [14], but no equilibrium data are to be found on the formation of polynuclear glycol–borate complex as the predominant form. In the case of mannite [9] and ascorbic acid [15] ligands it might be assumed that owing to the high stability of the mononuclear complex, the borate polyions depolymerize. However, KALACHEVA *et al.* [16] found even in boric acid of higher concentration only mononuclear ethylene glycol complexes. Since the stability of the latter is low [7, 17, 18], the question arises, whether it is due to structural causes that glycol is not bound by the polyborate ion, or whether the absence of data can be ascribed to the neglections introduced into the calculations?

Experimental

The preparation of the stock solutions and the potentiometric method were the same as described in our previous communication [7]. Changing the boric acid/borate ratio by alkaline titration between 6.5 and 9.5 pH, boric acid solutions of 0.050, 0.100 and 0.200 *M* were investigated in the presence of 0, 0.100, 0.200, 0.500, 1.000 and 2.000 *M* of ethylene glycol, and in 1.000 *M* $Na(ClO_4)$ at 25 ± 0.1°C. A Hewlett–Packard HP9100A computer was used for the calculations.

Symbols

HB mononuclear boric acid: $B(OH)_3$

B^- $B(OH)_4^-$ ion

D ethylene glycol

C_B total concentration of boron

C_D total concentration of glycol

C_A titration data, denoting the total concentration of borate anions. (In the pH-range investigated, C_A is equal to the quantity of the weighed in sodium hydroxide.)

Equilibria and constants

The following process:

$$q\,HB + r\,D \rightleftharpoons H_p B_q D_r^{(q-p)-} + (q-p)\,H^+ \tag{1}$$

denotes in the case of $r = 0$ the equilibrium of formation of the borate polyions, and in the case of $r > 0$ that of the glycol–borate complexes.

$$K_{pqr} = [H_p B_q D_r^{(q-p)-}]\,[H^+]^{(q-p)}\,[HB]^{-q}\,[D]^{-r} \tag{2}$$

K_w ion product of water

Auxiliary functions

$$W = \frac{[H^+]\,C_A}{C_B - C_A} \tag{3}$$

as defined in our previous communication [7]. In the equilibria to be discussed here:

$$W = \frac{\sum_{p=0}^{p_{max}} \sum_{q=1}^{q_{max}} \sum_{r=0}^{r_{max}} (q-p) K_{pqr} [HB]^{(q-1)} [H^+]^{(p-q+1)} [D]^r}{1 + \sum_{p=0}^{p_{max}} \sum_{q=1}^{q_{max}} \sum_{r=0}^{r_{max}} p K_{pqr} [HB]^{(q-1)} [H^+]^{(p-q)} [D]^r}$$

R serves for the comparison of the calculated and measured values:

$$R = [H^+] C_A = W(C_B - C_A) \tag{4}$$

$$R = \sum_{p=0}^{p_{max}} \sum_{q=1}^{q_{max}} \sum_{r=0}^{r_{max}} (q-p) K_{pqr} [HB]^q [H^+]^{(p-q+1)} [D]^r \tag{5}$$

R^* $|(-\log R)_{measured} - (-\log R)_{calculated}|$ (absolute value)
$\bar{R}^*$ arithmetic mean of the individual R^* values.

Discussion

Polyborate equilibria

For the conversion of the constants given by INGRI [1], which describe the polyborate equilibrium with the formation of boron-hydroxo complexes, to the equilibrium constants [2] used by us, the value of the ion product of water in 1.000 *M* $Na(ClO_4)$ is needed. Since we did not find accurate enough data in the literature [2], we used the $\log K_w = -14.22$ value [1] valid in 3.000 *M* $Na(ClO_4)$ for the conversion of INGRI's constant, and obtained $-\log K_{010} = 8.95$ for the dissociation constant of boric acid. We have measured in 1.000 *M* $Na(ClO_4)$ a value of 8.85 [7], and assumed therefore that in this medium $\log K_w = -14.12$. This approximation is thought to be permissible, since the functions of formation published by INGRI [19] for polyborate solutions run practically parallel to the curves which can be calculated from the data measured by us. The three variations of the constants, which according to INGRI [1] describe almost equally well the experimental data, are given in Table I.

Data measured by us are shown in Fig. 1, in form of $-\log W$ *vs.* $f(pH)$ functions. At $C_B = 0.010$, and in the case of 0.020 *M* (with good approximation) out of the K_{pq0} constants the others besides K_{010} can be neglected (boric acid is present in monomeric form), so that the straight line $-\log W = -\log K_{010}$ is obtained. In more concentrated solutions, curves with inflection indicate the appearance of polyanions.

The K_{pq0} constants were calculated on a computer [20]. The [HB] variable has been calculated from experimental pH and C_B data, with read-in

K_{pq0} starting values by the iteration method of Newton—Rawson. The agreement between calculated and measured values has been investigated by INGRI on the basis of the Z auxiliary formation function [1]. Since C_B used for iteration is included also in the definition of Z, its back-calculation is superfluous, so that we used the considerably simpler R control value. This value obtained directly from experimental data [4] can be also calculated with the aid of Eq. (5). That K_{pq0} constant-variation was accepted, which gave the lowest $\bar{R}^*$ value.

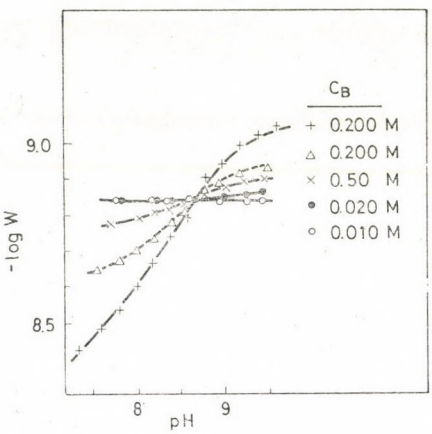

Fig. 1. Shape of the —log W *vs.* f(pH) plots, characteristic of the formation of borate polyions, at various boron concentrations

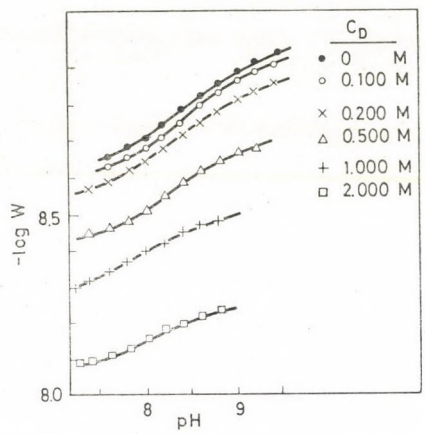

Fig. 2. —log W *vs.* f(pH) plots for solutions containing $C_B = 0.100$ M boron and ethylene glycol of various concentrations

Starting from data in the literature (Table I), the values $q_{max} = 4$ and $p_{max} = q_{max} - 1$ have been taken into consideration in our calculations, as the $H_4B_5^-$ ion is formed only in the $C_B > 0.2$ M and pH < 7 ranges.

Our results support the conclusions of INGRI [1]: the polyborate equilibria can be described almost equally well with either of the three variations of the constants (a, b and c in Table II). The closest agreement between the calculated and measured values was obtained under the assumption of the formation of all three polyions (variant a), but even in the case of b and c the value of $\bar{R}^*$ was less than the error of reproducibility of the measurements.

Under consideration of the uncertainty of the conversion factor K_W, agreement with data in the literature [1] is acceptable.

Formation of polynuclear ethylene glycol-borate complexes

Figure 2 shows a representative part of our data of measurement [20]. The slope of the curves decreases with increasing glycol concentration, and this indicates according to Fig. 1 a decrease in the average degree of polymerization.

Table I

Equilibrium constants of polynuclear borate anions ($-\log K_{pq} \pm 3\sigma$) in the literature (Data of INGRI [1] *recalculated using $-\log K_w = 14.12$. σ is the standard deviation)*

3.000 *M* $Na(ClO_4)$, 25°C

	a	b	c
$-\log K_{01}$	8.85 ± 0.01	8.85 ± 0.02	8.84 ± 0.02
$-\log K_{23}$	6.71 ± 0.07	6.58 ± 0.08	6.65 ± 0.11
$-\log K_{13}$	16.51 ± 0.24	16.15 ± 0.13	—
$-\log K_{24}$	14.69 ± 0.12	—	14.45 ± 0.08
$-\log K_{45}$	6.70 ± 0.70	6.70 ± 0.70	6.70 ± 0.70

Table II

Equilibrium constants of the formation of polynuclear borate anions ($-\log K_{pq0} \pm \Delta$) according to our measurements (Δ is the standard error of mean)

1.000 *M* $Na(ClO_4)$, 25°C
$C_B = 0.050$—0.200 *M*, pH = 6.5—9.5

	a	b	c
$-\log K_{010}$	8.85 ± 0.01	8.85 ± 0.01	8.85 ± 0.01
$-\log K_{230}$	7.00 ± 0.05	6.95 ± 0.08	6.95 ± 0.08
$-\log K_{130}$	16.55 ± 0.05	—	16.50 ± 0.08
$-\log K_{240}$	14.90 ± 0.05	14.85 ± 0.08	—
$\bar{R}^*$	0.006	0.009	0.009

Thus, no stable ethylene glycol–tetraborate complex is to be assumed. (Moreover, neither is the existence of an anion with charge —3 probable below pH 10, yet it can be seen from Fig. 5 that glycol could be linked only by the formation of a further tetracoordinated boron to the tetraborate ion, which would correspond according to equilibrium 1 to the dissociation of a third proton.)

Similarly as in the case of mononuclear complexes, here too it is to be expected that the probability of the linkage of the second ethylene glycol ligand is lower than that of the first. On the basis of all this, if ethylene glycol–polyborate complex is formed, this will be $H_2B_3D^-$ or HB_3D^{2-}.

In the course of our calculations, in the first step only the formation of mononuclear glycol–borates (BD^-, BD_2^-) has been taken into account, and the existence of the forms HB, B^-, $H_3B_3^-$, HB_3^{2-}, $H_2B_4^{2-}$ was considered

in the calculations. However, the $\bar{R}^*$ value obtained in this way was threefold of the $\bar{R}^*$ value found best in the description of the polyborate equilibrium.

Next, we investigated what improvement can be achieved between the calculated and measured data, when the formation of the $H_2B_3D^-$ complex is also considered.

It was assumed as a starting point that glycol is bound with the same probability to the borate and triborate ions, so that the equilibrium constants of the two following processes:

$$B^- + D \rightleftharpoons BD^-$$

$$H_2B_3^- + D \rightleftharpoons H_2B_3D^-$$

β_{011} [7] and K_{231}/K_{230} are identical.

The $\bar{R}^*$ value obtained in this way was also too high. Changing the ratio of the constants systematically, a constant was found, at which the difference between the measured and calculated data was minimal (Fig. 3).

A qualitatively similar result was obtained also in the cases, when variation b or c of Table II has been used, but the $\bar{R}^*$ values were higher than 0.01.

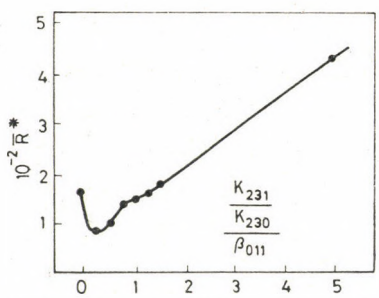

Fig. 3. Comparison of calculated and measured data for solutions containing ethylene glycol and borate polyions. (The local extreme value is indicative of the formation of the $H_2B_3D^-$ complex)

Table III

Equilibrium constants of the formation of ethylene glycol–borate complexes $(-\log K_{pqr} \pm \Delta)$

1.000 *M* $Na(ClO_4)$, 25 °C, pH = 6.5—9.5
C_B = 0.010—0.200 *M*
C_D = 0.100—2.000 *M*

$-\log K_{011}$	8.60 ± 0.02
$-\log K_{012}$	9.77 ± 0.11
$-\log K_{231}$	7.35 ± 0.20

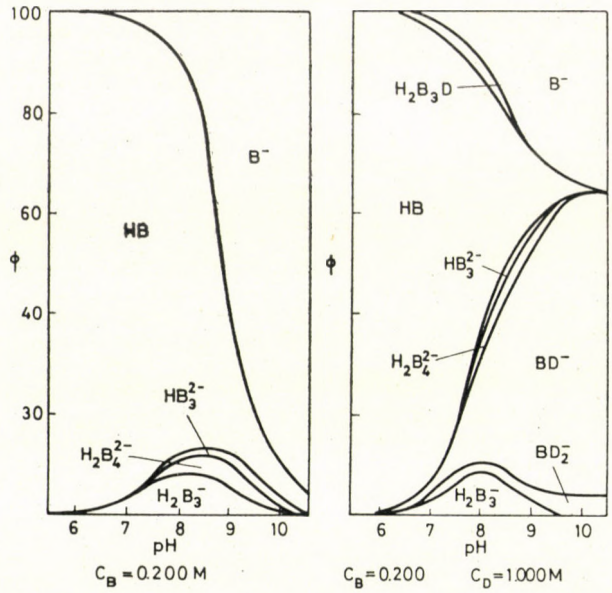

Fig. 4. Percentage distribution of the ions formed (Φ) as a function of the pH value. (The value of Φ is represented by the length of the given section of the vertical line of intersection)

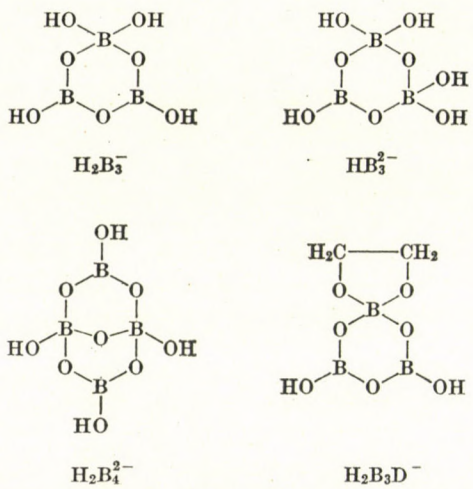

Fig. 5. Probable structures of borate polyions existing in aqueous solutions and of the polynuclear ethylene glycol–borate complex described on the basis of equilibrium measurement

When assuming the formation of HB_3D^{2-}, the agreement with experimental data was poorer than above.

Thus, according to our results, the probability of the linkage of glycol to the H_2B_3 ion is about four times lower than the probability of the formation of the BD^- complex. Equilibrium constants are compiled in Table III.

On the basis of our data, the formation of other ethylene glycol–boron adducts cannot be made probable. The distribution of the ions as a function of pH is shown in Fig. 4, and the assumed structure of the polyions in Fig. 5.

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DISCUSSION OF THE THERMODYNAMIC EQUATION OF MOTION ON THE BASIS OF THE THERMOSTATIC THEORY OF STABILITY

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In the one-variable form of the thermodynamic equation of motion there is a thermostatic coefficient of stability, which is the basis for the classification of homogeneous equilibrium states. On the basis of this fact, the peculiar forms and solutions of the thermodynamic equation of motion for different classes of homogeneous equilibrium states are discussed. The results permit interpretation of the deceleration of thermodynamic equalization processes, observed in the vicinity of the critical state.

1. Introduction

The linear theory of nonequilibrium thermodynamics developed by Onsager states that:

$$\dot{\alpha} = \mathbf{L}X(\alpha) \tag{1}$$

where α is a number vector consisting of the nonequilibrium state variables α_1, $\alpha_2, \ldots \alpha_n$, $\dot{\alpha}$ is the time derivative of α, X is the number (row) vector of the thermodynamic forces, $\mathbf{L}$ denotes the matrix of conductivity coefficients, n is the number of interactions between the system and its surroundings. System of equations (1) describes the change of quantities $\alpha_i = a_i - a_{i0}$ with time; a_i denotes the molar extensive quantities and index $_0$ refers to the equilibrium values. Elements of X are the corresponding $\Delta\Gamma_i'$ differences of the entropic intensive variables.

Matrix $\mathbf{L}$ is positive definite since, as is well known, it is connected with the entropy production by the relation

$$\dot{s} = \frac{1}{2}\bar{X}\mathbf{L}X \tag{2}$$

where $\bar{X}$ denotes a column vector composed of the elements of X; s however is positive according to the Second Law of thermodynamics (if $X \neq O$).

The so-called thermodynamic equation of motion can be obtained by the expansion of functions X into series around the point of $\alpha = O$, neglecting

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higher than first order terms. Its more general derivation on the basis of the axiomatic description of thermodynamics is due to GYARMATI [1, 2]. This system of differential equations was applied in the investigation of many important questions of non-equilibrium thermodynamics [2—6]; GYARMATI and OLÁH deduced the Prigogine—Glansdorff Theorem for discontinuous systems on this basis [3]. The nonlinear generalization of the system of differential equations

$$\dot{\alpha} = \mathbf{C}\alpha \tag{3}$$

was treated by GYARMATI in his work on the nonlinear generalization of the Onsager theory [2, 3]. In Eq. (3)

$$\mathbf{C} = \mathbf{L} \cdot \mathbf{g} \tag{4}$$

where **g** denotes the matrix obtainable from the second derivatives of the entropy function, **C** is a matrix of the kinetic coefficients, or, according to GYARMATI, the coupling matrix between the non-equilibrium state space α and the velocity space $\dot{\alpha}$.

Matrix **g** appears in the series expansion of the entropy function around the equilibrium state:

$$\Delta s = \frac{1}{2}\bar{\alpha}\mathbf{g}\alpha + \ldots \tag{5}$$

where $\bar{\alpha}\mathbf{g}\alpha$ denotes the quadratic form $\mathrm{d}^2 s$. So far as we know, Eq. (3) was investigated only in the case when the entropy has a maximum in the equilibrium state, *i.e.* when the quadratic form $\mathrm{d}^2 s$ was negative definite.

The thermostatic theory of stability, like non-equilibrium thermodynamics, has been developed during the last years [8—11]. According to this theory, if $\alpha = 0$ corresponds to the homogeneous state of the system investigated, this state can be stable, neutral or unstable, depending on which of the following conditions for the quadratic form $\mathrm{d}^2 u$ is satisfied:

$$\mathrm{d}^2 u > 0 \tag{6}$$

$$\mathrm{d}^2 u \geq 0 \tag{7}$$

$$\mathrm{d}^2 u \gtreqless 0 \tag{8}$$

Here u denotes the internal energy function.

Relations (6)—(8) represent a classification within the framework of the theory of 'local stability'. Investigation of 'global stability' involves higher order terms of $\mathrm{d}^2 u$ [8]. Locally stable states characterized by condition (6) can be further classified on the basis of this theory. Matrix **g** shows a characteristic behaviour for the different types of equilibrium states, accordingly,

in certain cases in Eq. (1) terms containing higher than first powers of parameters α can play an important role, too. In the present work we investigate the characteristic behaviour of the thermodynamic equation of motion and of its solutions for the different classes of homogeneous states. For the sake of simplicity, we shall deal only with the special case when all but one thermodynamic force disappear, and the remaining one can be arbitrarily chosen.

2. Thermodynamic equation of motion in the one-variable case

In the case mentioned above we have for the entropy production:

$$\dot{s} = \frac{1}{2} L_{nn} X_n^2 \tag{9}$$

where X_n is the thermodynamic force, which has a nonzero value, and L_{nn} is the appropriate conductivity coefficient, which is positive according to Eq. (2). From now on this will be referred to as the one-variable case.

We again restrict our investigations to those states described by Eq. (1), but we shall also consider the cases when in the series expansion of $X_n = (\Delta\Gamma'_n)_{\Gamma'_1,\ldots\Gamma'_{n-1}}$ according to variable α_n the first or the first and second order terms vanish, so that the first term retained is a higher order term. Accordingly, we investigate the thermodynamic equation of motion in the following form:

$$\alpha_n = L_{nn}\left[\Phi_n \alpha_n + \frac{1}{2}\frac{\partial \Phi_n}{\partial \alpha_n}\alpha_n^2 + \frac{1}{6}\frac{\partial^2 \Phi_n}{\partial \alpha_n^2}\alpha_n^3 + \ldots\right] \equiv$$
$$\equiv A_1 \alpha_n + A_2 \alpha_n^2 + A_3 \alpha_n^3 + \ldots \tag{10}$$

In Eq. (10) quantity $(\partial\Gamma'_n/\partial a_n)_{\Gamma'_1,\ldots\Gamma'_{n-1}}$ is denoted by Φ_n, Γ'_n is the entropic intensive quantity of the n-th interaction. This quantity is connected with the intensive quantity of the n-th interaction Γ_n via the equations:

$$\Gamma'_n = -\Gamma_n/T \qquad (\Gamma_n \neq T) \tag{11}$$

$$\Gamma'_n = 1/T \qquad (\Gamma_n = T) \tag{12}$$

Using (11) and (12):

$$\Phi_n = -\frac{1}{T}\left(\frac{\partial \Gamma_n}{\partial a_n}\right)_{\Gamma_1,\ldots,\Gamma_{n-1}} \qquad (\Gamma_n \neq T) \tag{13}$$

$$\Phi_n = -\frac{1}{T^2}\left(\frac{\partial T}{\partial s}\right)_{\Gamma_1,\ldots,\Gamma_{n-1}} \qquad (\Gamma_n = T) \tag{14}$$

If T is one of the quantities $\Gamma_1, \ldots \Gamma_{n-1}$, then, according to Eq. (13), we have

$$\Phi_n = -\frac{1}{T}\Pi_n \tag{15}$$

while if $\Gamma_n = T$, then according Eq. (14)

$$\Phi = -\frac{1}{T^2}\Pi_n \tag{16}$$

Here by Π_n we denote the so-called isodynamic coefficient of stability connected with the n-th interaction.

In the following we investigate the thermodynamic equation of motion in the form of (10) in different homogeneous equilibrium states classified according to the behaviour of the quantity Π_n if $\Gamma_n \neq \Gamma$. Solutions will be described taking into account only the first non-vanishing term. The classification of the equilibrium states according to the properties Π_n is based on the thermostatic stability theory and will be reviewed in detail in another paper [12].

3. Stable equilibrium states

In stable equilibrium states we have

$$\Pi_n > 0 \tag{17}$$

Then, according to (15) and (16),

$$\Phi_n < 0 \tag{18}$$

so that Eq. (10), with only the first non-vanishing term assumes the form:

$$\dot{\alpha}_n = A_1 \alpha_n \tag{19}$$

where

$$A_1 < 0 \tag{20}$$

according to relations (17)—(18) and the definition of A_1 given in (10). From Eq. (19) we have:

$$\alpha_n(t) = \alpha_n(0) e^{+A_1 t} \tag{21}$$

According to (21), the perturbation with an initial value of $\alpha_n(0)$ decays exponentially in time. This is the case treated so far in the literature. We wish to complete this treatment by emphasizing that, taking into account higher than first order terms in (10) leads to a modification of solution (21) and thus

we can describe the decay of perturbations into stable equilibrium states more accurately. In special cases we can have a limiting value of $\alpha_n(0)$ beyond which stability will cease.

4. Unstable equilibrium states

In unstable equilibrium states we have

$$\Pi_n < 0 \tag{22}$$

so that according to (15) and (16),

$$\Phi_n > 0 \tag{23}$$

The first approximation of Eq. (10) still has the form of (19) and its solution will have the form (21), but now we have:

$$A_1 > 0 \tag{24}$$

and, because of this, however small $|\alpha_n(0)|$ is, $\alpha_n(t)$ will tend to infinity in time. This is, of course, excluded on physical grounds, and in the search for a physically meaningful solution we shall have to take into account higher than first order terms in Eq. (10). If we terminate the expansion at the quadratic term, we shall have:

$$\dot{\alpha}_n = A_1\alpha_n + A_2\alpha_n^2 \tag{25}$$

Equation (25) at $\alpha_n = 0$ will have

$$a_n \equiv -\frac{A_1}{A_2} \tag{26}$$

as an equilibrium solution, *i.e.* as a solution at which $\dot{\alpha}_n = 0$. Clearly if the sign of $\alpha_n(0)$ is the same as that of $-A_1/A_2$, the increase of the absolute value of α_n will stop at that α_n which is the solution of (26).

This mathematical statement reflects the following physical facts. From the thermostatic theory of stability it is known that unstable homogeneous states are connected with first order phase transitions. In these states, because of the instability of the homogeneous equilibrium, the thermodynamic system investigated cannot exist, but a stable heterogeneous equilibrium state develops. This latter is nothing else but the state of phase equilibrium. Equation (25) or more exact approximations of (10) are suitable for the quantitative description of such changes in time.

5. Neutral equilibrium states

On the basis of the thermostatic theory of stability the homogeneous states which are characterized by

$$\Pi_n = 0 \tag{27}$$

are referred to as neutral. From Eqs (27) and (10) it is clear that we then have

$$A_1 = 0 \tag{28}$$

so that according to (10), the first approximation of the thermodynamic equation of motion will be:

$$\dot{\alpha}_n = A_2 \alpha_n^2 \tag{29}$$

which has the solution

$$\alpha_n(t) = \frac{1}{\frac{1}{\alpha_n(0)} - A_2 t} \tag{30}$$

It is clear from (30) that perturbation $\alpha_n(0)$ will disappear in time in this case too, but its decay will be 'slower'. Firstly, α_n may temporarily increase in time, secondly, in the case of $t \to \infty$ it disappears as a function of $1/t$ which means a slower change than in the case of an exponential decay.

Neutral homogeneous states are lying on the boundary of the set of stable homogeneous states: these are designed as 'spinodal' in the theory of thermostatic stability. Accordingly, Eq. (30) quantitatively reflects the difference which we have between stable and neutral equilibrium states.

All three main classes of homogeneous states have been reviewed. In what follows, we shall discuss two special states which have great practical importance.

6. States of maximum stability

In the thermostatic theory of stability the term 'maximally stable' is applied to those homogeneous states for which the so-called 'determinant stability' tends to infinity [10, 13—14]. We have shown [13] by the trivial factorization of the determinant of stability and by the quantitative expression of the static Braun—Le Châtelier principle that in such states one of the isodynamic coefficients of stability tends to infinity and that any state at which one of the isodynamic coefficients of stability tends to infinity is a state of maximum stability.

Let us suppose that in the equilibrium state investigated we have

$$\Pi_n \to \infty \tag{31}$$

then, according to (15) and (16),

$$\Phi_n \to \infty \tag{32}$$

i.e. if L_n is finite:

$$A_1 \to \infty \tag{33}$$

From this, taking into account Eq. (21), it is apparent that any perturbation can exist only for an infinitesimally short time. This fact shows that in maximally stable states a nonequilibrium state cannot develop. This statement shows a property of the states of maximum stability, which was not treated in the literature connected with the theory.

7. The critical state

In the thermostatic theory of stability the states characterized by a minimum, and a zero determinant of stability are designated as critical. It can be shown that in these states all isodynamic stability coefficients have minimum values of zero, *i.e.* in these special states of neutral equilibrium:

$$\left(\frac{\partial \Pi_n}{\partial a_n}\right)_{\Gamma_1,\ldots,\Gamma_{n-1}} = 0 \tag{34}$$

$$\left(\frac{\partial^2 \Pi_n}{\partial a_{n^2}}\right)_{\Gamma,\ldots,\Gamma_{n-1}} > 0 \tag{35}$$

According to (15) and (16)

$$(\partial \Phi_n / \partial a_n) = 0 \tag{36}$$

$$\left(\frac{\partial^2 \Phi_n}{\partial a_{n^2}}\right) < 0 \tag{37}$$

that is Φ_n takes on a maximum value of zero. From Eqs (36) and (37) it follows that

$$\dot{\alpha}_n = A_3 \alpha_n^3 \tag{38}$$

in the first approximation of Eq. (10).

Upon integrating (38) we will have:

$$\alpha_n(t) = \pm \sqrt{\frac{1}{\frac{1}{\alpha_n(0)^2} - 2A_3 t}} \tag{39}$$

From (39) it is apparent that any perturbation $\alpha_n(0)$ tends to zero in a monotonous way, however, now we have an asymptotic decay according to $1/\sqrt{t}$, *i.e.* a slower one than in the states of the spinodal and a much slower one than that in the stable equilibrium states. This result is a dynamic expression of TISZA's characterization of the critical state. According to this, critical states are stable, but their stability diminishes as compared with 'normal' stable states [8].

The recently established fact [16] that the thermodynamic equalization processes decelerate at the critical point can be regarded as an experimental verification of Eq. (39) obtained theoretically.

8. Discussion

We have shown that in a thermodynamic system whose state can be characterized by thermostatic variables $\Gamma_1, \ldots, \Gamma_{n-1}$, a_n, and only the value of a_n may differ from its equilibrium value, and further, if T is among $\Gamma_1, \ldots, \Gamma_{n-1}$, then the equation of motion (10) is sufficient to characterize the variation of α_n in time. We have taken into account only the first non-vanishing terms, and the equilibrium states were classified according to the resulting behaviour.

This treatment can be generalized from more than one aspect. First, even in this one-variable approximation one can take into account higher terms. Thus one obtains a more refined description. We have disregarded this case mainly because in this work we were relying only on the results of the investigations of thermostatic stability in a local sense. The analysis of the higher order terms requires an analytical treatment of macroscopic stability. Though we have made some progress in this direction [17], the theory cannot yet be considered as fully elaborated.

A consideration of the higher order terms in expansion (10) is particularly necessary in unstable states on physical grounds, as has been indicated in Chapter 4. It is needed also in neutral but not critical states because of similar reasons since, as indicated by (30), for $\alpha_n(t)$ we will then have an expression the denominator of which may become zero. This belongs to a certain value of t defined by $1/\alpha_n(0) = A_2 \cdot t$ in the case if $\alpha_n(0)$ and A_2 have the same sign. Strictly speaking, in the vicinity of this singular state, the absolute value of α_n will increase beyond any limit, which contradicts the assumption on the basis of which (10) has been replaced by (29), *viz.* that $|\alpha_n|$ is small. We have no such difficulty in stable and critical equilibrium states.

We wish to note that, according to (30), in neutral equilibrium states α_n varies with time, a fact that contradicts the usual meaning of a neutral equilibrium in physics. This apparent contradiction arises from the fact that the classification of neutral equilibria is made in the range of the theory of

local stability and this study is limited to an analysis of Φ_n or Π_n. Accordingly, in this case in (10) $\dot{\alpha}_n = 0$ when $\Pi_n = 0$ in this rough approximation. Thus the variation of quantity α_n in time arises from a consideration of higher order terms; if these are neglected, then the state we obtain upon perturbation remains unchanged in time in accord with the usual definition of a neutral equilibrium.

Investigation of the case when $T = \Gamma_n$ would probably lead to new results.

Naturally, this treatment can be extended to the case of many variables, however, this would yield the new results in a more complicated way.

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CATHODIC REDUCTION OF Ce(IV) ON GERMANIUM-SEMICONDUCTOR ELECTRODE*

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The cathodic reduction of ceric ions on the surface of *n*- and *p*-Ge cathodes has been studied in the presence of 2.0 *N* and 1.0 *N* sulphuric acid. *E vs.* log CD curves have been plotted for *X* $(NH_4)_2[Ce(NO_3)_6]$; *X* denotes gram mole litre^{-1}. Tafel relation is valid in a fairly long range of CDs. Overpotential increases on the introduction of ceric ions to sulphuric acid solutions. The reduction process at the surface of *n*-Ge cathode occurs in a comparatively narrow range of CDs, at higher CDs the discharge of hydrogen ions dominates over the reduction of the oxidant. On illumination, the saturation current density observed for *n*-Ge cathode decreases. The process of reduction seems to occur through the participation of valence band electrons.

Redox reactions on a semiconductor electrode differ considerably from those occurring on metal electrodes. A redox reaction may involve the transfer of either of two types of current carriers. The conduction band mechanism involves electron extraction or injection and the valence band mechanism may involve hole depletion or hole injection on the semiconductor electrode. GERISCHER [1] and DEWALD [2] suggested that in the reduction and oxidation of ion in a solution on the semiconductor electrode the electron transfer was dependent on the potential of the redox system along with the usual dependence upon the bias potential and equilibrium concentrations of holes and electrons. Anodic and cathodic processes on semiconductor electrodes lead to typical saturation currents which are affected by the addition of oxidant and reductant and are light sensitive [3—6]. The redox reaction occurs without either anodic dissolution or cathodic hydrogen evolution in a very narrow range of potential [7].

The present investigations emphasize the kinetic study of the reduction of Ce^{4+} ions at the surface of Ge-semiconductor electrode with particular reference to ascertain the nature of current carrier involved during the process.

Experimental

Ge single crystals of rectangular shape with a large face to edge ratio were used as electrodes. The resistance, plane orientation and type of germanium crystals were ascertained by the usual procedure [8]. The ohmic contact of germanium electrode was made by soldering

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copper wire with Pb–Sn alloy using $ZnCl_2$ flux. The copper wire was drawn through a Jena glass tube and was fixed with araldite. The surface of the crystals was rubbed with carborundum powder and etched with CP—4 solution (0.3 ml of bromine dissolved in 15.0 ml of glacial acetic acid, 15.0 ml of hydrofluoric acid and 25.0 ml of concentrated nitric acid) for one minute followed by immediate rinsing with conductivity water. The surfaces were covered with extra-pure E. Merck paraffin wax and an area of 1.0 cm × 0.5 cm was cut into it and the bare surface was used in the polarization measurements.

The chemicals used unless otherwise stated were B.D.H., AnalaR grade. Stock solution of sulphuric acid was prepared in fresh doubly distilled water and kept in Jena glass reagent bottles. The desired concentrations were obtained using volumetric method followed by appropriate and accurate dilutions.

H-shaped pyrex conductivity cell [8] was used for the experimental work. Platinum auxiliary electrode was used as counter electrode. The experiments were carried out in the dark at 25 ± 0.01°C in an air thermostat. The results were recorded galvanostatically in stirred solution and potential of Ge-electrode against saturated calomel electrode (SCE) was measured after one minute polarization. The graphs were plotted taking mean of at least six readings varying in a very narrow range of ±0.005 V.

A pyrex mercury vapour lamp operating at 240 V DC was used for illumination. The ilght was condensed on the surface of germanium using green monochromator.

Results and discussion

Tafel curves for the reduction of ceric ions on Ge-cathode are represented in Figs 1 and 2, in the presence of 2.0 *N* and 1.0 *N* sulphuric acid, respectively. The nature of polarization curve is substantially changed on the addition

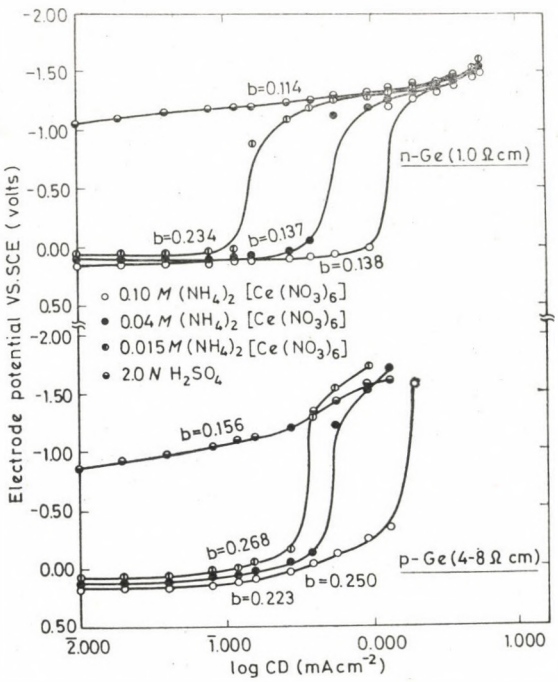

Fig. 1. Cathodic polarization curves for the reduction of Ce^{4+} ions in the presence of 2.0 *N* H_2SO_4 at 25°C

of ceric ions to sulphuric acid solutions. Cathodic saturation currents are observed for all the stated compositions but those obtained on *n*-Ge are sharper than the saturation current observed on the surface of *p*-Ge cathode. On *n*-Ge cathode a steady increase in electrode potential with applied current density is observed at potentials lower than about —0.125 V. The saturation current density in all the cases is found to decrease with the concentration of ceric ions.

Tafel relation is obeyed in all the solutions in a fairly long range of current density (CD). The slopes of the curves have comparatively lower values for *n*-Ge cathode. For *n*-Ge cathode, the values of *b* for various concentrations of ceric ions in 2.0 *N* sulphuric acid vary from 0.183 V to 0.234 V per unit of CD and in presence of 1.0 *N* sulphuric acid from 0.178 to 0.226 V per unit of CD. With some exceptions, the values of *b* decrease with a parallel decrease in the concentration of ceric ions. The nature of the curves obtained for the cathodic reduction of Ce^{4+} ions at *p*-Ge cathode is analogous; the values lying between 0.233 and 0.268 V per unit of CD in 2.0 *N* sulphuric acid and between 0.208 and 0.250 V per unit of CD in 1.0 *N* sulphuric acid are obtained. The values of *b* in the absence of the oxidant are in all cases lower than those in presence of oxidant, and range from 0.114 to 0.156 V per unit of CD.

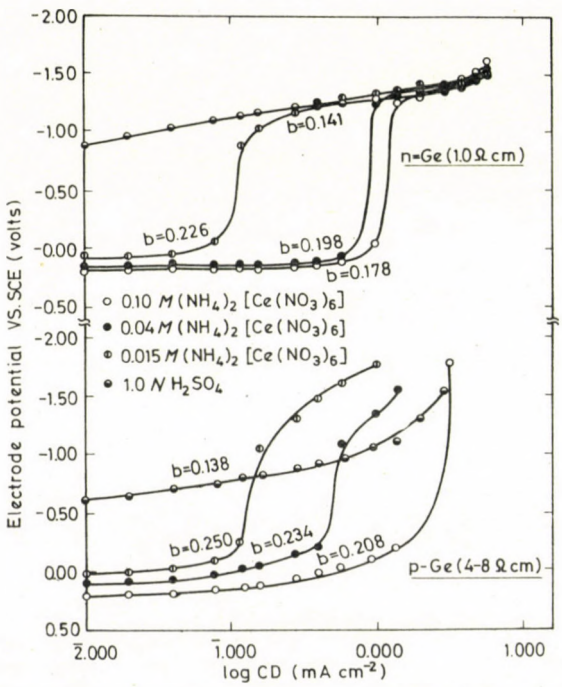

Fig. 2. Cathodic polarization curves for the reduction of Ce^{4+} ions in the presence of 1.0 *N* H_2SO_4 at 25°C

Fig. 3 illustrates the effect of illumination on the polarization behaviour of *n*- and *p*-Ge cathode during the reduction process of ceric ions. A remarkable change in the cathodic polarization behaviour on illumination is observed on *n*-Ge cathode. The saturation current density shifts towards lower cathodic current and this effect is multiplied on increasing the time of exposure. The change in overpotential is negligible at CDs less than saturation current density, but at higher CDs it becomes sufficiently large. The *p*-Ge cathode behaves in quite a different manner. The change in the electrode potential due to illumination is so small that the three curves almost overlap each other. The nature of curves thus remains apparently unaltered on illumination.

The results obtained for the cathodic reduction of cerium ions in acidic solutions reveal that the cathodic polarization curves are influenced remarkably by the introduction of cerium ions to sulphuric acid solutions. The overpotential is increased by about 1.0 volt, by the addition of ceric ions to sulphuric acid. The change in overpotential may be due to change in the nature of cathodic reaction, occurring at the surface of germanium electrode.

Well expressed saturation current densities are observed on *n*-Ge cathode, the saturation current densities observed on *p*-Ge cathode are rather diffuse. The shift of saturation current density towards more negative value with increasing concentration of the oxidant is in essential agreement with

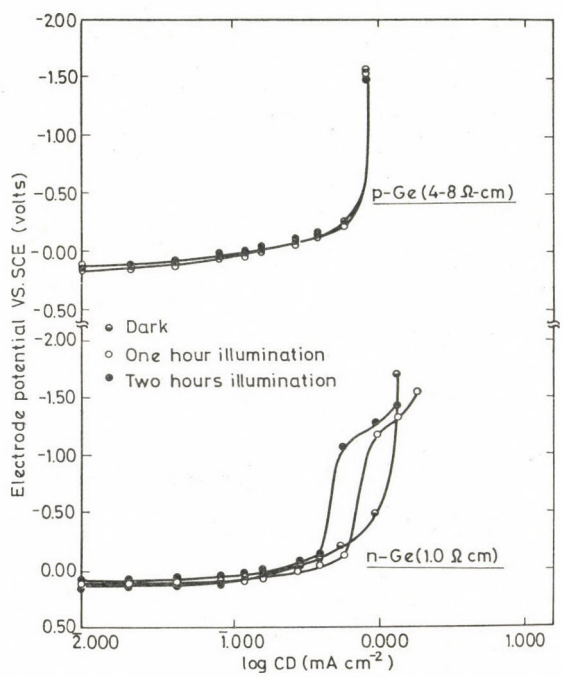

Fig. 3. Influence of illumination on the cathodic polarization curves

the observations of GERISCHER and BECK [7]. The presence of saturation current densities can be explained on the assumption that valence band electrons are involved during the reduction of ceric ions, that is, holes are produced during the reduction.

The process of reduction involving injection of holes at germanium cathode may be represented as:

$$Ce^{4+} \xrightarrow{i^-} Ce^{3+} + e^+ \qquad (1)$$

where Ce^{4+} ions are reduced to Ce^{3+}, e^+ is the hole produced in germanium and i^- indicates the current flowing in the direction of the cathode. Thus, the reduction process involves the transfer of electrons from the bulk of the semiconductor to the electrode electrolyte interface, which in turn are consumed by the ions of the oxidant. The transfer of electrons does not depend upon the concentration of holes in germanium bulk, but does depend upon the concentration of ions to be reduced [9]. As ceric ions are reduced at the surface of germanium, holes are produced which are to be transported to the bulk from the surface by diffusion. When the rate of reduction of ceric ions becomes higher than the rate of diffusion of holes, holes begin to accumulate at the surface. Consequently, saturation current density is observed when the rate of reduction is maximum. This explains our findings that the saturation of CD is reached on both germanium surfaces irrespective of the type of their conductivity, in accordance with the observations of PLESKOV [10].

A support to our assumption that ceric ions are reduced mainly through the participation of valence band electrons is given by the fact that the saturation current density observed on *n*-Ge cathode is sharper. Since holes are the minority carriers in *n*-Ge and as a rule transport of minority carrier is governed by diffusion only [11], the concentration gradient produced in this case is large and leads to well defined saturation current density. In the case of *p*-Ge, the rate of transference of holes is accelerated under the influence of electric field and, consequently, the saturation current observed is not so sharp. If the conduction band electrons were to participate, the saturation current density would have been observed on *p*-Ge surface only, electron being minority carrier in *p*-Ge. Since *n*-Ge is electron rich and when biased cathodically it is enriched in electron concentration, no saturation current density will be obtained in this case. The injection of holes in valence band during reduction of ceric ions has been reported by GERISCHER and BECK [12] and others [13]; our findings are in accordance with them.

The curves in Figs 1 and 2 show that on *n*-Ge cathode a flat region is observed in the post-saturation current density range. In this region the curves, both in the absence and presence of ceric ions, become parallel and obey Tafel relation. This region may be due to the discharge of hydrogen ions on

the cathode at the place of reduction of ceric ions. At the saturation current density ceric ions are reduced as fast as they arrive at the surface by diffusion; and the potential increases until the next cathode reaction, namely, hydrogen ion discharge occurs. GERISCHER and BECK [12] have also noticed such a behaviour in the polarization curves of *n*-Ge cathode and suggested that at potentials more negative than —1.0 V, the preferred reaction at the germanium cathode is the liberation of hydrogen rather than the reduction of ceric ion. This explanation is justified as such a polarization behaviour is associated with *n*-Ge cathode only. The discharge of hydrogen ions requires electrons which are minority carriers in *n*-Ge and hence is preferred on this electrode. The reduction of ceric ion, thus, occurs in a rather very narrow range of electrode potential at *n*-Ge cathode.

It is difficult to correlate the values of Tafel slopes with the kinetics of redox reaction, however, it may be considered as a measure of the extent of polarization. The numerical values of *b*, the Tafel slope, for *p*-Ge are found to be greater than the respective values of *b* for *n*-Ge. The difference in the extent of polarization may be due to different rates of diffusion of holes under the influence of applied electric field in two types of germanium electrodes. The lower value of *b* indicates that *n*-Ge is more polarized than the *p*-Ge cathode, which is obvious since holes can move through diffusion only, and is not affected by biased potential.

The illumination of the surfaces of germanium injects holes in valence band and thus *n*-Ge tends to attain the behaviour of *p*-Ge on illumination. If holes were to be injected during electrochemical reaction also, the saturation current density should be observed at lower CD on *n*-Ge cathode; a deduction in good agreement with our experimental findings. Prolonged illumination may further shift it to still lower CD which may ultimately become diffused. No change is observed in electrode potential at *p*-Ge, which further supports the reduction mechanism suggested by us. Thus it is well established that the reduction of Ce^{4+} ions involves injection of holes at the germanium surface.

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INVESTIGATION OF THE STOICHIOMETRY OF Pt(IV) AND Pd(II) COMPLEXES

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p-Dimethylaminoanil of anthracene glyoxal forms 1 : 1 complexes with Pt(IV) and Pd(II) as revealed by the method of FENGER *et al.*, a modified version of the method of continuous variation. Stoichiometry of the adducts was obtained by elemental analysis and conductometry. Non-electrolytic nature of the adducts was established by molar conductance measurements.

Introduction

In the continuation of our previous work [1—6] on the ketoanil complexes, the present communication describes the stoichiometric studies on Pt(IV) and Pd(II) complexes of *p*-dimethylaminoanil of anthracene glyoxal which separate from acetonic medium by following FENGER's method of preparation [7] developed recently.

FENGER *et al.* modified the method of continuous variation for the determination of stoichiometry of complexes which form a precipitate during the course of experimentation. They have shown that irrespective of the components (simple or complex) and complete insolubility of the compound, the maximum occurs at the stoichiometric composition of the precipitate on the curve obtained by extrapolation of the weight of the precipitate *vs.* composition of the mixture (obtained by mixing equimolar or non-equimolar component solutions). Composition of the complexes was verified also by elemental analysis and conductometry. Molar conductance values in alcoholic medium were used to establish their electrolytic nature. *p*-Dimethylaminoanil of anthracene glyoxal functions as a bidentate ligand as has been reported earlier [1—6, 8].

Experimental, results and discussion

Two sets of equimolar solutions of the reactants [Pt(IV)-ligand, 0.005 *M* and 0.0025 *M*; Pd(II)-ligand, 0.002 *M* and 0.00143 *M*] were prepared in acetone, stored overnight and mixed in varying proportions according to Job's

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method. After precipitation the samples were filtered through sintered glass crucible, washed successively with acetone and ether and dried under reduced pressure.

The weight of the precipitate was plotted as a function of the mole ratio of the samples and typical plots are shown in Fig. 1 [Curve 1, Pt(IV) complex; Curve 2, Pd(II) complex]. These results suggest a stoichiometry of 1 : 1 (metal : ligand) for each complex. The same ratio was also established by

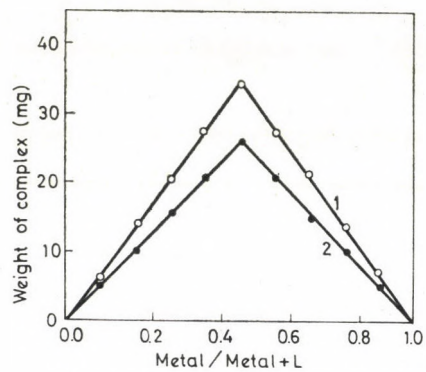

Fig. 1. Plot of the weight of the precipitate *vs.* composition of the mixture obtained by mixing the component solutions. (Curve 1, 0.005 *M*; Curve 2, 0.002 *M*)

elemental analysis [Pt-complex — Found: N 3.95%, Pt 28.16%, Cl 20.33%, $Pt(C_{24}H_{20}N_2O)Cl_4$. Calculated: N 4.06%, Pt 28.31%, Cl 20.53%. Pd-complex — Found: N 5.20%, Pd 19.92%, Cl 13.18%, $Pd(C_{24}H_{20}N_2O)Cl_2$. Calculated: N 5.29%, Pd 20.08%, Cl 13.33%] and conductometrically. Conductometric titrations were performed with 0.005 *M* ligand and 25 ml of 0.001 *M* metal chloride solutions in acetone. Titration curves showing minima at 5 ml of the ligand added evidently show the formation of only 1 : 1 complexes.

Molar conductance (ΛM) value of few Mhos determined with 0.001 *M* solutions of the adducts in acetonitrile suggested their nonelectrolytic nature. This was further verified by adding silver nitrate to the solution, no precipitate was formed.

The suitability of the ligand as a gravimetric reagent for the quantitative determinations [9] of Pt(IV) and Pd(II) was also explored and the results have been published elsewhere.

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BENZOYL SALICYLAL HYDRAZONE AS A CHROMOGENIC REAGENT FOR COPPER (II) AND PALLADIUM (II)

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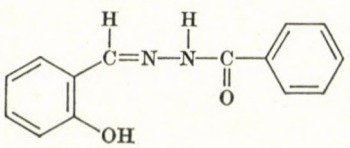
Benzoyl salicylal hydrazone (BSH) has been found to form leaf-green and greenish yellow 1 : 1 complexes with copper(II) and palladium(II), respectively. These complexes were isolated and analysed. Spectrophotometric studies show that in the respective pH regions of 4.5—6.5 and 1.7—2.3, Beer's law is obeyed within the optimum metal ion concentration ranges of 0—5.0 and 0—15.0 ppm at 385 nm and 395 nm, respectively. The molar absorptivities and sensitivities of reaction are 15,500 and 0.0041 $\mu g/cm^2$ for copper, and 7180 and 0.014 $\mu g/cm^2$ for palladium. The effect of a number of foreign ions has been studied. The ratio of metal to ligand is 1 : 1 in both complexes.

Introduction

Recently there has been renewed interest in the chemistry of hydrazones [1—7] because of their use in the detection and determination of many metals by spectrophotometric and gravimetric methods. They give quite sensitive reactions and can be made selective by the appropriate variation of pH or solvent concentration and by the use of suitable masking agents. KATIYAR and TONDON [5] and others [6, 7] have reported 1-isonicotinoyl-2-salicylidene hydrazine as a suitable chelatometric reagent for a number of bivalent, trivalent and tetravalent cations. Other hydrazones, *viz.* pyridine-2-aldehyde-2′-pyridyl hydrazone [8], pyridine-2-aldehyde-2-quinonoyl-hydrazone [9], and picoline aldehyde-2-quinonoyl hydrazone [10] have been suggested to be good chromogenic reagents for the study of copper(II) and palladium(II). This paper describes the spectrophotometric study of copper(II) and palladium(II) with benzoyl salicylal hydrazone (BSH). BSH(I) contains both oxygen and nitrogen as donor atoms, and is therefore a potential chelating agent.



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Experimental

Reagents

BSH solution — A stock solution of the reagent was prepared in acetone. It was synthesized by STRUVE's [11] procedure.

Copper sulphate solution — A standard solution of copper(II) sulphate was prepared from a weighed sample of electrolytic copper after dissolving in nitric acid, fuming with sulphuric acid and diluting it with water to a definite volume.

Palladium chloride solution — The standard solution of palladium(II) chloride was prepared by dissolving palladium(II) chloride (supplied by Johnson and Matthey) in a definite volume of 0.1 *M* hydrochloric acid; the palladium content was determined by the dimethylglyoxime method [12].

Weaker solutions of the metal ions were made by appropriate dilution, as required. Other chemicals used were of reagent grade quality and their solutions were prepared in bidistilled water.

Isolation of the complexes

Mono-(benzoyl salicylal hydrazone) copper(II)

A leaf-green precipitate was obtained by adding 50 ml of 0.05 *M* aqueous solution of copper(II) sulphate to 100 ml of an equimolar solution of the ligand in acetone and raising the pH of the reaction mixture to 5.0 by the addition of acetic acid and sodium hydroxide solutions. The precipitate was digested on a water bath for about 30 minutes, cooled, filtered and washed successively with water, acetone and ether. It was dried and analysed. Yield 90 per cent. Found: Cu, 20.86; C, 55.33; H, 3.46; N, 9.24 per cent. Calcd: for $[Cu(C_{14}H_{10}N_2O_2)]$ Cu, 21.06; C, 55.71; H, 3.34; N, 9.28 per cent. The complex does not melt or decompose up to 300°C. It is soluble in dimethyl formamide, dimethyl sulphoxide, partially soluble in dioxane and insoluble in other common organic solvents.

Monochloro mono-(benzoyl salicylal hydrazone) palladium(II)

A greenish yellow precipitate was obtained between pH 1.7 and 2.3 by mixing 50 m of 0.05 *M* palladium(II) chloride solution with 100 ml of equimolar BSH solution in acetone. The precipitate was digested, cooled, filtered and washed successively with water, acetone and ether. Yield 80 per cent. Analysis of the compound gives the formula $[Pd(C_{14}H_{11}N_2O_2)(Cl)]$ which requires: Pd, 27.93; C, 44.10; H, 2.91; N, 7.35; Cl, 9.09 per cent and was found to contain: Pd, 28.28; C, 44.40; H, 2.99; N, 7.46; Cl, 8.97 per cent. The complex does not melt or decompose up to 300°C. It is partially soluble in common organic solvents.

Apparatus — All spectrophotometric measurements were carried out on a Unicam SP—600 spectrophotometer in 1-cm quartz cells. A Metrohm pH meter model E—350 was used for adjusting the pH of the solutions.

Results

Spectral behaviour of the complexes

The effect of pH, time, solvent, etc., on the coloured systems was investigated.

A series of solutions containing a fixed amount of metal (copper or palladium) and excess of the reagent was prepared and the different pH values were adjusted by means of acetic acid and sodium hydroxide in the case of copper, and hydrochloric acid and sodium hydroxide in the case of palladium. The final acetone concentration was 50 v/v per cent. The absorption spectra were recorded against reagent blanks prepared under identical conditions. In both cases the absorbance increased as the pH was raised, becoming maxi-

mum and practically constant between pH 4.5 and 6.5 (copper), and between 1.7 and 2.3 (palladium), then decreasing again at higher pH values at which the ligand itself becomes highly coloured. The nature of the spectral curves and the position of the λ_{max} (385 nm for copper and 395 nm for palladium) indicate the formation of only one complex in each case. The maximum in colour intensity is reached after about half an hour but the colour remains stable even up to 48 hours.

Higher percentage of acetone had no effect on the absorbance but a minimum concentration of 30 v/v per cent of acetone was necessary below which the solutions become turbid. In view of this a 50 v/v per cent acetone concentration was chosen.

For the copper–BSH system, a minimum of 5-fold molar excess of the reagent is required for the development of the colour (30-fold for the palladium system).

Validity of Beer's law and sensitivity of the reaction

The complexes were found to obey the Lambert—Beer's law over the concentration range 0—5.0 ppm of copper at 385 nm and 0—15.0 ppm of palladium at 395 nm. The optimum range of concentration obtained from RINGBOM [13] plot is 1.0—3.5 and 3.5—11.5 ppm for copper and palladium, respectively. The sensitivity of the colour reaction in terms of SANDELL's [14] definition is 0.0041 μg of Cu^{2+}/cm^2 at 385 nm and 0.014 μg of Pd^{2+}/cm^2 at 395 nm for 0.001 absorbance. The molar extinction coefficients are 15,500 (copper) and 7180 (palladium).

Composition and apparent instability constant

The stoichiometric ratio of metal to ligand in the complexes under the conditions mentioned above was determined by the method of continuous variations [15], mole ratio [16], slope ratio [17] and BENT and FRENCH [18]. These methods all confirm the metal to ligand ratio in both complexes to be 1 : 1. This was further confirmed by the analysis of the complexes.

The apparent instability constant K, calculated from the equation

$$K = \frac{\alpha^2 \cdot c}{(1 - \alpha)}$$

is 6.77×10^{-8} and 7.01×10^{-5} for copper and palladium complexes, respectively (where α is the degree of dissociation and c is the molar concentration of the complex). The respective free energy change of formation ($-RT \log K$) has been calculated to 10.10 and 5.855 kcal per gram mole at 35°C.

Effect of foreign ions

To evaluate the tolerance limits for different ions solutions containing either 2.54 ppm copper(II) or 5.32 ppm palladium(II), and varying amounts of other ions were analysed by the method described above. Absorbance errors above 0.005 were considered to indicate interference.

In the copper system EDTA, oxalate, thiosulphate and Co^{2+}, Zn^{2+}, Sn^{2+}, UO_2^{2+}, Sc^{3+}, Fe^{3+}, Ce^{3+}, Al^{3+}, Ru^{3+}, Ga^{4+}, Os^{4+}, V^{5+} and Mo^{6+} interfered at all concentrations. The system, however, tolerates the presence of the following ions, the tolerance limits of which in ppm are given in parentheses: citrate (275), tartarate (30), thiocyanate (725), thiourea (100), borate (25), F^- (1000), Cl^- (3550), Br^- (2000), I^- (650), SO_4^{2-} (240), SO_3^{2-} (80), PO_4^{3-} (480), NO_3^- (650), IO_3^- (400), Hg^{2+} (200), Tl^+ (400), Be^{2+} (100), Mg^{2+} (100), Mn^{2+} (100), Ba^{2+} (275), Cd^{2+} (110), Sr^{2+} (175), Sb^{3+} (120).

In the palladium system, it was found that EDTA, thiosulphate, thiourea, thiocyanate, IO_3^-, SO_4^{2-} and the cations Cu^{2+}, Co^{2+}, Zn^{2+}, Mn^{2+}, Sn^{2+}, UO_2^{2+}, Sb^{3+}, Fe^{3+}, Ce^{3+}, Al^{3+}, Sc^{3+}, Ru^{3+}, Ga^{4+}, Os^{4+}, V^{5+} and Mo^{6+} interfere even when present in traces, while the tolerance limits are given in parentheses in ppm for: NO_3^- (6200), Br^- (400), I^- (300), CH_3COO^- (590), SO_4^{2-} (384), $C_2O_4^{2-}$ (200), PO_4^{3-} (470), BO_3^{3-} (660), citrate (284), tartarate (360), Be^{2+} (18), Pb^{2+} (207), Cd^{2+} (112), Mg^{2+} (120), Ba^{2+} (200), Hg^{2+} (200), Sr^{2+} (428) and Ti^{4+} (19). Calculated amount of sodium fluoride was added to mask Ti^{4+}. Platinum group metals except ruthenium and osmium, *viz.* Rh^{3+}, Ir^{3+}, Pt^{4+}, also do not interfere.

Discussion

A general review of the methods used for the spectrophotometric determination of copper(II) and palladium(II) reveals that mostly oximes were used for this purpose. Recently another class of compounds, namely, hydrazones have been tried and were found suitable. A comparison of the suitability of hydrazones, *viz.* pyridine-2-aldehyde-2′-pyridyl hydrazone, pyridine-2-aldehyde-2-quinonoyl hydrazone, and picoline aldehyde-2-quinonoyl hydrazone with benzoyl salicylal hydrazone shows that in case of BSH larger amounts of anions are tolerated. Further, since the determination of palladium is carried out in highly acidic medium, therefore, the possibility of hydroxide precipitation is greatly reduced. In addition to this, owing to the validity of Beer's law over a wider range (0—15.0 ppm) of concentration larger amounts of palladium can be determined with greater accuracy. For the copper system the sensitivity of the reaction is higher as compared to other hydrazones.

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A NOVEL TYPE OF N-ALKYLATION REACTION*

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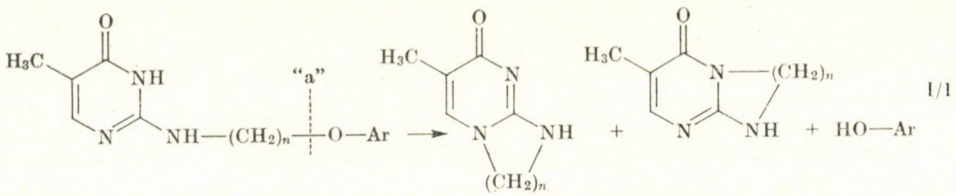
The general validity of the N-alkylation reaction shown by active arylalkyl ethers and observed by us earlier was demonstrated. This reaction differs from the well-known aromatic nucleophilic substitution of nitroarylalkyl ethers leading to the corresponding N-arylated products. On the basis of preparative, mass spectrometric and reaction kinetic measurements, an S_n2 mechanism is proposed.

As it has been reported earlier [1—5, 7—8], 2-(ω-aryloxyalkyl)amino-5-methylpyrimidin-4[3*H*]-ones (**1**) undergo further conversion during their preparation or on thermal treatment, to give the corresponding phenol (**4**) and two molecules each of condensed cyclic compounds with structures **2** and **3**, respectively.

The formation of compounds **2** and **3** (Reaction I/1) can be regarded as an intramolecular N-alkylation process, where the alkylating agent is the terminal arylalkyl ether in the side chain of compound **1**.

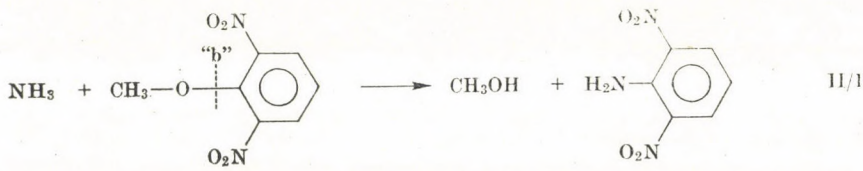


1 **2** **3** **4**

1a	Ar = phenyl	$n = 2$	**2a—f**	$n = 2$	**3a-f**	$n = 2$	**4a = 4g** Ar = phenyl
1b	Ar = 2,6-dimethylphenyl	$n = 2$	**2g—i**	$n = 3$	**3g-i**	$n = 3$	**4b = 4h** Ar = 2,6-dimethylphenyl
1c	Ar = 2,6-dichlorophenyl	$n = 2$					**4c = 4i** Ar = 2,6-dichlorophenyl
1d	Ar = pentachlorophenyl	$n = 2$					**4d** Ar = pentachlorophenyl
1e	Ar = 4-methoxyphenyl	$n = 2$					**4e** Ar = 4-methoxyphenyl
1f	Ar = 2,6-dimethoxyphenyl	$n = 2$					**4f** Ar = 2,6-dimethoxyphenyl
1g	Ar = phenyl	$n = 3$					
1h	Ar = 2,6-dimethylphenyl	$n = 3$					
1i	Ar = 2,6-dichlorophenyl	$n = 3$					

* Preliminary communications on this subject are Refs [1, 3, 4]

The alkylation of amines by phenylalkyl ethers substituted with nitro groups in the *o*- and *p*-positions (first of all by nitroanisoles) has been described [11] (*e.g.*, Reaction II/1), and explained by nucleophilic substitution of the aromatic ring [12].

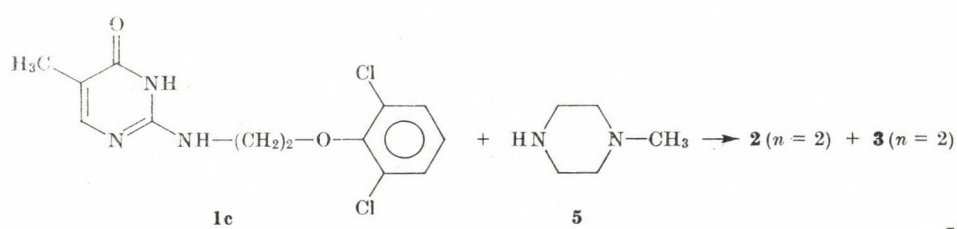


II/1

In the course of Reaction I/1 observed by us, the arylalkyl ethers undergo splitting at the O-alkyl bond ('a'-type splitting) to yield alkylamines, whereas in the known aromatic nucleophilic substitution reaction the O-aryl bond is ruptured ('b'-type splitting) (Reactions of type II), thus arylamines are obtained.

Since the intramolecular N-alkylation reaction I/1 could be equally accomplished in the presence of widely different substituents on the phenyl group of the terminal active arylalkyl ether [*e.g.* with substituents exhibiting $-I$ (Cl), $+I$ (CH_3), $-M$ (Cl) and $+M$ (OCH_3) effects], its rather general character could be assumed. Thus it seemed promising to attempt intermolecular N-alkylation reactions of type I with other arylalkyl ethers, too.

For this purpose, **1c** was allowed to react with secondary amines [N-methylpiperazine (**5**) and piperidine (**6**)] using them in excess as solvents. No significant conversion was, however, observed at the boiling points of the amines. Under more severe conditions (200°C, sealed tube), however, Reaction I/1 leading to intramolecular cyclization became prevailing and only compounds **2** ($n = 2$) and **3** ($n = 2$) were formed (Reactions I/2).

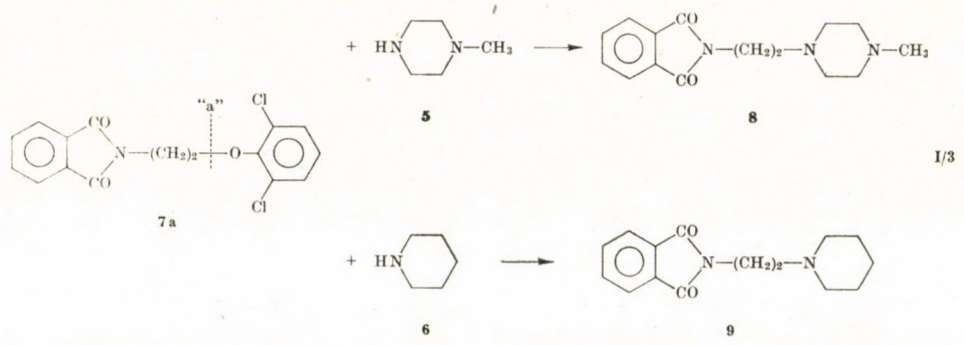


I/2

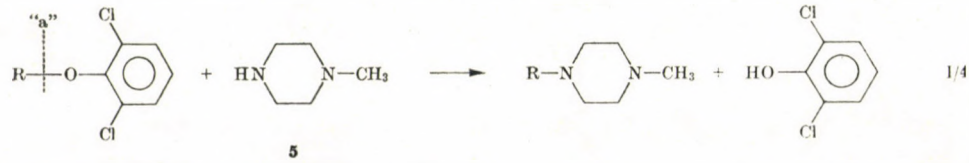


In order to exclude the above reaction leading to intramolecular cyclization a model compound similar to **1c** was required, which, in spite of comprising the 2-(2,6-dichlorophenoxy)ethylamino structural unit, should be in-

capable of undergoing intramolecular N-alkylation. Such a compound is, *e.g.*, 2-(2,6-dichlorophenoxy)ethylphthalimide (**7a**) [13], which actually yielded — besides 2,6-dichlorophenol — the expected 1-methyl-4-(2-phthalimidoethyl)piperazine (**8**) and 1-(2-phthalimidoethyl)piperidine (**9**), when heated with N-methylpiperazine (**5**) and piperidine (**6**), respectively, in a sealed tube at 190°C (Reactions I/3) [1].



After successful accomplishment of the above intermolecular N-alkylation reactions, primary and secondary alkylaryl ethers, such as 2,6-dichlorophenyl isopropyl- (**10a**), 2,6-dichlorophenyl *n*-butyl- (**10b**) and 2,6-dichlorophenyl *sec*-butyl ether (**10c**) were also subjected to this type of reactions. These compounds were heated with an excess of N-methylpiperazine (**5**) at 200—250°C for several hours. The products of the reaction, 1-methyl-4-isopropylpiperazine (**11a**), 1-methyl-4-*n*-butylpiperazine (**11b**) and 1-methyl-4-*sec*-butylpiperazine (**11c**) (Reactions I/4) confirm unambiguously that the new N-alkylation reaction involving the 'a'-type splitting of the O-alkyl bond in arylalkyl ethers is independent of the nature of the alkyl group present. Since in describing Reactions I/1 it has already been demonstrated that this reaction does not depend on the nature of the aryl group either, Reaction I may be considered to be *of general validity*.



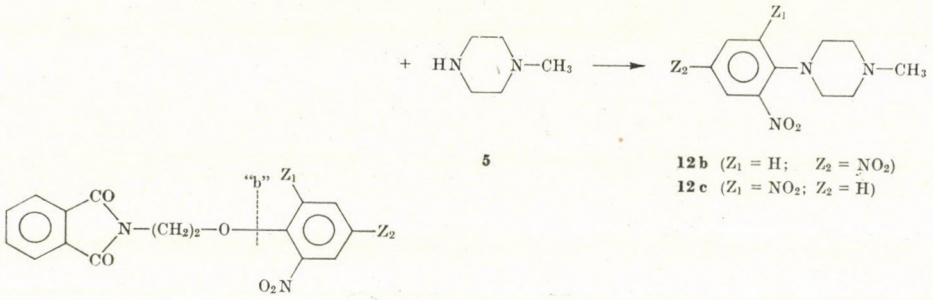
10a R = isopropyl
10b R = *n*-butyl
10c R = *sec*-butyl

11a
11b
11c

4c

On the basis of the above experiences it was also examined, whether the alkyl chain of the various nitro- and dinitroarylalkyl ethers — of which only the methyl and ethyl derivatives were studied up to now — affects the N-arylation capability of these products or not. In these experiments the nitro

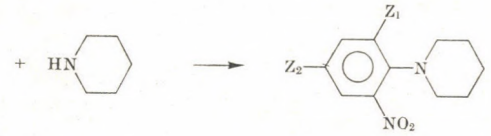
and dinitroarylalkyl ethers with alkyl chains already studied in Reaction I/3 were applied. Thus, 2-(2,4- and 2,6-dinitrophenoxy)ethylphthalimide (**7b** and **7c**) analogous to **7a** were prepared, and allowed to react with N-methylpiperazine (**5**) and piperidine (**6**), respectively (Reactions II/2).



5 **12b** (Z_1 = H; Z_2 = NO_2)
12c (Z_1 = NO_2; Z_2 = H)

II/2

7b (Z_1 = H; Z_2 = NO_2)
7c (Z_1 = NO_2; Z_2 = H)



6 **13b** (Z_1 = H; Z_2 = NO_2)
13c (Z_1 = NO_2; Z_2 = H)

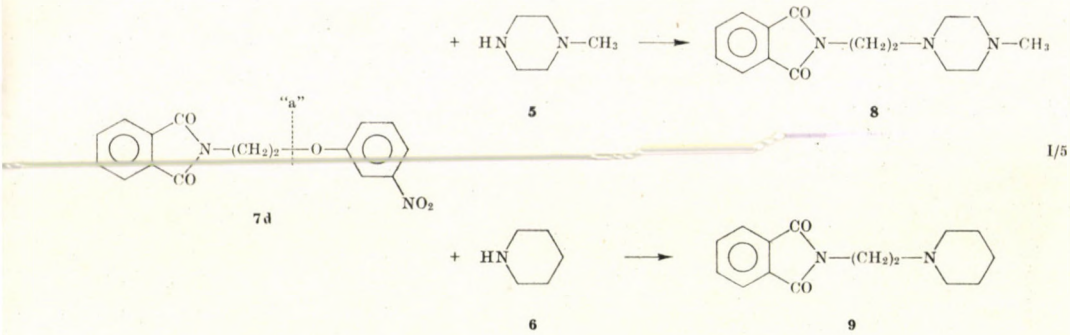
The products of the reaction, 1-(2,4-dinitrophenyl)-4-methylpiperazine (**12b**) and 1-(2,6-dinitrophenyl)-4-methylpiperazine (**12c**), as well as 1-(2,4-dinitrophenyl)piperidine (**13b**) and 1-(2,6-dinitrophenyl)piperidine (**13c**) give an unambiguous *evidence* of the fact that the N-arylation ability of *o*- and *p*-nitroarylalkyl ethers is not affected by variation of the alkyl group. The reactivity of these compounds leading to aromatic nucleophilic substitution is thus decided exclusively by the $-M$ effect of the *o*- and *p*-nitro groups [12].

The above results are also confirmed by N-alkylation experiments carried out with 2-(3-nitrophenoxy)ethylphthalimide (**7d**) having a structure analogous to that of **7b** and **7c** (Reactions I/5), where — since in these cases the nitro group in *m*-position cannot exert a $-M$ effect — the N-alkylating tendency becomes again predominating, as expected, yielding derivatives **8** and **9**.

This newly observed N-alkylating ability of active arylalkyl ethers, involving 'a'-type splitting may be interpreted in various possible ways.

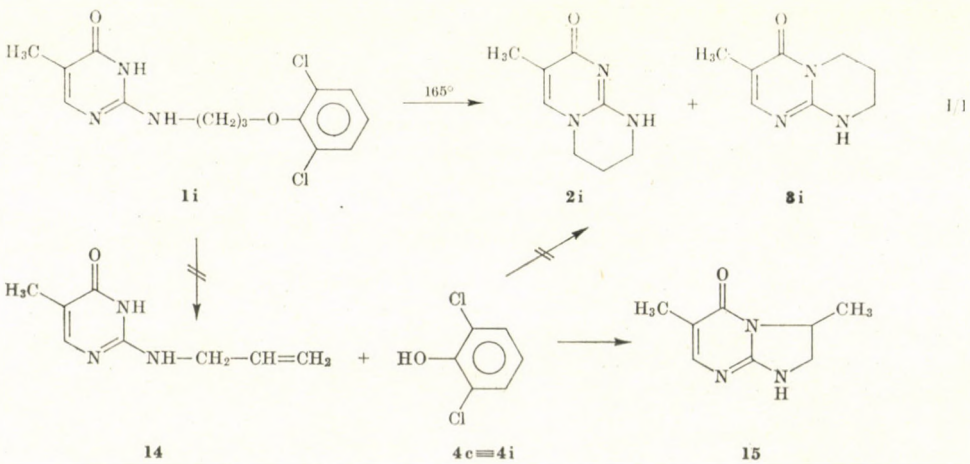
(a) It could be assumed that a phenol molecule leaves the aryloxyalkyl group by β-elimination, and this is followed by addition of the amine onto the unsaturated bond formed.

This reaction path could be excluded on the basis of the following experiments: on thermal treatment, compound **1i** yielded **2i** and **3i**, in addition to 2,6-dichlorophenol (**4c** = **4i**) in reaction I/1 [1, 7]. If the first step



I/5

in the reaction were β-elimination, the intermediate accompanying the 2,6-dichlorophenol would be 2-allylamino-5-methylpyrimidin-4(3*H*)-one (**14**), a compound prepared earlier [6]; the addition of the NH group of the pyrimidone ring to the formed unsaturated bond should then take place on the effect of 2,6-dichlorophenol (**4c**) (or simply on thermal effect). The above reaction path was imitated by heating a 1 : 1 mixture of **14** and **4c** in a sealed tube;* however, neither **2i** nor **3i** could be detected in the resulting reaction mixture. In chromatographic isolation, 2,3-dihydro-3,6-dimethylimidazo[1,2-*a*] pyrimidin-5(1*H*)-one (**15**) was found to be the main product of the reaction. This provides unambiguous evidence that **14** cannot be the intermediate in reaction I/1 occurring by 'a'-type splitting, that is, phenol **4c** *was not* split off from the active arylalkyl ether by a β-elimination process.

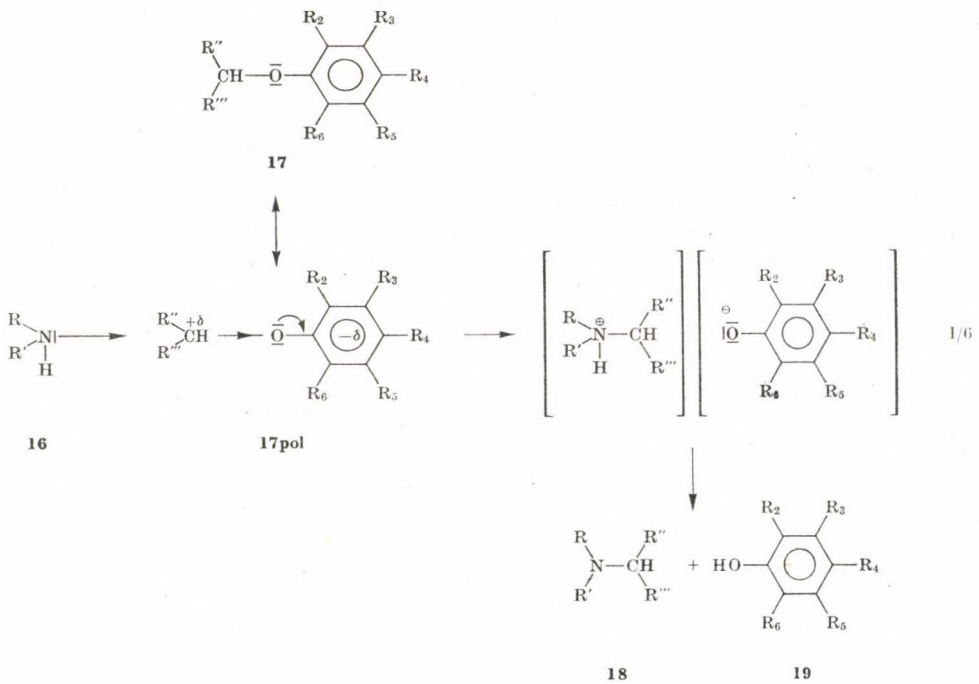


I/1

* An analogous reaction was effected by MAJIMA [14], when heating 2-allylamino-6-methylpyrimidin-4(3*H*)-one with concentrated hydrochloric acid in a sealed tube, to obtain 2,3-dihydro-3,7-dimethylimidazo[1,2-*a*]pyrimidin-5(1*H*)-one.

(b) The N-alkylation reaction accompanying the 'a'-type splitting could only be realized at high temperatures (150—250°C), therefore the possibility of cleavage of the phenoxy ethers by radical mechanism could not be excluded. In order to examine this possibility, we tried to record the ESR spectrum [15] of 2-[2-(2,6-dichlorophenoxy)ethylamino]-5-methyl-pyrimidin-4(3*H*)-one (**1c**) in the presence of nitrosobenzene as a radical trapping agent, under the conditions of the thermal decomposition (reaction I/1). The presence of radicals could not be detected in the ESR spectrum.

(c) Finally, the splitting of arylalkyl ethers (**17**) can also be assumed to proceed in such manner that the O-alkyl bond becomes polarized owing to the electron-withdrawing effect of the aromatic ring, giving rise to structure **17pol**, followed by nucleophilic attack on the positive centre by nitrogen atom of the amine (**16**) (Mechanism I/6).



The development of the polarized structure **17pol** is facilitated, when the $-I$ effects of the R_2—R_6 substituents on the aromatic ring are stronger, *i.e.* if a more stable phenolate ion can be formed. According to our earlier results [7], reaction I/1 proceeds at far lower temperatures with derivatives **1** carrying chloro substituents on the aromatic ring, than in the case of analogous non-substituted or methyl-substituted compounds. On the other hand, with derivatives **1** substituted with methoxy groups exhibiting negligible $-I$, but

strong $+M$ effects, thermal decomposition requires temperatures still higher than those necessary in the case of the analogous non-substituted derivatives **1**. This experimental result has supported the assumption of the appearance of polarized structure **17pol**, which may also be regarded as one of the main driving forces of the reaction.

The presence of the hypothetic polarized structure **17pol** could also be demonstrated by mass spectrometry [9], by comparing the ratio of ions formed owing to splitting of the O-alkyl ('a') and O-aryl ('b') ether bonds in the primary fragmentation of various arylalkyl ethers under the effect of electron bombardment.

In reactions I, splitting of the polarized arylalkyl ether (**17pol**) may take place prior to the nucleophilic attack by the amine (**16**) (S_n1 mechanism), or splitting may start just owing to this effect (S_n2 mechanism).

In order to decide this problem, reaction kinetic measurements were made [10] on a selected model, which was the reaction between 2,6-dichlorophenyl *n*-butyl ether (**10b**) and N-methylpiperazine (**5**) (Reaction I/4). The reaction was monitored by measuring the amount of 2,6-dichlorophenol (**4c**) formed. The rate of the reaction was found to depend on molar concentrations of both **10b** and **5**, thus an S_n2 *mechanism of reaction I* could be suggested unambiguously.

It is to be noted, however, that the progress of reaction I may be influenced not only by the extent of the polarization of the O-alkyl bond, but also by other factors.

For example, the reaction can advantageously be influenced by the ease of the formation of five- or six-membered rings. This may be responsible for the fact that, while in the reaction of **7a** and **10b** with **5** (Reactions I/3 and I/4, respectively) temperatures as high as 190°C and 200°C are necessary, in reaction I/1 the analogous compounds **1c** and **1i** — although all these are 2,6-dichlorophenyl ethers — undergo thermal decomposition at 150 and 165°C, respectively, yielding the appropriate condensed cyclic compounds **2** and **3**. Of the two possible cyclization processes, the one leading to the formation of a five-membered ring is favoured, presumably because of the formation of the nearly planar 2,3-dihydroimidazo[1,2-*a*]pyrimidones (**2a** and **3a**), similarly to the case of 2,3-dihydroimidazo[1,2-*a*]pyridines studied by PAUDLER and BLEWITT [16]; the two rings in 2,3,4,5-tetrahydroimidazo[1,2-*a*]pyrimidones (**2g** and **3g**) can never be coplanar. Consequently, a difference of about 20°C was observed between the reactivities of the analogous derivatives **1** carrying ethyl and propyl chain, respectively, to the advantage of the ethyl compound [7].

Experimental

M.p.'s were determined with Kofler—Böetius apparatus.

MS measurements were carried out with a single-focussed MX—1303 instrument. The samples were introduced into the ion source by direct evaporation at 5—100°C. IR spectra were recorded with a Zeiss UR—10 and a Perkin—Elmer 457 spectrophotometer, in KBr pellets. NMR spectra were recorded with a Jeol C—60 (at 23°C) and a Varian A—60D (at 36°C) instrument; tetramethyl silane and sodium 2,2-dimethyl-2-sila-pentanesulfonate were used as internal standards. ESR studies were accomplished with a JES—ME—3X apparatus.

The thin-layer chromatographic examinations were made on silic agel; the method of chlorination [17] was used for detection. Compositions of the most frequently used developing solvent mixtures were:

A: ethyl acetate (60 ml), pyridine (20 ml), acetic acid (6 ml), water (11 ml).
B: ethyl acetate (30 ml), pyridine (20 ml), acetic acid (6 ml), water (11 ml).

Reaction of 2-[2-(2,6-dichlorophenoxy)ethylamino]-5-methylpyrimidin-4[3*H*]-one (1c) with N-methylpiperazine (5)

A mixture of 2-[2-(2,6-dichlorophenoxy)ethylamino]-5-methylpyrimidin-4[3*H*]-one (**1c**) [6] (1.57 g; 0.005 mole) and N-methylpiperazine (**5**) (15 ml) was allowed to react in a sealed tube at 200°C for 3 hrs. The reaction mixture was evaporated to dryness in vacuum, then separated in solvent mixture **A** by column chromatography. The products obtained, in the order of their appearance, were: 2,6-dichlorophenol (**4c**) (0.78 g; 95.7%), m.p. 65—66°C (lit. [18] m.p. 66—67°C); 2,3-dihydro-5[1*H*]-oxo-6-methylimidazo[1,2-*a*]pyrimidine (**3**, $n = 2$), (0.25 g; 33.1%), m.p. 229—231°C (lit. [7] m.p. 232—233°C); and 2,3-dihydro-6-methyl-7[1*H*]-oxoimidazo[1,2-*a*]pyrimidine (**2**, $n = 2$) (0.37 g; 47.7%), m.p. 295—298°C (lit. [7] m.p. 299—300°C).

Reaction of 2-[2-(2,6-dichlorophenoxy)ethylamino]-5-methylpyrimidin-4[3*H*]-one (1c) with piperidine (6)

A mixture of 2-[2-(2,6-dichlorophenoxy)ethylamino]-5-methylpyrimidin-4[3*H*]-one (**1c**) [6] (1.57 g; 0.005 mole) and piperidine (**6**) (15 ml) was allowed to react in a sealed tube at 200°C for 3 hrs. The reaction mixture was evaporated to dryness in vacuum, then separated by column chromatography in solvent mixture **A**. The products obtained, in the order of their elution, were: 2,6-dichlorophenol (**4c**) (0.75 g; 92.0%), m.p. 65—66°C (lit. [18] m.p. 66—67°C); 2,3-dihydro-5[1*H*]-oxo-6-methylimidazo[1,2-*a*]pyrimidine (**3**, $n = 2$) (0.24 g; 31.8%), m.p. 230—232°C (lit. [7] m.p. 232—233°C); and 2,3-dihydro-6-methyl-7[1*H*]-oxo-imidazo[1,2-*a*]pyrimidine (**2**, $n = 2$) (0.41 g; 54.3 %; m.p. 296—298°C (lit. [7] m.p. 299—300°C).

Reaction of 2-(2,6-dichlorophenoxy)ethylphthalimide (7a) with N-methylpiperazine (5)

A mixture of 2-(2,6-dichlorophenoxy)ethylphthalimide (**7a**) [13] (2.52 g; 0.0075 mole) and N-methylpiperazine (**5**) (10 ml) was heated in a sealed tube at 190°C for 7 hrs. The excess of N-methylpiperazine was evaporated from the reaction mixture in vacuum, the residue was dissolved in absolute ethanol containing hydrochloric acid, evaporated to dryness, then separated by column chromatography on silica gel in solvent mixture **A**. The following products were obtained: 2,6-dichlorophenol (**4a**) (1.1 g; 90.2%), m.p. 65—66°C (from gasoline) (lit. [18] m.p. 66—67°C), and 1-methyl-4-(2-phthalimido)ethylpiperazine hydrochloride (**8**.HCl) (2.0 g; 86.3%), m.p. (after recrystallization from absolute ethanol) 241—243°C; $R_f = 0.27$ (in solvent mixture **A**).

IR: νC=O 1780 and 1715 cm^{-1}; νNH + NH^+ 2750—2350 cm^{-1}.

$C_{15}H_{20}ClN_3O_2$ (309.79). Calcd. C 58.12; H 6.50; N 13.57; Cl 11.12. Found C 57.88; H 6.76; N 13.34; Cl 10.98%.

When the above product was dissolved in absolute ethanol, then treated with absolute ethanol containing hydrochloric acid, 1-methyl-4-(2-phthalimido)ethylpiperazine dihydrochloride (**8**.2HCl) was obtained, m.p. 259—262°C (from dimethylformamide) (lit. [19] m.p. 243—244°C).

IR: $\nu C{=}O$ 1770 and 1700 cm^{-1}. νNH^+ 2800—1900 cm^{-1}.
$C_{15}H_{21}Cl_2N_3O_2$ (346.26). Calcd. C 52.03; H 6.11; N 12.14; Cl 20.48. Found C 52.20; H 6.32; N 12.10; Cl 20.60%.
MS: molecular weight of the base: 273; molecular formula: $C_{15}H_{19}N_3O_2$.

Reaction of 2-(2,6-dichlorophenoxy)ethylphthalimide (7a) with piperidine (6)

A mixture of 2-(2,6-dichlorophenoxy)ethylphthalimide (**7a**) [13] (2.52 g; 0.0075 mole) and piperidine (**6**) (10 ml) was heated in a sealed tube at 190°C for 7 hrs. The excess of piperidine was evaporated in vacuum and the residue separated on a silica gel column using solvent mixture **A**. The following products were obtained (in the order of their elution): 2,6-dichlorophenol (**4c**) (1.0 g; 82.1%), m.p. 66—67°C (from gasoline) (lit. [18] m.p. 66—67°C); 1-(2-phthalimidoethyl)piperidine (**9**) (1.3 g; 67.2%). The latter was converted into the hydrochloride with absolute ethanol containing hydrochloric acid; m.p. 241—242°C (from isopropanol) (lit. [20] m.p. 241—243°C); $R_f = 0.4$ (in solvent mixture **A**).
IR: $\nu C{=}O$ 1775 and 1715 cm^{-1}; νNH^+ 2700—2300 cm^{-1}.
MS: molecular weight of the base: 258; molecular formula: $C_{15}H_{18}N_2O_2$.

Reaction of 2,6-dichlorophenyl isopropyl ether (10a) with N-methylpiperazine (5)

A mixture of 2,6-dichlorophenyl isopropyl ether (**10a**) [9] (20.5 g; 0.1 mole) and N-methylpiperazine (**5**) (20.0 g; 0.2 mole) was heated in a sealed tube at 220°C for 30 hrs.; by distillation of the reaction mixture 1-methyl-4-isopropylpiperazine (**11a**) (6.9 g; 48.8%) was obtained; b. p. 35°C at 0.4 torr; $R_f = 0.14$ (in solvent mixture **A**).
NMR: $\delta = 1.00$d (6H, $J = 6.5$ Hz, $CHCH_3$), $\delta = 2.20$s (3H, NCH_3), $\delta = 2.45$s (8H, NCH_2), $\delta = 2.70-3.00$m (1H, $N-CH(CH_3)_2$); [lit. [21] data: $\delta = 1.0$d (6H, J=6 Hz, $CHCH_3$), δ= =2.10s (3H, NCH_3), $\delta = 2.18-2.74$m (also including the heptet, 9H, $NCH(CH_3)_2$, NCH_2), $\delta = 2.54$h ($J = 6$ Hz, $N-CH(CH_3)_2$].

Reaction of 2,6-dichlorophenyl *n*-butyl ether (10b) with N-methylpiperazine (5)

A mixture of 2,6-dichlorophenyl *n*-butyl ether (**10b**) [9] (4.38 g; 0.02 mole) and N-methylpiperazine (**5**) (4.00 g; 0.04 mole) was heated in a sealed tube at 240°C for 20 hrs. The reaction mixture was then separated on a silica gel column by means of an 1 : 3 mixture of methanol and chloroform. 1-Methyl-4-*n*-butylpiperazine (**11b**) (1.5 g; 48.1%) was obtained, which was dissolved in ethanol and converted into the hydrochloride by the addition of absolute ethanol containing hydrochloric acid; m.p. 239—241°C (from isopropanol); $R_f = 0.17$ (in solvent mixture **A**).
NMR: $\delta = 0.94$t (3H, CCH_3, $J = 6$ Hz), $\delta = 1.10-2.00$m (4H, CCH_2CH_2C), $\delta = 3.09$s (3H, NCH_3), $\delta = 3.36$t (2H, NCH_2C, $J = 8$ Hz), $\delta = 3.77$s (8H, NCH_2).
MS: molecular weight of the base: 156; molecular formula: $C_9H_{20}N_2$.

Reaction of 2,6-dichlorophenyl *sec*-butyl ether (10c) with N-methylpiperazine (5)

A mixture of 2,6-dichlorophenyl *sec*-butyl ether (**10c**) [9] (13.14 g; 0.06 mole) and N-methylpiperazine (**5**) (12.0 g; 0.12 mole) was heated in a sealed tube at 250°C for 30 hrs. The reaction mixture was then separated on a silica gel chromatographic column in a mixture of methanol and chloroform (3 : 1). Thus, 1-methyl-4-*sec*-butylpiperazine (**11c**) (4.5 g; 48%) was obtained, which was converted into the hydrochloride with absolute ethanol containing hydrochloric acid; m.p. 241—243°C (from isopropanol); $R_f = 0.25$ (in solvent mixture **B**).
NMR: $\delta = 1.00$t (3H, CH_2CH_3), $\delta = 1.37$d (3H, $CHCH_3$, $J = 7$ Hz), $\delta = 1.55-1.97$m (3H, $N-CH-CH_2$), $\delta = 3.10$s (3H, NCH_3), $\delta = 3.62$s (8H, NCH_2).
MS: molecular weight of the base: 156; molecular formula: $C_9H_{20}N_2$.

2-(2,4-Dinitrophenoxy)ethyl bromide

A mixture of potassium 2,4-dinitrophenolate [22] (11.1 g; 0.05 mole), 1,2-dibromoethane (93.9 g; 43.2 ml; 0.5 mole) and dimethylformamide (50 ml) was stirred on an oil bath at 120—130°C for 15 min. After cooling, the reaction mixture was filtered, and the filtrate

evaporated to dryness in vacuum. The product was dissolved in chloroform, extracted with 2×10 ml of 5% $NaHCO_3$ then with water, dried over $CaCl_2$, and evaporated to dryness in vacuum. In this way 2-(2,4-dinitrophenoxy)ethyl bromide (8.55 g; 58.8%) was obtained; m.p. (after recrystallization from methanol) 60.5—61°C; $R_f = 0.94$ (in solvent mixture **A**).

IR: νNO_2 1610 and 1520 cm^{-1}.

NMR: $\delta\ BrCH_2 = 3.75t$ (2H), $\delta OCH_2 = 4.53t$ (2H, $J = 6$ Hz), $\delta ArH_6 = 7.30d$ (1H), $\delta ArH_5 = 8.54$ quartet (1H), $\delta ArH_3 = 8.70d$ (1H), $J_{ortho} = 9$ Hz, $J_{meta} = 3$ Hz.

$C_8H_7BrN_2O_5$ (291.07). Calcd. C 33.01; H 2.42; N 9.63; Br 27.46. Found C 33.25; H 2.65; N 9.58; Br 27.20%.

2-(2,4-Dinitrophenoxy)ethylphthalimide (7b)

A mixture of 2-(2,4-dinitrophenoxy)ethyl bromide (2.91 g; 0.01 mole), potassium phthalimide (9.25 g; 0.05 mole) and dimethylformamide (30 ml) was stirred in an oil bath at 100°C for 3 hrs., then water (150 ml) was added to the still warm reaction mixture, with stirring. After cooling, 2-(2,4-dinitrophenoxy)ethylphthalimide (**7b**) separated, which was filtered off and washed with water. The product weighed 3.05 g (85.5%), m.p. (after recrystallization from acetonitrile) 190—191°C; $R_f = 0.77$ (in solvent mixture **A**).

IR: $\nu C{=}O$ 1780 and 1720 cm^{-1}.

$C_{16}H_{11}N_3O_7$ (357.27). Calcd. C 53.77; H 3.10; N 11.76. Found C 54.00; H 3.32; N 12.03%.

Reaction of 2-(2,4-dinitrophenoxy)ethylphthalimide (7b) with N-methylpiperazine (5)

A mixture of 2-(2,4-dinitrophenoxy)ethylphthalimide (**7b**) (3.57 g; 0.01 mole) and N-methylpiperazine (**5**) (20 ml) was refluxed in an oil bath at 160—170°C for 7 hrs. The reaction mixture was evaporated to dryness in vacuum, the residue dissolved in 5*N* HCl (40 ml) and extracted with benzene (3×50 ml). The hydrochloric solution was made alkaline with conc. ammonium hydroxide solution, the product was dissolved in benzene, the benzene solution was dried and the solvent removed in vacuum. The residual oily product (1.8 g) was converted into the hydrochloride with absolute ethanol containing hydrochloric acid to obtain 1-(2,4-dinitrophenyl)-4-methylpiperazine hydrochloride (**12b**.HCl) (1.4 g; 46.4%); its melting point was (after recrystallization from acetonitrile) 240—242°C (lit. [23] m.p. 233—234°C); $R_f =$ = 0.38 (in solvent mixture **A**).

IR: $\nu NH + NH^+$ 2800—2200 cm^{-1}, νNO_2 1615 and 1515 cm^{-1}.

$C_{11}H_{15}ClN_4O_4$ (302.72). Calcd. C 43.64; H 4.66; N 18.51; Cl 11.71. Found C 43.70; H 4.92; N 18.78; Cl 11.44%.

Reaction of 2-(2,4-dinitrophenoxy)ethylphthalimide (7b) with piperidine (6)

A mixture of 2-(2,4-dinitrophenoxy)ethylphthalimide (**7b**) (3.57 g; 0.01 mole) and piperidine (**6**) (20 ml) was heated in a sealed tube at 180°C for 7 hrs. After cooling, the reaction mixture was dissolved in chloroform (200 ml), extracted with 5*N* HCl (2×100 ml), then with water; finally, the solvent was removed in vacuum to obtain 1-(2,4-dinitrophenyl)piperidine (**13b**) (1.9 g; 75.7%) m.p. (after recrystallization from isopropanol) 90—91°C (lit. [24] m.p. 92°C); $R_f = 0.95$ (in solvent mixture **A**).

IR: νNO_2 1615 and 1515 cm^{-1}.

NMR: $\delta NCH_2 = 3.3m$ (4H), $\delta CH_2 = 1.7m$ (6H), $\delta ArH_6 = 7.35d$ (1H), $\delta ArH_5 = 8.25$ quartet (1H), $\delta ArH_3 = 8.55d$ ($J_{ortho} = 9$ Hz, $J_{meta} = 2$ Hz).

$C_{11}H_{13}N_3O_4$ (251.25). Calcd. C 52.58; H 5.22; N 16.72. Found C 52.52; H 5.47; N 16.72%.

2-(2,6-Dinitrophenoxy)ethyl bromide

A mixture of potassium 2,6-dinitrophenolate [25] (20.8 g; 0.094 mole), 1,2-dibromoethane (93.9 g; 43.2 ml; 0.5 mole) and dimethylformamide (80 ml) was stirred in an oil bath at 130°C for 45 min. After cooling, water (300 ml) and chloroform (300 ml) were added to the reaction mixture, the phases were separated, the chloroform phase was washed with water, dried, and evaporated to dryness in vacuum. Yellow, oily, non-distillable 2-(2,6-dinitrophenoxy)ethyl bromide (22.2 g; 81.1%; it decomposes at 160°C/0.2 torr) was obtained. This product was used in the subsequent synthetic steps without further purification.

$C_8H_7BrN_2O_5$ (291.07). Calcd. C 33.01; H 2.42; N 9.63; Br 27.46. Found C 33.38; H 2.63; N 9.31; Br 27.70%.

2-(2,6-Dinitrophenoxy)ethylphthalimide (7c)

A mixture of 2-(2,6-dinitrophenoxy)ethyl bromide prepared as described above (20.3 g; 0.07 mole), potassium phthalimide (43.5 g; 0.20 mole) and dimethylformamide (300 ml) was stirred in an oil bath at 100°C for 3 hrs. Water (1100 ml) was added to the hot reaction mixture and, after cooling, the crystalline product which separated was filtered off and washed with water to obtain 2-(2,6-dinitrophenoxy)ethylphthalimide (23.6 g; 94.8%), m.p. (after recrystallization from acetonitrile) 143—144°C; $R_f = 0.86$ (in solvent mixture **A**).

IR: νC=O 1775 and 1730 cm^{-1}.

$C_{16}H_{11}N_3O_7$ (357.27). Calcd. C 53.77; H 3 10; N 11.76. Found C 54.04; H 3.24; N 11.95%.

Reaction of 2-(2,6-dinitrophenoxy)ethylphthalimide (7c) with N-methylpiperazine (5)

A mixture of 2-(2,6-dinitrophenoxy)ethylphthalimide (**7c**) (1.78 g; 0.05 mole) and N-methylpiperazine (10 ml) (**5**) was refluxed in an oil bath at 150—160°C for 7 hrs. The reaction mixture was evaporated to dryness in vacuum and the residue dissolved in 5*N* HCl (20 ml); the solution was extracted with benzene (3×25 ml). The hydrochloric acid solution was made alkaline with conc. ammonium hydroxide solution, the product was dissolved in benzene, the benzene solution was dried and the solvent evaporated in vacuum. The residual oily product (0.8 g) was converted into the hydrochloride with absolute ethanol containing hydrochloric acid. Thus, 1-(2,6-dinitrophenyl)-4-methylpiperazine hydrochloride (**12c**.HCl) (0.6 g; 39.6%) was obtained, m. p. (after recrystallization from acetonitrile) 238—240°C; $R_f = 0.34$ (in solvent mixture **A**).

MS: molecular weight of the base: 266, molecular formula: $C_{11}H_{14}N_4O_4$.

$C_{11}H_{15}ClN_4O_4$ (302.72). Calcd. C 43.64; H 4.66; N 18.51; Cl 11.71. Found C 43.82; H 4.78; N 18.40; Cl 11.68%.

Reaction of 2-(2,6-dinitrophenoxy)ethylphthalimide (7c) with piperidine (6)

A mixture of 2-(2,6-dinitrophenoxy)ethylphthalimide (**7c**) (1.786 g; 0.005 mole) and piperidine (**6**) (10 ml) was heated in a sealed tube at 160°C for 7 hrs. After cooling, the reaction mixture was dissolved in chloroform (150 ml), extracted with 5*N* HCl (2×50 ml), then with water, dried and evaporated to dryness in vacuum to obtain 1-(2,6-dinitrophenyl)piperidine (**13c**) (0.45 g; 35.7%), m.p. (after recrystallization from isopropanol) 106.5—107.5°C (lit. [26] m.p. 106—107°C), $R_f = 0.97$ (in solvent mixture **A**).

IR: νNO_2 1600 and 1525 cm^{-1}.

$C_{11}H_{13}N_3O_4$ (251.25). Calcd. C 52.58; H 5.22; N 16.72. Found C 52.52; H 5.64; N 16.89%.

2-(3-Nitrophenoxy)ethylphthalimide (7d)

Potassium phthalimide (27.8 g; 0.15 mole) was added to a solution of 2-(3-nitrophenoxy)ethyl bromide [27] (24.6 g; 0.1 mole) in dimethylformamide (270 ml), then the mixture was stirred at 100—110°C for 6 hrs. After cooling, water (680 ml) was added to the reaction mixture; the crystalline product which separated was filtered off and washed with water to obtain 2-(3-nitrophenoxy)ethylphthalimide (**7d**) (28.5 g; 91.2%) m.p. (after recrystallization from acetonitrile) 139—140°C; $R_f = 0.90$ (in solvent mixture **A**).

IR: νC=O 1770 and 1715 cm^{-1}.

$C_{16}H_{12}N_2O_5$ (312.27). Calcd. C 61.54; H 3.87; N 8.97. Found C 61.81; H 3.84; N 8.93%.

Reaction of 2-(3-nitrophenoxy)ethylphthalimide (7d) with N-methylpiperazine (5)

A mixture of 2-(3-nitrophenoxy)ethylphthalimide (**7d**) (1.56 g; 0.005 mole) and N-methylpiperazine (**5**) (5 ml) was heated in a sealed tube at 200°C for 6 hrs. The excess of N-methylpiperazine was removed from the reaction mixture in vacuum, the residue was dissolved in absolute ethanol containing hydrochloric acid, evaporated to dryness, then separated on a silica gel chromatographic column in solvent mixture **A**.

First, 3-nitrophenol (**4j**) (0.81 g; 91.4%) was obtained (m.p. 96—97°C, lit. [28] m.p. 97°C), followed by 1-methyl-4-(2-phthalimidoethyl)piperazine hydrochloride (**8**.HCl) (1.24 g; 80.1%) (m.p. 241—243°C). The IR spectrum is identical with that of the product obtained n the reaction of **7a** with **5**.

Reaction of 2-(3-nitrophenoxy)ethylphthalimide (7d) with piperidine (6)

A mixture of 2-(3-nitrophenoxy)ethylphthalimide (**7d**) (1.56 g; 0.005 mole) and piperidine (**6**) (5 ml) was heated in a sealed tube at 200°C for 6 hrs. The excess piperidine was evaporated from the reaction mixture in vacuum and the residue was subjected to chromatographic separation on a silica gel column in solvent mixture **A**, to obtain 3-nitrophenol (**4j**) (0.84 g; 94.8%; m.p. 96—97°C, lit. [28] m.p. 97°C), and 1-(2-phthalimidoethyl)piperidine (**9**) (0.97 g; 65.8%). The latter was converted into the hydrochloride in absolute ethanol containing hydrochloric acid; m.p. 240—242°C (lit. [20] m.p. 241—243°C). The IR spectrum was identical with that of the sample prepared in the reaction of **7a** with **6**.

Heating of 2-allylamino-5-methylpyrimidin-4[3*H*]-one (14) with 2,6-dichlorophenol (4c)

A mixture of 2-allylamino-5-methylpyrimidin-4[3*H*]-one (**14**) [6] (8.28 g; 0.05 mole) and 2,6-dichlorophenol (**4c**) (9.00 g; 0.055 mole) was heated in a sealed tube at 220°C in an oil bath for 14 hrs. The dark brown reaction mixture was subjected to chromatographic separation on a silica gel column in solvent mixture **A**. In the order of their appearance the following substances were obtained from the column:

(1) 2,6-Dichlorophenol (**4c**), 8.8 g (97.8% of the amount introduced), m.p. 65—66°C (gasoline) (lit. [18] m.p. 66—67°C); $R_f = 0.95$ (in solvent mixture **A**).

(2) 2,3-Dihydro-3,6-dimethylimidazo[1,2-*a*]pyrimidin-5[1*H*]-one (**15**) (3.1 g; 37.5%); m.p. 158—159°C (from ethyl acetate), $R_f = 0.73$ (in solvent mixture **A**).

IR: νC=O 1670 cm^{-1}.

NMR: $\delta CCH_3 = 1.35$d, ($J = 6$ Hz), $\delta ArCH_3 = 1.75$s, $\delta CH = 3.15$m ($J_{AB} = 10$ Hz, $J_{AC} = 3$ Hz), $\delta ArH = 7.00$s, $\delta NH = 4.5$m ppm (overlapping with the light isotope contamination of the solvent D_2O).

$C_8H_{11}N_3O$ (165.19). Calcd. C 58.16; H 6.71; N 25.44. Found C 58.10; H 6.81; N 24.32%.

MS: molecular weight: 165; molecular formula: $C_8H_{11}N_3O$.

*

The authors' thanks are due to Dr. P. SOHÁR for the IR and NMR spectra, to Dr. L. LÁNG and Dr. J. LIPTÁK for the UV spectra, to Dr. J. TAMÁS (Central Research Institute for Chemistry of the Hungarian Academy of Sciences) for recording the MS spectra and for valuable discussions.

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RECENSIONES

Topics in Current Chemistry, Vol. 52: Medicinal Chemistry

Springer-Verlag, Berlin, Heidelberg, New York, 1974

The 52nd volume of the series "Topics in Current Chemistry", entitled *Medicinal Chemistry*, deals with some of the most actual problems of the design and mode of action of biologically active compounds.

The topic is introduced by a comprehensive study of Everardus J. ARIËNS and Anna-Maria SIMONIS on the general *Design of Bioactive Compounds* (61 pages with 172 references). Bioactive compounds are treated in the broadest sense of the term including not only drugs but also food additives, pesticides, industrial chemicals, etc. All relevant pharmacodynamic and pharmacokinetic aspects are discussed with special emphasis on the effects and site of actions of metabolites, modulation of drug metabolism by molecular manipulation, modification of transport properties and other pharmacokinetic parameters in order to decrease toxicity or to obtain particular time-effect profiles.

The following five works deal with the design and properties of particular drugs. *Antimetabolites: Molecular Design and Mode of Action* by Thomas J. BARDOS (32 pages, 133 references) gives a thorough description of "classical" antimetabolites which are close structural analogues of essential metabolic factors, and of 'non-classical' antimetabolites acting as enzyme inhibitors *per se* with large structural variations. Special chapters deal with the problem of the "dual antagonists" and the macromolecular antimetabolites (antitemplates). Prakash CHANDRA's study on the *Molecular Approaches for Designing Antiviral and Antitumor Compounds* (41 pages, 63 references) describes the problems connected with Distamycin A, Daunomycin and derivatives, tilorone hydrochloride and modified nucleic acids. A work on *Alkylating Agents* (31 pages, 97 references) written by Thomas A. CONNORS after reviewing the properties and mode of action of these compounds, discusses the selectivity of their action and the development of resistance; separate chapters deal with triazenes, nitrosoureas and platinum compounds of antitumour activity. This is followed by a review of Erik De CLERCQ on *Synthetic Interferon Inducers* (36 pages, 202 references) giving a general picture on natural and synthetic interferon inducers, on the structural requirements for the design of such compounds (polycarboxylates, polynucleotides and low molecular weight compounds), on their biological activities and on the mechanism of interferon production by the exposed cells. The last study of the volume, by Christoph WOENCKHAUS, is devoted to the *Synthesis and Properties of Some New NAD Analogues*, dealing with the elucidation of the chemical and physical nature of the active center in dehydrogenases involved in complex formation. The problems of coenzyme–enzyme complexes, coenzyme analogues, the role of the ribose moiety in the coenzyme molecule and the effect of modification of amino acids at the active center are discussed.

The studies in the volume have been written by prominent experts, and represent the highest level of the respective fields.

J. KNOLL

P. TÉTÉNYI, L. GUCZI, Z. PÁL and L. BABERNICS:

Heterogeneous Hydrocarbon Reactions Catalysed by Metals Recent Results in Chemistry, Vol. 19.

The authors of Volume 19 of the series "Recent Results in Chemistry" give, of the reactions catalyzed by metals, a systematic, concise, critical survey on research results concerning the reaction mechanism of hydrocarbons. The actuality and importance of the problems

treated in the monograph are justified in addition to the well known enormous practical importance of catalytic hydrocarbon reactions also by the circumstance that a research of these reactions is particularly suitable for studying certain general theoretical and practical problems of heterogeneous catalysis.

The monograph consists of eight chapters. The first, and to a certain degree also the last chapter, deal with the general problems of heterogeneous catalysis. The contents of these chapters exceed the sphere of theme of heterogeneous hydrocarbon reactions catalysed by metals. By giving an up-to-date survey and summary on some problems arising in heterogeneous catalysis research, it complements usefully the further chapters of the book and facilitates at the same time a better understanding of the problems treated for readers less versed in the field of heterogeneous catalysis.

Chapter 2 treats the adsorption of hydrocarbons, chapters 3—7 discuss the single types of heterogeneous hydrocarbon reactions catalysed by metals. These are: hydrogen exchange reactions of hydrocarbons, isomerization reactions, reactions accompanied by loss of hydrogen, hydrogenation reactions, and the hydrogenolysis of hydrocarbons.

The monograph gives a detailed picture of the main results achieved all over the world in the research of the reactions mentioned, and discusses the results of the own, extensive work of the authors in this field. Characteristics of the individual reaction types are shown by the more detailed discussion of well selected 'model reactions'. One of the merits of the monograph is that contested or not fully cleared problems are critically analysed in most of the cases.

Each chapter closes with a bibliography, listing the most important literature on the subject. The up-to-dateness of the study could have been further increased, if in addition to their own recent works the authors would have relied to a greater extent on publications of recent years dealing with heterogeneous catalytic hydrocarbon reactions.

Indubitably, this valuable work will be used to good advantage in addition to researchers dealing with metal-catalysed heterogeneous hydrocarbon reactions also by specialists interested in heterogeneous catalysis and hydrocarbon chemistry.

F. MÁRTA

Advances in Chemistry, Vol. 22

Ed. Béla Csákvári. Akadémiai Kiadó, Budapest 1974, 180 pages

This volume of the series, which has become popular within a short time, informs the reader on recent advances in new fields of chemistry. For those who have been following with attention the richness in content of these valuable booklets of nice presentation, it might be surprising, but in no way objectionable, that after the discussion of theoretical problems, now summaries of technological character, involving organic chemical technology and chemical operations, are also included.

Gyula GYOMBOLAI and Oszkár SZIMÁN give a clear picture in their paper "Diazo compounds and their application in the photochemical and telecommunication industries" on the practical uses of diazonium compounds. The simplicity and cheapness of diazotypy alone justify its great technological and economic importance and explain the dynamic development of this already almost classical technology.

The authors first elucidate the relevant theoretical problems, the structure of diazo compounds and the light sensitivity of diazonium compounds, then discuss practical problems. This comprises the mode of development of diazotypic compounds, as well as the manufacture and practical application of diazo substances. Their role in photochemical and telecommunication industry is described in detail. The last chapter of the review deals with the application of diazotypy in other new fields. The literature lists the patents, grouped under consideration of practical aspects.

The survey serves excellently the original purpose of the series: orientation of readers interested in chemistry of new advances in a given field.

The survey by Lajos MÉSZÁROS and Károly VARGA "Intensification of multiphase chemical operations and processes" is interesting in addition to its technical character from the aspect that it gives in essence the summary of the views and results of a Hungarian research group, engaged since a considerable time in the investigation of this subject. The review reports, according to the nomenclature of the authors, on the most important achievements

in the field of "dispersion operations". First, spraying operations are discussed, and this is followed by the description of the novel possibilities of intensification with agitators of point and line type. The reviewer is unfamiliar with this particular field, but in spite of this, or for this very reason, he has read the survey with interest, which calls attention to a special field of neglected publicity.

Gy. DEÁK

ZIESSOW, DIETER: *On-line Rechner in der Chemie. Grundlagen und Anwendung in der Fourierspektroskopie*

W. de Gruyter, Berlin—New York 1973, 376 Seiten

Das äußerst interessante Buch füllt eine wesentliche Lücke. Es sind nämlich zahlreiche Bücher über Fourierspektroskopie erschienen, die vor allem optische Beziehungen behandeln. Anderseits gibt es viele Arbeiten über die verschiedenen Anwendungen der Fouriertransformation. Auch gibt es zahllose Veröffentlichungen über problemorientierte Rechner. Im vorliegenden Buch erhält der Leser eine einheitliche, gründliche und knapp gefaßte Erläuterung, um die Grundlagen und Praxis der optischen bzw. NMR-Fourierspektroskopie verstehen und anwenden zu können.

Der Verfasser setzt keine besonderen theoretischen Kenntnisse voraus. Der erste Teil behandelt die Grundlagen und Verfahren der Datenverarbeitung. Unter anderem werden die Wahrscheinlichkeitsvariablen, die endliche Fouriertransformation, die Linienerkennung, die Reduktion der Zahl der Punkte erläutert. Dieser Teil macht den größeren Teil des Buches aus. Die kurzgefaßten Erklärungen sind präzise und die vorgetragene Theorie wird durch Beispiele klarer gemacht. Gerade wegen dieser Knappheit ist der Text jedoch keine leichte Lektüre. Es wäre nützlich gewesen, wenn der Verfasser das Wesentliche am Beginn oder Ende des Abschnitts kurz zusammengefaßt oder die besonders wichtigen Teile mit typographischen Mitteln hervorgehoben hätte.

Der nächste, sehr kurze Abschnitt behandelt Hardware und Software von problemorientierten Rechnern. Dabei werden on-line Rechner-Datenquelle-Systeme vor allem betont. Die Grundlagen der Assembler-Programmierung werden erörtert. Dieser Abschnitt gibt nur eine allgemeine Übersicht. Der Leser kann, falls er mit einem bestimmten on-line-System zu tun hat, eine gründliche Kenntnis dieses Systems nicht entbehren.

Der letzte, ziemlich umfangreiche Abschnitt befaßt sich mit der Fourierspektroskopie. Für diesen Abschnitt gilt das gleiche wie für den Abschnitt über die Datenverarbeitung. Die theoretischen Grundlagen werden ausführlich, jedoch mit der gewünschten Knappheit erörtert. Im Rahmen der NMR-Fourierspektroskopie wird das Impulsverfahren hervorgehoben, jedoch werden auch andere Verfahren diskutiert. Die Apparatur, das Blockschema des Steuerprogramms werden erörtert und ein Steuerprogramm für einen IBM—1800-Rechner wird angegeben und ausführlich behandelt.

Der weitere Teil des Abschnittes befaßt sich mit der optischen Fourierspektroskopie. Es wird das Problem der endlichen Apertur, die Ergänzung des Interferogramms, die Korrektion der Grundlinie und die Verbesserung der Daten durch Filter, Apodisation und Phasenkorrektion erörtert. Endlich werden die Grundlagen der Hadamard-Spektroskopie kurz behandelt.

Im Anhang vergleicht der Verfasser verschiedene Typen von problemorientierten kleinen Rechnern. Besonders hervorgehoben wird der IBM—1800-Rechner; die Maschine und sein Anweisungssystem werden ausführlich behandelt. Endlich wird ein für diesen Rechner in der Assembler-Sprache geschriebenes schnelles Fouriertransformationsprogramm (FFT) angegeben. Zum Schluß enthält das Buch eine nützliche Tabelle der Konvolutionskoeffizienten zum Glätten von diskreten Funktionen und zu ihrer Differenzierung.

Es sind etwa 200 Literaturangaben, einschließlich 1972, angeführt.

Der Rezensent empfiehlt dieses interessante Buch Studenten und Forschern, die sich für die in Ungarn noch wenig verbreitete NMR- und optische Fourierspektroskopie interessieren.

F. BILLES

JAMES L. COPELAND: *Transport Properties of Ionic Liquids*

Gordon and Breach Science Publishers New York—London—Paris, 1974. 76 pages.

This book gives an up-to-date theoretical picture and a concise review of the transport processes — viscosity, diffusion and electric conduction — of ionic melts very important in the practice. It provides a very satisfactory, strict theoretical treatment of the rapidly growing amount of experimental information. Such a concise and objective review of this field practically had not existed before publication of this book.

In the introductory part of the work (Chapters I and II) the author outlines his aims and the method of treatment, and summarizes the general phenomenological concepts, principles and definitions connected with the above-mentioned three transport properties. Chapter III gives a general account of the structures and fundamental physicochemical properties of ionic melts. In effect, Chapter IV contains the most important material. Here the author discusses the main models and theories describing the mechanism of transport in ionic melts: the hole theory, the absolute reaction rate theory, the free volume theories and the glassy state conception. He also deals with special phenomena appearing at higher temperatures, and with some new views relating to viscosity, primarily the Macedo—Litovitz concept and certain criticisms of this. At the end of the book, in addition to the explanation of the symbols and subject and name indexes, we find a collection of 105 references representing the main results of the past 15 years, supplementing and documenting the critical discussion of the author. These strengthen the view that this brief monograph provides a good review of the main trends, and is well worthy of study.

E. BERECZ

Molecular Complexes

Edited by Roy Foster, Volume 2, Elek Science, London, 1974. XI + 309 pages cloth, £ 9.40

This volume contains five independent reviews on some important problems:
Chemical effects of molecular complexing by A. K. COLTER and M. R. J. DACK;
Interactions in binary systems containing aromatic fluorocarbon by F. L. SWINTON;
Determination of association constants of electron-donor-acceptor complexes by R. FOSTER;
Intermolecular complexes in polymerisation processes by P. HYDE and A. LEDWITH;
The interactions of amines and amino-acids with p-benzoquinones and with tetracyanoethylene by R. FOSTER.

Each of these reviews provides a critical and informative treatment. As a whole the standard and style of this volume match with the former one. The first review is a continuation of the article published in the first volume by the same authors. The review on the problems of the determination of the association constants is particularly interesting for the reviser and it helps to make order in an apparently simple but in fact most complicated field.

When the first volume was published it was difficult to judge the editorial policy, after the publication of the second one it is impossible. These two volumes are valuable contributions to the literature of an important subject and they can be recommended to both libraries and individuals, although the high price will disappoint particularly the latter. But they do not provide a comprehensive treatment of the field, they can be better regarded as first volumes of a continuous series. No information is given, however, that any further volume is planned for publication.

M. BECK

B. CSÁKVÁRI (editor): *A kémia újabb eredményei (Recent Advances in Chemistry), Vol. 23*

Akadémiai Kiadó, Budapest, 1974 (In Hungarian)

This volume contains two chapters:
Mechanism of catalytic double bond isomerization of olefins (pp. 7 133) by Gy. GÁTI;
Mechanism of electrophilic aromatic substitution reactions (pp. 135- 197) by J. MÁRTON L. P. SIMON, L. BURSICS and L. HORVÁTH.

It seems interesting to note the different meanings of the term 'mechanism' in the two titles. In the first case, the chemical reaction proceeds in monomolecular layers adsorbed on the surface of the solid catalyst particles. Such reactions always comprise important consecutive physical elementary steps (*e.g.*, adsorption of gaseous reactants on the surface of the catalyst, diffusion in the surface layer, desorption from the surface, etc.) which may influence the overall rate of the chemical changes. Even the 'chemical part' of heterogeneous catalytic reactions is very complex involving several possible simultaneous pathways and consecutive steps. This complexity is connected with powerful surface forces breaking the σ and π bonds of the reactant molecule which are stable in most homogeneous conditions. The physical and chemical properties of the catalyst are also major factors influencing catalytic activity and the course of the chemical reactions. Although the field is extensively developing owing to essential implications in the petrochemical industry, generally accepted concepts of the mechanism of catalytic action and isomerization are still lacking. The first chapter surveys the ideas proposed so far, and an attempt is made to define the main characteristics of the mechanism. The principles of systematization involve the manner of hydrogen movement, the type of binding of the intermediate to the catalyst and the partial charge of the intermediate. Experimental methods are critically outlined and their capacity and relevance to the problem of mechanism are pointed out. There are 204 references, involving some of 1973.

The topic of the second chapter is one of the most extensively studied fields of organic chemistry. The scope is limited to the following problems:

(a) Origin of the primary kinetic hydrogen isotope effects in electrophilic aromatic substitution reactions,

(c) Conclusions concerning the probable structure of transition states, on the basis of the magnitude of isotope effects.

Since the two-step S_E2 mechanism involving a σ-complex intermediate is widely accepted (the proposal by OLÁH of a π-complex intermediate being doubtful), the discussion attempts to separate the steps and to consider the influence of several effects on the single steps. These effects include steric hindrance in the aromatic reactant, the electrophilicity of the electrophilic reactant, the role of proton-accepting bases and their basicity, the role of the solvent, etc. Although many aspects of the isotope effects in electrophilic aromatic substitution reactions are open to debate, the chapter offers recent information in the field, with emphasis on mechanistic considerations and the underlying principles. 86 references are given up to 1972.

M. SIMONYI

M. HARGITTAI and I. HARGITTAI

Vapour-phase Molecular Geometry of Coordination Compounds Recent Results in Chemistry, Vol. 23

Akadémiai Kiadó, Budapest 1974. 283 pages

The authors discuss a special and rather new field of coordination chemistry, the investigation of the molecular structure of coordination compounds existing in the vapour phase.

The structure of coordination compounds is investigated predominantly in solid phase or possibly in solution. In the course of these investigations, the structure and the symmetry conditions of the molecules may be influenced by various intermolecular interactions. Structural investigation completely free of these secondary effects is possible only in vapour phase. In vapour phase, the molecules are separated from each other to a great extent and their structure depends only on intramolecular forces. Thus, for the interpretation of the electron structure and of the chemical and physical properties of the molecules, an exact knowledge of the geometry of complex compounds in the gas phase will furnish substantially more information and easier to correlate, than results obtained in condensed phases. This is the reason why in the last 10 – 15 years, owing to the development of suitable methods, the structural investigation of complexes in vapour phase has been steadily gaining ground. This trend of development is well reflected by the detailed bibliography with 632 references, closing the volume.

Among the methods of investigation in this field, the authors deal extensively with two methods, *i.e.* with electron diffraction and microwave spectroscopy. The other methods are mentioned each on hand of an example.

The subject is discussed according to groups of compounds. After the introductory part summarizing general knowledge (36 pages), the following groups of compounds are treated: addition compounds, electron-deficient molecules, halogen bridge complexes, salts of oxy-acids, polymer oxides, complexes with hydrogen bond, carbonyls and metallocenes.

For the coordination chemists, particularly investigations concerning associates with halogen bridge, metal carbonyl and compounds of sandwich type are of interest, but from the point of view of inorganic chemistry, the other parts of the monograph are also interesting.

The better understanding of relationships is facilitated by 76 figures, mostly very illustrative, and by more than 50 tables. A very useful part of the book is the bibliography compiled evidently with a claim to monographic completeness.

In addition to researchers interested directly in this field, the book will be of interest also to wider circles dealing with structural inorganic chemistry, and particularly with coordination chemistry.

K. BURGER

J. MIKA and T. TÖRÖK: *Emission Spectral Analysis, II*

The book of J. MIKA and T. TÖRÖK "Emission Spectral Analysis II, Practical Part", which was written with the contribution of E. GEGUS, meets old demands and fills a fundamental gap. Its theme is connected to theoretical knowledges discussed in the first volume.

The book was published by Akadémiai Kiadó (Budapest) in 1974. The nine chapters of 718 pages contain several hundred figures and tables. Each chapter closes with a detailed bibliography. An extensive subject index and errata of the first volume close the book. The reader gets acquainted with the most important aspects of the preparation of test samples, the properties and fields of application of the various radiation sources, and with physical and chemical effects affecting the intensity of the spectral lines. A separate chapter contains the description of spectrographic, spectrometric and spectroscopic analysis procedures, and within these, the prescriptions of analysis of the substances most often analysed. Finally, the book gives the necessary bases of error calculation, based on modern statistical methods, and their application in the field of emission spectral analysis. The last chapter contains valuable tables for specialists active in this field.

This volume too represents a great help both for scientific research workers and for experts working in the most various industrial fields, in selecting methods, procedures and instruments best suited to their work. One of the chief merits of the book is that in addition to the description of instruments and methods proved well so far it calls the attention to the directions and possibilities of further development.

I. KEREKES

R. K. FREIER: *Water Analysis*

Second edition. Published by Walter de Gruyter, Berlin—New York, 1974. 214 pages (In German)

The book is divided into two main parts. The first part comprises the chemical and physicochemical methods used in water analysis while in the second one the radiochemical analytical methods are discussed. Altogether 49 photometric, flame photometric, titrimetric, gravimetric, conductometric and electrometric methods are given for the quantitative determination of ions and compounds that are of importance from the point of view of water quality. A paragraph is devoted to the fundamentals of photometry and a compilation of extinction data (correlation between D and E values) enables the easy evaluation of results obtained in photometric determinations. Several diagrams and tables are also included, *e.g.* the conductivities of a number of compounds as a function of different ranges of concentration, the correlation between the amount of dissolved carbon dioxide and the pH as well as the conductivity of the resulting aqueous solution.

Each chapter is divided into three parts. The first part describes the method to be followed in the practical work, the second one discusses the theoretical backgrounds, wile the third one contains the composition of the necessary reagents. If there are any, the disturbing interferences and their elimination are also described. The second part of the book consists of radiochemical analytical methods suitable in connection with water cooled atomic reactors for the determination of the isotopes of 13 elements. Most of the determinations are based on γ spectrometry and only a few methods make use of α spectrometry and β radiation measurement, respectively. A separate paragraph deals with the taking and evaluation of γ spectra. Also in this part figures and diagrams make th nderstanding easier.

The book with its up-to-date methods is a very useful tool and can be recommended for those engaged in water analysis.

L. ACKERMANN

P. HEDVIG: *Experimental Quantum Chemistry*

Akadémiai Kiadó, Budapest, and Academic Press, New York, London, 1975, pp. 533

Despite the misleading title, "the author intends to give a basic quantum mechanica viewpoint" to his readers on the diverse methods of chemical structure analysis. This concep is useful and modern but the author has failed in achieving his goal. Throughout the book, the lack of a thorough theoretical treatment can be noticed.

Chapter 1 is a well-written survey on the foundations of quantum theory. Unfortunately, no mention is made of perturbation theory which is an essential tool in quantum chemistry. Chapter 2 deals with protons while Chapter 3 discusses the properties of electrons and positrons. Isolated atoms and ions are treated in Chapter 4. This may be the best part of the book with a concise discussion of many-electron atoms, spin properties and experimental methods. Chapter 5 deals with the structure of nuclei as well as with NMR, NQR and Mössbauer spectroscopy. Molecules and free radicals are discussed in Chapters 6 and 7, respectively. Here a good survey on experimental techniques is given, while the theoretical part is obsolete. Important methods, *e.g.* IR spectroscopy, are handled too shortly. However, an exhaustive treatment of different ESR methods can be found here. The discussion of chiral properties is omitted Chapter 8 is devoted to the organic solid phase.

The most serious drawback of the book is the lack of recent literature citations. For example 101 of the 157 references, given to Chapter 7, are dated before 1965. Thus the book can be recommended primarily to graduate students and non-specialists who wish to gain a survey on the methods of structural chemistry.

G. NÁRAY-SZABÓ

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C. Sellei — S. Eckhardt — L. Németh

Chemotherapie der Geschwulstkrankheiten

Die medikamentöseBehandlung der Geschwulstkrankheiten findet immer größere Verbreitung. Dieses Werk will die zeitgemäßen Methoden zur Erprobung neuer Cytostatika dem Leser vermitteln. Die Technik der Tierversuche sowie die Messung der Toxizität und der zytostatischen Wirkung werden praktisch dargelegt, die zweckdienlichsten klinischen Erprobungsverfahren, die Problematik der Dosierung, die Resultate und Risiken erläutert und die Wirksamkeit der einzelnen Medikamente wird besonders auseinandergesetzt. Der Leser findet auch alles Wissenswerte über die in der Therapie heute allgemein anerkannten Cytostatika — ihre chemische Struktur, ihre günstigsten Dosierungen sowie die Nebenwirkungen, und die bisher erzielten Erfolge. Ein besonderes Augenmerk widmen die Verfasser der modernsten medikamentösen Therapie der einzelnen Krankheitsbilder, einschließlich der kombinierten Anwendung der verschiedenen Heilverfahren. Der Anhang enthält ein ausführliches, und die Spitzenleistungen der internationalen onkochemotherapeutischen Forschung treu wiedergebendes Literaturverzeichnis.

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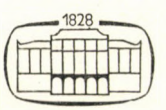

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K. VUKOV

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VOL. I: REPRINTS OF CONTRIBUTED PAPERS

Edited by E. WOLFRAM

This volume contains papers presented at the International Conference on Colloid and Surface Science held in September, 1975 in Budapest, Hungary. The purpose of this IUPAC-sponsored meeting was to cover as many subjects as possible of this broad field of science. The following areas have been dealt with: surface structure and surface chemistry of solids; adsorption at solid/gas and solid/liquid interfaces; wetting; thin liquid films; adsorption of polymers; adsorption of surfactants; formation of disperse systems; stability and structure of disperse systems; electrical phenomena; rheology; gels; micellization and related phenomena; monolayers and foams; molecular interactions; applications; methods. — The second volume containing the discussions of the Conference will follow at a later date.

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Edited by *Ilona Buzás*

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РЕЗЮМЕ

Исследование соединений осмия с помощью бумажной и тонкослойной хроматографии

Э. ПОМОГАЧ

Метод бумажной и тонкослойной хроматографии был разработан для разделения и определения соединений осмия в более высоком валентном состоянии. Соединения OsO_4 и $KOsO_3N$, а также K_2OsO_4 и $KOsO_3N$ были разделены с помощью элюирующей смеси этанол-вода-соляная кислота при комнатной температуре и в системе, поднимающейся на хроматографической бумаге MH 214. С помощью тонкослойной хроматографии на Кизель-геле, импрегнированном KOH, все три соединения осмия были разделены из смесей, содержащих ацетон, бутанол, пиридин и уксусную кислоту. Содержание осмия в пятнах, разделенных и проявленных с помощью солянокислого тиокарбамида, было определено количественно спектрофотометрическим путем.

Молекулярное силовое поле для некоторых молекул типа XY_6

К. РАМАСВАМИ и Л. ЯЯРАМАН

Силовое поле гексафторидов некоторых элементов групп IIIB, VIA, BIB и VIII было представлено с помощью параметрического изображения, используя изотопные частоты и наблюдаемые константы связи Кориолиса. Для SF_6 было зафиксировано единственное силовое поле и наиболее вероятная величина параметра R равна 23°23′. Изменение силовых постоянных для этих молекул было исследовано, исходя из того, что SF_6 является родственной молекулой, и используя для репрезентации внутренних координат функции Грина. Средняя амплитуда колебаний для всех этих молекул была рассчитана при 298,16°K.

Критический обзор теории переходного состояния

М. ШИМОНИ и И. МАЙЕР

Сравниваются кинетические схемы, соответствующие классическому и «квази» равновесиям в случае бимолекулярных процессов второго порядка. Рассмотрение, обычно применяемое в теории переходного состояния (ТПС), включает в себя результаты двух противоположных предельных случаев кинетического формализма. Обсуждаются некоторые характерные черты ТПС. Показано, что главным недостатком теории является необоснованное применение распределения Больцманна и сумм по состояниям для «активированного комплекса». Указаны характерные ошибки в некоторых выводах, использованных для получения основной формулы ТПС на основе различных моделей. Исходя из выражения, данного ТПС для скорости, и произведя рассуждения в обратном порядке по сравнению с

обычным, получена модель, следующая из самого выражения ТПС при условии более тщательного применения сумм по состояниям. Показано, что модель далека от реальности.

ТПС следует рассматривать как эвристический приближенный метод, не имеющий теоретического обоснования. Выводы, полученные на основе ТПС могут быть реалистичными, главным образом, благодаря внесению подгоняемых параметров. Понятия «энтропии активации» и «энтальпии активации» не имеют термодинамического смысла.

Образование боратов этиленгликоля в водных растворах, II

Т. ПААЛ и Л. БАРЦА

Были исследованы равновесия, устанавливающиеся в растворах, содержащих 0,05—0,02 М борной кислоты, 0,100—2,000 М этиленгликоля и 1,000 М $Na[ClO_4]$ в качестве инертной соли. Измерения проводились при 25°С, потенциометрическим методом в интервале pH = 6,5—9,5. Обозначая борную кислту — $B(OH)_3$ — через HB и этиленгликоль — $C_2H_6O_2$ — через D, система может быть представлена полианионами $H_2B_3^-$ HB_3^{-2} и $H_2B_4^{-2}$ и гликольными комплексами BD^-, BD^- и $H_2B_3D^-$. $\log K_{231} = 7{,}35 \pm 0{,}20$.

Обсуждение термодинамического уравнения движения на основе теории термостатической стабильности

Л. МЕЗЕИ

В термодинамическом уравнении движения в форме с одной переменной фигурирует «коэффициент термостатической стабильности», служащий основой классификации гомогенных равновесных состояний. На основе этого факта указаны те особенности, какими обладает термодинамическое уравнение движения и его решения для различных классов состояний гомогенных равновесий. На основе результатов может быть объяснено замедление процессов выравнивания, наблюдаемое экспериментально вблизи критического состояния.

Катодное восстановление Ce IV на полупроводниковом электроде германия

М. М. СИНГ и Д. СИНГ

Было изучено катодное восстановление ионов церия на поверхности катодов *n*- и *p* Ge, в присутствии 2N и 1N серной кислоты. Были построены зависимости E от логарифма плотности тока (пт) для $X(NH_4)_2Ce(NO)_{36}$ (X означает грамм-моль.$л^{-1}$). Уравнение Тафеля справедливо в весьма широком интервале пт. Потенциал сверхнапряжения увеличивается с введением ионов церия в раствор серной кислоты. Процесс восстановления на поверхности катода *n*—Ge протекает в сравнительно узком интервале пт; при повышенных пт разряд ионов водорода доминирует над восстановлением окислителя. При освещении плотность тока насыщения на катоде *n*—Ge уменьшается. Вероятно, что процесс восстановления протекает через участие электронов валентной связи.

Стехиометрические исследования комплексов Pt IV и Pd II

Р. К. УПАДХАЙ, Р. ПРАСАД и У. ВАЙПАИ

п-Диметиламиноанил антрацен-глиоксаля образует комплексы с Pt(IV) и Pd(II) с составом 1 : 1, как это было обнаружено методом Фенгера и сотр., представляющим модифицированный метод непрерывных вариаций. Стехиометрия аддуктов подтверждалась на основе данных их элементарного анализа и кондуктометрии. Неэлектролитная природа аддуктов была установлена на основе измерений молярной проводимости.

Бензоил-салициловый гидразон как хромогенный реактив для меди (II) и палладия (II)

Д. К. РУСТОГИ, С К. ДУА, ШРИ ПРАКАШ и Р. П. СИНГ

Бензоил-салициловый гидразон образует зеленые комплексы с медью(II) и зеленожелтые комплексы с палладием(II). Эти комплексы были изолированы и проанализированы. Состав комплексов равен 1 : 1. Спектрофотометрические исследования указывают на то, что в соответствующих областях pH $=4{,}5 \div 6{,}5$ и $1{,}7 \div 2{,}3$ закон Бэра соблюдается в пределах оптимальных концентраций иона металла, в области $0 \div 5{,}0$ и $0 \div 15{,}0$ ppm при длинах волн 385 и 395 nm, соотстветственно. Коэффициент молярной экспинкции и чувствительность реакции равны 15 500 и 0,0041 мг/см² для меди и 7190 и 0,014 мг/см² для палладия. Был изучен эффект некоторых ионов и было найдено, что многие из них допустимы в значительных количествах. Отношение металла к лиганду равно 1 : 1 в обоих комплексах.

Реакция N-алкилирования нового типа

Й. РАЙТЕР и Л. ТОЛЬДИ

С помощью препаративных исследований было доказано, что реакция N-алкилирования активных арил-алкиловых эфиров, наблюдаемая нами ранее, справедлива и в общем случае и отличается от N-арилирующей способности нитро-арил-алкильных эфиров, объясняемой ароматическим нуклеофильным замещением.

На основе дальнейших препаративных, масс-спектрометрических и кинетических измерений предлагается SN_2 механизм для наблюдаемой реакции N-алкилирования.

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UNTERSUCHUNG DER ZUSAMMENSETZUNG VON EINHEIMISCHEN UND AUSLÄNDISCHEN ÄTHERISCHEN ÖLEN, IV

BEITRÄGE ZUR ZUSAMMENSETZUNG DES UNGARISCHEN LAVENDELÖLES

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Die chemische Zusammensetzung des ungarischen Lavendelöles wurde durch Infrarotspektrometrie und magnetische Kernresonanz-Spektrometrie der mittels Rektifikation und präparativer Gaschromatographie isolierten Komponenten eingehend untersucht. Unter den durch Gaschromatographie unmittelbar nachgewiesenen 44 Komponenten konnten 27 Einzelbestandteile mit einem Anteilverhältnis von etwa 97,3 Gew.% identifiziert oder verwahrscheinlicht werden. Zahlreiche aliphatische Alkohole, Terpenalkohole, deren verschiedene Fettsäureester sowie das Äthyl-*n*-amylketon konnten nicht in der aufgrund der Fachliteratur erwarteten Konzentration gefunden werden. Auch im ungarischen Lavendelöl wurde neben den in höherer Konzentration vorhandenen üblichen Komponenten ein charakteristisch geringer Gehalt an Borneol, Campher und Cineol gemessen. Anhand der Forschungsergebnisse konnte im Lavendelöl noch die Anwesenheit des *p*-Cymols und vermutlich des Tricyclens, des Alloocymens und des *n*-Hexylisobutyrats bestätigt bzw. vorausgesetzt werden.

Die Zusammensetzung — und damit auch die Qualität und der Wert — des aus der Lavendel-Pflanze (Lavandula angustifolia) gewonnenen ätherischen Öles weist neben den genetischen Gegebenheiten eine bedeutende, durch die Bodenart und durch das Klima bedingte Variabilität auf. Außer der Variabilität wird die Wichtigkeit der Materialprüfung durch die Tatsache betont, daß die in der kosmetischen Industrie verwendeten wertvollen ätherischen Öle sehr oft verfälscht sind. Daraus folgt, daß verhältnismäßig viele Informationen über die Zusammensetzung des Lavendelöles zur Verfügung stehen [1—53].

Bis in die letzten Zeiten befaßte man sich nur wenig mit der ausführlichen Untersuchung des ungarischen Lavendelöles. Die früheren Forschungsarbeiten hatten die Bestimmung der verschiedenen physikalischen Eigenschaften [11], die Identifizierung der Hauptkomponenten [53] und die gaschromatographische Beurteilung des Lavendelöles zum Ziel [16, 27]. Nur eine einzige Arbeit beschäftigte sich mit der eingehenderen Erforschung der chemischen Zusammensetzung aufgrund wirksamer Rektifikation und chemischer Analyse [24]. Das Ziel unserer Arbeit war die Ergänzung der Kenntnisse über die Zusammensetzung des ungarischen Lavendelöles mit durch Instrumentalanalyse gewonnenen Angaben.

Literaturangaben über die Zusammensetzung des Lavendelöles

Zur Bestimmung der chemischen Zusammensetzung der ätherischen Öle wurden seit Ende des vorigen Jahrhundertes [3, 43] bis heute [11, 12] verschiedene Methoden angewandt. Unter den *Trennmethoden* ließen sich die anfangs verwendeten *chemischen* Stofftrennungen (Hydrolyse, Verseifung, Borsäure-Reaktion, Bisulfit-Reaktion usw. [z. B. 21, 52]) einerseits durch wirksame *physikalische* Trennverfahren (Rektifikation, Flüssigkeitschromatographie, präparative Gaschromatographie, präparative Dünnschichtchromatographie [z. B. 24, 47]), andererseits durch die *Kombination* physikalischer und chemischer Trennmethoden [z. B. 31, 32] ersetzen. Zur *Identifizierung* der isolierten Komponenten hatte man zuerst spezifische *chemische Reaktionen* oder spezifische *Eigenschaften der Derivative* (Urethanbildung, Semicarbazonbildung usw. [z. B. 2, 50]) verwendet. In den späteren Zeiten sind neben den angeführten Verfahren die *spektrometrischen Methoden* (Infrarotspektrometrie, magnetische Kernresonanz-Spektrometrie usw. [z. B. 1, 34]) und die *chromatographischen* Verfahren (Gaschromatographie, Dünnschicht-Chromatographie usw. [z. B. 13, 27]) in den Vordergrund getreten. Aufgrund der Fachliteratur kann also behauptet werden, daß die chemische Zusammensetzung der ätherischen Öle oder die Anwesenheit bestimmter Komponenten einwandfrei nur mittels wirksamer physikalischer (und teilweise auch chemischer) Trennungen und danach folgender spektrometrischer (und teilweise auch chemischer) Identifizierungen aufgeklärt werden kann [z. B. 34, 48]. Man kann ferner aus der Fachliteratur feststellen, daß zur Beurteilung der Qualität der ätherischen Öle und zur Bestimmung des Komponenten-Verhältnisses in erster Linie die Gaschromatographie am besten geeignet ist [z. B. 16, 46].

Über die Zusammensetzung des *französischen* Lavendelöles publizierten Naves, Tullen und Mitarbeiter [28—34], dann Peyron, Benezet und Mitarbeiter [2, 37—39] ausführliche Angaben. Berichte über das *bulgarische* Lavendelöl sind von Ognyanov, Vlakhov und Mitarbeitern [35, 47—49] erschienen. Mit der Zusammensetzung der ätherischen Öle aus *Italien* befassen sich die Publikationen von Calvarano [4], Fenaroli [9] und Franchi [10]. Über die Untersuchung verschiedener ätherischer Ölproben aus der *Sowjetunion* liegen Publikationen von Lazurewskij und Mitarbeitern [17, 25], dann von Karetnikowa und Mitarbeitern [18—20] vor. In den letzten Jahren haben Kolšek und Mitarbeiter [23] die Zusammensetzung des *jugoslawischen*, Ille [15] die des *rumänischen* und Kolta [24] die des *ungarischen* Lavendelöles eingehend untersucht. Einige der Verfasser haben nur vergleichende Untersuchungen mit ähnlichen ätherischen Ölen durchgeführt [z. B. 14, 46], andere haben die Qualitätsabweichungen der Lavendelöle von unterschiedlicher Herkunft [z. B. 10, 23] oder die durch das Pflanzenwachstum bedingten Zusammensetzungsänderungen [z. B. 45] untersucht.

Tabelle I

Im Lavendelöl vorhandene Komponenten aufgrund der Fachliteratur
(Die Spuren wurden mit <0,X gezeichnet)

a) Kohlenwasserstoffe

Komponenten (Monoterpene)	Menge, Gew.%	Literatur	Komponenten (Sesquiterpene)	Menge, Gew.%	Literatur
Camphen	0,0X—0,X	[23, 32]	Bergamoten	<0,X	[48]
Δ^3-Caren	0,X	[23, 32]	Bisabolen	<0,X	[42]
Limonen	0,0X—0,X	[32, 43]	γ-Cadinen	<0,X	[48]
β-Myrcen	0,0X—0,X	[32]	δ-Cadinen	<0,X	[42, 48]
β-Ocymen	X	[5, 24, 32]	Caryophyllen	X	[24, 33, 42, 48]
α-Phellandren	<0,X	[46]	Cedren	<0,X	[50]
β-Phellandren	<0,X	[46]	Curcumen	<0,X	[48]
α-Pinen	0,0X—0,X	[23, 32, 51]	Farnesen	<0,X	[48]
β-Pinen	0,0X—0,X	[23, 32]	Sabinen	0,0X	[32]
γ-Terpinen	<0,X	[4]	α-Santalen	<0,X	[48]
Terpinolen	<0,X	[46]	β-Santalen	<0,X	[48]
α-Thujen	0,X	[46]			

b) Alkohole

Komponenten (Monoterpen-alkohole)	Menge, Gew.%	Literatur	Komponenten (Sonstige Hydroxylderivate)	Menge, Gew.%	Literatur
Borneol	0,X—X	[13, 23, 35, 52]	N-Amylalkohol	<0,X	[52]
Izo-Borneol	0,X—X	[23]	Iso-Amylalkohol	0,X—X	[51]
Citronellol	0,X	[24, 41]	Bisabolol	<0,X	[42]
Geraniol	0,0X—X	[13, 24, 33, 52]	Cadinol	<0,X	[42]
Lavandulol	0,X	[8, 24, 33, 41]	Cuminalkohol	0,00X	[33, 42]
Linalool	0,X	[3, 20, 43]	N-Hexanol	0,X	[2, 24, 41, 52]
Nerol	0,X	[8, 13, 24, 41	3-Methylbuten-2-ol-1	<0,X	[44]
Perillalkohol	<0,X	[46]	N-Oktanol-3	0,00X—0,X	[2, 24, 34, 52]
Terpinen-1-ol-4	X	[24, 30, 34, 46]	N-Okten(?)ol-1	<0,X	[5]
Terpineol-4	0,X—X	[20, 23, 35, 49]	N-Okten-1-ol-3	0,X	[28, 34]
			Thymol	0,00X	[2, 8]

Tabelle I

c) Ester

Komponenten (Monoterpenderivate)	Menge, Gew.%	Literatur	Komponenten (Sonstige Ester)	Menge, Gew.%	Literatur
Bornylacetat	0,X—X	[23, 52]	Butylbutyrat	0,0X	[34]
Iso-Bornylacetat	0,X—X	[23]	Cuminacetat	0,00X—0,0X	[33]
Geranylacetat	0,X	[33, 52]	Cuminbutyrat	0,00X—0,0X	[33]
Isogeranylacetat	<0,X	[34, 48]	Cumincapronat	0,00X—0,0X	[33]
Geranylbutyrat	0,00X—0,0X	[51, 52]	Cuminbenzoat	0,00X—0,0X	[33]
Geranylvalerianat	0,00X—0,0X	[51, 52]	N-Hexylacetat	0,X	[5, 24, 34]
Geranylcapronat	0,00X—0,0X	[52]	N-Hexylbutyrat	0,X	[30, 31, 38]
Lavandulylacetat	0,X—X	[19, 33, 39, 46]	N-Hexylcapronat	0,0X	[3]
Linalylacetat	X—CO	z. B. [3, 20, 21, 43]	N-Heptylacetat	0,00X	[34]
Linalybutyrat	0,0X—X	[3, 24, 33, 51]	N-Okten-1-yl-3-acetat	0,X	[5, 24, 34]
Linalylvalerianat	0,0X—X	[24, 51, 52]			
Linalylcapronat	0,0X—X	[24, 52]	Sec. Oktylacetat	0,X—X	[5, 24]
Nerylacetat	0,X	[33]			
Terpenylacetat	0,X	[23]			

In Tabelle I sind fast alle zur Verfügung stehende Informationen über die Zusammensetzung des Lavendelöles zusammengefaßt. In der Tabelle sind die betreffenden Literaturangaben und auch die mitgeteilten oder verwahrscheinlichten Größenordnungen der Zusammensetzungsdaten wiedergegeben. Unter den Angaben sind beträchtliche Widersprüche zu finden, die sich auf die Anwesenheit verschiedener Terpene oder Terpenderivate (z. B. γ-Terpinen, Nerol, Isogeranylacetat) oder auf die Größenordung ihrer Konzentrationen (z. B. Borneol, Campher, Cineol) beziehen. Aus den Angaben ist ersichtlich, daß man im ungarischen Lavendelöl mit etwa 35—40 Komponenten zu rechnen hat, deren Konzentration jeweils 0,1 Gew.% übersteigt.

Die Methode der Untersuchung und die untersuchte Probe

Zur Untersuchung des ungarischen Lavendelöles wurde eine für die Analyse der ätherischen Öle ausgearbeitete Methode gewählt, die auf der Kombination von wirksamen Stofftrennungen und instrumentellen Komponentenidentifizierungen beruht [54—56]. Die annähernde quantitative Zusammensetzung des ätherischen Öles wurde *gaschromatographisch* mit einem Gerät Typ Chrom III unter Verwendung einer mit Carbowax 1500 benetzten Kapillarsäule [56] bei 150 °C und bei einer Argon-Trägergasgeschwindigkeit von 2 l/h

(Fortsetzung)

d) Aldehyde, Ketone, Säuren und sonstige Sauerstoffderivate

Komponenten (Aldehyde, Ketone)	Menge, Gew.%	Literatur	Komponenten (Säuren, sonstige Sauerstoffderivate)	Menge, Gew.%	Literatur
Butyraldehyd	0,0X	[2]	Benzoesäure	<0,X	[42]
Campher	0,0X—X	[5, 23, 26]	Buttersäure	0,00X	[2]
Capronaldehyd	<0,X	[46]	Capronsäure	0,00X	[2]
Caprylaldehyd	0,0X	[2, 46]	Caprinsäure	0,00X	[2]
Caprinaldehyd	0,0X	[2, 46]	Cineol	0,X—X0	[6, 14, 34, 36]
Citral	0,0X	[2]	Cumarin	0,0X	[2, 21, 25, 52]
Citronellal	0,0X	[2]	Cumarsäure	<0,X	[50]
Cuminaldehyd	0,0X	[2]	Cuminsäure	<0,X	[42]
Crypton	0,0X	[30]	Epoxy-dihydrocaryophyllen	0,0X	[30]
Etylamylketon	0,X—X	[24, 40, 51]	Epoxydihydrolinalool	0,0X	[30, 34]
Furfurol	0,00X	[2, 36, 52]	Essigsäure	0,00X	[2]
Hexen-2-al-1	0,0X	[2]	Eugenol	0,00X	[2]
Nonanal	<0,X	[4]	α-Methylessigsäure	<0,X	[42]
Önantaldehyd	<0,X	[46]	γ-Methyl-γ-vinyl-butyrolakton	0,0X	[22]
Perillaaldehyd	<0,X	[46]	Oktenylsäure	<0,X	[42]
Phellandral	<0,X	[46]	Pelargonsäure	<0,X	[42]
Valeraldehyd	<0,X	[52]	Tiglinsäure	<0,X	[42]
Iso-Valeraldehyd	0,0X	[2]	Umbelliferon	<0,X	[25]
			Umbelliferonmethyl-äther	<0,X	[7, 42]

ermittelt. Unter ähnlichen Umständen wurde auch der Wirkungsgrad der Trennprozesse des ätherischen Öles bzw. der Ablauf der Komponentenanreicherung kontrolliert. Die Komponenten der untersuchten Probe wurden durch *Rektifikation*, dann durch eine grobe und eine feine *gaschromatographische Präparation* in einem zur Identifizierung erforderlichen Reinheitsgrad bereitgestellt. Zur Rektifikation wurde eine mit Heli-Pak-Füllkörper versehene Kolonne (Abmessungen: 600 mm×24 mm) verwendet und ein Refluxverhältnis von 15 : 1 gewählt. Zur präparativen gaschromatographischen Anreicherung wurde ein Pye Gerät Typ 105 (unter den folgenden Arbeitsbedingungen — Füllmittel: Celit; Verteilungsphase: Carbowax-20 M; Temperatur 120—200 °C; Einwaage: 0,5 ml—50 μl) [56] eingesetzt. Die gewonnenen reinen Komponenten wurden mit einem ZEME *Massenspektrometer* Typ MI-1305, einem Zeiss *Infrarotspektrometer* Typ UR-20 und einem Varian *Kernresonanz-Spektrometer* Typ T-60 identifiziert. Zur Identifizierung ließen sich neben der

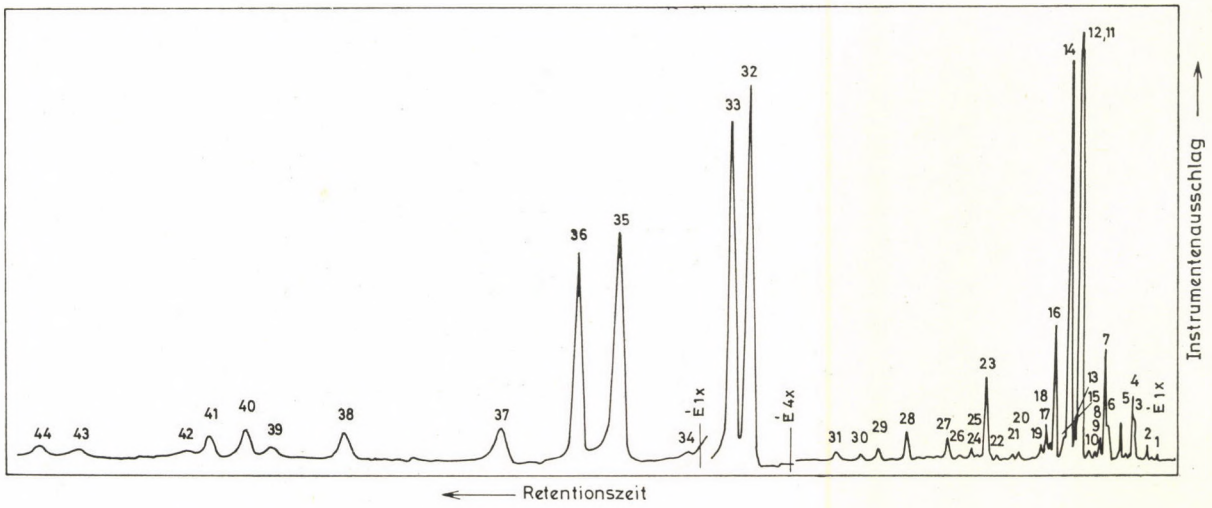

Abb. 1. Gaschromatogramm des untersuchten Lavendelöles. Versuchsbedingungen: Chrom III Gaschromatograph, Kapillarsäule: 50 m lang, Verteilungsphase: Carbowax-1500, Temperatur: 150 °C, Argon-Trägergasgeschwindigkeit: 2 l/h

Tabelle II

Identifizierung der Komponenten

Reihenzahl der Komponenten	Trennung			Spektrum-aufnahme		Identifizierung					
	Ohne Trennung	Anreicherung	Reindarstellung	Infrarot-Spektrum	Kernresonanz-Spektrum	Retentions-Verhalten	Bekanntes Spektrum	Spektrum-Zuordnung	Nicht identifiziert	Verwahrscheinlicht	Identifiziert
1.	+								+		
2.	+					+				+	
3.	+					+				+	
4.		+		+	+	+	+				+
5.		+		+	+	+	+	+			+
6.		+		+	+	+	+				+
7.			+	+	+	+	+				+
8.		+		+	+	+	+				+
9.		+		+				+		+	
10.		+		+				+		+	
11.		+		+		+	+	+		+	
12.		+		+		+	+	+		+	
13.	+								+		
14.		+		+	+	+	+	+		+	
15.		+		+	+	+	+	+		+	
16.			+	+	+	+	+				+
17—22.	+								+		
23.			+	+		+	+			+	
24—26.	+								+		
27.		+		+	+	+	+			+	
28.			+	+	+	+	+				+
29—31.	+								+		
32.			+	+	+	+	+				+
33.			+	+	+	+	+				+
34.			+	+	+	+	+				+
35.			+	+	+			+		+	
36.			+	+	+		+	+			+
37.			+	+	+	+	+				+
38.			+	+	+	+	+				+
39.	+								+		
40.			+	+	+		+	+			+
41.		+		+	+		+	+		+	
42.			+	+	+		+	+		+	
43—44.	+								+		

Tabelle III

Zusammensetzung des Lavendelöles

Reihenzahl der Komponenten (Abb. 1)	Komponenten	Menge, Gew.%	Reihenzahl der Komponenten (Abb. 1)	Komponenten	Menge, Gew.%
1.	—	0,0X	23.	*cis*-Alloocymen	0,9
2.	Tricyclen	0,0X	24.	—	0,0X
3.	α-Thujen	0,2	25.	—	0,1
4.	α-Pinen	0,2	26.	—	0,0X
5.	Camphen	0,2	27.	*n*-Hexylisobutyrat	0,3
6.	β-Pinen	0,2	28.	*n*-Hexylbutyrat	0,4
7.	β-Myrcen	0,7	29.	—	0,2
8.	Δ^3-Caren	0,2	30.	—	0,1
9.	Alkylacetate	0,0X	31.	—	0,2
10.	Alkylacetate	0,0X	32.	Linalool	35,1
11.	Limonen	4,8	33.	Linalylacetat	31,8
12.	β-*cis*-Ocymen	4,8	34.	Campher	0,0X
13.	—	0,1	35.	Lavandulylacetat	7,4
14.	β-*trans*-Ocymen	3,6	36.	Terpinen-1-ol-4	5,2
15.	Cineol	0,3	37.	Caryophyllen	1,4
16.	*p*-Cymol	1,1	38.	Lavandulol	0,9
17.	—	0,0X	39.	—	0,5
18.	—	0,2	40.	Terpineol-4	1,1
19.	—	0,1	41.	Borneol + Nerylacetat(?)	0,9
20.	—	0,0X	42.	Geranylacetat	0,3
21.	—	0,0X	43.	—	0,5
22.	—	0,0X	44.	—	0,5

Auswertung des Retentionsverhaltens auch die Spektren der Modellverbindungen, die in der Fachliteratur veröffentlichten Spektrumangaben und die zwischen Strukturteile und Spektren bestehenden Zusammenhänge verwenden.

Das untersuchte Lavendelöl wurde aus dem in Darányipuszta (Komitat Somogy) im Jahre 1971 gebauten Lavendel durch Wasserdampfdestillation gewonnen. Das Gaschromatogramm der ätherischen Ölprobe ist in Abb. 1 dargestellt. Wie ersichtlich, beträgt die Zahl der unter den gegebenen Bedingungen unmittelbar nachweisbaren Komponenten (Konzentration über 0,03—0,05 Gew.%) 44, und nach der quantitativen Auswertung sind 33 Komponenten mit einer Konzentration über 0,1 Gew.% zu finden.

Die Ergebnisse der Analyse des einheimischen Lavendelöles

Die qualitative und quantitative Analyse hatte das Ziel, jene Komponenten des untersuchten Lavendelöles zu erfassen, deren Konzentration 0,1 Gew.% übersteigt. Die Identifizierungsmethoden sind in Tabelle II in der Reihenfolge der Komponenten aufgeführt. Eine angereicherte oder reine Komponente haben wir nur dann als einwandfrei identifiziert anerkannt, wenn diese sich mit der entsprechenden Modellverbindung als vergleichbar erwies, oder wenn alle Versuchsdaten mit den entsprechenden Angaben aus der Literatur übereinstimmten. Wenn die Identifizierung sich nur auf ein einziges Spektrum, nur auf eine Spektrum-Zuordnung oder nur auf das gaschromatographische Retentionsverhalten beschränkte, wurde die betreffende Komponente nur für wahrscheinlich betrachtet.

Die Zusammensetzung der Untersuchungsprobe aus dem ungarischen Lavendelöl ist aus Tabelle III ersichtlich. Dementsprechend ist es gelungen, von den chromatographisch unmittelbar nachgewiesenen 44 Komponenten **27** *Einzelbestandteile* entweder einwandfrei zu identifizieren oder mit großer Wahrscheinlichkeit zu bestimmen. Das Anteilverhältnis der in der untersuchten Probe identifizierten Komponenten beträgt etwa 97,3 Gew.%.

Zur Bestimmung des *Cumaringehaltes* des Lavendelöles wurden bei angereicherten Fraktionen gesonderte gaschromatographische Untersuchungen (mit Diäthylenglykolsuccinat-Verteilungsphase benetzte 2 m lange Säule) verwendet. Die gaschromatographischen und die parallel ausgeführten ultravioletttspektrometrischen Untersuchungen haben die Anwesenheit von Cumarin bestätigt, dessen Konzentration aber unter der Größenordnung von 0,0X blieb.

In der Versuchsprobe waren unter den nachweisbaren Komponenten — bei den gegebenen Arbeitsbedingungen — die *in nachweisbarer Konzentration* erwarteten folgenden Komponenten *nicht* zu finden: Isoborneol, Citronellol, Geraniol, Nerol, verschiedene aliphatische Alkohole sowie Acetate, Butyrate und sonstige Fettsäureester der aliphatischen und der Terpenalkohole, dann Äthyl-*n*-amylketon und Cumarin.

Auch im ungarischen Lavendelöl konnte man eine für das Lavendelöl charakteristische *hohe Konzentration* an Linalool und an Linalylacetat bestimmen, und auch das Terpen-, das sonstige Terpenalkohol- und der sonstige Estergehalt erreichten die erwarteten Konzentrationen. In Einklang mit den Angaben verschiedener Publikationen haben wir auch im ungarischen Lavendelöl einen typisch *geringen Gehalt* an Borneol, Campher und Cineol (Größenordnung: 0,0X—0,X) gefunden. Außer den mit der Literatur übereinstimmenden Versuchsergebnissen scheint es wahrscheinlich zu sein, daß auch wenig *Tricyclen*, *cis-Alloocymen* und *n-Hexylisobutyrat* vorhanden sind. Das einwandfrei identifizierte *p-Cymol* entstand vermutlich teilweise während der Herstellung und der Lagerung des Lavendelöles.

Die spektrometrischen Untersuchungen ermöglichten es, die Spektren der isolierten reinen Komponenten näher kennenzulernen. Als Beispiele sind in Abb. 2 das Infrarotspektrum und in Abb. 3 das Kernresonanz-Spektrum des *Lavandulylacetats* wiedergegeben, die in der Literatur außer anderen gleichfalls nicht zu finden sind.

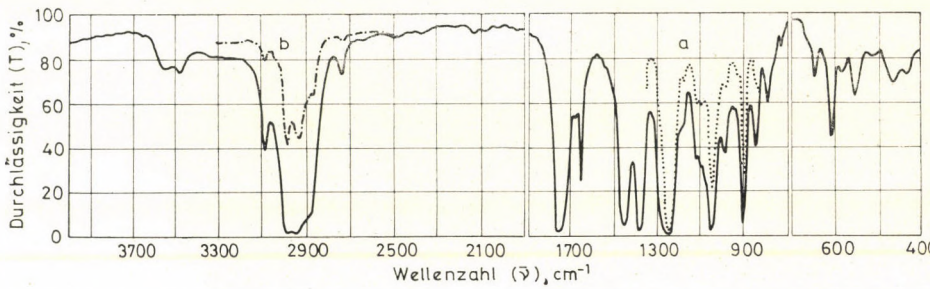

Abb. 2. Das Infrarotspektrum des isolierten Lavandulylacetats. Versuchsbedingungen: Zeiss UR-20; Schichtdicke: 0,004 cm; ···· *a* 200 g/l CS_2-Lösung; — — — *b* 20 g/l CS_2-Lösung

Einige charakteristischen Absorptionsbanden des Infrarotspektrums des Lavandulylacetats sind wie folgt: starke Banden der Acetatgruppe: $\nu_{C=O}$ = = 1743 cm^{-1}, $\nu_{as,\,C-O-C}$ = 1240 cm^{-1}, $\nu_{s,\,C-O-C}$ = 1143 cm^{-1}; starke und wenig intensive Banden der C=C Gruppen und deren Umgebung: $\nu_{=CH_2}$ = = 3085 cm^{-1}, $\nu_{C=C(H)}$ = 1676 cm^{-1}, $\nu_{C=C(H_2)}$ = 1650 cm^{-1}, $\gamma_{=CH_2}$ = 900 cm^{-1}, $\gamma_{=CH-}$ = 845 cm^{-1}.

Im Kernresonanz-Spektrum können die Peaks mit der Struktur wie folgt in Verbindung gebracht werden: δ_1 = 5,02 ppm, Triplett, 1 Proton (H_a), J_{ae} = 7 cps; δ_2 = 4,78 und 4,72 ppm, Doppeldublett, 2 Protonen ($H_{bb'}$), $J_{bb'}$ = 1,5 cps; δ_3 = 3,97 ppm, Dublett, 2 Protonen (H_c), J_{cd} = 7 cps; δ_4 = 2,34 ppm, Multiplett, 1 Proton (H_d), J_{de} = 7 cps; δ_5 = 2,10 ppm, Dublett, 2 Protonen (H_e); δ_6 = 1,94 ppm, Singulett, 3 Protonen (H_f); δ_7 = 1,66 und 1,58 ppm, zusammenfallende Peaks, insgesamt 9 Protonen ($H_{gg'h}$).

Die Identifizierung der wichtigsten Komponenten des einheimischen Lavendelöles sowie die sich darauf stützende gaschromatographische Schnellanalyse kann zum Ausgangspunkt der Untersuchung weiterer wissenschaftlicher (z. B. Pflanzenphysiologie), technischer (z. B. Raffination) oder wirtschaftlicher (z. B. Qualitätsbeurteilung, Reinheitskontrolle) Lavendelölfragen dienen.

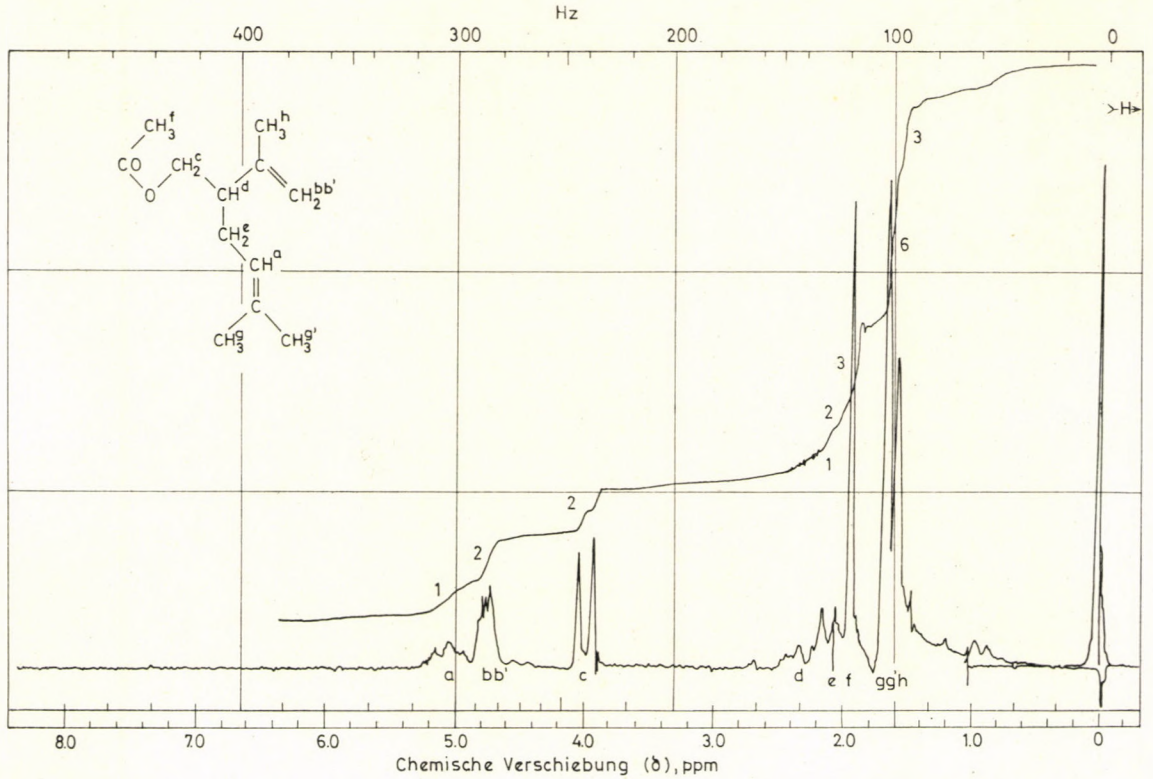

Abb. 3. Kernresonanz-Spektrum des isolierten Lavandulylacetats. Versuchsbedingungen: Varian T-60, 60 MHz, Tetramethylsilan enthaltende Tetrachlorkohlenstoff-Lösung

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UNTERSUCHUNG DER ZUSAMMENSETZUNG VON EINHEIMISCHEN UND AUSLÄNDISCHEN ÄTHERISCHEN ÖLEN, V

BEITRÄGE ZUR ZUSAMMENTSEZUNG DES LAVANDINÖLES UND DES MUSKATELLER SALBEIÖLES

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Die qualitative Zusammensetzung der ätherischen Öle von Lavandula hybrida und Salvia sclarea wurde durch präparative gaschromatographische Trennung und spektrometrische Identifizierung der Komponenten untersucht; die quantitative Zusammensetzung wurde mittels analytischer Gaschromatographie bestimmt. Im Lavandinöl wurden in meßbaren Mengen ($>0{,}03\%$) 34 Komponenten, in bedeutenden Mengen ($\geq 0{,}1\%$) 29 Komponenten gefunden, 22 von diesen wurden identifiziert. Im ätherischen Öl der Muskateller Salbei wurden in Mengen über 0,03% 24 Komponenten und in Mengen über 0,1% 22 Komponenten nachgewiesen, von denen 14 Komponenten mit unmittelbaren Untersuchungen identifiziert wurden.

Das *Lavandinöl* und das *Muskateller Salbeiöl* sind herkömmliche Erzeugnisse der heimischen Industrie von ätherischen Ölen und herkömmliche Rohstoffe der kosmetischen Industrie. Für beide ätherischen Ölen ist — neben einigen anderen gleichen Komponenten — ein erheblicher Gehalt an freiem oder gebundenem Linalool charakteristisch. Die Zusammensetzung des ätherischen Öles der heimischen *Lavandula hybrida* und teils auch der heimischen *Salvia sclarea* wurde im Vergleich zur Zusammensetzung des ätherischen Öles der heimischen *Lavandula angustifolia* [42] untersucht.

Angaben über die Zusammensetzung in der Fachliteratur

In den Sammelwerken und Fachartikeln über die Zusammensetzung der ätherischen Öle findet man relativ viele Angaben [1—27] über das Lavandinöl und verhältnismäßig wenige [28—37] über das Muskateller Salbeiöl. In bezug auf die Zusammensetzung der entsprechenden *einheimischen* ätherischen Öle wurden bis jetzt nur Angaben über die Hauptkomponenten veröffentlicht [38].

Die ersten ausführlicheren Veröffentlichungen über das *Lavandinöl* haben RIPERT [21], NAVES und ANGLA [17], BENEZET und IGOLEN [1], SFIRAS und VANDERSTREER [22] sowie IGOLEN [7] und NAVES [14] zwischen 1937 und 1945 publiziert. Zur Bestimmung der chemischen Zusammensetzung wurden

Tabelle I

Die bisher nachgewiesenen Komponenten des Lavandinöles nach der Fachliteratur

Komponenten	Größenordnung	Literatur
a) Kohlenwasserstoffe		
Alloocymen	<0,X	[14, 24]
β-Bisabolen	0,X	[7, 8, 20]
δ,γ-Cadinen	<0,X	[20, 24]
Camphen	0,X—X	[10, 14, 17, 24]
3-Caren	0,0X—0,X	[2, 10, 24]
Cariophyllen	0,X—X	[20, 22, 24]
p-Cymol	0,0X	[24]
α,β-Farnesen	0,X	[20, 24]
Limonen	0,X—X	[10, 14, 24]
β-Myrcen	0,X	[2, 24]
Ocymen	X	[14, 22, 24]
β-Phellandren	<0,X	[26]
α-Pinen	0,X—X	[7, 10, 14, 24]
β-Pinen	0,X—X	[2, 10, 24]
Sabinen	0,X	[2, 24]
α-Santalen	0,X	[24]
γ-Terpinen	<0,X	[2, 24]
Terpinolen	0,X	[24]
Tricyclen	0,0X	[14]
b) Alkohole		
Borneol	X	[z. B. 10, 17, 24]
Geraniol	0,X	[7, 22]
Hexan-1-ol	0,X	[1, 7]
Lavandulol	0,X	[14, 20, 24, 27]
Linalool	X0	[z. B. 7, 12, 22]
Linalooloxyd	0,X	[14, 22, 24]
2-Methyl-3-buten-2-ol	0,00X	[23, 24]
Nerol	0,X	[14]
Oktan-1-ol	0,X	[7, 8]
Oktan-3-ol	<0,X	[8, 24]
1-Okten-3-ol	0,X	[22, 24]
Perillylalkohol	0,X	[14]
Terpinen-4-ol	X	[22, 26]
α-Terpineol	0,X—X	[10, 14, 22, 24]

Tabelle I (Fortsetzung)

Komponenten	Größenordnung	Literatur
c) Säuren		
Essigsäure	<0,X	[7, 8]
Buttersäure	<0,X	[7, 8]
Capronsäure	<0,X	[8]
d) Ester		
Bornylacetat	X—X0	[2, 10]
i-Bornylacetat	X	[10]
n-Butylacetat	0,0X	[24]
Epoxylinalylacetat	0,X	[14]
Geranylacetat	0,X	[22, 24]
n-Hexylacetat	0,X	[7, 8]
n-Hexylbutyrat	0,X	[19, 24]
n-Hexylisobutyrat	0,0X	[24]
n-Hexyltiglat	0,X	[24]
Lavandulylacetat	0,X	[20, 24, 26]
Lavandulylbutyrat	0,X	[24]
Lavandulylbenzoat	<0,X	[27]
Lavandulylcapronat	0,X	[27]
Lavandulyl-2-methyl-butyrat	0,X—X	[24, 27]
Linalylacetat	X—X0	[z. B. 10, 22, 26]
Linalylbutyrat	<0,X	[22]
Linalylformiat	0,X	[22]
Nerylacetat	0,X	[24]
n-Oktylacetat	0,X	[7, 8]
1-Okten-3-ylacetat	0,X	[22, 24]
1-Okten-3-ylbutyrat	<0,X	[22]
Terpenylacetat	0,X	[10, 22]
e) Ketone		
Aceton	0,0X	[24]
Campher	X—X0	[z. B. 11, 16, 21]
Carvon	<0,X	[23]
Crypton	<0,X	[23]
Diacetyl	<0,X	[7, 8, 23]
Diisopropylketon	<0,X	[23]
Menthon	<0,X	[26]
p-Menthylacetophenon	<0,X	[26]

Tabelle I (Fortsetzung)

Komponenten	Größenordnung	Literatur
6-Methyl-hepta-3,5-dienon-2	<0,X	[23]
Methylheptenon	0,X	[23]
Nopinon	0,X	[23]
3-Oktanon	0,X—X	[7, 22, 23, 24]
Sabinaketon	<0,X	[23]
f) Aldehyde		
Cuminaldehyd	<0,X	[7, 8, 23]
Furfural	<0,X	[7, 8]
1-Hexanal	<0,X	[7, 8]
1-Oktanal	<0,X	[7, 8]
Phellandral	<0,X	[23]
g) Sonstige Sauerstoffverbindungen		
n-Butylmethyläther	0,00X	[24]
Cariophyllenoxyd	0,X	[24]
i-Cariophyllenoxyd	0,0X	[24]
Cineol	X	[z. B. 10, 22, 26]
Cumarin	<0,X	[7, 8]
Eugenol	<0,X	[7, 8]
h) Schwefelverbindungen		
Dimethylsulfid	0,00X	[24]

neben der Destillationstrennung vor allem chemische Trennungs- und Identifizierungsmethoden verwendet.

Die Verfasser der neueren Veröffentlichungen stützen sich bei der Trennung der Komponenten in erster Linie auf die präparative Gaschromatographie, zur Identifizierung der Komponenten werden meist spektrometrische oder gaschromatographische Methoden verwendet. Die Untersuchungen von STADLER [23], PEYRON, BENEZET und GARNERO [20], STELTKAMP und CASAZZA [24] sowie von TERHEIDE, TIMMER und WOBBEN [26] erlaubten aufgrund der angewandten wirksamen Anreicherung des empfindlichen Nachweises und der charakteristischen Identifizierung vor allem das eingehende Studium einiger Lavandinöle französischen Ursprungs.

Tabelle I enthält eine Zusammenfassung der Angaben der Fachliteratur über die Zusammensetzung des Lavandinöles.

Die ersten Veröffentlichungen über die Hauptkomponenten des *Muskateller Salbeiöles* stammen von CHIRIS [28], ROVESTI [33] sowie RUTOWSKI und

Tabelle II

Die bisher nachgewiesenen Komponenten des Muskateller Salbeiöles nach der Fachliteratur

Komponenten	Literatur	Komponenten	Literatur
a) Kohlenwasserstoffe		c) Ester	
Alloocymen	[35]	Linalylacetat	[28, 31, 34]
Cadinen	[35]	Nerolidylacetat	[34]
Camphen	[35]	Terpinylacetat	[35]
p-Cymol	[35]		
Limonen	[35]	d) Keton	
β-Myrcen	[29, 35]	Carvon	[32]
β-Ocymen	[29, 35]		
α-Pinen	[33, 35]	e) Aldehyde	
β-Pinen	[35]	Acetaldehyd	[32]
Salven	[33]	Benzaldehyd	[34, 35]
β-Santalen	[34]	Butyraldehyd	[32]
		Heptanal	[35]
b) Alkohole		Hexanal	[32, **35**]
Borneol	[33]	Nonanal	[35, 36]
Geraniol	[29, 35]	Oktanal	[35]
n-Hexanol	[35, 36]	Propionaldehyd	[32]
cis-2-Hexenol	[35]	Valeraldehyd	[32]
Linalool	[z. B. 28, 31]	Furfural	[32]
Nerol	[29, 35]		
Nerolidol	[34]	f) Sonstige Sauerstoffverbindung	
Oktan-3-ol	[35]	Cineol	[33, 35, 36]
1-Okten-3-ol	[35, 36]		
Sclareol	[35]		
α-Terpineol	[29, 35]		

GUSSEWA [34] aus den Jahren 1924 bis 1932. Die Kenntnisse über die Zusammensetzung des ätherischen Öles beruhen hauptsächlich auf chemischer Trennung und Identifizierung [z. B. 32, 37], doch erscheint in den Arbeiten von TEISSEIRE bereits die Kombination der chemischen Analysenmethoden und der gaschromatographischen Untersuchungen [35, 36]. Bei der Bewertung der Zusammensetzungsdaten sollte in Betracht gezogen werden, daß die einzelnen nachgewiesenen Komponenten (z. B. Myrcen, Ocymen) auch bei der Herstellung des ätherischen Öles durch Wasserdampfdestillation entstehen können [29].

Tabelle II enthält die bei der Aufarbeitung der Fachliteratur gesammelten Zusammensetzungsdaten für das *Muskateller Salbeiöl.*

Die Untersuchungsmethode und die untersuchten Proben

Ein Teil der Angaben der Fachliteratur ist im Falle der qualitativen und quantitativen Zusammensetzung der viele Komponenten enthaltenden ätherischen Öle — wegen der Funktionsgruppenanalyse mittels chemischer Methoden oder der gaschromatographischen Analyse ohne Modellsubstanzen — nicht genügend belegt.

Demgemäß wurde bei uns zur Untersuchung der Zusammensetzung der einheimischen ätherischen Öle, neben der *quantitativen Analyse* mittels Gaschromatographie, eine *kombinierte qualitative Analysenmethode* entwickelt,

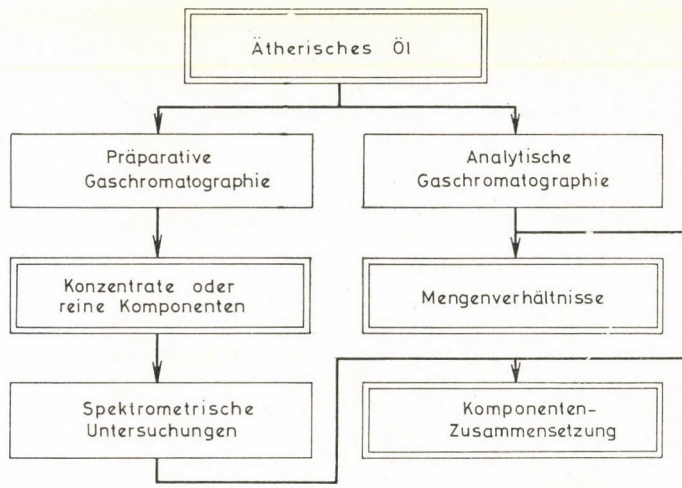

Abb. 1. Schematische Darstellung der qualitativen und quantitativen Analyse der ätherischen Öle

die auf präparativer Trennung und spektrometrischer Identifizierung der Komponenten beruht [39]. Die Methode wurde zur Untersuchung des einheimischen Pfefferminzöles [40], Dillöles [41] und Lavendelöles [42] bereits erfolgreich eingesetzt. Im Falle des Lavandinöles und des Muskateller Salbeiöles führte auch eine vereinfachte Variante der kombinierten Trennungs-Identifizierungs-Methode zur ausreichenden Kenntnis der Zusammensetzung der ätherischen Öle.

Abb. 1 zeigt die schematische Darstellung der verwendeten Untersuchungsmethode.

Die quantitative Zusammensetzung wurde gaschromatographisch mit dem *Gerät Typ ChromIII* bestimmt. Zur Prüfung wurde eine mit Carbowax 1500 Verteilungsphase benetzte, 50 m lange Kapillare verwendet, die Meßtemperatur betrug 150 °C, die Argongas-Geschwindigkeit war 2 Liter/Stunde.

In dem zur gaschromatographischen Präparierung verwendeten *Pye-Gerät, Typ 105* wurde eine 9 m lange Kolonne mit 6 mm Durchmesser bzw. eine 7 m lange Kolonne mit 3 mm Durchmesser, mit Carbowax-20M als Verteilungsphase in Mengen von 15% auf einen Celitträger aufgetragen verwendet. Das Präparieren wurde bei 120—200 °C aus Proben von etwa 0,5 ml bzw. 50 μl vorgenommen.

Die Infrarotspektren wurden mit einem *UR-20-Spektrometer der Firma Carl Zeiss, Jena* mit KBr-Fenster und einer Küvette mit 0,003 cm Schichtdicke oder mit KBr-Tablette im Wellenlängenbereich von 4000—400 cm^{-1} aufgenommen. Die Kernresonanzspektren wurden mit dem *Gerät Varian T-60*, in einer etwa 10%igen Tetrachlorkohlenstoff-Lösung, im Verschiebungsbereich von 0—8 ppm aufgenommen.

Die *untersuchten ätherischen Ölproben* stammten aus Pflanzungen von Lavandula hybrida und Salvia sclarea am Südufer des Balaton, aus dem Jahre 1971. Die Proben wurden uns vom Betrieb für Kosmetik und Haushaltschemie, Budapest zur Verfügung gestellt.

Zusammensetzung des Lavandinöles

Abb. 2 zeigt das analytische Gaschromatogramm des untersuchten Lavandinöles. An der ohne vorherige Trennung gemachten Aufnahme lassen sich 34 Komponenten nachweisen; unter den angewandten Umständen entsprach die Nachweisbarkeit einer Konzentration über 0,03 Gew.%. In bedeutenden Mengen ($\geq$0,1 Gew.%) fanden sich im ätherischen Öl 29 Komponenten.

Mit der Identifizierung der Komponenten Nr. 1, 12, 14—18, 21—23, 31 und 34, die am Gaschromatogramm nachweisbar waren, jedoch in geringen Mengen auftraten, haben wir uns nicht befaßt.

Die Anwesenheit von *Thujen* (Komponente 2) wurde ohne Anreicherung, aufgrund des Retentionsverhaltens für wahrscheinlich gehalten.

Das *α-Pinen* (Komponente 3) wurde außer durch die gaschromatographischen Daten durch die Prüfung der Spektren der isolierten reinen Komponente und der Modellsubstanz identifiziert. Die Identität wurde auch durch die in der Fachliteratur befindlichen Spektren des α-Pinens [44, 45] belegt.

Von der Anwesenheit des *Camphens* (Komponente 4) haben wir uns durch den Vergleich der Infrarotspektren der angereicherten Komponente und des bekannten Spektrums [44] sowie auch durch die Prüfung des Kernresonanzspektrums der angereicherten Komponenten überzeugt.

Der Nachweis des *β-Pinens* (Komponente 5) erfolgte aufgrund des Retentionsverhaltens und der identischen Spektren der hergestellten Reinkomponente sowie der Modellsubstanz. Die in der Fachliteratur veröffentlichten Spektren haben die Richtigkeit der Identifizierung bewiesen [44, 45].

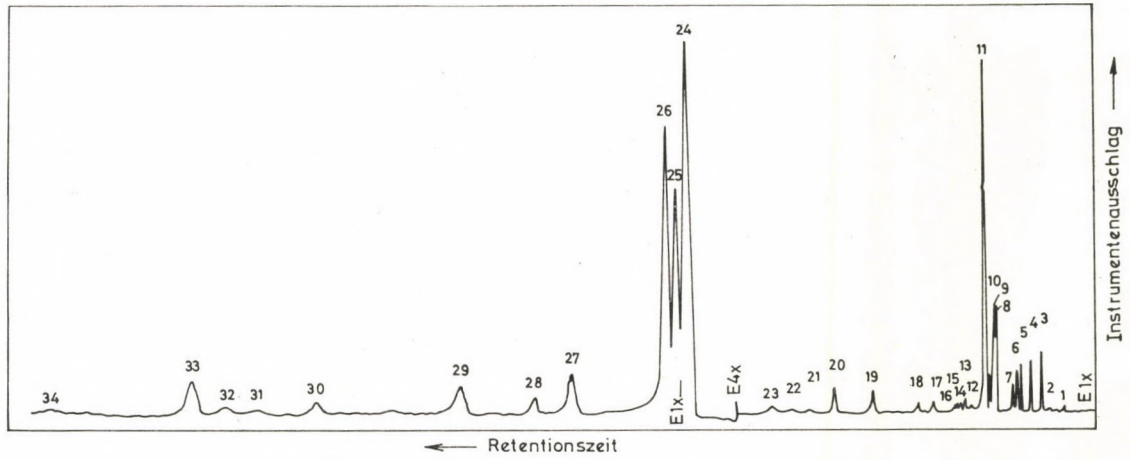

Abb. 2. Gaschromatogramm des Lavandinöles. Versuchsbedingungen: 50 m lange Kapillare, Verteilungsphase: Carbowax 1500, Temperatur: 150 °C, Argon-Trägergasgeschwindigkeit: 2 Liter/Stunde

Die Identifizierung des *β-Myrcens* (Komponente 6) erfolgte durch den Vergleich der Spektren der rein hergestellten Komponente mit den Spektren der Fachliteratur [46].

Zum Beweis der Anwesenheit des *3-Carens* (Komponente 7) wurden neben der Bewertung der Spektren der angereicherten Komponenten auch die mit Modellsubstanzen aufgenommenen und aus der Fachliteratur zugänglichen Spektren herangezogen [44, 45].

Das *Limonen* und das *β-cis-Ocymen* (Komponenten 8 und 9) wurden aufgrund des Retentionsverhaltens [43] sowie der Spektren ihres getrennten Gemisches und der bekannten Spektren [46] identifiziert.

Das *β-trans-Ocymen* (Komponente 10) wurde aus dem Lavandinöl in reiner Form nicht isoliert; seine Anwesenheit wurde bei der Untersuchung und Identifizierung der Spektren des angereicherten und mit *β-trans*-Ocymen verunreinigten 1,8-*Cineols* (Komponente 11) mit Hilfe der Spektren der Modellsubstanz nachgewiesen. Von beiden Komponenten sind in der Fachliteratur Spektren zu finden [44—46].

Das *p-Cymol* (Komponente 13) wurde durch Anreicherung und spektrometrische Untersuchung der Komponente, dann durch Vergleich der Spektren mit denen der Modellsubstanz und der Fachliteratur identifiziert [44].

Die Anwesenheit des *n-Hexylisobutyrats* (Komponente 19) wurde aufgrund der Interpretierung des Spektrums einer angereicherten Probe nachgewiesen.

Der Nachweis des *n-Hexylbutyrats* (Komponente 20) gelang durch die Untersuchung der hergestellten reinen Komponente, mittels der identischen Spektren der syntetisierten Modellsubstanz sowie aufgrund des gleichen Retentionsverhaltens.

Bei der Identifizierung der drei Hauptkomponenten: des *Linalools*, des *Linalylacetats* und des *Camphers* (Komponenten 24, 25 und 26) stützten wir uns auf den Vergleich der Spektren der isolierten reinen Komponenten, der zur Verfügung stehenden Modellsubstanzen sowie der Spektren aus der Fachliteratur [44].

Die Anwesenheit des *Lavandulylacetats* (Komponente 27) wurde nach der Trennung mit Hilfe der Modellsubstanz spektrometrisch nachgewiesen.

Das *Terpinen-4-ol* (Komponente 28) wurde durch Analyse der Spektren der isolierten reinen Probe, unter Einbeziehung des Infrarotspektrums aus der Fachliteratur identifiziert.

Beim Nachweis des *Cariophyllens* (Komponente 29) wurde neben dem Retentionsverhalten die Identität der Spektren der angereicherten Probe mit denen der Fachliteratur verwertet.

Die Identifizierung des *Lavandulols* (Komponente 30) erfolgte mittels des Infrarotspektrums aus der Fachliteratur [48].

Der Nachweis des *α-Terpineols* (Komponente 32) stützte sich auf die

Prüfung der Spektren der angereicherten Komponente unter Berücksichtigung des bekannten Infrarotspektrums von α-Terpineol [47].

Schließlich wurde die Anwesenheit des *Borneols* (Komponente 33) durch Untersuchung der Spektren der rein hergestellten Komponente und durch ihren Vergleich mit Spektren aus der Fachliteratur festgestellt.

Tabelle III

Zusammensetzung des untersuchten, einheimischen Lavandinöles

Reihenzahl nach Abb. 2	Komponenten	Menge, Gew.%	Reihenzahl nach Abb. 2	Komponenten	Menge, Gew.%
1	—	0,0X	18	—	0,2
2	α-Thujen	0,0X	19	*n*-Hexylisobutyrat	0,5
3	α-Pien	0,5	20	*n*-Hexylbutyrat	0,6
4	Camphen	0,6	21	—	0,1
5	β-Pinen	0,4	22	—	0,1
6	β-Myrcen	0,4	23	—	0,2
7	3-Caren	0,3	24	Linalool	57,4
8	Limonen	1,2	25	Linalylacetat	8,0
9	*β-cis*-Ocymen	1,3	26	Campher	11,6
10	*β-trans*-Ocymen	0,4	27	Lavandulylacetat	2,4
11	Cineol	5,4	28	Terpinen-4-ol	0,9
12	—	0,0X	29	Caryophyllen	2,2
13	*p*-Cymol	0,1	30	Lavandulol	1,0
14	—	0,0X	31	—	0,4
15	—	0,2	32	α-Terpineol	0,5
16	—	0,0X	33	Borneol	2,6
17	—	0,2	34	—	0,1

Tabelle III enthält die qualitativen und quantitativen Zusammensetzungsangaben des untersuchten Lavandinöles. Obwohl einige der Zahlreichen nachgewiesenen, in erheblicheren Mengen anwesenden Komponenten nicht identifiziert wurden, fehlen aufgrund der Fachliteratur viel mehr, in bedeutenden Mengen erwartete Komponenten aus der qualitativen Zusammensetzung. Wir können mit Sicherheit behaupten, daß im einheimischen Lavandinöl *Bornylacetat* nicht in Mengen von einigen Prozenten vorkommt, die Menge des *Camphens* ist ebenfalls viel kleiner, als aufgrund der Fachliteratur zu erwarten ist, und die Konzentration des *3-Oktanons* erreicht die in ähnlichen ätherischen Ölen nachgewiesene Menge ebenfalls nicht. Das nach den Untersuchungen wahrscheinlich in Spuren anwesende *α-Thujen* ist die einzige Komponente des einheimischen Lavandinöles, die die bisherigen Veröffentlichungen nicht erwähnt haben.

Kennzeichnend für die quantitative Verteilung der Komponenten ist, daß vier von ihnen (Linalool, Campher, Linalylacetat und Cineol) mehr als 82 Gew.% des ätherischen Öles ausmachen und die identifizierten Komponenten 98,3 Gew.% des Lavandinöles darstellen. Die Zusammensetzungsangaben erlauben auch einen Vergleich mit der Zusammensetzung des früher geprüften Lavendelöles [42].

Bei der Trennung und Identifizierung der Komponenten wurden mehrere rein hergestellt, deren Spektren unbekannt oder nicht zugänglich sind. Wir

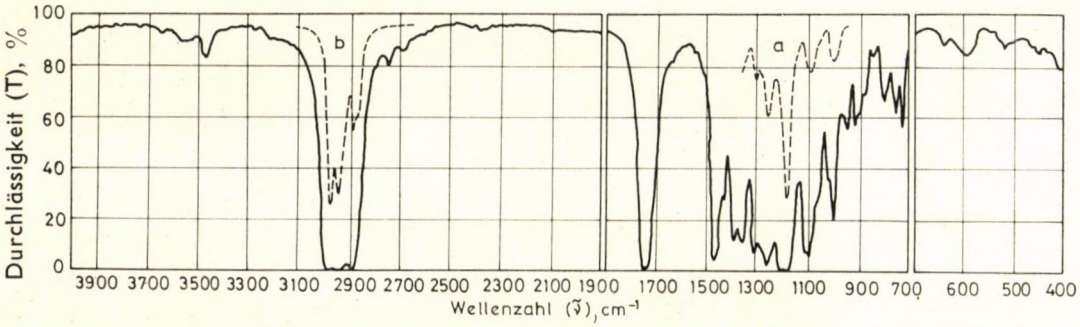

Abb. 3. Infrarotspektrum des *n*-Hexylbutyrats. Aufnahmebedingungen: Schichtdicke 0,0035 cm, ohne Lösungsmittel; a) und b) Details wurden in Tetrachlorkohlenstoff-Lösung aufgenommen. $\nu_{C=O} = 1740\ cm^{-1}$; $\nu_{C-O-C} = 1180\ cm^{-1}$; $\nu_{s,C-H} = 2890\ cm^{-1}$; $\nu_{ass,C-H} = 2940$ und $2980\ cm^{-1}$; $\delta_{C-H} = 1380$ und $1440\ cm^{-1}$; $\beta_{C-H} = 1460\ cm^{-1}$

zeigen hier beispielsweise in Abb. 3 und 4 das Infrarot- und magnetische Kernresonanzspektrum sowie die charakteristischen Spektrumdaten des *n-Hexylbutyrats* und unten auch die Daten des magnetischen Kernresonanzspektrums von Camphen und Terpinen-4-ol.

Das Protonenresonanzspektrum des *Camphens* zeigt vier charakteristische Protonengruppen: $\delta_1 = 4{,}70$ und 4,48 ppm, Doppelspitze, 2 Protonen ($H_2C=CH_2$); $\delta_2 = 2{,}68$ ppm, breite Spitze, 1 Proton ($H-\overset{|}{C}H-\overset{|}{C}=$); $\delta_3 = 2{,}0-1{,}1$ ppm, aus Multipletts verschiedener chemischer Verschiebungen bestehende Spitzengruppe, insgesamt 7 Protonen ($H-CH_2-$ und $H-CH-$); $\delta_4 = 1{,}05$ und 1,03 ppm, Doppelspitze, insgesamt 6 Protonen ($H-C(CH_3)$).

Im Protonenresonanzspektrum des *Terpinen-4-ols* kann man fünf verschiedene Protonen unterscheiden: $\delta_1 = 5{,}26$ ppm, breite Spitze, 1 Proton ($H=\overset{|}{C}H$); $\delta_2 = 1{,}97$ ppm, breite Spitze, insgesamt 4 Protonen ($H=\overset{|}{C}-CH_2-$); $\delta_3 = 1{,}68$, Singulett, 3 Protonen ($H=C-CH_3$); $\delta_4 = 2{,}0$ und 1,6 ppm, doppelte Spitzengruppe, teils verschmolzen mit dem vorigen Singulett, insgesamt 7 Protonen ($H-CH_2-$ und $H-\overset{|}{C}H-$); $\delta_5 = 0{,}90$ ppm, Dublett, insgesamt 6 Protonen ($H-\overset{|}{C}(CH_3)_2$), $J_{CH-CH_3} = 7$ cps.

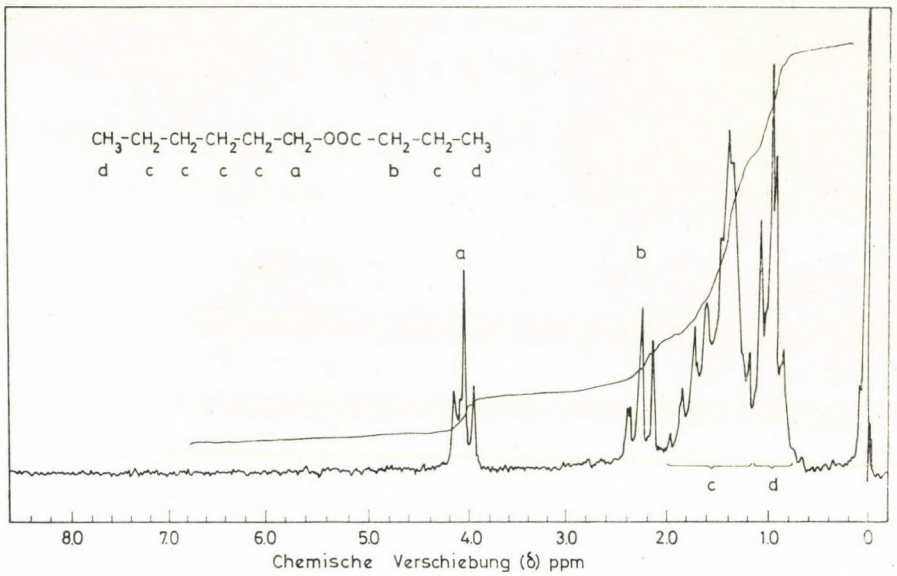

Abb. 4. Protonenresonanzspektrum des *n*-Hexylbutyrats. Aufnahmebedingungen: Lösung in Tetrachlorkohlenstoff mit Tetramethylsilan. $\delta_1 = 4{,}03$ ppm, Triplett (H_a), $J_{ac} = 7$ cps, 2 Protonen; $\delta_2 = 2{,}22$ ppm, Triplett (H_b), $J_{bc} = 7$ cps, 2 Protonen; $\delta_3 = 2{,}0-1{,}2$ ppm, aus Multipletts bestehende Spitzengruppe (H_c), insgesamt 10 Protonen; $\delta_4 = 0{,}96$ und 0,90 ppm, zwei Tripletts (H_d) $J_{cd} = 7$ cps, insgesamt 6 Protonen

Analyse des Muskateller Salbeiöles

Abb. 5 zeigt das analytische Gaschromatogramm der Probe des ätherischen Öles. Unter unseren Versuchsbedingungen wurden in der Aufnahme 24 Komponenten nachgewiesen, deren Konzentrationen jeweils über 0,03 Gew.% liegen. Im untersuchten Muskateller Salbeiöl waren 22 Komponenten in bedeutenderen Mengen ($\geq$0,1 Gew.%) anwesend.

Nicht identifiziert wurden die nachgewiesenen Komponenten Nr. 1, 8, 10—12, 16, 17, 19, 21 und 24, die meist geringe Konzentrationen aufwiesen. Die Identifizierung der Monoterpen-Komponenten (Nr. 2—6) des *α-Pinens*, *β-Pinens*, *β-Myrcens*, *Limonens* und *β-Ocymens* erforderte ähnliche Verfahren, wie bei den entsprechenden Komponenten des Lavandinöles beschrieben, teils aufgrund der aus dem Lavandinöl gewonnenen reinen Komponenten. Ähnlich wurde bei der Identifizierung des *p-Cymols* (Komponente 9), *Linalools*, *Linalyacetats*, *Camphers* (Komponenten 13—15), *Lavandulylacetats* (Komponente 18), *Cariophyllens* (Komponente 20), *α-Terpineols* (Komponente 22) sowie des *Borneols* (Komponente 23) verfahren. Tabelle IV enthält die Angaben über die qualitative und quantitative Zusammensetzung des untersuchten Muskateller Salbeiöles.

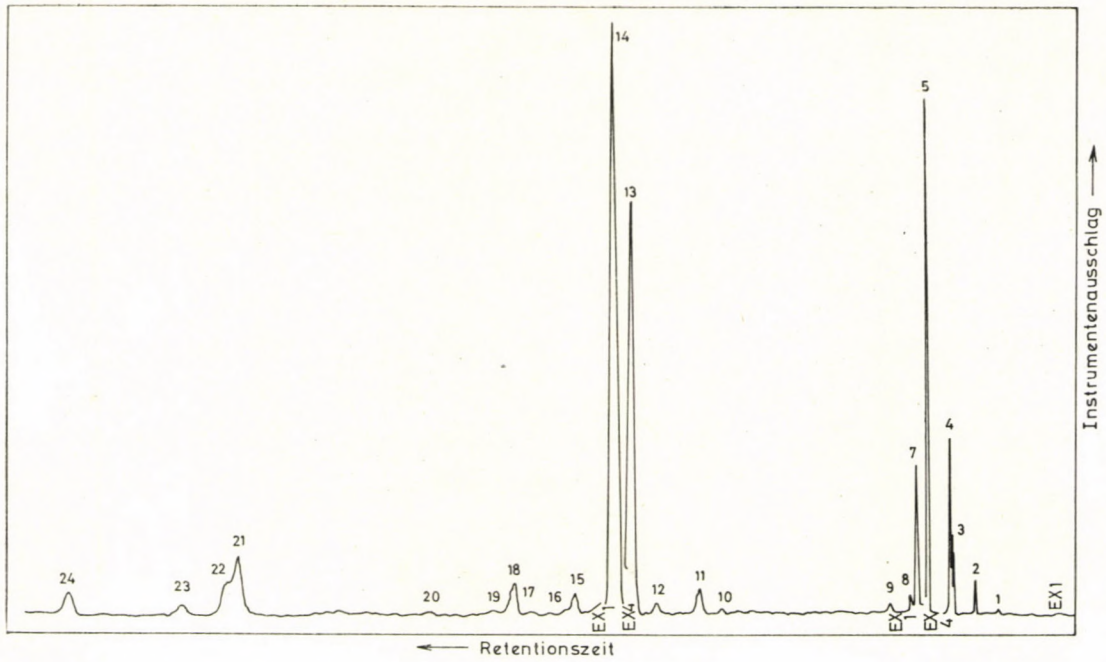

Abb. 5. Gaschromatogramm des Muskateller Salbeiöles. Versuchsbedingungen gleich wie in Abb. 2

Tabelle IV

Zusammensetzung des untersuchten, einheimischen Muskateller Salbeiöles

Reihenzahl nach Abb. 5	Komponenten	Menge, Gew.%	Reihenzahl nach Abb. 5	Komponenten	Menge, Gew.%
1	—	0,0X	13	Linalool	9,5
2	α-Pinen	0,2	14	Linalylacetat	59,9
3	β-Pinen	0,6	15	Campher	0,5
4	β-Myrcen	1,3	16	—	0,1
5	Limonen (+β-*cis*-Ocymen)	18,9	17	—	0,1
6	β-*trans*-Ocymen	0,0X	18	Lavandulylacetat	1,0
7	Cineol	1,2	19	—	0,1
8	—	0,2	20	Caryophyllen	0,1
9	*p*-Cymol	0,1	21	—	2,9
10	—	0,1	22	α-Terpineol	1,0
11	—	0,6	23	Borneol	0,5
12	—	0,3	24	—	0,7

Wie man sieht, haben die Untersuchungen im einheimischen Muskateller Salbeiöl überwiegend die Anwesenheit der bekannten Komponenten bewiesen. Außer den in der Fachliteratur erwähnten Komponenten kann aufgrund der Identifizierung die Anwesenheit des *Lavandulylacetats* und des *Cariophyllens* als wahrscheinlich angenommen werden. Die quantitative Verteilung der Komponenten wird durch die relativ hohe Menge des Linalylacetats, Limonens und Linalools gekennzeichnet, deren gesamter Prozentanteil fast 90% beträgt. Die identifizierten Komponenten stellen 94,8 Gew.% des Muskateller Salbeiöles dar.

Die Identifizierung des überweigenden Teiles der Komponenten und die Untersuchung ihrer quantitativen Verhältnisse ermöglichte die Bestimmung der Eigenheiten der einheimischen ätherischen Öle, die Bewertung und den Vergleich von Proben ätherischer Öle und hat auch die weitere eingehendere Untersuchung der Zusammensetzung begründet.

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SPECTROPHOTOMETRIC STUDIES OF SOME STYRYL CYANINE DYES

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The ultraviolet and visible absorption spectra of some 2-styrylpyridine and -quinoline ethiodides have been studied in ethanol. The bands observed are assigned to certain electronic transitions. The effect of substituents on the band position and intensity is discussed. The pK values for some compounds have been determined.

Introduction

The preparation of 2-styrylpyridine- and -quinoline-N-alkyl iodides has been described previously by MILLS [1, 2], KOELSCH [3] and PHILLIPS [4]. Some correlation has been noted between the colour of 2-styrylpyridine methiodide and the substituents in the nucleus of the aldehyde condensed with α-picoline [4]. Some of the compounds are known to be powerful photosensitizers for light of certain wavelengths; however, spectrophotometric studies with these substances have been rather scarce. The present work deals with the assignment of the ultraviolet and visible absorption bands in ethanol solutions. The effect of substitution on the band position and extinction is also discussed. Furthermore, the absorption spectra in buffer solution have been utilized for the determination of the acid dissociation or deprotonation constants for some of these compounds, in order to permit selection of the suitable pH when the compounds are applied as photosensitizers.

Experimental

The compounds were prepared by mixing an excess of the aromatic aldehyde with α-picoline or quinaldine ethiodide in the presence of piperidine as catalyst, in a way similar to the method described before [4].

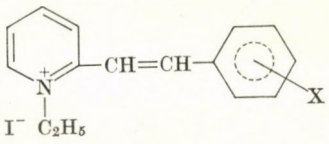
10^{-3} M solutions of the dyes were prepared by dissolving the accurate weight of the recrystallized product in the appropriate volume of pure ethanol.

Ethyl alcohol, used as a solvent, was purified according to recommended methods [5]. Buffer solutions were prepared as given by BRITTON [6].

The spectra of the compounds were recorded within the wavelength range 210—600 nm with a Carl Zeiss VSU 2-P spectrophotometer, using 1 cm matched silica cells.

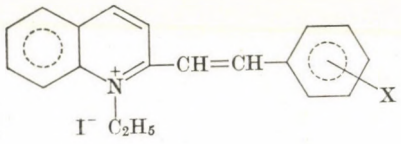
Results and discussion

The compounds under investigation belong to two main series having the structure **I** and **II**, respectively.



I

X = *p*-H (**a**); *p*-OCH_3 (**b**); *p*-OH (**c**); *p*-$N(CH_3)_2$ (**d**); *m*-NO_2 (**e**); *p*-OH-*m*-OCH_3 (**f**)



II

X = *p*-H (**a**); *p*-OCH_3 (**b**); *p*-OH (**c**); *p*-$N(CH_3)_2$ (**d**); *m*-NO_2 (**e**).

Table I

Spectral bands obtained in ethanol

No.	1st band $\pi \rightarrow \pi^*$ aromatic		2nd band $\pi \rightarrow \pi^*$ aromatic		Charge transfer band	
	λ_{max}	ε_{max}	λ_{max}	ε_{max}	λ_{max}	ε_{max}
	(A) Results for series **I**					
Ia	215	17,300	290 sh	5,300	340	14,300
Ib	215	21,300	270	5,300	370	10,100
Ic	225	30,300	260 sh	9,600	385	25,300
Id	225	32,500	265	9,500	460	33,300
Ie	215	21,600	265	13,600	325	11,000
	(B) Results for series **II**					
IIa	245	23,500	295	12,000	380	34,000
IIb	240 sh	40,000	310	13,500	410	25,500
IIc	262	21,300	305	13,500	430	35,000
IId	285	10,000	330	12,500	530	67,500
IIe	240	62,500	316	21,000		

λ_{max} in nm; ε_{max} in cm^2 $mole^{-1}$

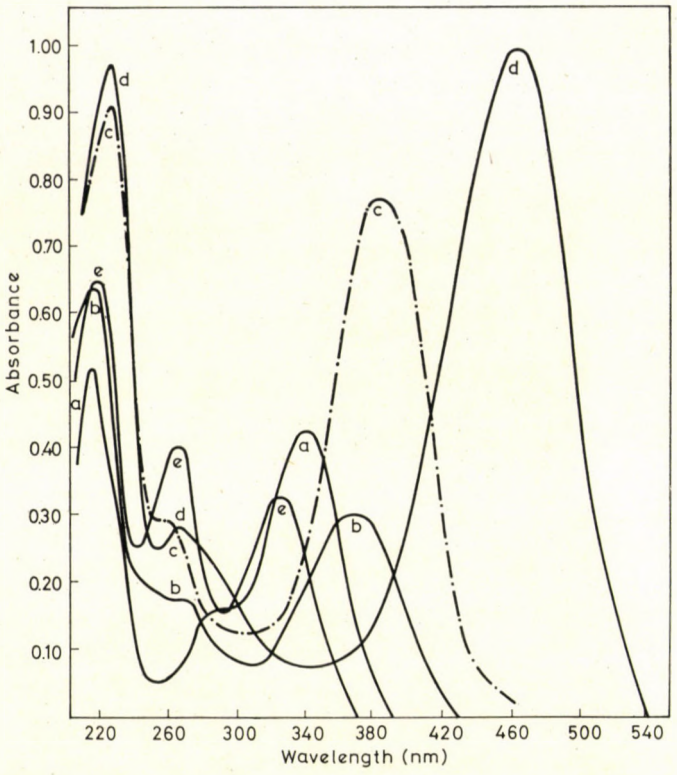


Fig. 1

The spectra of the 2-styrylpyridine or -quinoline ethiodides represented in Figs 1 and 2 are more or less identical. Each spectrum essentially consists of three bands, except for *m*-nitro-2-styrylquinoline ethiodide whose spectrum has two bands only. Generally, the absorption bands of compounds **II** are found at longer wavelengths than those of the corresponding derivatives of **I**. This is due to the higher coplanarity of **II** resulting from the greater bulk of the heterocyclic moiety attached to the —CH=CH— centre. This leads to a stronger interaction of the electrons within the whole molecule, hence a lower excitation energy is required.

Considering previous spectrophotometric studies on substituted benzenes, pyridine and quinoline [7], it seems plausible to consider the bands below 290 nm in **I** and 330 nm in **II** as being due to electronic transitions ($\pi \rightarrow \pi^*$) within the benzenoid and heterocyclic rings (Table I). Comparable bands are observed in the spectrum of 2-methylpyridine ethiodide ($\lambda_{max} = 265$ nm; $\varepsilon_{max} = 7{,}000$ cm^2 $mole^{-1}$) and 2-methylquinoline ethiodide ($\lambda_{max} = 238$ and 320 nm; $\varepsilon_{max} = 48{,}000$ and 14,500 cm^2 $mole^{-1}$), respectively.

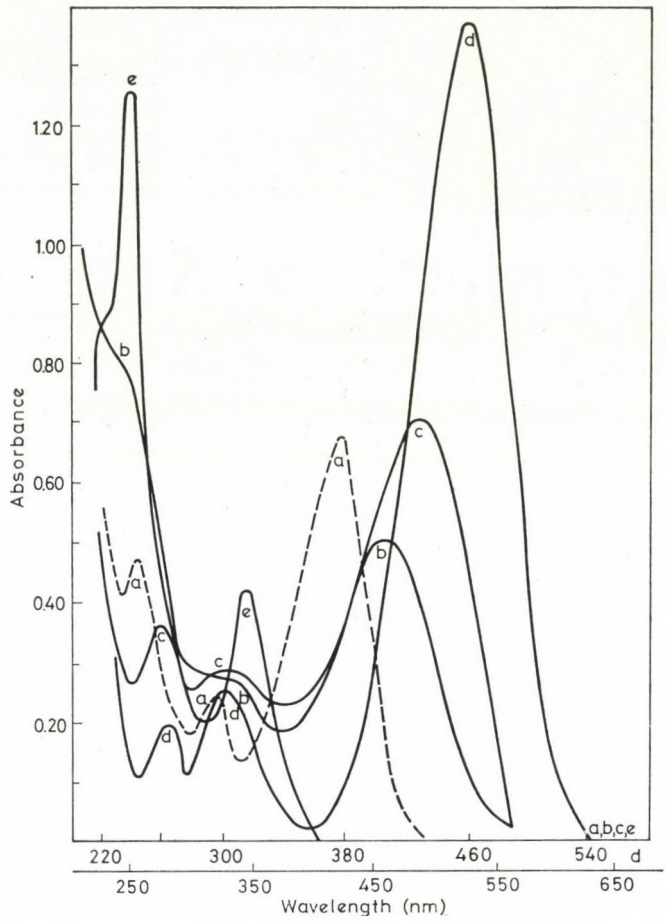


Fig. 2

These bands, however, exhibit some red shifts in **I** and **II**, probably due to higher conjugation resulting from the condensation of these compounds with the aromatic aldehyde and the influence of a possible charge transfer from the phenyl moiety on the electronic transitions of the heterocyclic system.

The band located at longer wavelength can be assigned to an intramolecular charge transfer. This charge transfer seems to originate from the phenyl moiety influenced by the substituent (X) directly bonded to it. The acceptor is the positively charged nitrogen atom.



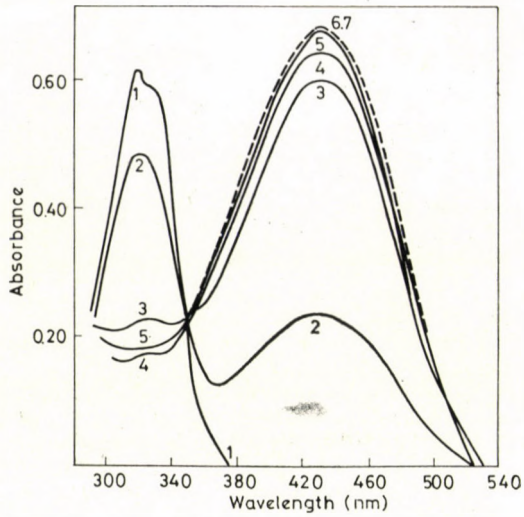


Fig. 3

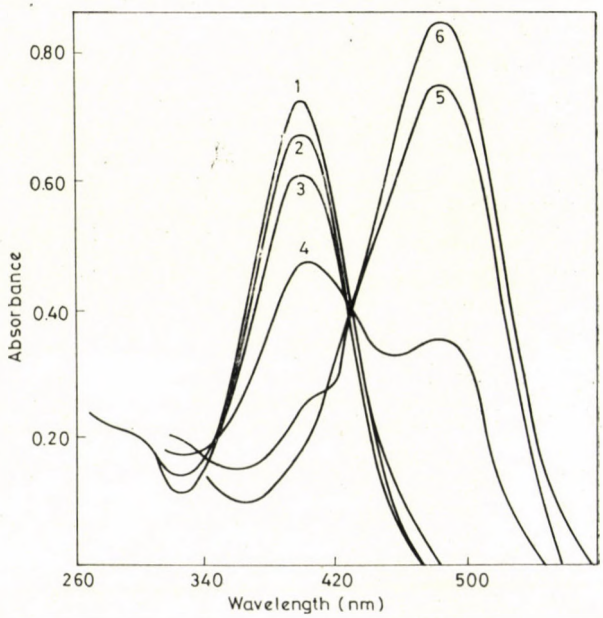
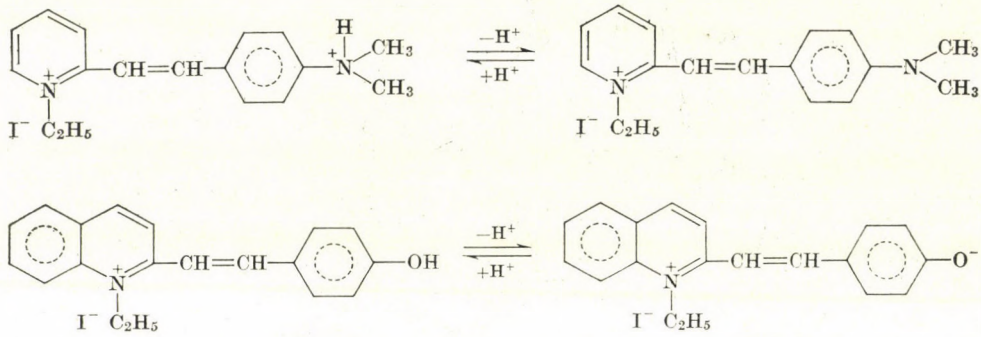


Fig. 4

The charge transfer nature of the transition leading to the band at longer wavelength can be supported by considering the spectral behaviour of the compounds in solutions of varying hydrogen ion concentrations (Figs 3, 4). It has been found that for compounds in which X = *p*-OH, *p*-OH-*m*-OCH_3,

and p-$N(CH_3)_2$, the band is largely red-shifted (in alkaline media for the p-OH derivatives, and at pH >4 for the N-dimethyl derivatives). This large red shift is mainly due to a relatively increased negative charge density on the substituent (phenolate ion or alkylamino group).



Effect of substitution on the spectra

Change of the substituent apparently influences both the position and molar extinction coefficient of the three bands observed, as seen from the results given in Tables I and II. This behaviour may be ascribed to the high coplanarity of the molecule, which is shown by the linear relation obtained on plotting $1/\lambda_{max}$ (charge transfer) *versus* the Hammett constants (σ) of the substituent X (Fig. 5).

The observed shifts and intensities of the charge transfer band run in a more or less regular manner, in accordance with the electronic character of the substituent. Within one and the same series, the charge transfer band is shifted to a longer wavelength as the electron donor character of the substituent increases. This can be explained by increased charge transfer to the positively

Table II

Spectral bands obtained in buffer solutions

No.	Non-ionic or protonated form		Ionic or non-protonated form		pK				
	λ_{max}	ε_{max}	λ_{max}	ε_{max}	1	2	3	4	Mean
Ic	360	22,500	425	28,700	8.30	8.37	8.35	8.32	8.33
Id	320	20,300	430	22,000	3.35	3.34	3.39	3.34	3.36
If	370	21,600	445	28,000	8.10	8.16	8.17	8.15	8.15
IIc	400	36,000	485	42,500	8.0	7.96	8.10	8.05	8.03
IId	360	35,000	495	46,000	3.05	3.07	3.10	3.05	3.07

charged heterocyclic atom, thus supporting the charge transfer nature of the band.

The blue shift observed in the positions of the charge transfer bands of the *m*-nitro-2-styrylpyridine or -quinoline ethiodides relative to the parent compounds is due to the acceptor character of the nitro group. This anatago-

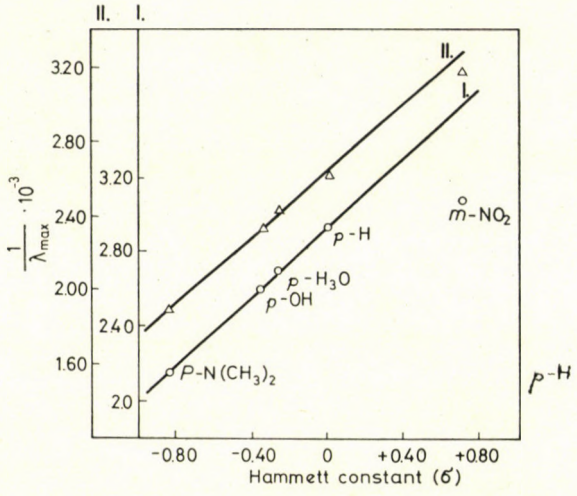


Fig. 5.

nizes the charge transfer from the phenyl moiety to the positively charged hetero atom.

The charge transfer band of *m*-nitro-2-styrylquinoline ethiodide is located at 316 nm and overlaps the second band due to the $\pi \rightarrow \pi^*$ transition of the aromatic system.

Determination of the pK values

The acid dissociation or protonation constants of some-2-styrylpyridine and -quinoline ethiodide derivatives have been determined, in order to ensure the optimal pH in the application of these dyes as photosensitizers. The effectiveness of the compounds as photosensitizers increases when they are present in the ionic form, which has a higher planarity. For this purpose the spectra of these compounds in aqueous solutions of varying pH were studied.

The spectra at pH > 9 for the *p*-hydroxy compounds, and at pH > 4 for the *p*-$N(CH_3)_2$ compounds, represent the absorption of the ionic and non-protonated forms of these substances, respectively, whereas those at lower pH of the medium are due to the non-ionic or protonated species. On decreasing

the pH of the medium, the absorbance of the band due to the ionic or non-protonated form decreases in intensity, whereas that of the non-ionic or protonated form increases (Figs 3, 4).

The spectra of these compounds exhibit a clear isosbestic point denoting the existence of an equilibrium between the two forms essentially of the acid–base type. The A-pH curves are typical dissociation or association curves, supporting the acid–base equilibrium.

The pK values of the compounds, obtained by applying the different spectrophotometric methods previously described [8, 9], are depicted in Table II. The results show that the pK values of compounds belonging to series **I** are higher than those belonging to series **II**. This behaviour may be explained on the same principle as above, *i.e.* by the higher planarity of **II** which favours the intramolecular charge transfer from the phenyl moiety. This leaves a lower negative charge density on the aromatic system resulting in weaker bonding of the proton.

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FORCE FIELD STUDY OF SOME XY_3 TYPE MOLECULES AND IONS

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A molecular force field study of some planar XY_3 type molecules and ions has been attempted using the parametric method of REDINGTON and ALJIBURY and additional parameters like Coriolis coupling constants and mean amplitudes of vibration. The rotational distortion constants are also calculated and reported.

1. Introduction

The force field of molecules can be unambiguously fixed using vibrational frequencies and additional parameters like isotopic frequencies [1, 2], Coriolis coupling constants [3], mean amplitudes of vibration [4] and rotational distortion constants [5]. The main difficulty in inverse vibrational problems lies in fixing the exact eigenvector matrix L, the transformation matrix between symmetry and normal coordinates. One of the methods of obtaining the true L is by multiplying L_0 (the matrix obtained from the relation $G = L_0\tilde{L}_0$ where G is the usual kinetic energy matrix) by a suitable orthogonal matrix C. This matrix in essence reduces to fixing one angular parameter in the case of $n = 2$ and $\frac{n(n-1)}{2}$ parameters for an nth order problem. Recently REDINGTON and ALJIBURY [6] attempted to fix the angle parameter Φ by maximizing the restoring force for the bond associated with the highest vibrational mode. In the present paper, an attempt is made to fix the unambiguous force field for some XY_3 planar type molecules and ions using the above method. For a 2×2 case the matrix C is represented by

$$\begin{bmatrix} C_\Phi & S_\Phi \\ -S_\Phi & C_\Phi \end{bmatrix}$$

where C_Φ and S_Φ denote the cosine and sine of angle Φ, and the force constants can be evaluated from the well-known relation

$$F = \tilde{L}^{-1}\Lambda L^{-1} \tag{1}$$

where Λ is the diagonal matrix of the vibrational eigenvalues ($\Lambda_i = 4\pi^2c^2\nu^2$).

To fix the C matrix, REDINGTON and ALJIBURY [6] calculated the restoring forces for each coordinate as a function of parameter Φ. The coordinate associated with the highest vibrational frequency is displaced and the other coordinates are allowed to relax in order to attain a restoring force balance and a minimum potential energy so that the restoring force takes the near maximum value. Each coordinate has to be considered in the order of descending vibrational frequencies and in identical potential energy conditions.

For a 2×2 case, the restoring force balance can be obtained by finding points of the function F_{stp}

$$F_{stp} = T_1 D_{11}^{-1/2} + T_2 D_{22}^{-1/2} \tag{2}$$

for all values of Φ, and some intersection solutions

$$T_1 D_{11}^{-1/2} = T_2 D_{22}^{-1/2} \tag{3}$$

where T_1 and T_2 are the geometrical constants of the molecule which can be obtained by the use of the virial theorem (for planar type XY_3, $T_1 = R_{X-Y}$ and $T_2 = 2 \sin \Phi$), D_{11} and D_{22} are the cofactors of the diagonal force constants

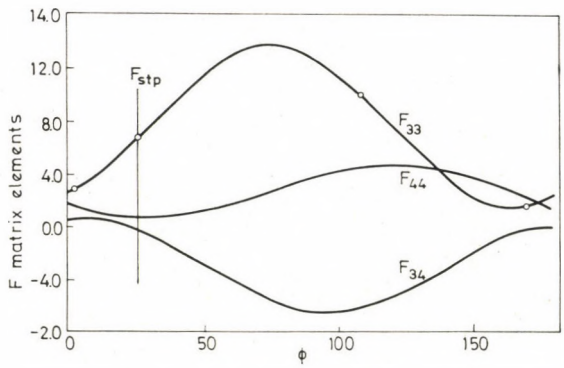

Fig. 1. The F matrix elements for the species of BF_3. The F_{stp} maximum and intersection solutions are indicated by dots. The correct solution is represented by the line

This type of approach, as shown in Fig. 1, yields two F_{stp} critical solutions and two intersection solutions, of which only one reproduces all the molecular constants satisfactorily.

Coriolis constants [7] can be used to fix the parameter Φ. The relation connecting Φ and ζ is given as

$$\zeta = L^{-1} C^{\alpha} \tilde{L}^{-1} . \tag{4}$$

The true L can be obtained from the relations connecting experimentally observed ζ 's with Φ. These relations were given by ANANTHAKRISHNAN and ARULDHAS [7].

The experimentally observed mean amplitude of vibration [8] for bonded atoms can also be used to fix the parameter Φ. The Σ matrix is expressed as

$$\Sigma = L\Delta\tilde{L} \tag{5}$$

where

$$\Delta_k = \frac{h}{8\pi^2 c\nu_k} \operatorname{cotan} \frac{hc\nu_k}{2KT} . \tag{6}$$

Equation (5), when substituted for L in terms of L_0 and Φ, yields

$$\Sigma^e_{33} = C^2_\Phi \left[L^{02}_{11}\Delta_{33} + L^{02}_{12}\Delta_{44}\right] + S^2_\Phi \left[L^{02}_{11}\Delta_{44} + L^{02}_{11}\Delta_{33}\right] + \\ + 2S_\Phi C_\Phi L^0_{11} L^0_{12} (\Delta_{44} - \Delta_{33}) \tag{7}$$

and

$$[\sigma_{X-Y}]^2 = \frac{\Sigma^a_{11} + 2\Sigma^e_{33}}{3} . \tag{8}$$

With values of σ_{X-Y} known from electron diffraction data, Φ can be obtained. The observed vibrational frequencies and other molecular parameters used in the present calculations are given in Table I.

Table I

Vibrational frequencies (cm^{-1}) and molecular parameters for some planar XY_3 type molecules and ions

Molecule or ion	Vibrational wavenumber (cm^{-1})				Bond distance (Å)		Mean amplitude of vibration (Å)	
	$\nu_1(A_1)$	$\nu_3(E)$	$\nu_4(E)$	Ref.	R_{X-Y}	Ref.	σ_{X-Y}	Ref.
$^{11}BF_3$	888	1449	479.36	[9, 10]	1.313	[11]	0.042 ± 0.002	[11]
$^{10}BF_3$	888	1502.5	481.13					
$^{11}BCl_3$	471	956	243	[12]	1.73	[12]	0.0505± 23	[13]
$^{10}BCl_3$	471	995	244					
$^{11}BBr_3$	278	820	150	[12]	1.87	[12]	0.0514± 63	[14]
$^{10}BBr_3$	278	856	156					
$^{11}BI_3$	190	704	100	[12]	2.10	[12]		
$^{10}BI_3$	190	734	100					
$^{15}NO_3^-$	1055.1	1352.2	714.4	[15]	1.243	[16]		
$^{14}NO_3^-$	1054.8	1383.2	715.6					
$^{11}BO_3^{3-}$	939	1284.5	603.75	[12]	1.36	[12]		
CO_{33}^{2-}	1063	1415	680	[17]	1.31	[16]		

Table II

Angle parameter Φ, force constants (mdyn/Å),[a] isotopic shifts (cm^{-1}), Coriolis coupling constants, type molecules

Molecule or ion	Method	Parameter	Force constants (mdyn/Å)		
			F_{33}	F_{34}	F_{44}
	F_{stp}	26° 3′	6.6660[b]	−0.3718	0.5104
	$\sigma_{X-Y} = 0.042$	28° 49′	7.2477	−0.5909	0.4982
$^{11}BF_3$	$\zeta_3 = 0.81$	25° 13′	6.4892	−0.3107	0.5174
	$\zeta_4 = -0.789$	25° 48′	6.6612	−0.3531	0.5122
	Isotopic frequency (Ref. [19])	26° 16′	6.7642	−0.4717	0.5125
			(6.561	−0.317	0.512)[20]
	Most probable value	25° 41′	6.5868	−0.3446	0.5132
	F_{stp}	14° 45′	3.3529	−0.1948	0.2272
$^{11}BCl_3$	$\sigma_{X-Y} = 0.050$	10° 44′	2.7696	−0.0273	0.2623
	Isotopic frequency (Ref. [19])	14°	3.3516	−0.1954	0.2268
			(3.174	−0.144	0.237)[20]
	F_{stp}	9°	2.7556	−0.1806	0.1901
$^{11}BBr_3$	$\sigma_{X-Y} = 0.054$	8° 10′	2.5978	−0.1367	0.1963
	Isotopic frequency (Ref. [19])	9°	2.8708	−0.2246	0.1999
			(2.461	−0.134	0.200)[20]
	Most probable value	8° 35′	2.6761	−0.1582	0.1929
$^{11}BI_3$	F_{stp}	6° 20′	2.1154	−0.1350	0.1314
			(1.820	−0.077	0.144)[20]
$^{14}NO_3^-$	F_{stp}	25° 45′	6.3652	−0.6604	1.6597
			(6.2	−0.75	1.68)[25]
$^{11}BO_3^{3-}$	F_{stp}	21° 20′	4.7181	−0.4059	0.7395
			(5.09	−0.43	0.73)[26]
CO_3^{2-}	F_{stp}	23° 33′	6.0916	−0.5088	0.9430
			(6.17	−0.53	0.94)[26]

a: 1. mdyn/Å = 10^2 N/m
b: This number of significant figures is retained to secure internal consistency in calculation

2. Results and discussion

The force field study of boron trihalides has been carried out by various authors using Coriolis coupling constants [3, 7], mean amplitudes of vibration [13] and isotopic frequencies [18] as additional parameters. Recently, ANANTHAKRISHNAN and ARULDHAS [7] and RAMASWAMY and JAYARAMAN [19] have attempted to fix the force field using a parametric technique.

mean amplitudes of vibration (Å) and rotational distortion constants (cm^{-1}) of some planar XY_3 and ions

Isotopic shifts (cm^{-1})		$\zeta_3 = -\zeta_4$	σ_{X-Y} in Å	Rotational distortion constants $\times 10^{-7}$ cm^{-1}		
$\Delta\nu_3$	$\Delta\nu_4$			D_J	D_K	$-D_{JK}$
52.92	1.98	0.793	0.0427	2.6203	1.8518	4.1963
51.10	1.60	0.730	—	2.5722	1.8453	4.1616
53.43	1.81	—	0.0428	2.6321	1.8642	4.2403
53.07	1.96	—	0.0427	2.6197	1.8873	4.2511
—	—	0.789	0.0430	2.8515	1.9972	4.8500
(53.5	1.77)[9,10]	—	(0.042)[23]	(4.00	2.0	5.0)[21]
—	—	0.800	0.0427	2.6246	1.8567	4.2253
39.45	0.71	0.870	0.0491	0.3087	0.2166	0.5057
40.69	0.38	0.930	—	0.3144	0.2317	0.5182
—	—	0.881	0.050	0.2991	0.2182	0.4900
(39.0	1.00)[12]	(0.874)[22]	(0.049)[23]			
37.00	5.79	0.940	0.0509	0.0449	0.0323	0.0730
37.18	5.82	0.950	—	0.0450	0.0323	0.0731
—	—	0.940	0.0515	0.0419	0.0298	0.0677
(36.0	6.0)[12]	(0.903)[22]	(0.051)[23]			
—	—	0.945	0.0511	0.0452	0.0326	0.0735
32.58	0.10	0.959	0.0551	0.0124	0.0091	0.0204
(30.0	)[12]	(0.978)[22]	(0.0554)[23]			
33.27	1.35	0.866	0.042	3.4341	2.1672	6.0860
(30.90	1.20)[15]		(0.0418)[23]			
47.93	1.48	0.966	0.0468	2.6743	1.7424	4.1060
(45.5	2.48)[12]		(0.047)[23]			
—	—	0.865	0.0433	2.6198	1.7094	4.0257
			(0.0428)[23]			

For $^{11}BF_3$ the value of Φ corresponding to F_{stp} maximum is 26° 3′. Using ζ_3 (= 0.810) and ζ_4(= − 0.789) values as reported by GINN *et al.* [9, 10] the values of Φ are fixed as 25° 13′ and 25° 48′, respectively. The experimentally observed mean amplitude of vibration for bonded atoms [11] σ_{X-Y} = 0.042 Å yields imaginary values for Φ, hence the discriminant of the quadratic equation in Φ is assumed to be zero to give a limiting value of Φ equal to 28° 49′. This value is rather high. Probably the orthogonal matrix C with Φ = 25° 41′ (mean value obtained from the various methods) represents the true transformation matrix. With this value of Φ, the values of symmetrized force constants agree well with those of SHIMANOUCHI *et al.* [20]. They are F_{33} = 6.5868 mdyn/Å;

$F_{34} = -0.3446$ mdyn/Å and $F_{44} = 0.5132$ mdyn/Å. The calculated isotopic shifts also compare very well with the observed results. The calculated ζ value is in good agreement with the average value (0.799), given by GINN *et al.* [9, 10]. The calculated rotational distortion constants for $\Phi = 25° 41'$ also generally agree well with the observed values [21], $D_J = 4 \times 10^{-7}$ cm^{-1}, $D_K = 2 \times 10^{-7}$ cm^{-1} and $D_{JK} = 4 \times 10^{-7}$ cm^{-1}. The mean amplitudes of vibration are not sensitive to angle Φ; the values obtained for all the angles Φ are essentially the same. Thus it is seen that the mean vibrational amplitude has a value of 0.0427 Å against the experimental value of 0.042 Å. This is in agreement with the observation of ANANTHAKRISHNAN and ARULDHAS [24] who have reported a value of 0.043 Å for $l_{(B-F)}$. All the results are summarized in Table II.

In the case of BCl_3, the F_{stp} criterion yields a solution of $\Phi = 14° 45'$ while the experimental value $\sigma_{X-Y} = 0.505$ Å yields $10° 44'$. RAMASWAMY and JAYARAMAN [19] computed the value of Φ as 14°, using isotopic frequencies, which is in good agreement with the present values obtained by REDINGTON's method. Probably $\Phi = 14° 45'$ is the true angle for in the case of BCl_3 and the molecular constants calculated from this represent the probable values. The molecular constants for BBr_3 and BI_3 were also obtained, using REDINGTON's method and the mean amplitudes wherever available. The results are summarized in Table II.

In the case of nitrate, carbonate and borate ions, the parameter Φ is fixed as $25° 45'$, $23° 33'$ and $21° 20'$, respectively, through REDINGTON's approach. The calculated symmetrized force constants and mean amplitudes of vibration compare well with the values reported by BECKMANN and MECKE [25], and FADINI and MULLER [26]. The Coriolis constants and rotational distortion constants are calculated and reported.

In conclusion it may be seen that REDINGTON's method of obtaining C yields reliable results in the case of the molecules under consideration. The mean vibrational amplitudes are insensitive and therefore they cannot be used to fix the force fields accurately.

*

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STUDY OF THE ASSOCIATION CONDITIONS OF STRAIGHT-CHAIN PRIMARY ALCOHOLS IN THE PRESENCE OF NORMAL PARAFFINS

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The associations of 1-pentanol, 1-hexanol and 1-heptanol were investigated in their mixtures with normal paraffins. Viscosity measurements indicated that the degree of association of the alcohols increased during dilution of the pure alcohol to a mole fraction of 0.6. This phenomenon was interpreted in terms of the dissociation of the cyclic associated species present in the pure alcohol. The linear polymers produced in this process are assumed to form longer chain-like species, resulting in an increase in the degree of association. This hypothesis is in agreement with previous results of dielectric and infrared spectroscopic measurements and calorimetric data on heats of mixing.

Many authors have studied the physical chemical properties of alcohol–hydrocarbon mixtures, and within this the effect of the association of the alcohols on the properties of the mixture [1—6]. Investigations with various methods have shown that the physical chemical properties of such mixtures in the liquid phase are determined primarily by the structure of the association complexes formed via the coupling of the alcohol molecules, by the degree of association, and by the strength of the hydrogen-bonds formed in the complexes. Comprehensive research work has already led to the clarification of many part-problems, but nevertheless it cannot be said that exact information is available on the association conditions of the alcohols. Looking over the literature it is evident that the various investigations were carried out with different methods, and that the results were interpreted with different physical models. In a comparison of the models used for the association of alcohols, many contradictory assumptions may be found. For example, DUNKEN and FRITZSCHE [7] interpret their results obtained in an infrared spectroscopic study of the tertiary isobutanol–CCl_4 mixture with five different, contradictory models, with approximately the same degrees of success. Those authors came to the conclusion that the agreement of the model and the experiments could be regarded as accidental. It appears that creation or selection of a model based on assumptions close to the physical reality can be achieved only by seeking a model which can be reconciled with all of the results obtained with different experimental methods.

Here we report on a study made on the association conditions of 1-pentanol and 1-heptanol in their mixtures with normal paraffins. We shall deal

with the questions of whether the viscosity data relating to the average association degree of the association complexes, the static dielectric properties of the mixtures, the results of infrared spectroscopic examinations, and the mixing heat data can be interpreted with one given association model, and whether they can be reconciled with our previous conceptions of this association.

Table I

Dynamic viscosity of the 1-pentanol (A)–n-hexane (B) mixture as a function of temperature

x_A	η (cP)			
	273 °K	293 °K	313 °K	333 °K
0.0000	0.383	0.308	0.264	0.221
0.1034	0.395	0.312	0.271	0.240
0.2086	0.438	0.348	0.289	0.251
0.3140	0.546	0.446	0.353	0.290
0.4020	0.681	0.533	0.406	0.321
0.5014	0.976	0.688	0.495	0.372
0.5982	1.31	0.926	0.629	0.458
0.6987	2.15	1.31	0.862	0.590
0.7887	2.83	1.65	1.06	0.700
0.8923	4.32	2.43	1.46	0.974
1.0000	5.89	3.302	1.899	1.164

Table II

Dynamic viscosity of the 1-heptanol (A)–n-octane (B) mixture as a function of temperature

x_A	η (cP)			
	273 °K	293 °K	313 °K	333 °K
0.000	0.714	0.545	0.428	0.350
0.113	0.792	0.598	0.459	0.361
0.224	0.882	0.630	0.472	0.371
0.334	1.14	0.809	0.592	0.447
0.440	1.51	1.04	0.717	0.530
0.535	2.23	1.40	0.902	0.642
0.637	3.05	1.84	1.14	0.763
0.730	4.33	2.44	1.48	0.947
0.823	5.51	3.11	1.92	1.15
0.915	7.65	4.17	2.36	1.42
1.000	10.56	5.42	2.99	1.82

Viscosity measurements

The dynamic viscosity of 1-pentanol–*n*-hexane and 1-heptanol–*n*-octane mixtures was studied as a function of composition and temperature. The measurement was carried out with a Höppler rheoviscosimeter, at atmospheric pressure, and in the temperature interval 0 to +60 °C. The compositions of the mixtures varied from pure hydrocarbon to pure alcohol. The experimental results are listed in Tables I and II, as functions of the temperature and the nominal mole fraction of the alcohol component (x_A); they are also plotted in Figs 1 and 2 (1 cP = 10^{-3} N sec m^{-2}).

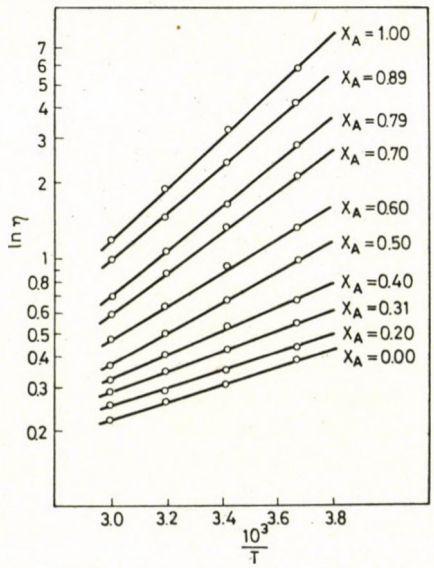

Fig. 1. Dynamic viscosity of the 1-pentanol (*A*)–*n*-hexane mixture as functions of the temperature and the composition

Discussion of results of viscosity measurements

The literature describes a number of methods for the calculation of the average association degree of associative components. These calculations are generally based on the simple assumption that the non-ideal behaviour of mixtures of the associative components with apolar substances is caused only by the decrease in the number of molecules as a result of association. Thus, for example, in the knowledge of the activity factors calculated from the vapour–liquid equilibrium data, or more exactly from the activity factor of the apolar component extrapolated to zero concentration, the average degree of

association of the pure associative component may be calculated [8]. From the freezing-point depression, on the other hand, we can calculate the degree of association of the associative component present in high dilution [8]. It was earlier shown that the activation enthalpy of viscous flow can be used to calculate the average degree of association of alcohols and amines [9]. This method is based on the fact that, in the case of a non-associating apolar com-

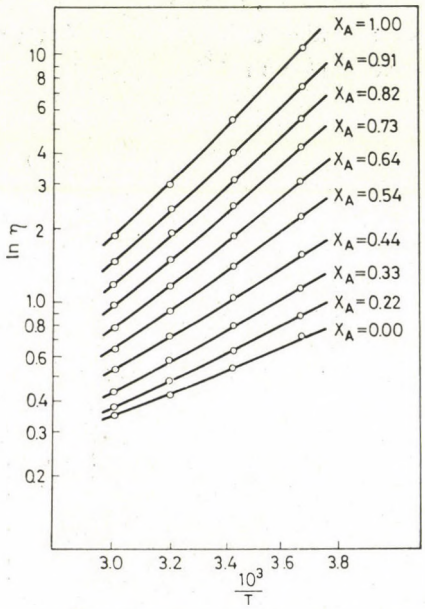

Fig. 2. Dynamic viscosity of the 1-heptanol (*A*)–*n*-octane mixture as functions of the temperature and the composition

ponent, the activation enthalpy of viscous flow is to a good approximation proportional to the molecular weight of the component, whereas in the case of associating components this activation enthalpy is significantly higher than would be expected from the molecular weight. Assuming that any deviation from the behaviour of apolar substances is caused only by the molecular weight increase due to association, the average degree of association can be calculated. The degrees of association calculated in this way exhibited good agreement with the results obtained by other methods. Determination of the degree of association from the activation enthalpy of viscous flow has an advantage over the other methods: in the case of an appropriately selected component (this selection is treated in the discussion of the results), this method is suitable for the calculation of the degree of association not only of pure alcohols, but also of alcohol–hydrocarbon mixtures, and it provides information on

the extent of association in just that concentration range where the other methods cannot be applied.

The relation given earlier [9] for the calculation of the average degree of association (α) of normal primary alcohols is as follows:

$$\alpha = \frac{\overline{M}}{M} = \frac{7.0133 \times 10^{-2}\, \Delta H_v}{M} - \frac{35.37}{M} \tag{1}$$

where ΔH_v is the activation enthalpy of viscous flow (kcal/mole);
M is the molecular weight of the monomer molecules; and
$\overline{M}$ is the average molecular weight, defined by the following relation:

$$\overline{M} = \sum_i x_i M_i \tag{2}$$

where M_i is the molecular weight of the ith associated complex; and
x_i is the mole fraction of the ith associated complex.

It should be noted that relation (1) with the substitution $\alpha = 1$ gives the activation enthalpy of viscous flow of normal paraffins as a function of the molecular weight.

Calculation of the degree of association of mixtures is simplified if the paraffin to be added to the alcohol is selected so that its molecular weight be the same as that of the alcohol monomer. In the two systems chosen for the present work this condition is met as far as possible, the molecular weights being 86.18 and 88.15, and 114.23 and 116.20 g/mole in the two cases.

In the calculations the arithmetical mean of the two similar molecular weights was taken as M. The average degrees of association calculated *via*

Table III

Activation enthalpy of viscous flow and degree of association of the 1-pentanol (A)–n-hexane (B) mixture as functions of temperature

x_A	ΔH_v (cal/mole)	α	α_A	α_A max	α_A min
1.000	4873± 88	3.52±0.06	3.5	—	—
0.892	4488± 68	3.20±0.05	4.4	4.5	4.3
0.789	4174± 38	2.95±0.03	6.2	6.4	6.0
0.699	3871± 18	2.71±0.02	10.3	10.6	10.0
0.598	3180±125	2.15±0.10	9.5	14.3	7.0
0.501	2900± 38	1.93±0.03	24.8	41.8	17.6
0.402	2270± 98	1.42±0.07	3.8	3.8	2.7
0.314	1914± 91	1.13±0.06	1.6	2.2	1.2

Table IV

Activation enthalpy of viscous flow and degree of association of the 1-heptanol (A)–n-octane (B) mixture as functions of temperature

x_A	ΔH_v (cal/mole)	α	α_A	α_A max	α_A min
1.000	5289± 36	2.88±0.03	2.9	—	—
0.915	5057± 79	2.77±0.05	3.8	4.0	3.6
0.823	4659±137	2.53±0.08	5.4	5.4	5 4
0.730	4557± 50	2.46±0.01	7.5	8.1	7.1
0.637	4173± 50	2.23±0.03	17.8	13.6	10.9
0.535	3762± 61	1.98±0.04	37.5	9.9	6.0
0.440	3161± 62	1.62±0.04	7.1	9.0	5.9

relation (1), and the activation enthalpy of viscous flow of the mixture are given in Tables III and IV as functions of the mole fraction of the alcohol component.

It must be noted that in the whole temperature range examined the activation enthalpies of viscous flow are practically constant for pure alcohols, mixtures containing alcohol, and pure paraffins. Thus, relation (1) does not contain the temperature as a variable, and is valid from −20 to +80 °C [9]. This finding requires explanation in the case of the alcohols. It is interpreted in that, besides the special association conditions of the alcohols, where both cyclic and chain-form association polymers are possible, the gradual rupture of the hydrogen bonds is conceivable at higher temperature: it is primarily the number of ring closures which decreases, and thus the average degree of association remains practically constant. Since there is one hydrogen bond for each associated alcohol monomer in the case of the formation of cyclic associations, it can readily be seen that there is no clear-cut correlation between the average degree of association and the number of hydrogen bonds developing in the liquid on cyclic association. Such a correlation can be written only on the basis of some model, but in the sense of what was said in the introduction we wish to avoid this here.

In the following a study is made of how the association degree (α_A) of the alcohol component in the alcohol–hydrocarbon mixture can be determined in the case of an average degree of association α referring to the mixture.

Let us denote the (nominal) numbers of moles calculated from the analytical molecular weight by N_A and N_B, where the index A refers to the alcohol, and B to the hydrocarbon component. If the total number of moles is N, then

$$N = N_A + N_B \,. \tag{3}$$

Let us denote the 'actual' numbers of moles of the various alcohol complexes by $n_1, n_2, \ldots, n_i$, and let the index refer to the number of monomers present in the complexes. Thus:

$$N_A = n_1 + 2n_2 + \ldots + in_i + \ldots + kn_k = \sum_{i=1}^{k} in_i \tag{4}$$

where k is the number of monomers in the associate with the highest possible degree of association.

The actual and nominal numbers of moles of the non-associating component are the same:

$$N_B = n_B. \tag{5}$$

Since the molecular weights of the alcohol monomer and the hydrocarbon practically agree ($M_1 \sim M_B \sim M$), the average molecular weight of the mixture is

$$\overline{M} = M\frac{n_1}{n} + 2M\frac{n_2}{n} + \ldots + iM\frac{n_i}{n} + \ldots + kM\frac{n_k}{n} + M\frac{n_B}{n} \tag{6}$$

where

$$n = n_1 + n_2 + \ldots + n_i + \ldots + n_k + n_B. \tag{7}$$

The average degree of association α of the mixture is thus

$$\alpha = \frac{\overline{M}}{M} = \frac{\sum_{i=1}^{k} in_i + n_B}{n}. \tag{8}$$

Taking into account (4) and (5):

$$\alpha = \frac{N_A + N_B}{n} = \frac{N}{n}. \tag{9}$$

Let us next consider the average molecular weight (M_A) and degree of association (α_A) of the alcohol component in the mixture:

$$\overline{M}_A = M\frac{n_1}{\sum_{i=1}^{k} n_i} + 2M\frac{n_2}{\sum_{i=1}^{k} n_i} + \ldots + iM\frac{n_i}{\sum_{i=1}^{k} n_i} + \ldots + kM\frac{n_k}{\sum_{i=1}^{k} n_i} = M\frac{\sum_{i=1}^{k} in_k}{\sum_{i=1}^{k} n_i} \tag{10}$$

where

$$\sum_{i=1}^{k} n_i = n_1 + n_2 + \ldots + n_i + \ldots + n_k = n - n_B . \tag{11}$$

From relations (4) and (10), the degree of association of the alcohol component in the mixture is

$$\alpha_A = \frac{\bar{M}_A}{M} = \frac{N_A}{\sum_{i=1}^{k} n_i} . \tag{12}$$

From this, with the use of (5), (9) and (11):

$$\alpha_A = \frac{N_A}{\frac{N}{\alpha} - N_B} . \tag{13}$$

Introducing the notations $x_A = N_A/N$ and $x_B = N_B/N$ for the nominal mole fractions, we have

$$\alpha_A = \frac{x_A}{\frac{1}{\alpha} - x_B} . \tag{14}$$

The results calculated in this way are listed in Tables III and IV. The data to be found here were calculated in the following manner:

$\ln \eta$ was plotted against $1/T$ (Figs 1 and 2), and the regression straight line fitting the experimental points for a given mole fraction was determined with the aid of the method of least squares. The scatter (σ) of the experimental data was calculated, and the equations of the straight lines running parallel to the regression straight line at distances of $\pm\sigma$ were also determined. Assuming that the scatter of the experimental results is due to chance errors, the individual experimental points must with 85% certainty lie within the area enclosed by these latter two straight lines. From the equations of the steepest and least steep straight lines crossing this area, the greatest and least values of the activation enthalpy of viscous flow were determined; the difference of these from the value calculated from the slope of the regression straight line is given in the Tables as the limiting error. The uncertainty in α arose directly from the uncertainty in ΔH_v. The final two columns of the Tables contain the α_A values calculated from the greatest and least α values for the given composition. The α_A values in the fourth columns of the Tables were calculated from the average α values in the third column.

In connection with the evaluation of the results, we wish to note that the reliability of the values obtained from the average degree of association of

the alcohol decreases with the increase of the mole fraction of the hydrocarbon. The cause of this is that, since the extent of association of the alcohol molecules is concluded from the average molecular weight of the mixture, the error of the correlation method increases with the decrease of the number of moles of the alcohol.

From the viscosity measurements, therefore, it appears that the degree of association of the alcohols in the mixtures examined increases during dilution of the pure alcohol with hydrocarbon; at around the equimolar composition it passes through a maximum, and in dilute solutions it again decreases. Since this surprising physical picture is based on the results of a single investigation method, it demands further study.

Dielectric investigations

One of the frequently used methods of studying liquid-phase alcohol association is based on the measurement of the dielectric properties [1, 2]. Despite the extensive literature, there is as yet no unified conception as to the structure of the association polymers formed from the monomeric alcohol molecules in the course of the hydrogen-bonding association [10—14]. BORDEWIJK *et al.* [15] studied the association of 1-heptanol in dilute (0.1—3.0 mole%) carbon tetrachloride solution in the temperature interval of 25—45 °C. By extending the Kirkwood—Fröhlich equation [16] to dilute solutions, they determined the permanent dipole moment of the alcohol as a function of concentration. From the variation of the dipole moment with concentration they found that monomer–dimer–tetramer and monomer–dimer–trimer equilibria develop in this system. They also assume that the dimer associations are not cyclic in structure. LISZI and NÁRAY [17] investigated the association of cyclohexanol in its mixtures with apolar solvents. The concentration-dependence of the Kirkwood g factor [16] led to the conclusion that cyclic tetramers predominate in the concentration range around an alcohol mole fraction of 0.1. HUYSKENS and CRACCO [18] found that in mixtures of butanols with apolar solvents the dipole moment of the alcohol passes through a minimum as a function of composition in the vicinity of an alcohol mole fraction of 0.1. It is generally characteristic of the papers cited that the model used gives a satisfactory approximation to reality only in a relatively narrow concentration range. The experimental results to be reported below similarly permit the development of only a qualitative picture. The question arises of whether this picture is in accordance with the results of investigations relating to the activation enthalpy of viscous flow.

The experimental work involved the study of the 1-heptanol–*n*-octane and 1-pentanol–*n*-hexane systems. The relative permittivities and densities

of the mixtures were determined at 25 and at 45 °C. The relative permittivity was measured at a frequency of 500 kHz with a Siemens Rel. 3R277 type bridge. It was found that at these temperatures the relative permittivity determined at 500 kHz for these systems agrees with the static relative permittivity. Density was measured with a DMA OZC type digital densitometer. The experimental results are given in Tables V and VI.

Table V

Density and relative permittivity of the 1-pentanol (A)–n-hexane (B) mixture

x_A	25 °C		45 °C	
	ϱ (g/cm³)	ε	ϱ (g/cm³)	ε
0.0000	0.6571	1.89	0.1780	1.87
0.1034	0.6674	2.06	0.5946	2.03
0.2086	0.6824	2.35	0.6136	2.33
0.3140	0.6978	2.98	0.6329	2.82
0.4020	0.7113	3.85	0.6497	3.46
0.5014	0.7269	5.22	0.6694	4.44
0.5982	0.7428	6.88	0.6894	5.73
0.6987	0.7603	8.94	0.7115	7.38
0.7887	0.7752	10.87	0.7320	9.08
0.8923	0.7937	12.54	0.7545	10.96
1.0000	0.8142	14.45	0.7810	12.83

Table VI

Density and relative permittivity of the 1-heptanol (A)–n-octane (B) mixture

x_A	25 °C		45 °C	
	ϱ (g/cm³)	ε	ϱ (g/cm³)	ε
0.0000	0.7026	1.95	0.6380	1.93
0.5009	0.7586	3.82	0.7081	3.52
0.5984	0.7705	5.02	0.7237	4.30
0.6942	0.7825	6.41	0.7390	5.28
0.7967	0.7957	8.11	0.7557	6.63
0.8966	0.8086	9.80	0.7719	8.07
1.0000	0.8226	11.45	0.7898	9.64

In these Tables ϱ is the density, ε the relative permittivity, and x_A the mole fraction of the alcohol component.

The data in Tables V and VI were employed to determine the molar polarization P of the mixture *via* the relation

$$P = \frac{\varepsilon - 1}{\varepsilon + 2} \frac{M^*}{\varrho} \tag{15}$$

where M^* is the average molecular weight of the mixture (calculated from the average weighted with the nominal mole fractions) at the given composition. The molar polarizations of the mixtures are shown in Tables VII and VIII.

Table VII

Molar polarization of the 1-pentanol (A)–n-hexane (B) mixture, and moler polarization of the alcohol in the mixture, as functions of the composition

x_A	25 °C		45 °C	
	P	P_A	P	P_A
0.0000	30.0	—	33.5	—
0.1034	33.7	65.5	37.1	68.7
0.2086	39.3	74.4	43.2	80.1
0.3140	49.4	91.7	51.7	91.4
0.4020	59.4	103.2	60.1	99.8
0.5014	70.0	109.7	69.4	105.1
0.5982	77.7	109.8	77.4	106.8
0.6987	83.4	106.4	83.5	105.1
0.7887	86.7	101.8	87.3	101.7
0.8923	87.7	94.7	89.4	96.2
1.0000	88.4	88.4	89.9	89.9

Table VIII

Molar polarization of the 1-heptanol (A)–n-octane (B) mixture, and molar polarization of the alcohol in the mixture, as functions of the composition

x_A	25 °C		45 °C	
	P	P_A	P	P_A
0.0000	39.1	—	42.2	—
0.5009	73.5	107.8	74.1	105.8
0.5984	85.6	116.3	83.4	111.1
0.6942	94.8	119.3	91.8	113.7
0.7467	102.2	118.4	99.8	114.5
0.8966	106.8	114.7	105.3	112.5
1.0000	104.6	109.6	109.0	109.0

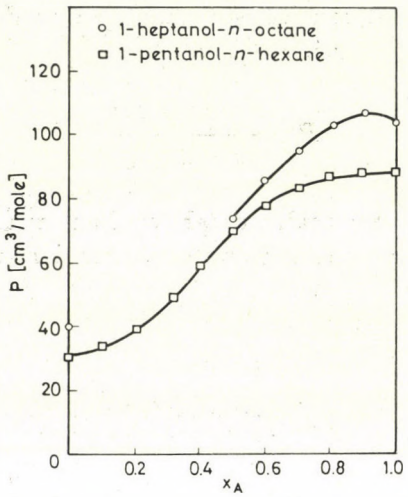

Fig. 3. Molar polarizations of alcohol–hydrocarbon mixtures at 25 °C

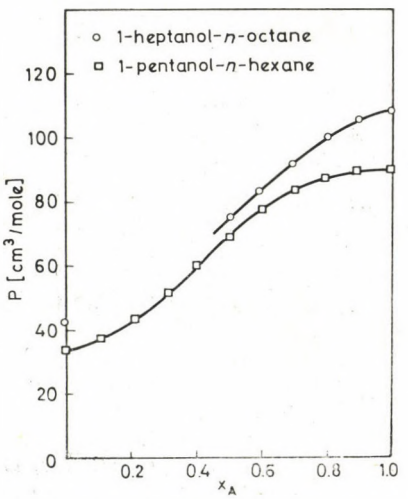

Fig. 4. Molar polarizations of alcohol–hydrocarbon mixtures at 45 °C

and Figs 3 and 4. The tabulated data include the molar polarization of the alcohol. This was calculated by assuming that the molar polarizations are additive, and that the molar polarization of the hydrocarbon component is constant:

$$P_A = \frac{P - x_B P_B}{x_A} . \tag{16}$$

In this latter equation the index A refers to the alcohol, and B to the apolar component forming the mixture with the alcohol.

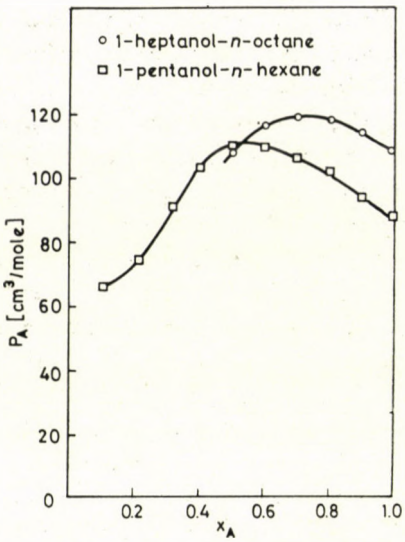

Fig. 5. Molar polarizations of the alcohols in the alcohol–hydrocarbon mixtures at 25 °C

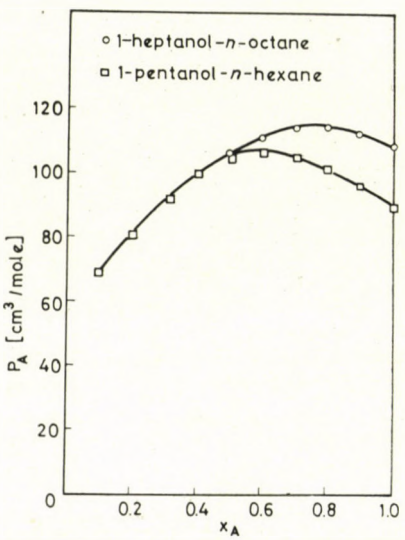

Fig. 6. Molar polarizations of the alcohols in the alcohol–hydrocarbon mixtures at 45 °C

Relation (16) involves the customary simplifying assumption that the deviations from ideal of the properties of the alcohol–hydrocarbon mixtures are caused solely by the association of the alcohol molecules.

The molar polarizations of the alcohols are given as a function of composition in Figs 5 and 6.

Figures 3 and 4 indicate that neither of the alcohol-containing systems is an ideal mixture: the molar polarization of the mixture does not agree with the sum of the molar polarizations of the components weighted by the mole fractions. More characteristic, however, is the variation of the molar polarizations of the alcohols with composition. Figures 5 and 6 show that at both temperatures in both systems P_A passes through a maximum as a function of composition. With the decrease of the temperature the position of the maximum is shifted towards lower alcohol concentrations. Such a change in the molar polarization of the alcohols can primarily be attributed to the change of the directional polarization. To a first approximation it may be assumed that the atom and electron polarizations are not affected by the dipole environment of the molecules. This means, however, that the dipole concentration in the mixtures also passes through a maximum as a function of composition. One possible explanation of this, which is in agreement with the results of other investigations, is as follows: in concentrated alcohol solution a significant proportion of the associates are present in cyclic forms with low (possibly zero) dipole moment. In the course of dilution with the apolar solvent these rings in part break down to give chain-like structures, which results in an increase of the directional polarization. In accordance with the mass action law, further dilution leads to the breakdown of the chain associates too, and hence to a decrease in the directional polarization. Finally, in infinitely dilute solution the value of this approximates to that valid in the vapour phase.

All things considered, it seems that the physical picture based on the determination of the activation enthalpy of viscous flow, according to which dilution of the alcohols with hydrocarbon in these systems is accompanied first by conversion of the cyclic associates to chains, and then at higher dilutions by the progressive breakdown of the chain associates too, can be reconciled with the findings made in the study of the molar polarization. It is true that the molar polarization maxima indicative of the formation of chain associations are not too sharp. Nevertheless, we may accept this interpretation, since the assumption of a chain association does not define the mutual spatial arrangement of the alcohol molecules coupled in the associate, though this may significantly affect the molar polarization increase due to chain formation. At any rate, it can be stated that the conclusions drawn from the results of the viscosity measurements are not in contradiction with the static dielectric properties.

Infrared spectroscopic studies

In this chapter we examine whether the infrared spectroscopic measurements can be brought into correlation with the previously developed physical picture. Since most of the published papers deal with solutions of alcohols in

carbon tetrachloride, with concentrations in the range $x_A = 0.0—0.4$ mole fraction, we studied the infrared spectrum of the 1-pentanol–*n*-hexane mixture over the entire concentration range (without a third component as solvent). A UR 2000 instrument was used, and recordings were made at 35 °C. Some of the most characteristic spectra are presented in Figs 7—11.

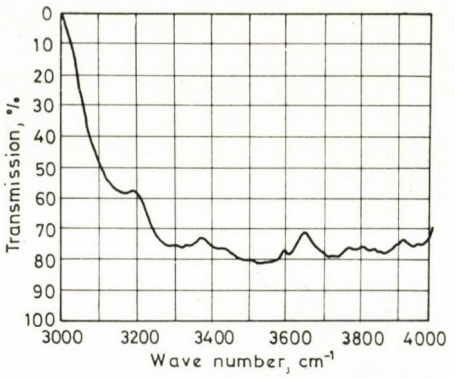

Fig. 7. Infrared spectrum. 1 mole% 1-pentanol, 99 mole% *n*-hexane. (Cell width: 0.16 mm)

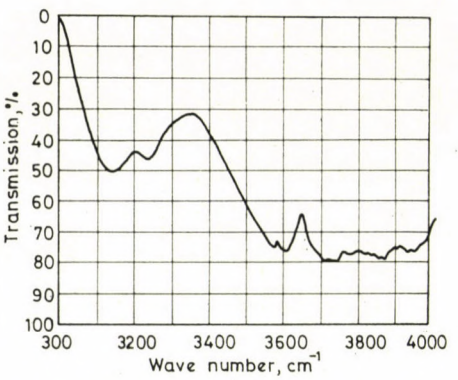

Fig. 8. Infrared spectrum. 4 mole% 1-pentanol, 86 mole% *n*-hexane. (Cell width: 0.028 mm)

Evaluation of the spectra led to the following findings:

1. In contrast with the phenomenon observed [19] in the investigation of alcohols dissolved in carbon tetrachloride, that the band of the monomer is well measurable at low alcohol mole fractions, with $x_A = 0.0—0.3$, in the mixtures examined here the monomer appears only at very high dilutions (ca. $x_A = 0.10$).

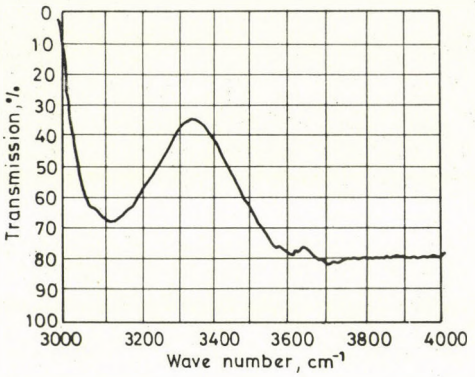

Fig. 9. Infrared spectrum. 10 mole% 1-pentanol, 90 mole% *n*-hexane. (Cell width: 0.028 mm)

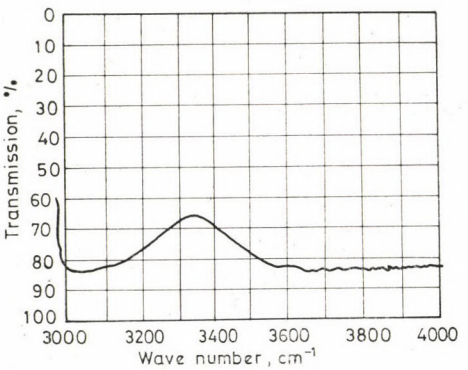

Fig. 10. Infrared spectrum. 50 mole% 1-pentanol, 50 mole% *n*-hexane. (Liquid film)

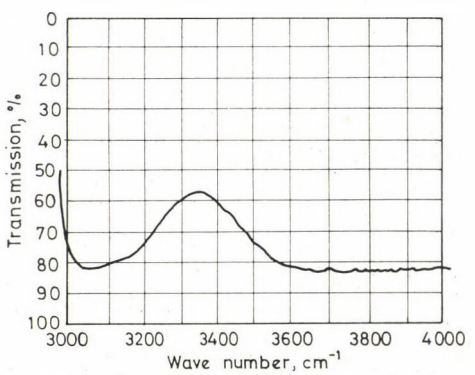

Fig. 11. Infrared spectrum of pure 1-pentanol. (Liquid film)

2. Four well-distinct absorptions are to be observed in the spectra. The OH group of the monomer gives a band at about 3650 cm^{-1}, the OH groups in the chain polymer one at 3500 cm^{-1}, the chain-terminal groups one at 3590 cm^{-1}, and the OH groups bonding in the ring one at 3350 cm^{-1} [20]; this band may include the bands of the cyclic and the chain-form dimers too. It is not considered probable that the OH groups in the inner members of the chains and in the larger cyclic associates are distinguishable, and accordingly only little information can be obtained on the nature of the association. The difficulties are increased by the fact that, since no solvent was employed, different cell sizes had to be used for practically every recording. Nevertheless, it can readily be seen that on proceeding along the concentration scale from pure alcohol towards pure hydrocarbon, the number of hydrogen-bonded OH groups first decreases without a significant change in the number of chain terminals. Later, the number of chain terminals increases ($x_A < 0.5$), and then the monomers too appear at a composition of about $x_A = 0.1$.

At concentrations $x_A < 0.04$ the band including the cyclic associates, cyclic dimers and chain-type dimers diminishes. There is a progressive increase in the relative amount of OH groups bound in chain polymers, chain terminals and monomers. At $x_A = 0.01$ we can observe the breakdown of the various associates, but it can also be stated that the band of the chain polymers is the last to disappear with the increase of the dilution.

This qualitative picture is in complete agreement with our earlier findings. It thus appears that for the clarification of the association conditions of alcohols a model must be created on the basis of the physical picture outlined above.

Study of the mixing heats

In our study of the heat of mixing (mixing enthalpy excess, H^E) of an alcohol–hydrocarbon mixture, we set out from the fact that the calorimetrically measured effect can be resolved into two components: the interaction between the hydrocarbon molecules and the carbon chain of the alcohol molecules, and the change in the number of hydrogen bonds between the alcohol molecules as a result of mixing. As the infrared spectroscopic data indicated that only few alcohol monomers are present in the concentration range $0.4 < x_A < 1.0$, their role was neglected in the investigation of the mixing heat.

The mixing heats of the systems in question were determined by the previously reported method [21], and are given in Fig. 12 and Tables IX–XIII, supplemented by the literature data [22] relating to the 1-pentanol–*n*-hexane and 1-hexanol–*n*-hexane systems.

It can be seen from the experimental data that the heat of mixing of the alcohol–hydrocarbon mixture is one order of magnitude larger than that of the

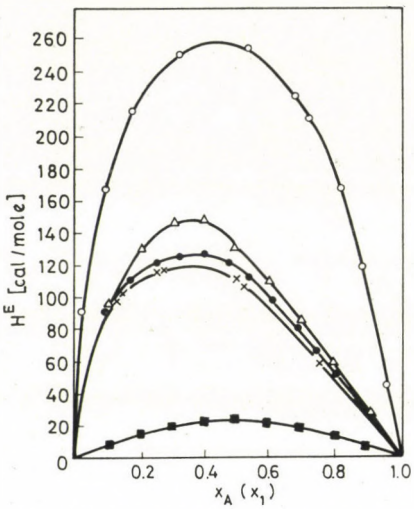

Fig. 12. Heats of mixing of the *n*-octane (1)–*n*-hexadecane (2) (■), the 1-heptanol (*A*)–*n*-hexadecane (*B*) (○), the 1-hexanol (*A*)–*n*-hexane (*B*) (×), the 1-hexanol (*A*)–*n*-nonane (*B*) (△), and the 1-pentanol (*A*)–*n*-hexane (●) systems as functions of the composition. ○, ▨ refer to 20 °C, and ×, △ and ● refer to 25 °C

Table IX

Heat of mixing of the 1-pentanol (A)–n-hexane (B) system as a function of the composition at 25 °C [25]

x_A	H^E (cal/mole)	$\frac{H^E}{x_A}$ (cal/mole)
0.09	90.0	1010.3
0.17	109.3	642.9
0.25	117.8	471.0
0.33	123.5	374.1
0.40	126.3	315.7
0.48	121.0	252.2
0.55	111.0	201.9
0.62	96.9	156.2
0.69	80.1	116.1
0.75	66.9	89.1
0.82	51.9	63.3
0.88	36.6	41.6

mixture of another hydrocarbon with the hydrocarbon having the same molecular weight as the alcohol. The magnitude of the heat of mixing in alcohol–hydrocarbon mixtures therefore depends primarily on the number of hydrogen bonds between the alcohol molecules. The cause of the strong endothermic

Table X

Heat of mixing of the n-octane (1)–n-hexadecane (2) system as a function of the composition at 20 °C

x_1	H^E (cal/mole)
0.1	8.0
0.2	13.5
0.3	19.5
0.4	22.5
0.5	23.0
0.6	21.5
0.7	19.0
0.8	13.0
0.9	8.5

Table XI

Heat of mixing of the 1-heptanol (A)–n-hexadecane (B) system as a function of the composition at 20 °C

x_A	H_A (cal/mole)	$\frac{H^E}{x_A}$ (cal/mole)
0.022	91.4	4150
0.092	167.0	1820
0.159	217.0	1360
0.316	251.0	794
0.540	259.0	479
0.667	226.0	339
0.713	212.0	307
0.811	164.0	202
0.880	120.0	136
0.952	44.4	46

effect is clearly to be sought in the fact that the hydrogen bonds in the alcohol are progressively broken as a result of the addition of the apolar component to the alcohol. The phenomenon may be interpreted qualitatively on the basis of the model of ideally associated systems [8]. In this model it is assumed that in the mixture the monomers and associates form an ideal mixture with each other, and the amounts of the various associates can be calculated in the entire concentration range with the aid of the association equilibrium constants given by the mole fractions. With different apolar components different heats of mixing may be observed, and the model cannot give an explanation for this

Table XII

Heat of mixing of the 1-hexanol (A)–n-hexane (B) system as a function of the composition at 25 °C

x_A	H^E (cal/mole)	$\frac{H^E}{x_A}$ (cal/mole)
0.1245	99.8	801
0.1371	102.7	749
0.2523	116.8	463
0.2686	118.0	439
0.5046	113.5	225
0.5216	108.5	208
0.7586	60.5	79

Table XIII

Heat of mixing of the 1-hexanol (A)–n-hexane (B) system as a function of the composition at 25 °C

x_A	H^E (cal/mole)	$\frac{H^E}{x_A}$ (cal/mole)
0.1	96.0	960
0.2	130.0	650
0.3	145.0	483
0.4	147.0	367
0.5	130.0	260
0.6	111.0	185
0.7	84.0	120
0.8	61.0	76
0.9	27.0	30

because of the assumption of an 'ideal' associative system: in this model the variation of the association equilibria as a function of the concentration is independent of the nature of the apolar component; thus, it is easy to see that the association conditions and their variations are much more complex than generally assumed. The concentration-dependence of the heat of mixing in alcohol–hydrocarbon mixtures is typified by the fact that the heat of solution of the alcohol (H^E/x_A) varies characteristically as a function of the mole fraction of the mixture; the resulting curve has more or less the same course in mixtures of the alcohol with any apolar component (Fig. 13).

It was shown by WÓYCICKA and RECKO [23] that the heat of solution of the alcohol gives an S-shaped curve in the alcohol mole fraction range 0—0.02; this falls only slightly in the infinite dilution range, much more rapidly

around an alcohol mole fraction of 0.005, and more slowly again at higher mole fractions. They found that in mixtures of a given alcohol with various paraffin homologues the values of the functions $H^E(x_A = f/x_A)$ practically agreed in the region of $x_A = 0$. In the case of 1-hexanol this value was 5590 ± 95 cal/mole, which is indicated in Fig. 13.

At alcohol mole fractions from 0.1 to 1.0 the heat of solution of the alcohol further decreases and generally gives a convex curve from below. The

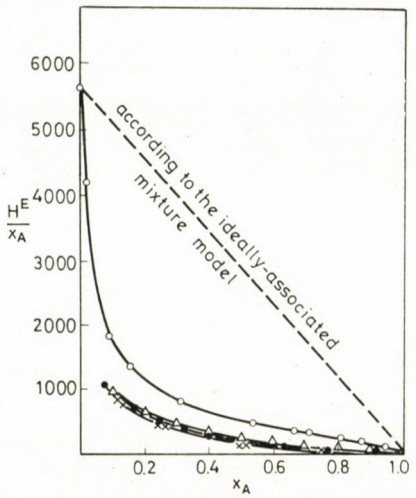

Fig. 13. The H^E/x_A *vs.* x_A curves for the 1-hexanol–*n*-hexadecane (○), the 1-hexanol–*n*-nonane (△), the 1-pentanol–*n*-hexane (●) and the 1-hexanol–*n*-hexane (×) systems

question to be considered here is whether these phenomena are in agreement with the results of the viscosity measurements, *i.e.* with the fact that in mixtures with hydrocarbons the average degree of association of the alcohol increases on proceeding from the pure alcohol to a mole fraction value of about 0.6.

In contrast with what was said on the actual change in the heat of solution, from the ideally-associated mixture model mentioned above a symmetric H^E *vs.* x_A relation is obtained about the equimolecular composition; from this, H^E/x_A is to a first approximation a linear function of the mole fraction. This can be seen in Fig. 13 [24].

Let us consider how the number of hydrogen bonds in the alcohols varies during dilution of the pure alcohol with hydrocarbon.

Let us take a nominally molar alcohol, and denote the number of moles of the alcohol monomer by n_1^0, and the number of moles of the various chain associations by m_1^0. All those alcohol molecules which are present not as monomer or in chain associates must form cyclic associates, in which every mole-

cule is associated with one hydrogen bond, independently of the degree of association. Thus, if the alcohol molecules were present only in cyclic associates, then 1 mole of pure alcohol would contain 1 mole of hydrogen bonds. The 'number of moles' of hydrogen bonds in the nominally molar pure alcohol (z) can be given as follows:

$$z = 1 - n_1^0 - \sum_{i=2}^{k} m_1^0 \tag{17}$$

where $i = 2, 3, \ldots, k$ is the number of molecules in the chain complexes. This relation utilizes the fact that each chain associate always contains one hydrogen bond less than the cyclic formation with the same degree of association.

Let us denote the numbers of monomers and chain complexes in one nominal mole of alcohol in the mixture by n_1 and m_1. Assuming that the enthalpies of formation of the various hydrogen bonds (ΔH) can be taken as the same, the following expression is then obtained for the molar heat of mixing:

$$\frac{H^E}{\Delta H} = x_A (z^0 - z) = x_A \left[n_1 - n_1^0 + \sum_{i=2}^{k} m_i - \sum_{i=2}^{k} m_i^0 \right], \tag{18}$$

where x_A is the nominal mole fraction of the alcohol in the mixture.

It can be seen that if there is a change (increase) in the quotient of either the monomers or the chain complexes to the given alcohol amount in the course of the mixing, then an endothermic heat of mixing is obtained.

Since it was found that the absorption band of the monomers appears on the infrared spectra only at high dilution, it must be assumed that, at least at mole fractions $x_A > 0.5$, the heat of mixing can be explained by the increase in the relative amount of the chain-like species. This conception is in agreement with the conclusions drawn from heat of mixing, infrared spectroscopic, static dielectric and viscosity measurements.

Summary

An effort was made to use not a model, but the experimental results, to draw conclusions on the association conditions of the alcohols studied, and their mixtures with normal paraffins. In our view the experimental results can be interpreted in that the pure alcohols are assumed to contain primarily cyclic complexes, the hydrogen of nearly every OH group being in a hydrogen bond. In the case of cyclic association the average degree of association is by no means as important as in the chain association, for independently of the number of monomers associated in the rings, each molecule is related with one hydrogen bond in such a system. In the case of the less highly associated dimers, trimers and tetramers it is conceivable that the hydrogen bonds formed on ring-closure differ significantly in energy from those involved in chain formation, but for larger complexes there can be no substantial difference between the enthalpy changes for the two types of association process. The fact that a degree of association of about 4 was found for alcohols in the pure state [9] shows that the formation of rings from the relatively few monomers is accompanied by the greatest free enthalpy decrease.

In our conception the addition of paraffin to pure alcohol causes some of the hydrogen bonds to break; the cyclic structure of the complexes is progressively lost, and the adjacent

alcohol molecules form a chain-type association complex. This process is accompanied by an endothermic heat change, and by the increase of the degree of association. If it is accepted as a fact that the average degree of association of the pure alcohol is about 4, and that it consists overwhelmingly of cyclic complexes, then it follows that splitting of the rings and coupling of the chains into units with higher degrees of polymerization may involve rupture of almost 1/4 of the hydrogen bonds. The viscosity measurement data permit the conclusion that in the mixtures examined this process takes place at concentrations close to a mole fraction of $x_A = 0.6$. If the mixture contains more hydrocarbon than this, the chain complexes dissociate to some extent. The average degree of association thus decreases, and the system becomes similar to those assumed in the model of ideally-associated $A_i - B$ type mixtures. The fact that it is the behaviour of just those mixtures which contain very little alcohol which cannot be described by this model shows that cyclic dimers may also be formed in this concentration range [26].

Overall, it appears that the different assumptions connected with the assciation conditions of the alcohols can be accepted only for individual well-defined systems and concentration ranges, and that the question is much too complex to be clarified on the basis of information acquired from a single investigation method. We feel that although our qualitative assumptions regarding the association conditions of the examined mixtures are not based on indisputable evidence, they are nevertheless closer to reality than the assumptions of most models, and can be maintained until contradicted by experimental facts.

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FLAVONOIDS, XXXI

SYNTHESIS OF FLAVAN-4α-OL AND THE ENANTIOMERS OF FLAVANONE*

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The hydrochlorides of optically active *cis*-4-aminoflavan were subjected to deamination with nitrous acid to obtain (+)- and (−)-flavan-4α-ol. Acetylation of the optical antipodes gave the corresponding optically active O-acetyl derivatives.

Both optically active enantiomers of flavanone have been prepared from the flavan-4α-ol enantiomers by oxidation with sodium dichromate.

In a previous paper we reported the resolution of racemic *cis*-4-aminoflavan, prepared by the reduction of flavanone oxime, by means of D-(+)-10-camphorsulfonic acid and dibenzoyl-D-(−)-tartaric acid [1]. Decomposition of the diastereomeric salt pairs yielded the hydrochlorides of the two enantiomeric 4-aminoflavans unknown up to that time, as well as the appropriate optically active free amines, and their N-acetyl and N-benzoyl derivatives.

The deamination process with nitrous acid described by us earlier [2] was applied to prepare (−)-flavan-4α-ol and (+)-flavan-4α-ol from the hydrochlorides of (+)-4-aminoflavan and (−)-4-aminoflavan, respectively. Acetylation of the optical antipodes yielded the corresponding optically active O-acetyl derivatives. Optically active (+)-flavan-4α-ol, and both acetates have been unknown so far. (−)-Flavan-4α-ol was obtained by UDUPA *et al.* [3] in 1968.

The enantiomeric flavan-4-ols comprising two asymmetric centres were treated with sodium dichromate to oxidize the C-4 hydroxyl group; this eliminated the C-4 centre of asymmetry. In this way (−)-flavanone and (+)-flavanone were obtained from (+)-flavan-4α-ol and (−)-flavan-4α-ol, respectively, in satisfactory yields; the physical constants of the products agreed with the literature data [4, 5].

The two enantiomeric flavanones were prepared first by KOTAKE and NAKAMINAMI [4] from racemic flavanone through the optically active 5-methyl-5-[α-methylphenethyl]-semioxamazone. Later, COREY and MITRA [5] accomplished the resolution of flavanone by separatory crystallization of the cyclic mercaptals formed with L-(+)-2,3-butanedithiol.

A stereochemical interpretation of the reactions may be summarized as follows. According to NMR investigations [1, 6], (±)-4-aminoflavan obtained

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by the reduction of flavanone oxime is the racemate of two enantiomers with *cis* configuration. After resolution the optical antipodes with 2*S*, 4*S* and 2*R*, 4*R* configuration were obtained. Deamination of the enantiomers with nitrous acid — involving inversion at the C-4 atom — gave two optically active flavan-4α-ols having *trans* configuration (2*S*, 4*R* and 2*R*, 4*S*), which was confirmed

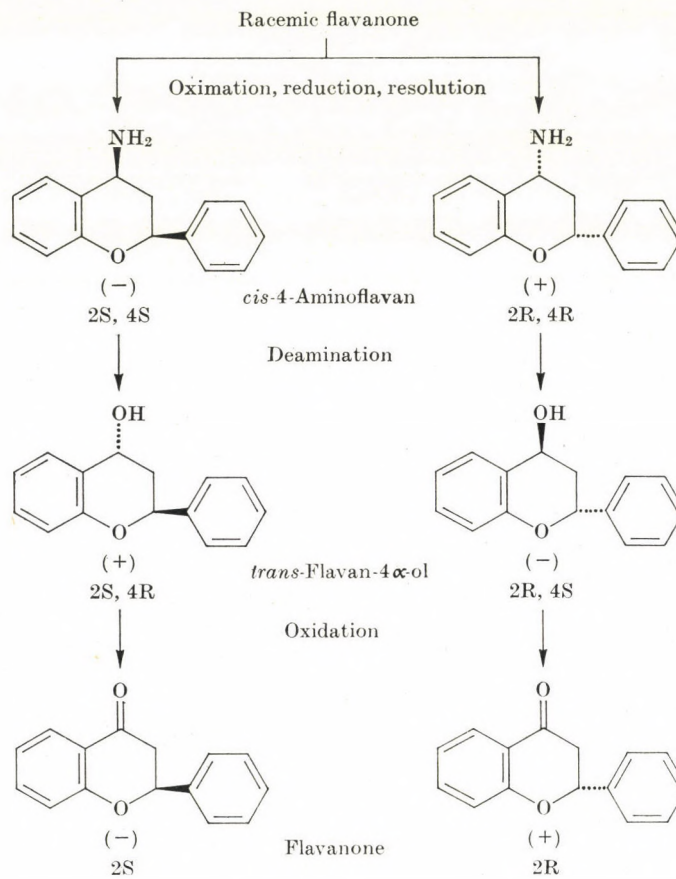

Fig. 1

unambiguously by the IR and NMR spectra [3, 6—12]. Oxidation of the C-4 atoms in the flavan-4α-ol enantiomers eliminated this asymmetric centre of the carbon atom, and the two optical antipodes of flavanone containing only one centre of asymmetry (2*R* and 2*S*) were obtained.

On the basis of investigations showing that natural flavanones isolated in optically active form up to now are all levorotatory compounds, and have identical, 2*S*, configuration at C-2 [7], it was assumed that (−)-flavanone prepared by us is the enantiostereomer of 2*S* configuration, while (+)-fla-

vanone has 2*R* configuration. This hypothesis has been verified by CD measurements [13]. Therefore, the absolute configurations of the optically active C-4-substituted flavan derivatives synthesized by us are given as shown in Fig. 1.

Experimental

(+)-flavan-4α-ol

Glacial acetic acid (20 ml) was added to a solution of sodium nitrite (4 g) in water (10 ml) under constant stirring. A solution of (−)-4-aminoflavan hydrochloride ($[\alpha]_D^{20}$ −26.5°, ethanol) (1.5 g) in a mixture of glacial acetic acid (50 ml) and water (50 ml) was added to the reaction mixture at room temperature during 45 min., with stirring. The mixture was stirred at room temperature for 30 min., then at 50 °C for 45 min. The cool solution was neutralized with solid sodium hydrogen carbonate (105 g). The product which separated was filtered off, washed with ice-cold water and crystallized from gasoline (50 ml). White, needle-shaped crystals were obtained (0.55 g; 42.6%), m. p. 127 °C; $[\alpha]_D^{20}$ +17° (c = 0.5, chloroform).

$C_{15}H_{14}O_2$ (226.26). Calcd. C 79.63; H 6.24. Found C 80.16; H 6.33%.

(−)-Flavan-4α-ol

The hydrochloride of (+)-4-aminoflavan ($[\alpha]_D^{20}$ +28.6°, ethanol) (1.5 g) was converted as described for (+)-flavan-4α-ol, into (−)-flavan-4α-ol (0.60 g; 46.5%), m. p. 126—127 °C; $[\alpha]_D^{20}$ −15° (c = 0.5, chloroform).

$C_{15}H_{14}O_2$ (226.26). Calcd. C 79.63; H 6.24. Found C 80.05; H 6.08%.

Literature data: m. p. 127 °C; $[\alpha]_D$ −27.3° [3].

(+)-4α-Acetoxyflavan

(+)-Flavan-4α-ol (0.3 g) was dissolved in absolute pyridine (1 ml) and acetylated with acetic anhydride (1 ml). After recrystallization from gasoline 0.2 g (57.0%) of the product was obtained, m. p. 86 °C; $[\alpha]_D^{20}$ +129° (c = 0.3, ethanol).

$C_{17}H_{16}O_3$ (268.30). Calcd. C 76.09; H 6.01. Found C 76.00; H 5.99%.

(−)-4α-Acetoxyflavan

(−)-Flavan-4α-ol (0.3 g) was converted in pyridine with acetic anhydride into 0.15 g of the product (42.8%); m. p. 85—86 °C; $[\alpha]_D^{20}$ −123° (c = 0.3, ethanol).

$C_{17}H_{16}O_3$ (268.30). Calcd. C 76.09; H 6.01. Found C 76.05; H 6.02%.

(+)-Flavanone

(−)-Flavan-4α-ol (0.4 g) was dissolved in ether (50 ml) and a solution of sodium dichromate (0.53 g) in a mixture of conc. sulfuric acid (0.3 ml) and water (1.5 ml) was added to it in small portions at 25 °C. After stirring the mixture for 2 hrs the ethereal phase was separated, washed with water and dried. After removing the ether by distillation, the crystalline residue was recrystallized from gasoline to yield 0.3 g (76.9%); m. p. 77 °C; $[\alpha]_D^{20}$ +67° (c = 0.35, chloroform).

Literature data: m. p. 76 °C; $[\alpha]_D$ +52° (c = 0.75, chloroform) [5].

(−)-Flavanone

(+)-Flavan-4α-ol (0.4 g) was converted in the above manner into (−)-flavanone (0.3 g; 76.9%), m. p. 76—77 °C, $[\alpha]_D^{20}$ −64° (c = 0.35, chloroform).

Literature data: m. p. 77—78 °C; $[\alpha]_D$ −53.5° (c = 2.27, chloroform) [5].

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REACTIONS OF 2,7- AND 2,8-DIMETHYLCHROMONES AND RELATED COMPOUNDS

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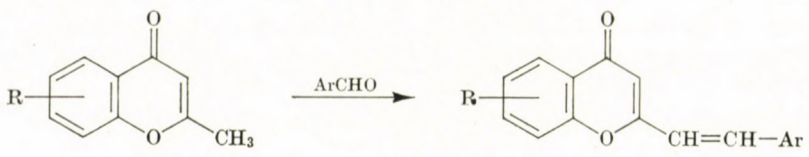
Several substituted chromones and β-aminocrotonylphenols have been prepared from 2,7- and 2,8-dimethylchromones and their 4-thio derivatives. Xanthone derivatives were obtained from the 2-stylrylchromones by Diels—Alder reaction with maleic anhydride. The methyl group in the 2-position in the chromone reacted with phthalic anhydride to give the phthalide. The action of hydrazines and hydroxylamine on th mentioned chromones was investigated.

The methyl group in the 2-position in 2,7- and 2,8-dimethylchromones (**Ia** and **Ib**) was condensed with aromatic aldehydes (benzaldehyde, anisaldehyde, *o*-chlorobenzaldehyde, *p*-nitrobenzaldehyde, *m*-nitrobenzaldehyde, 2,4-dimethoxybenzaldehyde, cinnamaldehyde and piperonal) to give the 2-styryl derivatives **IIa—o.**



I **II**

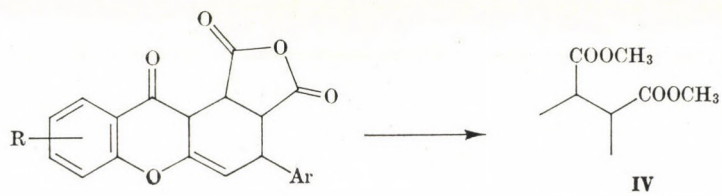
I	R	II	R	Ar
a	7-CH_3	**a**	7-CH_3	C_6H_5
b	8-CH_3	**b***	7-CH_3	$C_6H_4OCH_3$ *(p)*
		c	7-CH_3	C_6H_4Cl *(o)*
		d	7-CH_3	$C_6H_4NO_2$ *(p)*
		e	7-CH_3	$C_6H_4NO_2$ *(m)*
		f	7-CH_3	$C_6H_3(OCH_3)_2$ (2',4')
		g	7-CH_3	$CH=CHC_6H_5$
		h	7-CH_3	$C_6H_3O_2CH_2$ (piperonyl)
		i	8-CH_3	C_6H_5
		j	8-CH_3	$C_6H_4OCH_3$ *(p)*
		k	8-CH_3	C_6H_4Cl *(o)*
		l	8-CH_3	$C_6H_4NO_2$ *(p)*
		m	8-CH_3	$C_6H_4NO_2$ *(m)*
		n	8-CH_3	$C_6H_3(OCH_3)_2$ (2',4')
		o	8-CH_3	$C_6H_3O_2CH_2$ (piperonyl)

* A. Zaki and R. C. Azzam, J. Chem. Soc. **1943**, 434.

The purpose of using the different aldehydes was to investigate the effect of substituents in the aldehyde on the condensation reaction and on the yield. It was found that the condensations proceeded readily and almost independently of the substituents present either in the aldehyde or in the chromone [1—4]. Good yields of the styryl derivatives were generally obtained.

Alkaline hydrolysis of both the chromone **Ia** and the 2-styrylchromone **IIa** effected cleavage at the same position, to give *o*-hydroxy-*p*-toluic acid. This cleavage occurred with sodium hydroxide, but also with sodium carbonate.

The 2-styryl derivatives **IIa, b, i** and **j** react as dienes undergoing Diels—Alder reaction with maleic anhydride to yield the xanthone derivatives **IIIa—d**. Succinic anhydride, however, failed to add to 2-styrylchromones.



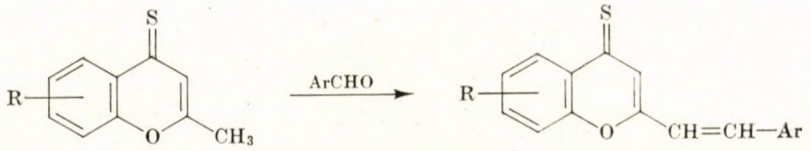
III IV

III	R	Ar
a	6-CH_3	C_6H_5
b	6-CH_3	$C_6H_4OCH_3$ *(p)*
c	5-CH_3	C_6H_5
d	5-CH_3	$C_6H_4OCH_3$ *(p)*

Structure **III** was based on IR measurements of **IIIb** whose spectrum had two bands at 1800 and 1790 cm^{-1} resulting from the asymmetrical and symmetrical stretching modes of $>C=O$, and on the similarity to other xanthone derivatives prepared by this method [2, 3, 5, 6]. Hydrolysis with methanolic sodium hydroxide of the anhydride **IIIc** gave the corresponding dicarboxylic acid which was difficult to isolate in pure crystalline form, therefore it was transformed to the dimethyl ester **IV**.

2,7- and 2,8-dimethyl-4-thiochromones (**Va** and **Vb**) were obtained by heating **Ia** and **Ib** with phosphorus pentasulfide in benzene. **Va** and **Vb** when condensed in the presence of piperidine [7] with benzaldehyde, anisaldehyde, *o*-hydroxybenzaldehyde and piperonal yielded **VIa—h** which are dark violet in colour. **VIa** was also made by heating **IIa** with phosphorus pentasulfide in benzene.

The action of hydrazine and phenylhydrazine on **Ia** and **Va** resulted in the same pyrazole derivatives **VIIa** and **VIIc**, respectively [3, 6, 8]. They yielded also the same isoxazole derivative **VIII** on reaction with hydroxylamine. **VIIa** and **VIII** were also synthesized by the action of hydrazines and hydroxylamine on the β-diketone **IXa**.



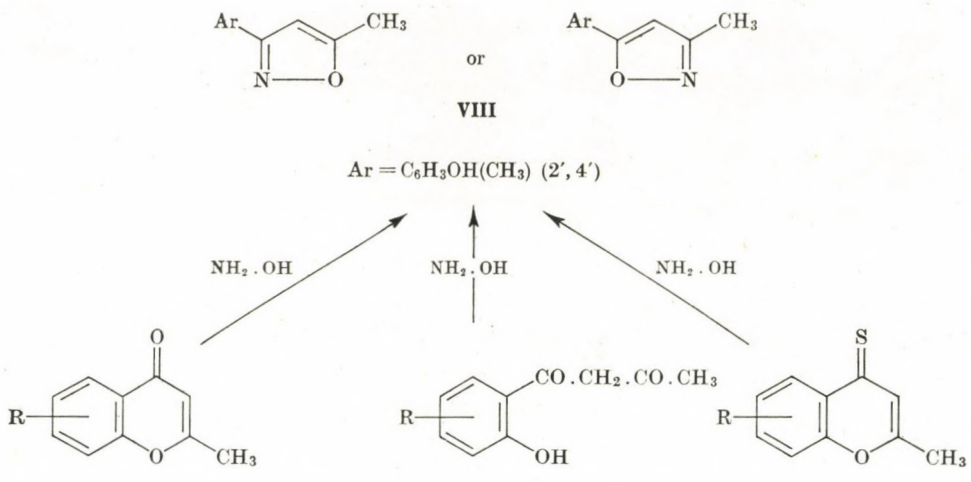
V **VI**

V	R	VI	R	Ar
a	7-CH_3	**a**	7-CH_3	C_6H_5
b	8-CH_3	**b**	7-CH_3	$C_6H_4OCH_3$ *(p)*
		c	7-CH_3	C_6H_4OH *(o)*
		d	7-CH_3	$C_6H_3O_2CH_2$ (piperonyl)
		e	8-CH_3	C_6H_5
		f	8-CH_3	$C_6H_4OCH_3$ *(p)*
		g	8-CH_3	C_6H_4CH *(o)*
		h	8-CH_3	$C_6H_3O_2CH_2$ (piperonyl)

Similarly, the action of hydrazines on **Ib** and **Vb** led to the pyrazole derivatives **VIIb** and **VIId** which can also be derived from the β-diketone **IXb**. The products **VII** and **VIII** dissolve in aqueous alkali and give colour reactions with ferric chloride (in cases **VIIa** and **VIb**) indicating the presence of a free phenolic hydroxyl group. They yielded mono- (*e.g.* in the case of **VIIb** and **VIII**) or di- (*e.g.* **VIIb**)-benzoyl derivatives. IR measurements of **VIIb** and **VIII**, taken as examples, showed the presence of a broad OH band with its centre at 3100 cm^{-1}. On the other hand, the IR spectra of the monobenzoyl derivative of **VIII** and the dibenzoyl derivative of **VIIb** had no OH peak. These facts support that the cleavage of the pyrone ring in chromone took place under the influence of the above-mentioned reagents with the formation of the isooxazole and pyrazole structures.

The heterocyclic oxygen ring in chromones opens when treated with primary amines to yield the enamine derivatives [9—13]. **Ia** and **Ib** reacted with primary alkylamines and gave the 2-alkylaminocrotonylphenols **Xa—h** which were found to be identical with the products obtained on reacting **IXa** and **IXb** with the same amines. The β-alkylamine derivatives give a deep green colour with ferric chloride and regenerate the chromone upon treatment with concentrated sulfuric acid or upon boiling with dilute hydrochloric acid. Refluxing an ethanolic solution of **Va** and **Vb** with butylamine and benzylamine, respectively, effected desulfurization and the formation of **Xc—f**.

Recently SAMMOUR *et al.* [6] have shown that 2-methyl-1,4-β-naphthopyrone reacts with phthalic anhydride and zinc chloride at elevated temperatures to give a phthalide derivative. We allowed **Ia** and **Ib** to react with phthalic anhydride under the same experimental conditions, but only a tarry material was obtained from which no pure product could be isolated. Other experiments

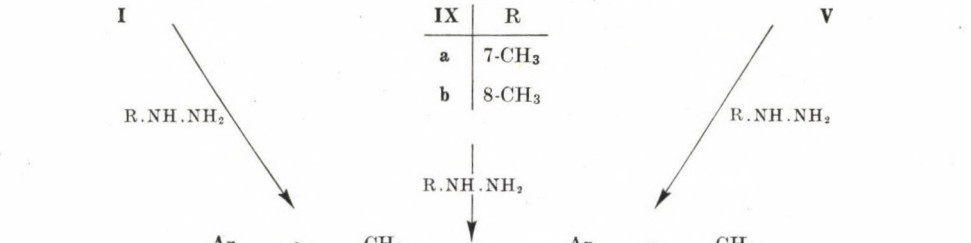


VIII

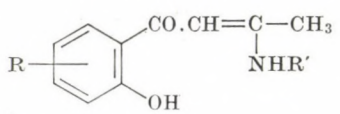
$Ar = C_6H_3OH(CH_3)$ (2', 4')

I **V**

IX	R
a	7-CH_3
b	8-CH_3



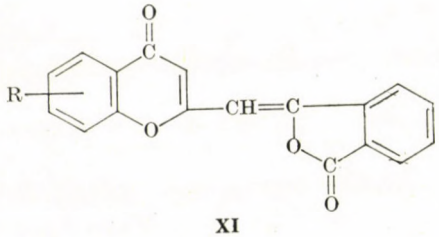
VII	R	Ar
a	H	$C_6H_3OH(CH_3)$ (2',4')
b	H	$C_6H_3OH(CH_3)$ (2',3')
c	C_6H_5	$C_6H_3OH(CH_3)$ (2',4')
d	C_6H_5	$C_6H_3OH(CH_3)$ (2',3')



X	R	R'
a	5-CH_3	C_2H_5
b	5-CH_3	C_2H_4OH
c	5-CH_3	*n*-C_4H_9
d	5-CH_3	$CH_2C_6H_5$
e	6-CH_3	*n*-C_4H_9
f	6-CH_3	$CH_2C_6H_5$
g	6-CH_3	C_2H_5
h	6-CH_3	C_2H_4OH

with zinc chloride at lower temperatures, or using boiling acetic anhydride-sodium acetate mixture as the dehydrating agent gave back unchanged material. However, when **Ia** and **Ib** were heated with fused sodium acetate at

240 °C, a reaction occurred and we were able to isolate the phthalide derivatives **XIa** and **b**, though in rather low yields. Attempts at improving the yield by prolonging the reaction period brought about insignificant change.



XI

XI	R
a	7-CH_3
b	8-CH_3

The structure of **XI** was established by formation of the original chromone **Ia** or **Ib** and N-phenylphthalimide upon heating with aniline at 180 °C; hydrolysis with aqueous sodium hydroxide when phthalic acid and *o*-hydroxytoluic acid (*m*-, and *p*-) were obtained [6]; and by the IR spectra which showed two well defined bands at 1780 and 1680 cm^{-1} attributable to lactonic and γ-pyrone C=O stretching vibrations, respectively.

Experimental

M. p.'s are uncorrected. The IR spectra were obtained with a Perkin-Elmer Infracord Spectrophotometer Model 137. The starting chromones were prepared according to the procedure given in the literature [14].

Condensation of 2,7- and 2,8-dimethylchromones (Ia and Ib) with aromatic aldehydes

The chromone **Ia** or **Ib** (1 mole) was dissolved in the minimum amount of absolute ethanol and treated at room temperature with an alcoholic solution of sodium ethoxide (1 mole). The aromatic aldehyde (1 mole) was then added to the solution, and the mixture was allowed to stand for 24 hrs at ordinary temperature. The yellow condensation product which usually separated was filtered off and purified by crystallization to give the 2-styryl derivatives **IIa—o** (*cf.* Table I). Dilution of the mother liquor with water gave an additional amount of the condensation product.

Hydrolysis of Ia and IIa

(a) With sodium hydroxide: A mixture of **Ia** or **IIa** (1 g), 20% sodium hydroxide (15 ml) and ethanol (30 ml) was refluxed for 4 hrs. The alcohol was evaporated and the solution acidified (H_2SO_4) to give 0.5 g (or 0.55 g) of *o*-hydroxy-*p*-toluic acid (m. p. and mixed m. p.).

IIa (1 g) using 2% sodium hydroxide and under the same conditions gave 0.5 g of *o*-hydroxy-*p*-toluic acid.

Table I

Condensation of 2,7- and 2,8-dimethylchromones with aromatic aldehydes

Compound	Yield, %	M. p., °C	Solvent of crystn.	Formula	Analysis					
					Carbon		Hydrogen		Nitrogen	
					Calcd.	Found	Calcd.	Found	Calcd.	Found
IIa	87	159.5—161	A	$C_{18}H_{14}O_2$	82.44	82.22	5.34	7.71		
c	90	163	B	$C_{18}H_{13}ClO_2$	72.86	73.17	4.38	4.72		
d	90	286	C	$C_{18}H_{13}NO_4$	70.37	69.74	4.23	4.64	4.56	4.65
e	93	214	C	$C_{18}H_{13}NO_4$	70.37	70.31	4.23	4.65	4.56	4.83
f	87	151	A	$C_{20}H_{18}O_4$	74.56	74.4	5.59	5.61		
g	54	156.5—158	D	$C_{20}H_{16}O_2$	83.23	82.78	5.55	5.72		
h	85	178	A	$C_{19}H_{14}O_4$	74.5	75.2	4.58	4.75		
i	80	145	E	$C_{18}H_{14}O_2$	82.44	82.66	5.34	5.69		
j	70	155—156.5	A	$C_{19}H_{16}O_3$	78.07	77.52	5.48	5.52		
k	90	221—222	B	$C_{18}H_{13}ClO_2$	72.85	72.32	4.38	4.66		
l	90	290	C	$C_{18}H_{13}NO_4$	70.37	70.77	4.23	4.81	4.56	4.51
m	91	219	C	$C_{18}H_{13}NO_4$	70.37	70.80	4.23	4.67	4.56	4.75
n	76	180	D	$C_{20}H_{18}O_4$	74.56	74.96	5.59	5.20		
o	85	198	F	$C_{19}H_{14}O_4$	74.5	74.33	4.58	4.89		

A, ethanol; B, benzene; C, acetic acid; D, methanol; E, aqueous ethanol; F, toluene

(b) With sodium carbonate: To a solution of **Ia** (0.5 g) in ethanol (35 ml) there was added a solution of sodium carbonate (1 g) in water (35 ml). The reaction mixture was refluxed for 6 hrs. The solution was concentrated, cooled and filtered to give 0.1 g of unchanged chromone; the filtrate upon acidification gave 0.15 g of *o*-hydroxy-*p*-toluic acid.

Using the same procedure, **IIa** (0.5 g) gave 0.3 g of unchanged starting material and 0.11 g of *o*-hydroxy-*p*-toluic acid.

Reaction of 2-styrylchromones (IIa, b, i and j) with maleic anhydride

A mixture of each of **IIa**, **b**, **i** and **j** (0.004 mole), maleic anhydride (0.04 mole) and dry xylene (30 ml) was refluxed for 15 hrs. Concentration of the solvent deposited the adducts **IIIa—d** (*cf.* Table II). Petroleum ether was added to the concentrate in portions and the oil formed was solidified by rubbing ethanol. Succinic anhydride did not react under the above conditions.

Methyl 3-phenyl-5-methyl-1,2,3,9a-tetrahydroxanthone-1,2-dicarboxylate (IV)

IIIc (0.8 g) in methanolic sodium hydroxide (1 g in 50 ml) was refluxed for 2 hrs. The reaction mixture was filtered while hot, cooled, and acidified with cold dilute hydrochloric acid to give 0.65 g of the dicarboxylic acid which was difficult to crystallize. The diacid was taken up in absolute methanol (15 ml) and dry hydrogen chloride was passed into the solution for 2 hrs. The mixture was allowed to stand overnight, concentrated, and the product which separated was crystallized from methanol to give 0.3 g of colourless crystals of **IV**, m. p. 175—176 °C.

$C_{24}H_{22}O_6$. Calcd. C 70.94; H 5.4. Found C 70.9; H 5.8%.

Table II

Reaction of 2-styrylchromones **IIa**, **b**, **i** *and* **j** *with maleic anhydride*

Compound	Yield, %	M. p., °C	Solvent of crystn.	Formula	Analysis			
					Carbon		Hydrogen	
					Calcd.	Found	Calcd.	Found
IIIa	40	260—262	A	$C_{22}H_{16}O_5$	73.33	73.07	4.66	4.91
b	40	248	B	$C_{23}H_{18}O_6$	70.76	70.30	4.61	4.70
c	35	263	C	$C_{22}H_{16}O_5$	73.33	73.70	4.66	4.70
d	35	232	A	$C_{23}H_{18}O_6$	70.76	70.60	4.61	4.60

A, xylene; B, benzene; C, toluene

2,7- and 2,8-Dimethyl-4-thiochromones (Va and Vb)

Va was obtained by refluxing a solution of **Ia** (0.83 g) in dry benzene (30 ml) with phosphorus pentasulfide (1 g) for 2 hrs. The reaction mixture was filtered while hot, the solvent was evaporated and the product crystallized from ethanol to obtain violet needles, m. p. 149—150 °C; yield 82%.

$C_{11}H_{10}OS$. Calcd. C 69.47; H 5.26; S 16.84. Found C 68.86; H 5.67; S 16.8%.

Similarly, **Ib** gave 80% of **Vb**, m. p. 133 °C (lit. m. p. 132 °C [15]).

Condensation of 2,7- and 2,8-dimethyl-4-thiochromones (Va and Vb) with aromatic aldehydes

A mixture of each of **Va** and **Vb** (0.006 mole) in absolute ethanol (20 ml) and an equimolecular amount of the appropriate aldehyde was treated with 4 drops of piperidine and refluxed for 6 hrs. The reaction product which separated upon cooling was crystallized from ethanol (or *n*-butanol in the cases of **VId** and **VIh**) to obtain violet needles of **VIa—h**. The results are given in Table III. Compound **VIa** was also synthesized in 70% yield by refluxing 2-styrylchromone (**IIa**) (1 g) with phosphorus pentasulfide (1 g) in dry benzene (30 ml) for 2 hrs.

Table III

Condensation of 2,7- and 2,8-dimethyl-4-thiochromones (**Va** *and* **Vb**) *with aromatic aldehydes*

Compound	Yield, %	M. p., °C	Formula	Analysis					
				Carbon		Hydrogen		Sulfur	
				Calcd.	Found	Calcd.	Found	Calcd.	Found
VIa	75	175	$C_{18}H_{14}OS$	77.71	77.96	5.01	5.41	11.52	11.60
b	70	148	$C_{19}H_{16}O_2S$	74.01	73.92	5.19	5.65	10.39	10.80
c	60	253	$C_{18}H_{14}O_2S$	73.47	73.33	4.76	4.80	10.88	11.00
d	60	202	$C_{19}H_{14}O_3S$					10.00	10.00
e	62	162	$C_{18}H_{14}OS$	77.71	78.22	5.01	4.50	11.52	11.50
f	63	183	$C_{19}H_{16}O_2S$	74.01	74.10	5.19	5.19	10.39	10.70
g	66	150	$C_{18}H_{14}O_2S$					10.88	10.60
h	60	217	$C_{19}H_{14}O_3S$	70.80	70.90	4.35	4.30	10.00	10.00

3-(or 5)-Aryl-5-(or 3)-methylpyrazole (VIIa and VIIb)

To a solution of each of **Ia** and **Ib** (1.25 g) in ethanol (15 ml) a solution of hydrazine hydrate (3.75 g) in warm ethanol (15 ml) was added. The reaction mixture was heated for 14 min, cooled, diluted with water and the solid which separated was crystallized from aqueous ethanol. The products were soluble in aqueous alkali and gave a deep green colour with aqueous $FeCl_3$ solution.

3-(or 5)-[4'-Methyl-2'-hydroxyphenyl]-5-(or 3)-methylpyrazole (VIIa)

This compound forms colourless crystals of m. p. 121—122 °C; yield 95%.
$C_{11}H_{12}N_2O$. Calcd. C 70.21; H 6.38; N 14.89. Found C 69.97; H 6.67; N 14.94%.

3-(or 5)-[3'-Methyl-2'-hydroxyphenyl]-5-(or 3)-methylpyrazole (VIIb)

This compound has the appearance of colourless crystals, m. p. 136 °C; yield 95%.
$C_{11}H_{12}N_2O$. Calcd. C 70.21; H 6.38; N 14.89. Found C 69.6; H 6.6; N 14.93%.
In the same manner compounds **VIIa** and **VIIb** were obtained in higher than 75% yield by the action of hydrazine hydrate on **Va** or **IXa** and **Vb** or **IXb**.

Benzoylation

Monobenzoyl derivative

A mixture of 0.8 g of **VIIb** in 10 ml pyridine and benzoyl chloride (0.65 g) was heated at 100 °C for 2 hrs. The cooled mixture was acidified with dilute hydrochloric acid and the solid which deposited was filtered off and crystallized from ethanol, m. p. 161 °C; yield 90%. The product was soluble in aqueous sodium hydroxide and gave a deep green colour with aqueous $FeCl_3$.
$C_{18}H_{16}N_2O_2$. Calcd. C 73.98; H. 5.48. Found C 74.27; H 5.54%.

Dibenzoyl derivatives

Benzoylation of **VIIb** (0.8 g) as described above using 1.16 g of benzoyl chloride, gave 91% yield of the dibenzoyl derivative which was crystallized from ethanol, m. p. 129—130 °C. The product was insoluble in aqueous sodium hydroxide and gave no colour with $FeCl_3$.
$C_{25}H_{20}N_2O_3$. Calcd. C 75.75; H 5.05; N 7.03. Found C 75.7; H 5.1; N 7.2%.

3-(or 5)-Aryl-5-(or 3)-methyl-1-phenylpyrazole (VIIc and VIId)

A mixture of each of **Ia** and **Ib** (1 g) in pyridine (10 ml) and phenylhydrazine hydrochloride (0.83 g) in water (3 ml) was refluxed for 4 hrs. The cooled mixture was acidified with dilute acetic acid and the product filtered off.

3-(or 5)-[4'-Methyl-p-hydroxyphenyl]-5-(or 3)-methyl-1-phenylpyrazole (VIIc)

This compound crystallized from aqueous ethanol, m. p. 188—189 °C; yield 90%.
$C_{17}H_{16}N_2O$. Calcd. C 77.27; H 6.09; N 10.6. Found C 77.15; H 6.17; N 10.72%.

3-(or 5)-[3'-Methyl-2'-hydroxyphenyl]-5-(or 3)-methyl-1-phenylpyrazole (VIId)

This product crystallized from petroleum ether (b. p. 60—80 °C), m. p. 134—135 °C; yield 90%.

$C_{17}H_{16}N_2O$. Calcd. C 77.27; H 6.08; N 10.6. Found C 77.02; H 6.16; N 10.56%.

Following the above procedure, compounds **VIIc** and **VIId** were also obtained in higher than 70% yield by the action of phenylhydrazine hydrochloride on **Va** or **IXa** and **Vb** or **IXb**

3-(4'-Methyl-2'-hydroxyphenyl)-5-methylisoxazole (VIII)

A mixture of **Ia** or **Va** or **IXa** (0.85 g) in pyridine (10 ml) and hydroxylamine hydrochloride (1.2 g) in water (5 ml) was refluxed for 4 hrs. The cooled mixture was acidified (AcOH) and the solid which deposited was filtered off and crystallized from benzene to obtain colourless needles of **VIII**, m. p. 206 °C; yields: 93%, 70% and 65%, respectively. The product was soluble in aqueous sodium hydroxide.

$C_{11}H_{11}NO_2$. Calcd. C 69.84; H 5.82; N 7.41. Found C 69.8; H 6.10; N 7.56%.

Benzoylation

To a solution of **VIII** (1 g) in 10% aqueous sodium hydroxide (25 ml), benzoyl chloride (1.25 g) was added. The mixture was vigorously shaken for 15 min. The solid which separated was collected and crystallized from aqueous ethanol or petroleum ether (b. p. 80—100 °C), m. p. 98 °C; yield 90%. The product was insoluble in aqueous sodium hydroxide.

$C_{18}H_{15}NO_3$. Calcd. C 73.7; H 5.5; N 5.0. Found C 73.79; H 5.26; N 4.97%.

Experiments with amines

(a) A solution of each of **Ia** and **Ib** (0.006 mole) in ethanol (8 ml) was treated with the appropriate amine (0.012 mole) and the mixture was kept at room temperature for 24 hrs. The product which separated was filtered off and crystallized from a proper solvent to obtain the yellow compounds **Xa—h** (*cf.* Table IV). They gave a deep green colour with $FeCl_3$.

(b) Compounds **Xa—h** were obtained directly in 85—90% yield by treating **IXa** and **IXb** (0.001 mole) with the corresponding amine (0.002 mole) in ethanol (1 ml), or in the absence of solvent at room temperature.

(c) Compounds **Xc—f** were prepared in 75—90% yield by refluxing a solution of **Va** and **Vb** (0.002 mole) with an excess of the corresponding amine in ethanol (3 ml) for 4 hrs.

Reaction of 2,7- and 2,8-dimethylchromones (Ia and Ib) with phthalic anhydride

A mixture of each of **Ia** and **Ib** (2 g), phthalic anhydride (2 g) and anhydrous sodium acetate (0.6 g) was heated at 240 °C for 15 min. After cooling, the reaction mixture was triturated with water and the product was crystallized from acetic acid to give 0.3 g brownish yellow crystals of **XI**. Evaporation of the mother liquor and heating the residue with boiling aqueous sodium carbonate for 5 min gave 1.5 g of unreacted **Ia** or **Ib**.

7-Methyl-2-phthalidenemethylenechromone (XIa) had m. p. 229—231 °C.
$C_{19}H_{12}O_4$. Calcd. C 74.99; H 3.94. Found C 75.50; H 4.30%.

8-Methyl-2-phthalidenemethylenechromone (XIb) had m. p. 290 °C.
$C_{19}H_{12}O_4$. Calcd. C 74.99; H 3.94. Found C 75.36; H 4.21%.

Table IV

Action of aliphatic amines on 2,7- and 2,8-dimethylchromone (**Ia** *and* **Ib**)

Compound	Yield, %	M. p., °C	Solvent of crystn.	Formula	Analysis					
					Carbon		Hydrogen		Nitrogen	
					Calcd.	Found	Calcd.	Found	Calcd.	Found
Xa	92	121	A	$C_{13}H_{17}NO_2$	71.24	70.92	7.76	8.08	6.39	6.40
b	93	98	B	$C_{13}H_{17}NO_3$	66.37	67.15	7.23	7.72	5.96	6.07
c	77	96—97	C	$C_{15}H_{21}NO_2$	72.88	73.64	8.50	8.64	5.67	5.38
d	90	129—130	A	$C_{18}H_{19}NO_2$	76.87	76.69	7.76	7.16	5.00	5.28
e	92	90	A	$C_{15}H_{21}NO_2$	72.88	73.50	8.50	8.60	5.67	5.40
f	81	126—127	A	$C_{18}H_{19}NO_2$	76.87	76.77	6.76	7.09	5.00	5.15
g	92	109	A	$C_{13}H_{17}NO_2$	71.24	71.40	7.76	8.18	6.39	6.32
h	96	103—104	B	$C_{13}H_{17}NO_3$	66.37	66.86	7.23	7.24	5.96	5.94

A, ethanol; B, benzene; C, petroleum ether (b.p. 60—80 °C)

Action of aqueous sodium hydroxide on the phthalides XIa and XIb

A mixture of **XIa** (0.3 g) and 10% aqueous sodium hydroxide (10 ml) was refluxed for 30 min. The reaction mixture was allowed to cool, acidified with dilute sulfuric acid and the product filtered off to give 0.1 g of *o*-hydroxy-*p*-toluic acid, m. p. 176 °C. Extraction of the filtrate with ether gave 0.1 g of phthalic acid.

Similarly, **XIb** gave *o*-hydroxy-*m*-toluic acid and phthalic acid.

Action of aniline on the phthalides XIa and XIb

A mixture of **XIa** (0.2 g) and an excess of aniline was heated at 180—190 °C for 15 min. After cooling, the reaction mixture was triturated with ether and the product was filtered off to obtain 0.1 g of N-phenylphthalimide (m. p. and mixed m. p.). Acidification of the mother liquor with dilute hydrochloric acid followed by extraction with ether gave 0.05 g of **Ia**.

Similarly, the reaction of **XIb** with aniline yielded 0.12 g of N-phenylphthalimide and 0.04 g of **Ib**.

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A NOVEL METHOD FOR THE PREPARATION OF 2,4-DIAMINO-5-(SUBSTITUTED BENZYL)-PYRIMIDINES

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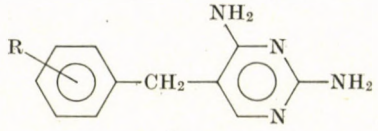
2,4-Diamino-5-(substituted benzyl)-pyrimidines (Trimethoprim, Diaveridine and Ormethoprim) were synthesized in the following way. A benzylcyanoacetic ester was prepared from ethyl cyanoacetate and an appropriately substituted benzyl chloride; this ester was cyclized with guanidine to give 2,4-diamino-5-(substituted benzyl)-6-oxo-5,6-dihydropyrimidine; the latter compound was transformed to the 6-chloro derivative which was in turn dehalogenated to the end-product.

Several 2,4-diamino-5-(substituted benzyl)-pyrimidines possess an outstanding sulfonamide potentiating effect. Well-known examples are the following:



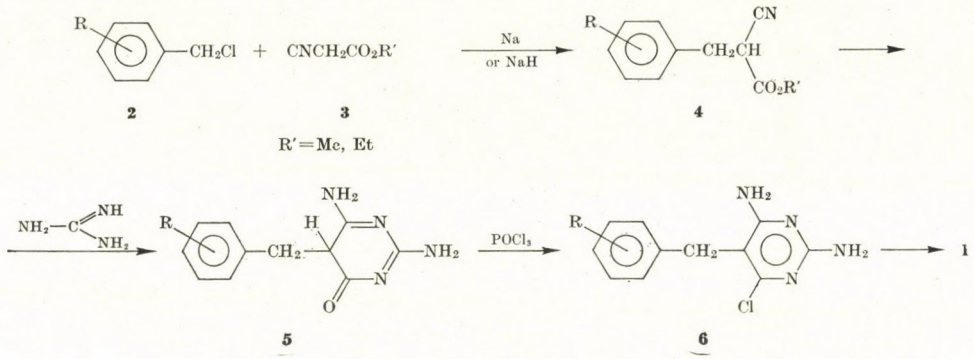
1

a	3,4-$(OMe)_2$ (Diaveridine)
b	3,4,5-$(OMe)_3$ (Trimethoprim)
c	2-Me-4,5-$(OMe)_2$ (Ormethoprim)
d	3-OMe-4,5-(OCH_2O)

Apart from some less significant procedures [1—4], the most useful method for the preparation of the above type of substance starts with a properly substituted benzaldehyde which is condensed with 3-ethoxypropionitrile to give 2-(substituted benzylidene)-3-ethoxypropionitrile. This is isomerized to the 2-(substituted benzyl)-3-ethoxyacrylonitrile and the latter condensed with guanidine to yield **1** [5].

According to an alternative route [6], the substituted benzaldehyde is condensed with cyanoacetaldehyde acetal, the so obtained 2-(substituted benzylidene)-2-cyanoacetaldehyde acetal hydrogenated and cyclized with guanidine to give **1**.

During our experiments, we aimed at a procedure for large-scale synthesis, requiring easily accessible starting materials. Favourable results were obtained by the following pathway [7]:



2 **3** **4**

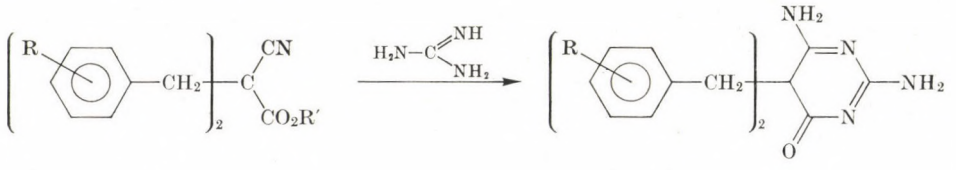
R′=Me, Et

5 **6**

A 2-(substituted benzyl)-cyanoacetic acid ester (**4**) was synthesized from a benzyl chloride (**2**) and alkyl cyanoacetate (**3**). Cyclization of **4** with guanidine resulted in 2,4-diamino-5-(substituted benzyl)-6-oxo-5,6-dihydropyrimidine (**5**); the oxo group in position 6 was then replaced by chlorine (**6**) and **1** was obtained by reductive elimination of the halogen.

To ensure a favourable yield of **4**, the suppression of dibenzylation is of prime necessity. In the course of the large-scale preparation of **4**, the reaction was carried out in an excess of **3** as solvent (the sodium salt of **3** was prepared with sodium or sodium hydride). The crude **4** so obtained could directly be used for subsequent cyclization. This latter reaction was accomplished with guanidine in the presence of sodium methoxide giving **5** in nearly quantitative yield. This step could be used for controlling the quality of crude **4** in the following manner.

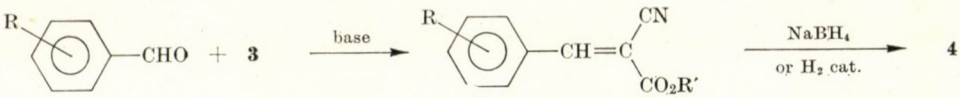
The 2,2-bis-(substituted benzyl)-cyanoacetic ester (**7**) that was present in crude **4**, also underwent cyclization with guanidine; the resulting **8**, however, was insoluble in aqueous alkali and could thus easily be separated from **5** which is readily soluble.



7 **8**

For the preparation of **6**, the chlorination of **5** with $POCl_3$ in the presence of dimethylaniline proved to be a satisfactory method. Reductive dehalogenation of **6** was accomplished by zinc powder in alkaline medium; this process, however, was strongly dependent on the quality of the metal. When the reduction was carried out in acetic acid, the result was independent of the quality of zinc, and the yield of **1** was nearly quantitative. The reduction could also be achieved catalytically.

The key intermediate (**4**) of the above route was also prepared by condensation with **3** of the substituted benzaldehyde (**9**) in the presence of a base (piperidine, sodium hydroxide, sodium alkoxide) and subsequent hydrogenation to **4** of the ylidene compound (**10**) obtained with sodium borohydride or catalytically [8].



9 **10**

Both latter reactions could be combined with the cyclization of **4** with guanidine, and thus **5** was prepared in a 'one-pot' synthesis, *i.e.* without separation of the intermediates.

Characteristic data of the products of the above reaction routes are summarized in Tables I to IV.

Table I

Esters of 2-(substituted benzyl)-cyanoacetic acids (**4**)*

Substance	M. p., °C	Formula
a	77—78	$C_{14}H_{17}NO_4$
b	57—58.5	$C_{15}H_{19}NO_5$
c	not isolated	$C_{15}H_{19}NO_4$
d	not isolated	$C_{14}H_{15}NO_5$

* Used subsequently as crude product

Table II

2,4-Diamino-5-(substituted benzyl)-6-oxo-5,6-dihydropyrimidines (**5**)

Substance	Method	M. p., °C	Yield, %	Formula
a	A	268—270	61.5	$C_{13}H_{16}N_4O_3$
	B		59.5	
b	A	278—281	78.8	$C_{14}H_{18}N_4O_4$
c	B	247—250	57.0	$C_{14}H_{18}N_4O_3$
d	B	245—248	52.0	$C_{13}H_{14}N_4O_4$

Method A: from crude **4** (by reaction of **2** with **3**)
Method B: from crude **4** (by reaction of **9** with **3**)

Table III

2,4-Diamino-5-(substituted benzyl)-6-chloropyrimidines (**6**)

Substance	M. p., °C	Yield, %	Formula
a	277—278	64.5	$C_{13}H_{15}ClN_4O_2$
b	218—221	61.0	$C_{14}H_{17}ClN_4O_3$
c	227—230	48.0	$C_{14}H_{17}ClN_4O_2$
d	300—304	83.0	$C_{13}H_{13}ClN_4O_2$

Table IV

2,4-Diamino-5-(substituted benzyl)-pyrimidines (**1**)

Substance	M. p., °C	Method	Yield, %	Formula
a	232—236	C	80.0	$C_{13}H_{16}N_4O_2$
		D	67.0	
b	200—202	C	89.0	$C_{14}H_{18}N_4O_3$
c	235—236	D	65.0	$C_{14}H_{18}N_4O_2$
d	236—237	D	63.0	$C_{13}H_{14}N_4O_2$ [10]

Method C: Zn/AcOH
Method D: H_2 on Pd/C in AcOH

The novel procedure is very useful for the large-scale preparation of substances of type **1**.

It should be noted that practically the same procedure was filed later by two companies for patent application [9].

Experimental

M. p.'s are uncorrected. The analyses were consistent with the structures of the products.

Preparation of esters of 2-(substituted benzyl)-cyanoacetic acids (4)

Method A: Sodium (0.442 kg; 19.25 atoms) was added to ethyl cyanoacetate (26 kg at a temperature below 35—40 °C with stirring, during 4 hrs. After complete dissolution, 3,4,5-trimethoxybenzyl chloride (2.08 kg; 9.6 moles) was added at 10 °C during 2—3 hrs, the mixture was stirred at room temperature for 18 hrs and then aqueous acetic acid solution (5%; 24 kg) was run in at 15—20 °C. After extraction with benzene (27, 12 and 12 l, successively), the organic layers were combined, washed with water (25 l), dried $MgSO_4$ and the benzene evaporated till attaining an internal temperature of 50 °C under reduced pressure. From the residue, ethyl cyanoacetate was completely removed at 1—2 torr and an internal temperature of 110 °C. The remaining crude product weighed 3.02 kg and could be used in the subsequent step without further purification.

Note: For obtaining an analytically pure sample of ethyl 2-(3',4',5'-trimethoxybenzyl) cyanoacetate, the crude product was recrystallized twice from aqueous ethanol; m. p. 57—58.5 °C.

Method B: A mixture of the substituted benzaldehyde **9** (1 mole), cyanoacetic ester (1.05 moles), ethanol (1 l) and piperidine (3 ml) was refluxed for 5 hrs. After cooling, the crystals were filtered off, washed with a little ethanol and the crude product (yield about 82%) was dissolved in ten volumes of ethanol and hydrogenated in the presence of Pd/C at atmospheric pressure and room temperature (about 2 hrs). After removal of the catalyst by filtration the solvent was evaporated under reduced pressure and the residual crude product was used in the subsequent cyclization.

Preparation of 2,4-diamino-5-(substituted benzyl)-6-oxo-5,6-dihydropyrimidines (5)

Sodium (0.995 kg; 43.3 atoms) was dissolved in methanol (10 kg), guanidine hydrochloride (2.75 kg; 28.8 moles) was added in portions with stirring, and the mixture was stirred and refluxed for 15 min. A solution of crude ethyl 2-(3',4',5'-trimethoxybenzyl)cyanoacetate (3.02 kg distillation residue of the preceding step, Method 'A', corresponding to 2.82 kg, *i.e.* 9.6 moles of product) in methanol (1.5 kg) was then added, and the mixture was refluxed and stirred for 14 hrs, then cooled to room temperature, filtered by suction and washed with methanol (3×1.5 l). The filtrate was evaporated under reduced pressure, the residue combined with the insoluble part, triturated thoroughly with water (20 l) and filtered. The precipitate was washed with 4% sodium hydroxide (2.5 l) and water (7 l). The filtrate was adjusted to pH 5.5—6 by acetic acid and allowed to stand overnight at 0 °C. The crystals were filtered off, washed with water and dried to give 2.32 kg (78.8% calculated for 3,4,5-trimethoxybenzyl chloride used in the preceding step, Method 'A') of 2,4-diamino-5-(3',4',5'-trimethoxybenzyl)-6-oxo-5,6-dihydropyrimidine, m. p. 278—284 °C, sintering at 276 °C, IR (KBr) νC=O 1695 cm^{-1}.

'One pot synthesis' for the preparation of 2,4-diamino-5-(2'-methyl-4',5'-dimethoxybenzyl)-6-oxo-5,6-dihydropyrimidine (5c)

A mixture of 2-methyl-4,5-dimethoxybenzaldehyde (24.0 g; 0.15 mole), ethyl cyanoacetate (17.0 g; 0.15 mole), methanol (250 ml) and sodium methoxide (2 g) was refluxed for 2.5 hrs; the mixture was cooled, methanol (200 ml) was added to it and it was hydrogenated in the presence of Pd/C at atmospheric pressure. After removal of the catalyst by filtration and evaporation of the ethanol, the residue was stirred and refluxed with an ethanolic guanidine solution (200 ml; 0.45 mole) for 10 hrs. After evaporation of the solvent, the residue was dissolved in hot water (200 ml) and the pH adjusted to 7 by acetic acid. The precipitate was filtered off, washed with water and dried to give 23.3 g (57.0%) of **5c**, m. p. 247—250 °C.

Preparation of 2,4-diamino-5-(substituted benzyl)-6-chloropyrimidines (6)

Dimethylaniline (1.275 kg; 10.52 moles) was added dropwise to a stirred mixture of 2,4-diamino-5-(3',4',5'-trimethoxybenzyl)-6-oxo-5,6-dihydropyrimidine (1.5 kg; 4.9 moles) and phosphorus oxychloride (12.7 kg; 83.1 moles), then the mixture was heated to boiling within 1 hr (internal temperature 105—108 °C) and refluxed for 4 hrs. The major part (50—60%) of the phosphorus oxychloride used was removed by distillation at 50—100 torr. The residue was cooled and poured cautiously onto crushed ice (60 kg), with stirring. The aqueous acidic mixture was let to stand at room temperature for 6 days and filtered. If the crystalline 2,4-diamino-5-(3',4',5'-trimethoxybenzyl)-6-chloropyrimidine hydrochloride did precipitate from the solution, this salt was used for liberation of the base; when no hydrochloride precipitated, the base was liberated directly from the filtrate. The process was carried out as follows: The crystalline hydrochloride or its solution was added portionwise to concentrated ammonium hydroxide solution (16.2 kg) below 20 °C and the mixture was allowed to stand 2—3 hrs at room temperature. The precipitate was filtered off, triturated with acetone (12 kg), filtered again, washed several times with water and dried to give 0.97 kg (61%) of 2,4-diamino-5-(3',4',5'-trimethoxybenzyl)-6-chloropyrimidine, m. p. 218—221 °C.

Preparation of 2,4-diamino-5-(substituted benzyl)-pyrimidines (1)

Method C: A mixture of 2,4-diamino-5-(3',4',5'-trimethoxybenzyl)-6-chloropyrimidine (1.62 kg; 5 moles), acetic acid (16.2 kg), water (1.62 l) and zinc powder (1.09 kg; 16.7 atoms)

was stirred and refluxed for 10 hrs, filtered while hot and the zinc precipitate washed with acetic acid containing 10% of water. The filtrate was run cautiously, with stirring and cooling below 20 °C, into concentrated ammonium hydroxide solution (40.5 kg) (pH 9). The precipitate was filtered off, washed with water and dried to give 1.292 kg (89%) of 2,4-diamino-5-(3',4',5'-trimethoxybenzyl)pyrimidine (Trimethoprim), m. p. 197—199 °C. An analytically pure sample, m. p. 200—202 °C, was obtained after recrystallization from ethanol containing 10% water.

Note: If the zinc powder is contaminated or not active enough, its amount should be increased to 1.43 kg and mercury(II) chloride (80 g) should be added to the reaction mixture (dissolved in the water used). The amount of the ammonium hydroxide may be increased to maintain the pH at 9.

Method D: A mixture of the chloro compound **6** (1 part) and 50% aqueous acetic acid (20 parts) was hydrogenated in the presence of Pd/C (10%; 0.15 part) at room temperature and atmospheric pressure. After the absorption of 1 mole of hydrogen the catalyst was filtered off, washed with hot 15% hydrochloric acid, and the filtrate was neutralized with conc. ammonium hydroxide. After cooling, the precipitate was filtered, washed with water and dried.

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A SIMPLE SYNTHESIS OF METHYL 9-OXO-*cis*-DEC-5-ENOATE, A USEFUL PROSTANOID INTERMEDIATE

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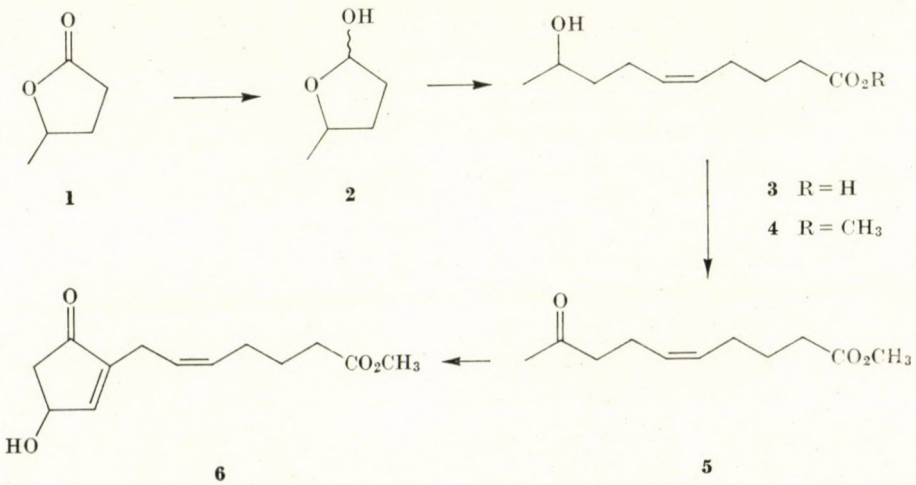
A simple synthetic route of the title compound as a useful prostanoid intermediate is described.

In a highly stereoselective synthesis [1] of E-prostaglandins the α-chain and the five-membered cycle is built up from the title compound *via* condensation with diethyl oxalate followed successively by partial and selective reduction and water elimination. Since addition of lithium dialkyl cuprates [2], $LiCuR_2$, upon the conjugated double bond affords directly the appropriate PG, the convenience of this synthetic route depends largely upon the availability of **5**. The synthesis of **5** by a multistep procedure has been reported in a preliminary communication by SIH *et al.* [1]. The method seems to require laborious steps which are further associated with comparatively low overall yield.

In this paper we describe a simple method for the preparation of **5** comprising only three steps, each of which can be carried out with high yield. The starting material and reagents are commercially available.



1 **2** **6** **5**

$Ph_3P{=}CH{-}(CH_2)_3{-}CO_2Na$

7

Reduction of γ-valerolactone (**1**) with diisobutylaluminium hydride afforded a diastereomeric mixture of the lactol **2**. Separation of the diastereomers can be readily achieved on silica gel plate (benzene–methanol), however, by virtue of the subsequent steps, preparative separation is unnecessary. Lactol **2** reacted smoothly with **7** in DMSO [3] to give, after esterification with diazomethane **4**. A one-pot preparation of **4** was carried out by allowing **2** to react with **7** prepared *in situ* from the corresponding phosphonium salt and sodium hydride dispersion in DMF and subsequent treatment with excess methyl iodide. Oxidation of the hydroxyl function either with Sarett or with Jones reagent led to **5** in practically quantitative yield and 59% overall yield based on γ-valerolactone. The unsaturated oxo-ester thus obtained was chromatographically homogeneous and could be used for the synthesis [1] of **6** without any further purification.

Experimental

γ-Valerolactol (2)

To a solution of diisobutylaluminium hydride (4.5 g; 31 mmoles) in dry toluene (20 ml) pre-cooled to -60 °C in argon atmosphere, γ-valerolactone (2 g; 20 mmoles) dissolved in dry toluene (10 ml) was added. The mixture was stirred and allowed to reach room temperature in 2 hrs, and was maintained at this temperature for additional 4 hrs. Excess reagent was decomposed by cautious addition of methanol (3.5 ml) and the gel formed was precipitated by ether–methanol (10 : 1, 110 ml). The insoluble material was filtered off and washed with methanol–ether (1 : 1, 120 ml). Evaporation of the solvent gave **2** as a clear liquid, yield: 1.66 g (80%).

IR (film): 3400 (OH), 1070 cm^{-1} (C—O). R_f: 0.65 and 0.45 (silica gel, benzene–methanol 9 : 1).

Methyl 9-hydroxy-*cis*-dec-5-enoate (4)

(A) 4-Carboxybutyltriphenylphosphonium bromide (1.772 g; 4 mmoles) dissolved in dry DMSO (10 ml) was treated dropwise under argon with a 1*N* solution of sodium methylsulfinylmethide in DMSO (8.2 ml). Addition of the reagent caused and instantaneous deep red coloration. After stirring for 20 min, the lactol **2** (366 mg; 3.58 mmoles) in dry DMSO (10 ml) was added, which led to the rapid decoloration of the ylid solution. After 2 hrs stirring most of the DMSO was removed in vacuum (0.1 torr, 35—40 °C) and the residue was diluted with water (60 ml). Triphenylphosphine oxide was filtered off and the mother liquor acidified to pH 2 with 1*N* hydrochloric acid, followed by extraction with ether–pentane (1 : 1, 2× 35 ml). Drying ($MgSO_4$) and evaporation of the solvent afforded **3** as a pale yellow oil, yield: 580 mg (78%).

IR (film): 3500—2300 (OH), 1720 (C=O), 720 cm^{-1} (C=C, *cis*).

The acid **3** was esterified with ethereal diazomethane in the usual manner to give **4**, yield: 600 mg (96%).

IR (film): 3400 (OH), 1730 cm^{-1} (C=O). R_f 0.19 (silica gel, benzene–methanol, 9 : 1).

$C_{11}H_{20}O_3$ (200.27). Calcd. C 65.96; H 10.06. Found C 66.30; H 10.54%.

(B) To a slurry of finely dispersed sodium hydride (4 mmoles) in dry DMF (10 ml) lactol **2** (3.58 mmoles) in DMF (5 ml) and 4-carboxybutyltriphenylphosphonium bromide (4 mmoles) in DMF (25 ml) were added simultaneously during 2 hrs, under argon. The mixture was stirred for 4 hrs at room temperature, treated with methyl iodide (2 ml), and allowed to stand for 36 hrs. Water (100 ml) was added and the product extracted with ether (3×30 ml), washed with water (4×10 ml) and dried ($MgSO_4$). Evaporation of the solvent afforded **4** (60%) which was identical with the compound prepared by method *(A)*.

Methyl 9-oxo-*cis*-dec-5-enoate (5)

To a solution of Sarett reagent [4] freshly prepared from chromic anhydrid (0.9 g; 9 mmoles) and pyridine (0.8 g; 9 mmoles) in methylene chloride (15 ml), **4** (300 mg; 1.5 mmoles) in methylene chloride (6 ml) was added (2 min.), with stirring. The reaction was complete in 15 min. Usual work-up afforded **5** as a faintly yellow oil, yield: 295 mg (99%).

IR (film): 1745 (C=O), 1715 (C=O), 722 cm^{-1} (C=C, *cis*).

$C_{11}H_{18}O_3$ (198.25). Calcd. C 66.64; H 9.15. Found C 66.28; H 9.52%.

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STUDIES ON 4-THIAZOLIDINONES, IV

STEREOCHEMISTRY AND REACTIONS OF 5-ARYLIDENE-4-THIAZOLIDINONES

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Condensation of 4-thiazolidinones with 5-bromovanillinal, 6-bromopiperonal and 6-bromoveratral gave isomeric mixtures of the 5-arylidene-4-thiazolidinones **1** and **2**, in a few of the examples studied. A tentative configurational assignment to these isomers is based on spectral data.

5-Arylidenerhodanines **1a—c** are converted to the corresponding 2-thiazolin-4-ones **3** on treatment with piperidine, morpholine, or pyrrolidine. 5-Arylidene-2-benzylimino-3-methyl-4-thiazolidinones **4a** and **b** are obtained on treating **1d** and **e**, respectively, with benzylamine.

Hydrazine reacts with 5-(6-bromo-3,4-dimethoxybenzylidene)-3-phenyl-2,4-thiazolidenedione **1k** to give 1-amino-3-phenyl-5β-(6-bromo-3,4-dimethoxyphenylethylideneamino) biuret **5**. The 3-unsubstituted derivatives **1g** and **h**, however, yield the corresponding triazinones **7**, with evolution of hydrogen sulfide gas. The route through which this latter transformation occurs is presented.

Although two geometrical isomers of 5-arylidene-4-thiazolidinones are theoretically possible, it seems that in none of the previously studied examples were two isomers isolated. In the present work it has been possible to isolate such isomers in a few of the newly studied examples.

Thus, 5-bromovanillinal condenses with rhodanine, 2,4-thiazolidinedione and 3-phenyl-2,4-thiazolidinedione, using the sodium acetate–acetic acid method [1] to give isomeric mixtures of **1** and **2c**, **1** and **2i**, and **1** and **2c**, respectively. Similarly, 6-bromoveratral condenses with 3-phenyl-2,4-thiazolidenedione to give an isomeric mixture of **1** and **2k**.

However, condensing 6-bromopiperonal with rhodanine, 3-methylrhodanine, and 2,4-thiazolidenedione gives **1a, d** and **g**, respectively. Similarly, 6-bromoveratral condenses with the above mentioned 4-thiazolidinones, in the order cited, to give **1b, e** and **h**, respectively. Also, 5-bromovanillinal condenses with 3-methylrhodanine to give **1f**.

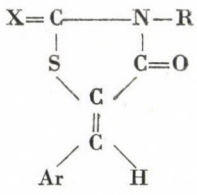
The structures of **1a—l** and **2c, i, k** and **l** are substantiated by analytical (Table I), as well as spectral data. Thus, the infrared spectra of the rhodanines **1a—f** and **2c** and the 2,4-thiazolidenediones **1g—l** and **2i, k** and **l** show one and two strong absorptions, characteristic of $\nu_{C=O}$ in the respective systems, respectively. Their electronic spectra are analogous to those previously reported for 5-arylidene-4-thiazolidinones [2]. Furthermore, the NMR spectra of **1** and **2c, i, k** and **l** support their structures. They show from low to high field

Table I

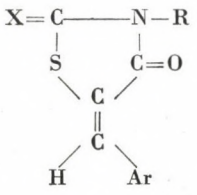
5-Arylidene-4-thiazolidinones **1** *and* **2**

Compound	M. p., °C	Yield, %	Formula	Analysis, Calcd. Found			
				C	H	N	S
1a	247—8*	87	$C_{11}H_6BrNO$	38.3 38.5	1.7 1.8	4.06 4.36	23.19[c] 23.10[c]
1b	266—7**	85	$C_{12}H_{10}BrNO_3S_2$	40.0 40.3	2.9 2.9	3.88 4.05	17.7 17.2
1c	273—4**	60	$C_{11}H_8BrNO_3S_2$	38.2 38.2	2.3 2.6	4.05 4.25	18.5 18.5
2c	240—2+	20	$C_{11}H_8BrNO_3S_2$	38.2 38.5	2.3 2.4	4.05 4.3	18.5 18.5
1d	220—2***	89	$C_{12}H_8BrNO_3S_2$	40.18 40.20	2.2 2.4	3.91 3.60	17.78 17.80
1e	201—3***	82	$C_{13}H_{12}BrNO_3S_2$	41.71 42.1	3.2 3.2	3.74 3.66	17.1 17.1
1f	218—20***	83	$C_{12}H_{10}BrNO_3S_2$	40.0 40.0	2.77 2.8	3.88 3.65	17.77 17.7
1g	244—6**	76	$C_{11}H_6BrNO_4S$	40.2 40.4	1.8 2.0	4.26 4.1	9.7 9.9
1h	266—7**	90	$C_{12}H_{10}BrNO_3S_2$	41.9 42.2	2.9 3.0	4.06 3.7	9.0 9.1
1i	230—1***	65	$C_{11}H_8BrNO_4S$	40.0 39.9	2.4 2.6	4.2 3.9	9.7 9.7
2i	245—8+	20	$C_{11}H_8BrNO_4S$	40.0 40.3	2.4 2.3	4.2 4.5	9.7 9.5
1j	175—7***	74	$C_{17}H_{10}BrNO_4S$	50.5 50.3	2.47 2.7	3.46 3.7	7.9 7.9
1k	176—8***	60	$C_{18}H_{14}BrNO_4S$	51.4 51.4	3.3 3.5	3.33 3.5	7.6 7.8
2k	229—30+	20	$C_{18}H_{14}BrNO_4S$	51.4 51.6	3.3 3.4	3.33 3.1	7.6 7.9
1l	193—5***	65	$C_{17}H_{12}BrNO_4S$	50.2 50.5	2.95 3.0	3.45 3.48	7.9 8.1
2l	200—201+	20	$C_{17}H_{12}BrNO_4S$	50.2 50.4	2.95 3.2	3.45 3.6	7.9 8.1

[c] Analysis for Br
\+ from ethanol
* from benzene
** from acetic anhydride
*** from glacial acetic acid



1 (Z)-isomer



2 (E)-isomer

	Ar	R	X
a	A	H	S
b	B	H	S
c	C	H	S
d	A	Me	S
e	B	Me	S
f	C	Me	S
g	A	H	O
h	B	H	O
i	C	H	O
j	A	Ph	O
k	B	Ph	O
l	C	Ph	O

A = 6-bromo-3,4-methylenedioxyphenyl
B = 6-bromo-3,4-dimethoxyphenyl
C = 5-bromo-4-hydroxy-3-methoxyphenyl

the signals characteristic of olefinic, aromatic and methoxyl protons. The disappearance of the signals characteristic of the phenolic protons in **1** and **2c, i** and **l** is attributed to intermolecular hydrogen bonding with the dimethyl sulfoxide solvent. This is consistent with the downfield shift observed for such interactions [3]. Data of these NMR spectra are listed in Table II.

The isomeric nature of **1** and **2c, i, k** and **l** is proved by the similarity of their NMR spectra (*cf.* Table II). Furthermore, **1** and **2** are easily converted to the corresponding 2-thiazolin-4-ones by treatment with secondary amines. This is taken as a further evidence for their rhodanine nature, since a similar conversion has been previously reported (Part II of this series [4]).

A tentative configurational assignment to **1** and **2** is based on some appreciable differences in their spectra. Thus the (Z)- and (E)-configurations* are assigned to **1** and **2**, respectively, since the olefinic proton signal of **1** appears at a relatively lower field as compared with those of **2**. This is attributed to the relatively stronger deshielding effect caused by a carbonyl group on a *β-cis* rather than a *β-trans* olefinic proton [5]. Further, the higher intensity observed in the electronic spectra of **1** as compared with **2** may be in favour of the above configurational assignment.

Refluxing the rhodanines **1a—c** and **2c** with piperidine, morpholine or pyrrolidine gives the corresponding 5-arylidene-2-piperidino-(**3a—c**), 5-arylidene-2-morpholino-(**3d—f**) and 5-arylidene-2-pyrrolidino-2-thiazolin-4-ones (**3g—i**), respectively, with the evolution of hydrogen sulfide gas. The route through which this transformation occurs was discussed in Part II [4].

Formation of the same thiazolinone on treating either **1c** or **2c** with secondary amines, infers the possibility of interconversion of these isomers.

* The nomenclature of *cis/trans* isomers used herein follows the IUPAC 1968 Tentative Rules, Section E, Fundamental stereochemistry, J. Org. Chem., **35**, 2894 (1970).

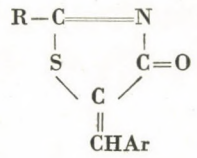
Table II

Spectral data of the 5-arylidene-4-thiazolidinones **1** *and* **2**

Compound	IR spectra, cm^{-1}			UV spectra, nm		NMR spectra (τ values)		
	νC=O	νNH	νOH	λ_{max}	ε_{max}	Olefinic proton	Aromatic protons	Methoxyl protons
1a	1700	3000	3200	405 283 266	25200 8156 10340	—	—	—
1b	1700	3000	3200	410 268	27870 10065	—	—	—
1c	1700	3262	3480	396 280 267	33227 8300 9220	2.5, 1H (s)	2.67, 1H (d) 2.75, 1H (d)	6.18, 3H (s)
2c	1710	3000 broad	3700	377 280 259	29690 7700 5865	2.55, 1H (s)	2.7 1H (d) 2.93, 1H (d)	6.13, 3H (s)
1d	1727	—	—	402 290 268	37000 12600 10500	—	—	—
1e	1725	—	—	407 290 268	37200 9200 10500	—	—	—
1f	1720	—	3460	398 287 264	36200 11600 11500	—	—	—
1g	1710, 1755	3280	—	367 ~310—25 255	16000 9040 8300	—	—	—
1h	1705, 1758	3140	—	271 258	21800 11200	—	—	—
1i	1690, 1745	3140	3600	360 258	22655 9040	2.23, 1H (s)	2.58, 1H (d) 2.7, 1H (d)	6.18, 3H (s)

2i	1700, 1755	2900 broad	3600	332 258	18035 7000	2.28, 1H (s)	2.62, 1H (d) 2.8, 1H (d)	6.12, 3H (s)
1j	1710, 1755	3280	—	364 ~310—25 256	13590 7655 10820	—	—	—
1k	1700, 1740	—	—	368 257	17800 12490	2.0, 1H (s)	2.4—3.2, 7H (m)	6.12, 6H (m)
2k	1700, 1745	—	—	367 256	20130 11710	2.05, 1H (s)	2.4—3.2, 7H (m)	6.15, 6H (m)
1l	1700, 1740	—	—	361 259	26200 11700	2.1, 1H (s)	2.25—2.8, 7H (m)	6.1 3H (s)
2l	1700, 1745	—	—	360 257	23900 11300	2.2, 1H (s)	2.35—2.9 7H (m)	6.1 3H (s)

(s) = singlet (d) = doublet (m) = multiplet ~ = inflection



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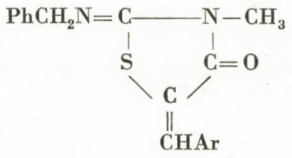


4

	Ar	R
a	A	piperidyl
b	B	piperidyl
c	C	piperidyl
d	A	morpholyl
e	B	morpholyl
f	C	morpholyl
g	A	pyrrolidyl
h	B	pyrrolidyl
i	C	pyrrolidyl

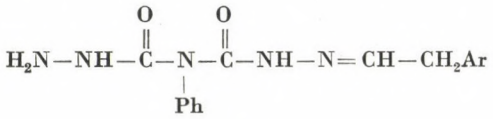
a: Ar = A
b: Ar = B

A = 6-bromo-3,4-methylenedioxyphenyl
B = 6-bromo-3,4-dimethoxyphenyl
C = 5-bromo-4-hydroxy-3-methoxyphenyl

However, the treatment of 5-arylidene-3-methylrhodanines **1d** and **e** with one mole of benzylamine gives 5-(6-bromo-3,4-methylenedioxybenzylidene)-(**4a**) and 5-(6-bromo-3,4-dimethoxybenzylidene)-2-benzylimino-3-methyl-4-thiazolidinone (**4b**), respectively, with the evolution of hydrogen sulfide.

Structures **4a** and **b** are substantiated by analytical and spectral data. The infrared spectra show the expected $\nu_{C=O}$ and $\nu_{C=N}$ bands (see Experimental). The appearance of two absorption maxima in the same regions as in the case of the starting rhodanines infers the presence of the same chromophoric systems in both groups of compounds, being consistent with the structures proposed.

It has been observed that substitution at the 3-position exerts a prominent effect on the mode of action of hydrazine on 5-arylidene-2,4-thiazolidenediones. Thus, treatment of 5-(6-bromo-3,4-dimethoxybenzylidene)-3-phenyl-2,4-thiazolidenedione **2k** with hydrazine gives 1-amino-3-phenyl-5β-(6-bromo-3,4-dimethoxyphenylethylideneamino)-biuret **5**, with the evolution of hydrogen sulfide. The route through which this transformation occurs has been reported in Part I [6].



5

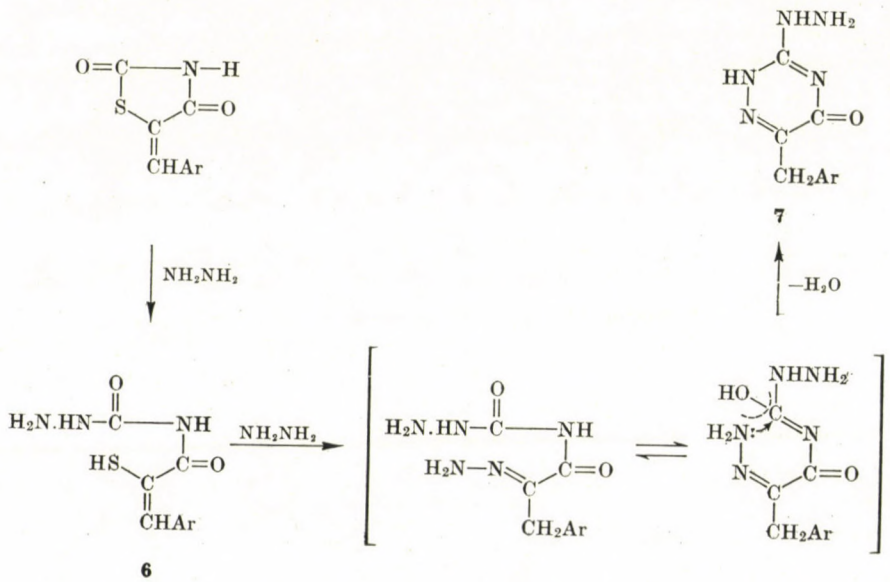
Ar = 6-bromo-3,4-dimethoxyphenyl

However, similar treatment of the 5-arylidene-2,4-thiazolidenediones **1g** and **h** gives 6-(6-bromo-3,4-methylenedioxybenzyl)- (**7a**) and 6-(6-bromo-3,4-dimethoxybenzyl)-3-hydrazinodihydro-1,2,4-triazin-5-one (**7b**), respectively, with the evolution of hydrogen sulfide.

The structure of **7b** is substantiated by analytical and spectral data. Thus the infrared spectrum (see Experimental) shows ν_{N-H} (primary and secondary amines) (**7a**), ν_{C-H} (CH_2 in- and out-of-phase streching) (**7b**) and $\nu_{C=O}$ (triazinone) [8] vibrations. The electronic spectrum has a medium intensity absorption at about 265 nm, which is far from a conjugated band and may be attributed to the heteroaromatic and auxochromically substituted benzenoid chromophores (see Experimental). The NMR spectrum (DMSO + D_2O) also supports the proposed structure. It has from low to high field the following absorptions: two singlets (aromatic protons), two doublets (benzyl protons) and two singlets (methoxyl protons) with the integrated proton areas of 1 : 1 : 1 : 1 : 3 : 3, respectively.

The structure of **7a** is substantiated by the analytical data and gains further support by its electronic spectrum which is analogous to that of **7b**.

The conversion of 5-arylidene-2,4-thiazolidenediones to the corresponding triazinones may be explained by the sequence of reactions represented in Scheme I.



a: Ar = 6-bromo-3,4-methylenedioxyphenyl
b: Ar = 6-bromo-3,4-dimethoxyphenyl

Scheme I

Although the 1,2-cleavage product **6** was not isolated in the present case, it was possible to isolate its analogue on treating 5-(6-bromo-3,4-methylenedioxybenzylidene)-2,4-thiazolidenedione with piperidine [9].

Formation of the cyclized triazinone **7b**, instead of the open-chain biuret derivative **5**, in the reaction with hydrazine of 5-(6-bromo-3,4-dimethoxybenzylidene)-2,4-thiazolidenedione **1h**, and its 3-phenyl-substituted analogue **1k**, may be explained by considering the different routes through which the 1,2-cleavage products react. It is suggested that there is a competition between two different routes. The first involves a nucleophilic attack at C-5, whereas the latter at C-4 (*cf.* Ref. [6]).

The first route is more favourable with the 3-unsubstituted 2,4-thiazolidenedione **1h**, while the latter one predominates with the 3-substituted analogue **1k**. This is based on the fact that a 3,4-tautomerization is possible only with the unsubstituted derivative **1h**. It is evident that this tautomerization retards the attack at C-4 and hence a condensation at C-5 is more favourable than cleavage at the 4,5-bond. 3,4-Tautomerizations in these systems have been reported previously by Girard and Dreux.

Experimental

M. p.'s are uncorrected. Infrared spectra were obtained with a Unicam SP 1200 spectrophotometer. Electronic spectra were recorded on a Unicam SP 8005 spectrophotometer in glacial acetic acid solutions. The NMR spectra were taken with a 90 MHz field locked Perkin-Elmer R32 spectrophotometer using DMSO as a solvent and TMS as internal reference.

Condensation of 4-thiazolidinones with 1a, b and c

Rhodanine, 3-methylrhodanine, 2,4-thiazolidenedione or 3-phenyl-2,4-thiazolidenedione (0.01 mole) was refluxed with each of 6-bromopiperonal, 6-bromoveratral and 5-bromovanillinal (0.01 mole) in glacial acetic acid using the method of CAMPAIGNE and CLINE [1].

The dried products were extracted several times with boiling alcohol and the insoluble fractions crystallized from a suitable solvent to give the (E)-5-arylidene-4-thiazolidinones **2c**, **i**, **k** and **l**.

Evaporation of the alcohol and fractional crystallization of the residual solids from methanol gave the (Z)-5-arylidene-4-thiazolidinones **1a—l**. The results are shown in Table I.

Action of cyclic secondary amines on 1a, b, c and on 2c

To a suspension of each of **1a**, **b**, **c** or **2c** (0.01 mole) in ethanol (50 ml), piperidine, morpholine or pyrrolidine (0.02 mole) was added and the mixture was refluxed until the evolution of hydrogen sulfide ceased. The reaction mixture was concentrated, treated with charcoal and allowed to stand overnight. The precipitated solid was filtered off and recrystallized from a suitable solvent to give the corresponding 2-piperidino- (**3a**, **c**), 2-morpholino- (**3d—f**), or 2-pyrrolidino-2-thiazolin-4-ones (**3g—i**), respectively. The results are shown in Table III.

Action of benzylamine on 5-arylidene-3-methylrhodanines (1d and e)

A mixture of each of **1d** or **e** (0.01 mole) and benzylamine (0.01 mole) was refluxed in ethanol (20 ml) on a boiling water bath for 15 hrs. The reaction mixture was treated with charcoal, concentrated and cooled. The dried products were recrystallized from ethanol to give the 2-benzylimino derivatives.

Table III

2-Thiazolin-4-ones **3a—i**

Compound	M. p., °C	Yield, %	Formula	Analysis, Calcd. Found			
				C	N	H	S
3a	199—201*	78	$C_{16}H_{15}BrN_2O_3S$	48.6 48.6	3.79 4.0	7.08 6.9	8.1 8.2
3b	218—20*	73	$C_{17}H_{19}BrN_2O_3S$	48.45 48.6	4.5 4.5	6.81 6.5	7.7 8.0
3c	226—7*	78	$C_{16}H_{17}BrN_2O_3S$	48.38 48.5	4.28 4.1	7.05 7.2	8.06 8.1
3d	262—4[c]	80	$C_{15}H_{13}BrN_2O_4S$	45.8 45.8	3.3 3.5	7.1 6.8	8.1 8.3
3e	233—5***	90	$C_{16}H_{17}BrN_2O_4S$	46.48 46.5	4.1 4.4	6.77 7.0	7.74 7.9
3f	253—5**	86	$C_{15}H_{15}BrN_2O_4S$	45.1 45.5	3.75 4.1	7.01 7.29	8.02 8.1
3g	242—4[c]	81	$C_{15}H_{13}BrN_2O_3S$	47.2 47.4	3.4 3.6	7.3 7.35	8.4 8.1
3h	221—3*	90	$C_{16}H_{17}BrN_2O_3S$	48.36 48.6	4.28 4.4	7.05 6.9	8.05 7.9
3i	228—30**	81	$C_{15}H_{15}BrN_2O_3S$	46.99 46.7	4.12 4.10	7.3 7.1	8.34 8.2

* from ethanol
[c] from acetic anhydride
** from glacial acetic acid
*** from n-butanol

5-(6-Bromo-3,4- methylenedioxybenzylidene) -2 - benzylimino-3-methyl -4- thiazolidinone (4a) (81%), m. p. 156—158 °C, ν_{C-H} (cm^{-1}) 2890, 2950, $\nu_{C=O}$ (cm^{-1}) 1720 and $\nu_{C=N}$ (cm^{-1}) 1675. λ_{max} (nm) (ε) 264 (18 000), 323 (9500) and 251.5 (9980).

$C_{19}H_{15}BrN_2O_3$. Calcd. C 54.9; H 3.61; Br 19.2. Found C 54.7; H 3.7; Br 18.7%.

5-(6-Bromo-3,4-dimethoxybenzylidene)-2-benzylimino-3-methyl-4-thiazolidinone (4b) (79%), m. p. 148—150 °C, ν_{C-H} (cm^{-1}) 2890, 2950, $\nu_{C=O}$ (cm^{-1}) 1645. λ_{max} (nm) (ε) 265 (20 800), ~325 (12 000) and 250 (13 000).

$C_{20}H_{19}BrN_2O_3$. Calcd. C 55.5; H 4.4; Br 18.5. Found C 55.2; H 4.5; Br 18.2%.

Action of hydrazine on 5-(6-bromo-3,4-dimethoxybenzylidene)-3-phenyl-2,4- -thiazolidenedione (1k)

A mixture of **1k** (0.003 mole) and hydrazine (0.009 mole) in ethanol was refluxed until hydrogen sulfide gas had ceased to evolve. The reaction mixture was concentrated and cooled. The precipitated solid was filtered off and recrystallized from ethanol to give 1-amino-3-phenyl-5β-(6-bromo-3,4-dimethoxyphenylethylideneamino)-biuret **5** (72%), m.p. 214—215 °C. ν_{N-H} (cm^{-1}) 3300, 3340, 3420, ν_{C-H} (cm^{-1}) 3205, 3180, $\nu_{C=O}$ (cm^{-1}) 1640. λ_{max} (nm) (ε) 267 (14 650).

$C_{18}H_{20}BrN_5O_4$. Calcd. C 47.9; H 4.65; N 15.55; Br 17.7. Found C 48.3; H 4.9; N 15.65; Br 17.5%.

Table IV

Spectral data of compounds **3a—i**

Compound	IR spectra, cm^{-1}		UV spectra, nm	
	$\nu C=O$	νOH	λ_{max}	ε_{max}
3a	1697	—	370 302 260	26386 18470 14512
3b	1690	—	372 307 260	25100 16100 14100
3c	1690	3000—3400*	365 262	30600 14800
3d	1690	—	372 305 259	23900 16240 13600
3e	1700	—	375 309 262	20100 13800 13400
3f	1685	3000—3400**	367 264	25200 12100
3g	1682	—	371 305 259	25850 11740 12200
3h	1685	—	370 305 259	26000 11740 12200
3i	1700	2800—3600*	374 269	27100 14200

* broad absorption
** weak and broad absorption

Action of hydrazine on 5-arylidene-2,4-thiazolidenediones (1g and h)

To a suspension of each of **1g** or **h** (0.001 mole) in *n*-butanol, hydrazine (0.001 mole) was added, and the whole mixture heated on a boiling water bath for 15 min. The crude product which separated after cooling was filtered off and recrystallized from ethanol to give the corresponding triazinones **7a** and **b**, respectively.

6-(6-Bromo-3,4-methylenedioxybenzyl)-3-hydrazinodihydro-1,2,4-triazin-5-one (7a) (80%), m. p. 183—184 °C (decomp.). ν_{N-H} (cm^{-1}) 3220, 3303, 3400, 3465, $\nu_{C=O}$ and $\nu_{C=N}$ (cm^{-1}) 1660 (broad). λ_{max} (nm) (ε) 262.5 (9480) and ~240 (3500).

$C_{11}H_{10}BrN_5O_3$. Calcd. C 38.8; H 2.8; N 20.58; Br 23.5. Found C 38.4; H 2.7; N 20.15; Br 23.3%.

6-(6-Bromo-3,4-dimethoxybenzyl)-3-hydrazinodihydro-1,2,4-triazin-4-one (7b) (90%), m. p. 187—188 °C (decomp.). ν_{N-H} (cm^{-1}) 3220, 3303, 3400, $\nu_{C=O}$ (cm^{-1}) 1680, and $\nu_{C=N}$ (cm^{-1}) 1660. λ_{max} (nm) (ε) 265 (9475) and ~240 (3540). τ (DMSO + D_2O) 2.72, 1H (singlet), 2.88, 1H (singlet) (aromatic protons); 5.83, 1H (doublet) and 5.95, 1H (doublet) ($-CH_2$ protons) and 6.28, 3H (singlet) and 6.35, 3H (singlet) (methoxyl protons).

$C_{12}H_{14}BrN_5O_3$. Calcd. C 40.44; H 3.93; N 19.66. Found C 40.1; H 4.0; N 19.2%.

*

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Исследование состава отечественных и иностранных эфирных масел, IV

К. БЕЛАФИ-РЕТИ, Э. КЕРЕНИ и Р. КОЛЬТА

Химический состав венгерского лавандового масла был определен с помощью ректификации и препаративной газовой хроматографии с дальнейшими ИК и ЯМР исследованиями. Среди 44 компонентов, разделенных с помощью газовой хроматографии, 27, составляющих суммарно 97,3%, удалось идентифицировать. Количества многих алифатических спиртов, терпеновых спиртов, различных эфиров жирных кислот, а также этиламилкетона отличались от количеств, сообщаемых в спецлитературе. Наряду с обычными компонентами, присутствующими в больших количествах, и в венгерском лавандовом масле были обнаружены борнеол, камфора и цинеол в весьма малых количествах. На основе полученных результатов удалось доказать также присутствие п-цимола и, вероятно, трициклена, аллооцимена и гексилизобутирата.

Исследование состава отечественных и иностранных летучих масел, V

Некоторые данные к составу лавандинового масла и эфирного масла мускатного шалфея

К. БЕЛАФИ-РЕТИ, Э. КЕРЕНИ и Р. КОЛЬТА

Качественный состав летучих масел гибрида лавандулы (**Lavandula hybrida**) и мускатного шалфея (**Salvia sclarea**) был получен на основе разделения компонентов с помощью препаративной газовой хроматографии с дальнейшей идентификацией их спектрометрическим путем, а количественный состав — с помощью аналитической газовой хроматографии. В лавандиновом масле было найдено всего 34 компонента (с содержанием $> 0{,}03\%$) и 29 основных компонентов (с содержанием $\geq 0{,}1\%$), среди которых 22 компонента удалось идентифицировать. В эфирном масле мускатного шалфея было найдено всего 24 компонента с содержанием, превышающим 0,03%, 22 компонента с содержанием выше 0,1%, среди которых 14 компонентов идентифицировали на основе непосредственных исследований.

Спектрофотометрическое исследование некоторых стирильных цианинных красителей

М. Р. МАХМУД, З. Х. ХАЛИЛ и Р. М. ИССА

Были исследованы УФ и видимые спектры поглощения некоторых 2-стирилпиридинов и хинальдин этиодидов. Наблюдаемые полосы поглощения были отнесены к некоторым электронным переходам. Обсуждается влияние заместителей на положение и интенсивность полосы. Были определены и обсуждаются величины pK для некоторых соединений.

Изучение силового поля некоторых молекул и ионов типа XY_3

К. РАМАСВАМИ и С. КАРУНАНИТИ

Было проведено изучение молекулярного силового поля некоторых плоских молекул и ионов типа XY_3, используя параметрический метод Рединтона и Алжибури, а также некоторые дополнительные параметры, такие, как константы связи Кориолиса и средние амплитуды колебаний. Были рассчитаны и приводятся константы вращательных искажений.

Исследование ассоциации неразветвленных первичных спиртов в присутствии нормальных парафиновых углеводородов

Т. ШАЛАМОН, Й. ЛИСИ и Ф. РАТКОВИЧ

Ассоциация 1-пентанола, 1-гексанола и 1-гептанола была исследована в их смесях с норм. парафиновыми углеводородами.

Измерения вязкости указывают на то, что степень ассоциации спиртов увеличивается по мере разбавления чистого спирта до 0,6 молярной доли. Это явление объяснялось на основе диссоциации циклических ассоциированных частиц, присутствующих в чистом спирте. Полагается, что линейные полимеры, образующиеся в данном процессе, дают более длинные цепнообразные частицы, приводящие к увеличению степени ассоциации. Эта гипотеза находится в согласии с предыдущими результатами, полученными как на основе диэлектрических и ИК спектроскопических исследований, так и на основе калориметрических данных теплоты смещения.

Флаваноиды, XXXI

Синтез энантиомеров флаван-4α-ола и флаванона

М. РАКОШИ, А. Л. ТЕКЕШ и Р. БОГНАР

Из солянокислых солей оптически активного цис-4-аминофлавана с помощью азотистокислого дезаминирования были получены (+)- и (—)-флаван-4α-олы. Ацетилирование оптических антиподов приводит к образованию соответствующих оптически активных О-ацетильных производных.

Окисление бихроматом натрия энантиостереомеров флаван-4α-ола дает два оптически активных энантиомера флаванона.

Реакции 2,7- и 2,8-диметилхромонов и родственных им соединений

А. А. САЙЕД, С. М. САМИ А. ЛАБИБ и С. С. ИБРАХИМ

Некоторые замещенные хромоны и β-аминокротонилфенолы были синтезированы из 2,7- и 2,8-диметилхромонов и их 4-тиопроизводных. Производные ксантона были получены из 2-стирилхромонов за счет реакции Дильс-Альдера с малеиновым ангидридом. Метильная группа в положении 2 хромона реагирует с фталевым ангидридом, давая при этом фталид. Было исследовано действие гидразинов и гидроксиламина на вышеупомянутые хромоны.

Новый метод получения 2,4-диамино-5-(замещенный бензил)-пиримидинов

Г. СИЛАДИ и Е. КАСТРЕЙНЕР

2,4-Диамины-5-(замещенный бензил)-пиримидины (Триметоприм, Диаверидин и Орметоприм) были синтезированы следующим путем. Бензилцианоуксусный эфир был приготовлен из этилцианоацетата и соответственно замещенного бензилхлорида; этот эфир был циклизирован с гуанидином, давая 2,4-диамино-5-(замещениый бензил)-6-оксо-5,6-дигидропиримидин; последнее соединение было превращено в его 6-хлорзамещенное производное, которое, в свою очередь, было дегалогенизировано до конечного продукта.

Простой синтез метил-9-оксо-цис-дек-5-эноата — важного промежуточного продукта простаноида

Л. ГРУБЕР, Э. МАЙОР и И. ТЁМЁШКЁЗИ

Был описан простой синтез заглавного соединения, являющегося важным промежуточным продуктом простаноида.

Исследование 4-тиазолидинонов, IV

Стереохимия и реакции 5-арилиден-4-тиазолидинонов

А. Р. А. РАУФ, М. Т. ОМАР и М. М. ЭЛЬ-АТАЛЬ

Конденсация 4-тиазолидинонов с 5-бромованилиналем, 6-бромоипероналем и 6-бромовератралем дает смесь изомеров 5-арилиден -4-тиазолидинонов 1 и 2 лишь в некоторых исследованных случаях. Вероятные конфигурационные ассигнации этих изомеров основаны на спектральных данных.

5-Арилиден роданиды (1a—c) были превращены в соответствующие 2-тиазолин-4-оны (3) при обработке их пиперидином, морфолином или пирролидином. При обработке 1e и 1f бензиламином были получены 5-арилиден-2-бензилимино-3-метил-4-тиазолидиноны 4a и 4b, соответственно.

Гидразин реагирует с 5-(6-бромо-3,4-диметоксифенил)-3-фенил-2,4-тиазолидендионом (1к), давая при этом 1-амино-3-фенил-5-β-(6-бромо-3,4-диметоксифенил-этилендиамино) биурет (5). 3-Незамещенные производные 1g и 1h, однако, дают соответствующие триазиноны 7 с выделением газообразного сероводорода. Описывается реакционный путь, по которому протекают эти превращения.

Organo-Phosphorchemie

Stand und Entwicklung

Von Prof. Dr. KURT ISSLEIB, Halle/S.

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KINETIC ANALYSIS OF TG CURVE

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After briefly reviewing the theoretical possibilities as well as the experimental difficulties of getting meaningful kinetic parameters on the basis of TG curves, trends of the effects of the experimental conditions on the shape of the TG curve are discussed. TG data are presented on the thermal dehydration reaction of calcium oxalate monohydrate obtained with samples of ~1 mg in air and vacuum. Results taken by different microbalances are compared and reasonable suggestions for minimizing the influence of the experimental conditions are outlined.

The dynamic thermal methods are often used to study the kinetics and mechanism of solid state reactions. The kinetics of thermal decomposition of solid state materials is a highly complex and frequently controversial subject.

Two of the major difficulties are:

a) all procedures of deriving kinetic parameters from thermal curves obtained under non-isothermal conditions are based upon a series of hypotheses which are not theoretically justified;

b) the experimental conditions greatly influence the shape of the thermal curves and consequently the values of the kinetic parameters calculated from them.

Thermal methods of analysis consist in measuring the changes in some physical properties of the sample. The measurement of weight is preferred due to ist high sensitivity and accuracy. The present paper concerns the analysis of thermogravimetric (TG) curve.

The reaction rate is generally defined as the derivative of conversion with respect to time. Conversion means the ratio of the actual weight loss to the total weight loss corresponding to a given stage of the reaction

$$\alpha = \frac{W_0 - W}{W_0 - W_f} \tag{1}$$

where W, W_0 and W_f stand for the actual, initial and final weight of the sample, respectively. In this case the reaction rate is presumed to be solely a function of the conversion and temperature.

It can be expressed by the following equations

$$\frac{d\alpha}{dt} = k(T) \cdot f(\alpha)$$

The conversion function $f(\alpha)$ is presumed to be of the following form

$$f(\alpha) = \alpha^a(1 - \alpha)^n \tag{3}$$

Supposing that the value of homogeneity factor a is zero, we have a formal analogy with homogeneous reactions.

In this case n can be called the apparent reaction order and the function $k(T)$ can formally be the specific rate constant. Under non-isothermal conditions k cannot remain constant. The Arrhenius equation expresses the temperature dependence of k as follows

$$k = A \cdot e^{-\frac{E}{RT}}$$

where A is the preexponential term and E is the apparent activation energy.

Taking into account the neglections indicated above, and assuming that the temperature increases linearly, after some mathematical substitutions the following equation can be derived for reactions proceeding under non-isothermal conditions

$$g(\alpha) = \int_0^{\alpha} \frac{d\alpha}{f(\alpha)} = \frac{A \cdot E}{R \cdot q} \int_x^{\infty} \frac{e^{-x}}{x^2} dx \tag{5}$$

where f and g are symbols of function, q is the heating rate, R is the universal gas constant and $x = \dfrac{E}{RT_\alpha}$

The right-hand side of Eq. (5) is called $p(x)$ function which cannot be integrated in finite form. This is the reason why a number of methods have been suggested to approximate this function; mentioning only the most important integral [1, 2], difference-differential [3], approximation [4] one-curve and many curves-methods.

The integral $p(x)$ can be resolved in finite form in case where a hyperbolic temperature program is used [5, 6] as follows

$$g(\alpha) = \int_0^{\alpha} \frac{d\alpha}{f(\alpha)} = -\frac{A}{b} \int_{\infty}^{1/T} e^{-\frac{E}{RT}} d\left(\frac{1}{T}\right) = \frac{A \cdot R}{b \cdot E} e^{-\frac{E}{RT}} \tag{6}$$

where b is a constant which depends upon the experimental conditions.

$f(\alpha)$ is a certain function of the weight. The different forms of this function represent the hypothetical models of the reaction mechanism. In practice, the best fitting rate-controlling process is estimated on the basis of the value of α obtained from the individual TG curves.

During the past few years considerable effort has been devoted to study the nature of the individual TG curves, using extremely different experimental

conditions and three types of instruments; the 'Derivatograph' produced by the Hungarian Optical Works, the Sartorius 'Thermogravimat' and the Mettler 'Thermoanalyser'. It is known that the last two ones can be used as microbalances under vacuum. Moreover, the 'Thermogravimat' is operating under presetting pressure program.

Our aim was to study the effect of experimental conditions, including the former mentioned instruments as well, on the shape of the TG curves and on the values of kinetic parameters, or rather to determine such conditions where these effects can be minimized.

On the basis of our results taken by the Derivatograph [7, 8] it can be stated that the experimental conditions (sample size, heating rate, particle size and atmosphere) influence the shape of the TG curve to a great extent. however, the smaller the sample size, the narrover is the temperature interval $(T_f - T_i)$ of the decomposition and the slope of the curve decreases with increasing sample size. The effect of heating rate is in accordance with the former statement. It can be established that the smaller the particle size, the narrower the temperature interval where the reaction proceeds. Talking about the influence of atmosphere, it can be observed that the higher is the partial pressure of the gases decomposed in the surroundings of the sample, the smaller is the $(T_f - T_i)$ range [9].

The value of kinetic parameters was calculated by Zsakó's integral method, using a DSC-3300 computer [10].

It can be observed that the values of apparent activation energy decrease with an increase in sample size and heating rate. The values of the apparent reaction order are rather varied in accordance with the different slopes of TG curves.

The dependence of the value of the activation energy upon the sample size and heating rate is a composite of at least two factors. The distribution of thermal flux is changed at a given geometry of the sample pile due to the self-cooling effect of endothermic reaction and the relative change in the partial pressure of gases evolved.

The second factor concerns the kinetic compensation law [11]. Namely, if A diminishes, also E diminishes: the former shifts the TG curves towards higher temperatures, the latter towards lower ones. Thus, we have two effects which act in opposite direction and partially compensate each other.

It is an established fact that the results obtained are not consistent, they represent rather the experimental conditions than the chemical process. In this manner the results published in the literature must be treated critically.

But how can we reduce the effect of the experimental conditions? By using such experimental conditions, the effect of which can be neglected to a first approximation.

From this point of view it seems reasonable to use as small amount of

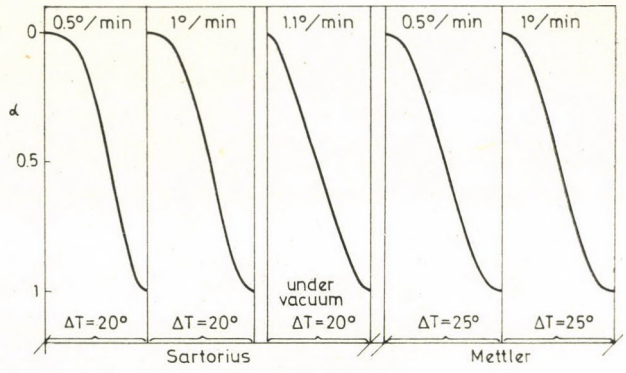

Fig. 1. TG curves obtained by microbalances. Dehydration step of crystalline $Ca(COO)_2 \cdot H_2O$

samples as possible to ensure the necessary experimental sensitivity, a relatively slow heating rate and a sample with very small particle size.

In this manner, the decomposition temperature is determined by the chemical reaction. Since the heat exchange between the sample and its surroundings is better, the quantity of gas evolved is less and its diffusion path is shorter. The self-cooling effect is essentially smaller.

A few TG curves are presented in Fig. 1 obtained under the recommended conditions by Sartorius and Mettler microbalances. The sample size is about 1 mg, and the heating rate is 0.5—1°/min, using platinum crucible. The dehydration process of calcium oxalate monohydrate starts at about 100°C at normal pressure, whereas at reduced pressure it starts below 100°C. The weight loss obtained agrees well with the theoretical value. The dehydration reaction takes place over a relatively narrow temperature interval: $(T_f - T_i)$ is between 20 and 25 degrees. The slope of the curves is nearly identical. The order of reaction was 2/3 in every case. The activation energy was between 37 and 40 kcal/mole. It is a fact that the results obtained at reduced pressure are quite similar to the others, consequently, the effect of atmosphere could be neglected.

An approximation of this type might mean the standardization of the experimental conditions, in other words, the results of measurement made in different laboratories could be compared.

It seems that only arbitrary limits can be given. Even 100 per cent difference either in sample size or heating rate in the range mentioned will slightly influence the value of the kinetic parameters, as may be seen in the figure. From this point of view it is important that the uncertainty due to the variation in experimental conditions does not exceed that of the mathematical methods of evaluation, which is, according to the literature, 6—10 per cent in the case of using integral methods.

On the basis of the results obtained by the above-mentioned conditions the effect of the experimental conditions seems to be eliminated. Consequently, from the evaluation of these data the existence of different rate-controlling processes might be evidenced. The procedure outlined could be a solution of the formal kinetics.

However, a final solution could be expected from the exact mathematical description of the phenomena on the basis of irreversible thermodynamics.

*

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RESIN-PHASE CONCENTRATION DEPENDENCE OF ANION-EXCHANGE EQUILIBRIA

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An equilibrium-column technique has been applied to evaluate the dependence of anion-exchange equilibrium constants for monovalent and bivalent organic acid anions on the resin-phase composition. Ion-exchange isotherms for monovalent and bivalent anions of maleic and fumaric acids were obtained, at various total normalities. The corrected selectivity coefficients show a remarkable change with the resin-phase concentration in all cases. Selectivity reversal was observed at higher resin loading in all cases, indicating a remarkable difference between the states of the resin hydration in the two different ionic forms. Dowex AG 1X4 (100—200 mesh) chloride form anion-exchange resin was used. All data were obtained for systems at 25°C, in aqueous media.

Introduction

For a quantitative definition of the selectivity of ion-exchange reactions the selectivity coefficient is generally used.* A number of experimental evidences prove, however, that the selectivity coefficient is not a true constant but for a given system and temperature it is a function of the ionic composition of the exchanger phase [1].

In the field of cation exchange a considerable number of measurements were published on the dependence of selectivity coefficient on the resin-phase concentration. The purpose of these studies was to obtain the thermodynamic equilibrium constant, and a selectivity scale thermodynamically established. Selectivity scales based on the equilibrium constants were presented for the equilibria of a number of monovalent [2] and bivalent [3] cation pairs, of which only a few examples are being mentioned here.

Much less information is available for analogous investigations on anion-exchange equilibria. Early works of WHEATON and BAUMAN [4] and PETERSON [5] and later GÜRTLER and SANTANA [6] present some values for anion–exchange equilibria, however, they are not true thermodynamic data but rather selectivity coefficients which are given together with the degree of transformation of the resin under equilibrium conditions.

*Apart from selectivity coefficients distribution coefficients are also widely used for comparing the selectivity of ions for resins. Their use is advantageous in chromatography where the distributing species is only a trace component.

Thermodynamically meaningful equilibrium constants for a number of univalent anions were measured by GREGOR *et al.* [7]. In some systems the selectivity coefficients varied little with the composition, while in others a marked dependence was observed. Examples of the former included systems made up of various pairs of ions from Group A: halide, acetate, iodate and nitrate, or of pairs of ions from Group B: thiocyanate, perchlorate, di- and trichloroacetate, trifluoroacetate, toluenesulphonate and naphthalenesulphonate. Examples of the systems, where the selectivity coefficient changed markedly, were made up of anion from Group A with one from Group B. This behaviour was explained by a special ion-pair cluster formation.

Equilibrium selectivity coefficients for the whole range of equivalent fraction of the preferred ion were also measured by BOYD *et al.* [8] for the exchange of bromide with chloride, iodide or fluoride. The connected selectivity coefficients slightly decreased with increasing resin loading. BUCHER *et al.* [9] studied the selectivity of the exchange of chloride with perchlorate and trichloroacetate as a function of resin composition. They found only a gentle increase in the selectivity coefficient with increasing of the chloride mole fraction in the resin. The phenomenom was explained on the basis of the ion–water interaction the importance of which was earlier recognized by CHU *et al.* [10].

A statistical thermodynamic treatment of the anion–exchange equilibria was introduced by HARVEY *et al.* [11]. The validity of the derived equation was successively proved for the exchange of chloride with sulphate, oxalate, carbonate and borate [12].

The purpose of our investigation was the experimental determination of the selecticity coefficients as a function of the equilibrium resin composition for monovalent and bivalent anions of maleic and fumaric acids. The chosen system lends itself for the study of the exchange of the monovalent and bivalent anions without a qualitative change of the chemical species and thereby the effect of the charge can be studied.

Experimental

Materials and solutions: Maleic (Schuchardt, München, GFR) and fumaric (Reanal, Budapest, Hungary) acids were reagent grade chemicals. Equilibrium measurements were carried out in total normalities, *viz.* 0.04 and 0.1.

For the investigation of the monovalent anions at the total normality of 0.04 and 0.1 stock solutions of maleic and fumaric acids were prepared (0.04 and 0.1 *M*, resp.) by dissolving the appropriate amount of acids in water. By addition of sodium hydroxide the pH of the above stock solutions was adjusted to 4.0 and 3.7, respectively.

For the investigation of the bivalent anions at total normality of 0.04 and 0.1 maleic and fumaric acid solutions (0.02 and 0.05 *M*, resp.) were prepared. The pH of the stock solutions was adjusted with sodium hydroxide to 8.0.

Corresponding to the above total normalities the concentration of the sodium chloride stock solution was 0.04 and 0.1 *M*, resp.

Ion-exchange resin. Dowex AG 1X4 (100—200 mesh) chloride form anion-exchange resin was used throughout. Approximately 20 g resin was placed in a 15 cm long glass filtered ion-exchange column of 3 cm in diameter. 1 *M* sodium hydroxide and 1 *M* hydrochloric acid

were then passed through, with intermediate water rinse, until a total of six cycles had been completed, leaving the resin in chloride form. The column was thoroughly washed with distilled water until the effluent gave no test for chloride with several drops of 10^{-1} M silver nitrate solution. The chloride-free resin was spread on a filter paper and dried at room temperature for two days. The air-dry resin was stored in a well closed glass vessel.

Capacity determination. No more than 1 g exactly weighed portion of the above resin was quantitatively rinsed in a column similar to that used in the equilibration experiment (see later). The resin bed was back-flushed with water to remove the air and allowed to settle. Then 1 M potassium nitrate solution was passed through the column and the effluent was collected in a 100 ml graduated flask. 20 ml aliquot was titrated with standard silver nitrate solution (0.1 M) according to the Mohr method. Capacity: 3.56 mval/g dry Cl^--form resin.

Equilibration procedure: Following SALMON's equilibration procedure [12] an equilibrium column technique was used. The column (of 1 cm inner diameter, 10 cm long) was equipped with a water jacket. The inlet and outlet of the water jackets were connected to a TB 150 (GDR) circulating thermostat which maintained the temperature of the system at 25 $\pm$ 0.05°C. For the measurements seven of the above columns were connected in series regarding their thermostation. Exactly 0.5 g portions of the above resin were placed in each column.

The equivalent fraction of the acid anions in the solution to be equilibrated was changed by mixing the stock solution of the acid salt in question with 0.04 M (or 0.1 M) sodium chloride solution in various column ratios but in a constant end volume (200 ml). Equivalent fractions of the acids varied from 0.05 to 0.9 at each total normality. With the solutions obtained, the columns were filled air-free. The effluent solution was collected in a 100-ml graduated flask. Approximate rate of dropping was 0.2 ml/min.

Analysis of the equilibrium solutions. The chloride concentrations of the influent and effluent solutions were determined by the Votocek method [13]. Usual argentometric chloride determinations cannot be used due to the interfering complex formation between the silver ion and the weak acid anions.

Results and discussion

To obtain ion-exchange, isotherms, equivalent fractions of the counter-ion were calculated. The equivalent ionic fractions in the solution and in the exchanger phase were calculated by the equation

$$x_i = \frac{z_i m_i}{\Sigma z_i m_i} \quad \text{and} \quad \bar{x}_i = \frac{\Delta \mathrm{Cl} \cdot V}{\mathrm{Q}\, w} \tag{1}$$

where: x_i, $\bar{x}_i$ equivalent ionic fractions of the i-th ion in the solution and in the exchanger phase,

z_i, m_i charge and mole concentration of the i-th ion,

ΔCl difference between the chloride concentration of the solutions after and before contact with the resin,

V collected volume of the effluent (100 ml),

Q, w resin capacity (mval/q) and the resin quantity used (0.5 g).

Ion-exchange isotherms of the monovalent anions of maleic and fumaric acids are shown in Figs 1 and 2, while for the bivalent anions they are presented in Figs 3 and 4. As can be expected within the limits of experimental error the isotherms are independent of the total normalities in the case of the monovalent ions. Practically no significant difference can be observed between the isotherms of the two anions. Selectivity reversal occurs at $\bar{x} > 0.85$ in both cases.

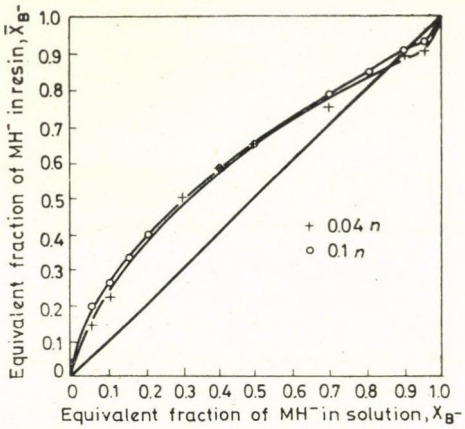

Fig. 1. Ion-exchange isotherms of the monovalent maleic acid anion at two total normalities (n), at 25°C. Resin: Dowex AG 1X4 (Cl, 100—200 mesh)

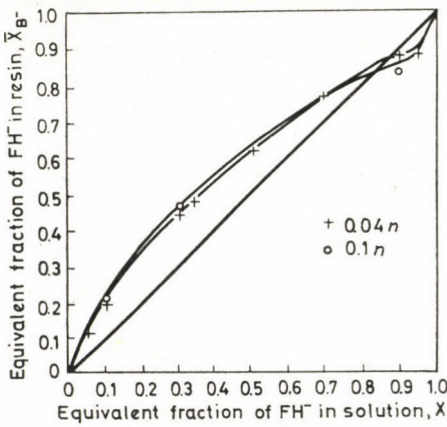

Fig. 2. Ion-exchange isotherms for the monovalent fumaric acid anion at two total normalities (n), at 25°C. Resin: Dowex AG 1X4 (Cl, 100—200 mesh)

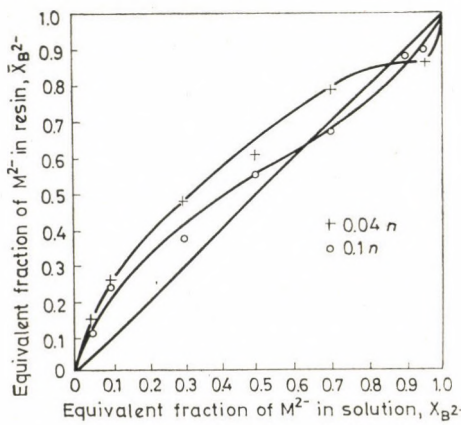

Fig. 3. Ion-exchange isotherms for the bivalent maleic acid anion at two total normalities (n), at 25°C. Resin: Dowex AG 1X4 (Cl, 100—200 mesh)

In the case of bivalent ions the principle of electroselectivity is valid. With increasing total normality curves show a progressively greater deviation from the unit slope. Occurrence of the selectivity reversal depends on the total normality.

For the following anion exchange between Cl^- in the resin and B^{z-} in the solution

$$zR\ Cl + B^{z-} \rightleftharpoons R_z B + z\ Cl^- \tag{2}$$

the equilibrium constant is:

$$\mathcal{K}_{B/Cl} = \frac{(\bar{x}_B z)\,(x_{Cl})^z}{(\bar{x}_{Cl})^z\,(x_B z)} \cdot \frac{\bar{\gamma}_B z\,\gamma_{Cl}^z}{\bar{\gamma}_{Cl}^z\,\gamma_B z} = K_{B/Cl}\,\frac{\bar{\gamma}_B z\,\gamma_{Cl}^z}{\gamma_B z\,\bar{\gamma}_{Cl}^z} = K'_{B/Cl}\,\frac{\bar{\gamma}_B z}{\bar{\gamma}_{Cl}^z} \tag{3}$$

where: x, $\bar{x}$ have the same meaning as in Eq. (1),

γ, $\bar{\gamma}$ ionic activity coefficients in the solution and in the resin phase, respectively,

$\mathcal{K}_{B/Cl}$ thermodynamic equilibrium constant,

$K_{B/Cl}$ selectivity coefficient,

$K'_{B/Cl}$ corrected selectivity coefficient.

To obtain the corrected selectivity coefficients, activity coefficients for the solution phase were calculated by the DAVIES equation [14]. It should be noted, however, that this type of calculation of the activity coefficients in mixed electrolyte solutions is very approximate. A slightly greater refinement in this correction might be made either by using the interaction coefficients introduced by GUGGENHEIM [15] or the empirical Harned's rule [16]. Neither of these methods can be applied here due to the lack of interaction coefficients and the isopiestic data for the organic acids studied. If $K_{B/Cl}$ is defined in terms of equivalent fractions, $K_{B/Cl}$ cannot be calculated directly from Eq. (3) in the case of heterovalent exchange ($B^{z-} \rightarrow Cl$) because its value will depend on the total normality of the solution. It can readily be shown that these calculated values should be multiplied by the $Q/\Sigma\, c_i m_i$ ratio to obtain $K'_{B/Cl}$ for heterovalent exchange.

Having the equivalent fraction of the anions in the resin and in the solution phase, moreover the activity coefficients of the chloride and the respective anion, $K_{B/Cl}$ was calculated by Eq. (3) considering the above remarks. The calculated values are presented graphically in Figs 5 to 8 as a function of the equivalent fraction of the acid anion in the resin phase. Figs 5 to 8 show that the corrected selectivity coefficients vary to a considerable degree with the resin composition in the cases of both monovalent and bivalent anions.

Since in the studied systems there is a little chance for ion-pair formation between the resin cation and the acid anion, therefore, the strong dependence cannot be attributed to any special ion-cluster-formation mechanism postulated by

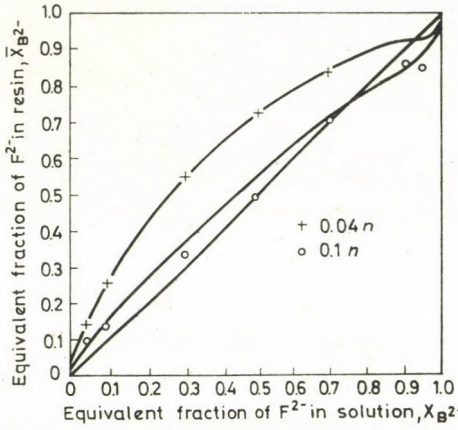

Fig. 4. Ion-exchange isotherms for the bivalent fumaric acid anion at two total normalities (n) at 25°C. Resin: Dowex AG 1X4 (Cl, 100—200 mesh)

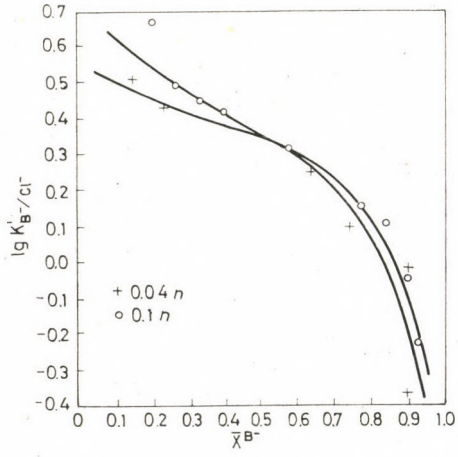

Fig. 5. Monovalent maleic acid anion–chloride exchange selectivity on Dowex AG 1X4 showing selectivity reversal

GREGOR *et al.* [7]. The strong dependence is rather a consequence of the significant difference between the hydration state of the resin in the two ionic forms ($R\,Cl \rightarrow R\,B^{z-}$). The resin selectivity for the chloride decreases since the possibility of the chloride hydration in the resin decreases with increasing $\bar{x}_{B^{z-}}$ and the chloride is preferred rather by the solution than by the exchanger phase.

With proper choice of the standard states of the electrolyte and the resin phase the thermodynamic equilibrium constant can be calculated from the corrected selectivity coefficients, as pointed out by ARGERSINGER *et al.* [17] and EKEDHAL *et al.* [18]. Application of the Gibbs—Duhem equation leads to the result:

$$\lg \mathcal{K}_{B/Cl} = \int_0^1 \lg K'_{B/Cl}\, d\,\bar{x}_{B^{z-}} \qquad (4)$$

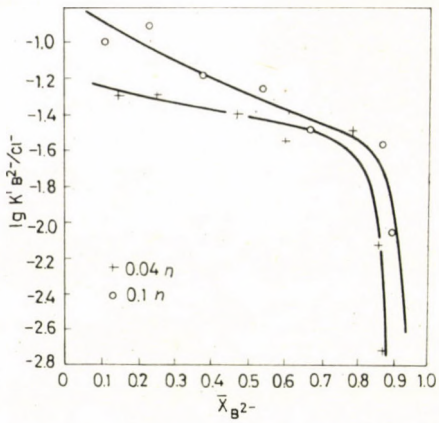

Fig. 6. Bivalent maleic acid anion–chlorid exchange selectivity on Dowex AG 1X4

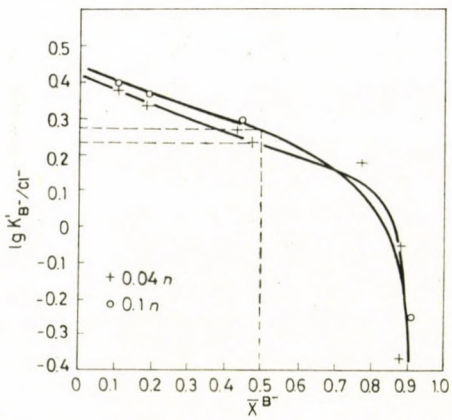

Fig. 7. Monovalent fumaric acid anion–chloride exchange selectivity on Dowex AG 1X4 showing affinity reversal

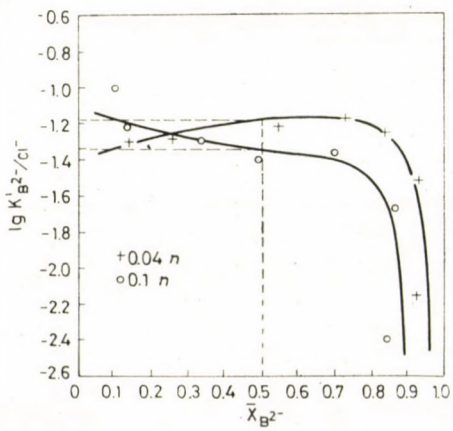

Fig. 8. Bivalent fumaric acid anion–chloride exchange selectivity on Dowex AG 1X4

The error is seldom very large if the value of the integral in Eq. (4) is approximated by taking the lg $K'_{B/Cl}$ value at $\bar{x}_B = 0.5$, *i.e.*:

$$\lg \mathcal{K}_{B/Cl} = [\lg K'_{B/Cl}]_{\bar{x}_B=0.5} \tag{5}$$

Table I gives the values of the thermodynamic equilibrium constants which were obtained using the above approximation.

Data in Table I corresponding to the total normality of 0.04 can be compared with previous results [19] obtained by trace equilibration experiments on Dowex AG 1X8. These values are reported again in brackets in Table I. Although there is a slight difference between the two resins, the difference between the values is not significant. It can be concluded that the constants of the bivalent ions are much lower than those of the monovalent ions. The order of the constants corresponds approximately to the order of the protonation constants of the anions.

Further information can be expected from the calorimetric study of the exchange equilibrium which throws light on the type of interactions which are responsible in a given system for the selective binding of an ion.

Table I

Thermodynamic equilibrium constants of maleic and fumaric acid anions calculated by Eq. (5)

Total normality	Thermodynamic equilibrium constants at 25°C			
	MH^-	FH^-	M^{2-}	F^{2-}
0.04	2.25	1.77	0.038	0.067
0.1	2.25	1.77	0.052	0.046
	(2.96)	(1.70)	(0.022)	(0.063) [19]

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MOLAR POLARIZATION OF NITROBENZENE IN POLAR SOLVENTS

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A study was made of binary mixtures of nitrobenzene with polar liquids. It was found that in the systems examined the variation of the molar polarization of nitrobenzene with the volume polarization of the mixture is determined by the molar polarization of pure nitrobenzene and by the equation

$$P_n^* = -P_{or}\left(\frac{\varepsilon - 1}{\varepsilon + 2} - 1\right)$$

The increase of P_n is limited by the Sugden equation valid for non-polar solvents. The lower limit of the decrease of P_n is the displacement polarization. A correlation was found between the relative permittivity of the polar liquid and its mutual solubility with nitrobenzene.

In an earlier publication [1] a study was made of the dipole association of nitrobenzene in non-polar solvents. It was found that in pure liquid nitrobenzene the molecules are present in a very significant proportion in antiparallel arrangements. Such an arrangement strongly decreases the molar polarization of nitrobenzene compared to that of the liquid consisting of molecules in the monomeric state. In the course of dilution with non-polar solvent the dipole associations break down, and the molar polarization of nitrobenzene increases to a considerable extent with the increase of the dilution. The phenomenon can be described by the Sugden equation [2].

If nitrobenzene is mixed with a polar solvent, the Sugden equation no longer holds. This can be seen, for example, in a plot of P_n *vs.* $\frac{\varepsilon - 1}{\varepsilon + 2}$; the data calculated for the molar polarization of nitrobenzene do not lie on the straight line characteristic for non-polar substances. The present work deals with such systems: binary mixtures of nitrobenzene with polar substances.

Experimental

The relative permittivity of the mixtures was measured with a SIEMENS Scheinwiderstandsmeßbrücke Rel. 3R 277 instrument. Measurements were made at 20°C, in special thermostated cells made from a combination of teflon and stainless steel. The relative permittivity values determined at a frequency of 500 kHz can be regarded as equal to the static relative permittivity.

The densities of the pure substances were determined in a pycnometer, while, in the knowledge of the densities of the pure substances, the densities of the mixtures were measured with a DMA OZC (Austria) digital densitometer. The mixtures of various compositions were prepared by weighing the components. The experimental results are listed in Tables I—IV.

Discussion

The data in Tables I–IV were used to calculate the molar polarizations of the mixtures as a function of the composition. The formula employed for calculating the molar polarization (P) was

$$P = \frac{\varepsilon - 1}{\varepsilon + 2} \cdot \frac{x_n M_n + x_b M_b}{\varrho} \tag{1}$$

The molar polarization data are given in Tables V—VIII and Fig. 1. The tables also contain the molar polarization of nitrobenzene; this was calculated from the relation

$$P_n = \frac{P - x_b P_b}{x_n} \tag{1}$$

assuming the additivity of molar polarizations.

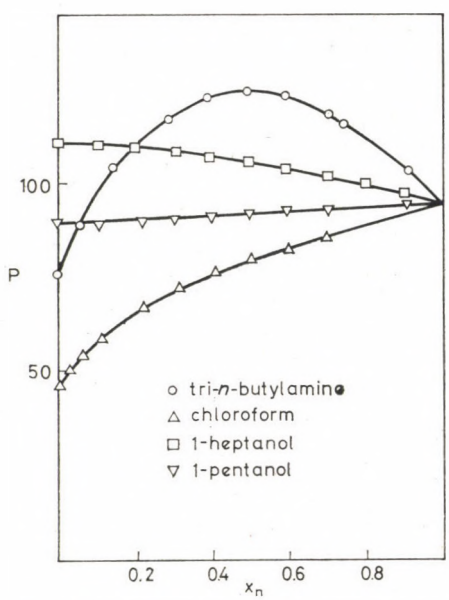

Fig. 1. Molar polarization of binary mixtures containing nitrobenzene at 20°C as a function of the mole fraction of nitrobenzene

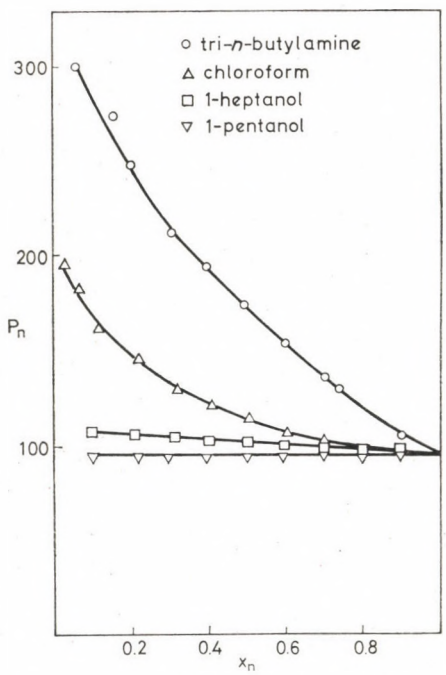

Fig. 2. Molar polarization of nitrobenzene at 20°C as a function of the composition of the mixture

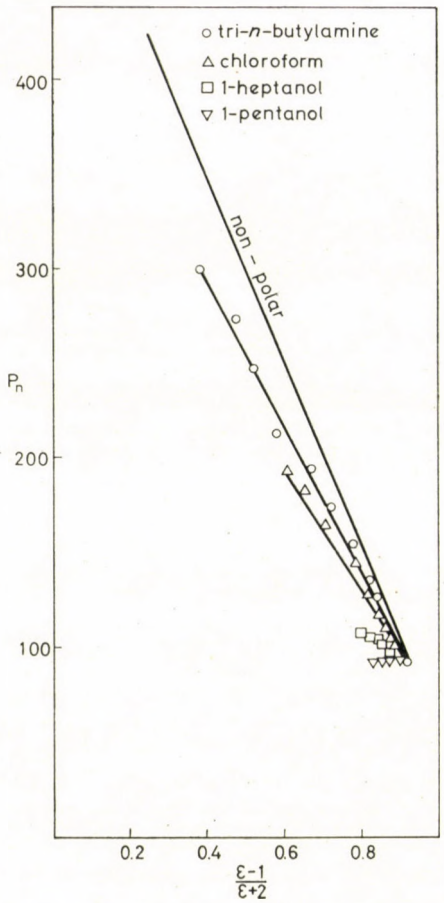

Fig. 3. Molar polarization of nitrobenzene as a function of the volume polarization of the mixture at 20°C

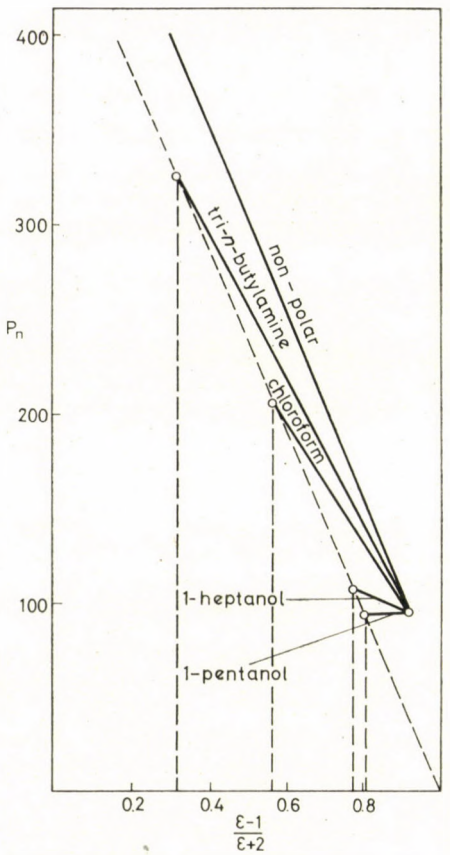

Fig. 4. The molar polarization values of nitrobenzene extrapolated to "infinitely dilute" solution lie on the straight line corresponding to Eq. (3)

The molar polarization of the mixture exhibits approximately ideal behaviour for the alcohol-containing systems, whereas there is a positive deviation from ideal behaviour in the systems containing tri-*n*-butylamine and chloroform. This positive deviation is so considerable in the case of the tri-*n*-butylamine system that the molar polarization passes through a maximum as a function of the composition.

Figure 2 shows the molar polarization of nitrobenzene as a function of the mole fraction of nitrobenzene. Tri-*n*-butylamine behaves similarly to the non-polar solvent systems presented earlier [1]. The molar polarization of nitrobenzene decreases with the increase of x_n, though not to such a great extent as for the mixtures with non-polar solvents. In the nitrobenzene–chloroform

Table I

Relative permittivity and density of nitrobenzene–tri-n-butylamine mixtures at 20°C as functions of the composition

x_n	ε	ϱ (g cm^{-3})
0	2.40	0.7782
0.0555	2.87	0.7912
0.1477	3.80	0.8104
0.1991	4.27	0.8208
0.2983	5.32	0.8459
0.3991	7.07	0.8752
0.4984	9.17	0.9086
0.6018	12.09	0.9492
0.7052	15.94	0.9987
0.7406	17.22	1.0167
0.9028	26.44	1.1224
1	34.74	1.1981

Table II

Relative permittivity and density of nitrobenzene–chloroform mixtures at 20°C as functions of the composition

x_n	ε	ϱ (g cm^{-3})
0	4.81	1.4791
0.0269	5.67	1.4752
0.0615	6.72	1.4637
0.1180	8.35	1.4516
0.2120	11.85	1.4157
0.3140	15.00	1.3858
0.4048	17.80	1.3552
0.5059	20.71	1.3284
0.5987	23.16	1.3058
0.6995	24.69	1.2797
1	34.74	1.1981

system this tendency is even less significant, while in the alcohol-containing mixtures P_n varies only slightly with composition. The phenomenon can presumably be explained by the formation of mixed nitrobenzene–solvent associations in place of the antiparallel nitrobenzene–nitrobenzene associations which break down upon dilution with the solvent. The variation of the apparent

Table III

Relative permittivity and density of nitrobenzene–1-heptanol mixtures at 20°C as functions of the composition

x_n	ε	ϱ (g cm^{-3})
0	11.48	0.8205
0.1053	13.02	0.8506
0.2061	14.59	0.8812
0.3112	16.51	0.9150
0.4004	18.15	0.9453
0.5003	20.32	0.9828
0.6001	22.69	1.0203
0.7045	25.30	1.0630
0.8003	28.19	1.1055
0.8982	31.51	1.1526
1	34.74	1.1981

Table IV

Relative permittivity and density of nitrobenzene–1-pentanol mixtures at 20°C as functions of the composition

x_n	ε	ϱ (g cm^{-3})
0	14.50	0.8142
0.1117	15.96	0.8561
0.2233	17.10	0.8953
0.3049	18.26	0.9286
0.4020	19.76	0.9671
0.5071	21.74	1.0076
0.6009	23.73	1.0440
0.7002	26.06	1.0843
0.8989	31.75	1.1631
1	34.74	1.1981

molar polarization of nitrobenzene with the composition is probably determined by the structure of the nitrobenzene–solvent associations formed in place of the nitrobenzene–nitrobenzene associations. It appears that the stronger the mixed interaction, the less P_n decreases with the increase of x_n.

Figure 3 shows the molar polarization of nitrobenzene as a function of the volume polarization of the mixture for the four systems examined. The figure also depicts the straight line corresponding to the Sugden equation obtained

Table V

Molar polarization of the nitrobenzene–tri-n-butylamine mixture (P) and molar polarization of nitrobenzene in the mixture (P_n) at 20°C as functions of the composition

x_n	P (cm³ mol⁻¹)	P_n (cm³ mol⁻¹)
0	75.8	—
0.0555	88.2	299.8
0.1477	105.0	273.4
0.1991	109.9	247.0
0.2983	116.3	211.7
0.3991	122.7	193.4
0.4984	124.2	173.0
0.6018	122.6	153.6
0.7052	118.0	135.6
0.7406	115.6	129.5
0.9028	102.9	105.9
1	94.3	94.3

Table VI

Molar polarization of the nitrobenzene–chloroform mixture (P) and molar polarization of nitrobenzene in the mixture (P_n) at 20°C as functions of the composition

x_n	P (cm³ mol⁻¹)	P_n (cm³ mol⁻¹)
0	45.1	—
0.0269	49.3	195
0.0615	53.6	183.1
0.1180	58.6	162.0
0.2120	66.5	145.9
0.3140	71.6	129.6
0.4048	75.7	120.7
0.5059	79.2	112.6
0.5987	82.0	106.8
0.6995	84.6	101.6
1	94.3	94.3

with non-polar solvents [1]. The data relating to the four systems examined in the present work do not lie on the straight line determined by the mixtures containing a non-polar second component, but at the same time they display an interesting regularity. The data for each of the systems lie on separate

Table VII

Molar polarization of the nitrobenzene–1-heptanol mixture (P) and molar polarization of nitrobenzene in the mixture (P_n) at 20°C as functions of the composition

x_n	P (cm³ mol⁻¹)	P_n (cm³ mol⁻¹)
0	110.1	—
0.1053	109.8	107.3
0.2061	109.2	105.8
0.3112	108.7	105.5
0.4004	107.0	102.3
0.5003	105.3	100.5
0.6001	103.5	99.1
0.7045	101.3	97.6
0.8003	99.1	96.3
0.8982	96.6	95.0
1	94.3	94.3

Table VIII

Molar polarization of the nitrobenzene–1-pentanol mixture (P) and molar polarization of nitrobenzene in the mixture (P_n) at 20°C as functions of the composition

x_n	P (cm³ mol⁻¹)	P_n (cm³ mol⁻¹)
0	88.5	—
0.1117	89.4	96.7
0.2233	90.2	96.3
0.3049	90.6	95.4
0.4020	91.0	94.8
0.5071	91.7	94.8
0.6009	92.2	94.9
0.7002	92.7	94.5
0.8989	93.6	94.2
1	94.3	94.3

straight lines. The slopes of these lines are different from one another, and in every case are smaller than the value of P_{or} given by the Sugden equation. If the latter straight lines are extended to the volume polarization values corresponding to the pure solvents, then the resulting end-points define a further straight line, shown as a dashed line in Fig. 4. Such an extension of the straight

lines leads to the value of the molar polarization of nitrobenzene relating to infinitely dilute solution. The equation of this straight line is

$$P_n^* = -P_{or}\left(\frac{\varepsilon^* - 1}{\varepsilon^* + 2} - 1\right) \tag{3}$$

It appears from the results, therefore, that the picture of binary mixtures with polar solvents in the P_n *vs.* $\frac{\varepsilon - 1}{\varepsilon - 2}$ diagram is a set of straight lines, the common point of which is the point corresponding to pure nitrobenzene, while the other end-points lie on the straight line defined by Eq. (3) (see Fig. 4).

If this regularity holds for any binary mixture containing nitrobenzene, then the molar polarization of nitrobenzene may increase, or it may decrease with the variation of the volume polarization (*i.e.* with the variation of the composition of the mixture), or may even be constant, as was observed in the case of the 1-pentanol system. The upper limit of the increase of P_n is given by the straight line obtained on the basis of the Sugden equation with non-polar solvents. The lower limit of the decrease of P_n is examined below.

According to the above, in the limiting case of $\varepsilon = \infty$ $\left(i.e.\ \frac{\varepsilon - 1}{\varepsilon + 2} = 1\right)$, P_n would decrease to zero. Experience shows, however, that the dipolar environment of the molecule does not affect (or does to a negligible extent only) the electron and atom polarizations [2]. In the book of HILL, VAUGHAN, PRICE and DAVIES [3] a value of 33 cm^3/mol is to be found for the sum of the electron and atom polarizations (this value was used in our previous publication [1]). According to the same book, the atom polarization is 3.8 cm^3/mol. PARTINGTON [2] gives a value of 8 cm^3/mol for the atom polarization. The data of SZKANAVI [5] include 33 cm^3/mol for the electron polarization. The shaded area in Fig. 5 shows the scatter of the literature data relating to the electron and atom polarizations. The present studies indicate that the value of the displacement polarization is given by the point of intersection of the straight line defined by Eq. (3), and the volume polarization (relative permittivity) of nitrobenzene (point 1 in Fig. 5). Our experimental results give a value of 37 cm^3/mol for the displacement polarization of nitrobenzene at 20°C. The molar polarization of nitrobenzene can thus not decrease below 37 cm^3/mol. If the substance forming a mixture with nitrobenzene is a polar component the volume polarization of which is greater than that of pure nitrobenzene [*i.e.* if ε^* (polar) $> \varepsilon^*$ (nitrobenzene)], then, according to Eq. (3), P_n might assume a smaller value than the displacement polarization of nitrobenzene. This is a physical impossibility, however, and in such a case the mixture separates to two phases. This is illustrated by the dashed straight line relating to water in Fig. 5: nitrobenzene will mix with water only so long as its molar polarization is not less than the dis-

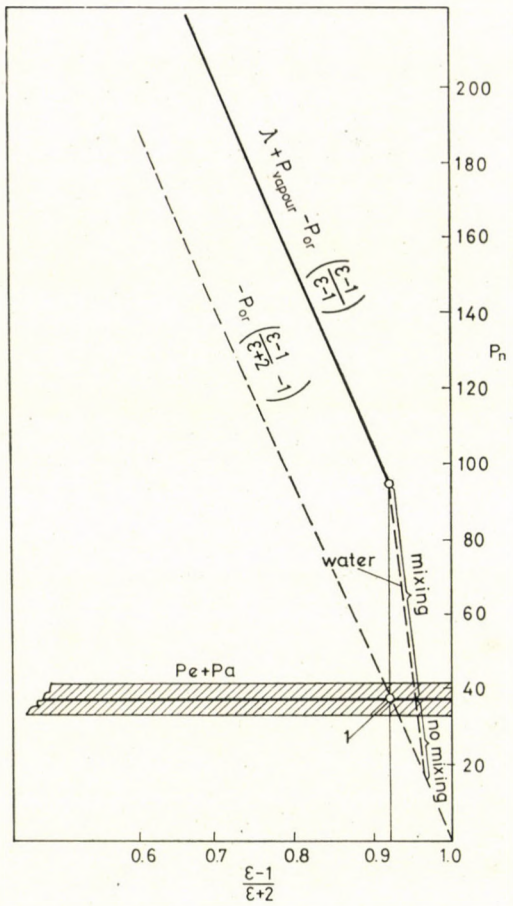

Fig. 5. Illustration of the connection between molar polarization and mutual solubility

placement polarization. Table IX contains data on a number of liquids which mix only to a limited extent with nitrobenzene.

According to the present investigation, those substance for which $\varepsilon^* < \varepsilon^*$, (nitrobenzene) will mix with nitrobenzene in all proportions.

Table IX

Liquids mixing to a limited extent with nitrobenzene

Liquid	Temperature (°C)	ε^* [4]	$\frac{\varepsilon^* - 1}{\varepsilon^* + 2}$
Water	20	80.2	0.9635
Glycol	25	38	0.925
Glycerol	25	42.5	0.9326
Formamide	20	109	0.973

Notations

x = mole fraction
ε = relative permittivity
ϱ = density
P = molar polarization

Indices

n = nitrobenzene
b = other component
$*$ = value extrapolated to 'infinitely dilute' solution, and referring to pure solvent
or = orientation

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HELICAL STRUCTURE OF POLY(VINYLENE CARBONATE) OBTAINED BY SOLID STATE POLYMERIZATION

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The IR spectra of poly(vinylene carbonates) obtained by solid and liquid state polymerization initiated by γ-rays were compared. Conformational energies of polymer chains built up either from *threo* or *erythro* segments in *iso-* or *syndio*tactic connections were computed, using atomic coordinates obtained by minimizing the strain energies of *threo-* and *erythro*-dimethylethylene carbonates. The results were compared with previous X-ray data. The primary polymer obtained in a solid state reaction is an *erythro-syndio*tactic 3_1 helix which partly turns into a 4_1 helix after precipitation. The polymer obtained in a liquid state process is a *threo-erythro* atactic chain.

It has been previously established that the first period of the solid state polymerization of vinylene carbonate [1, 2] consists of a topotactic process. The crystal structure of the monomer has been determined, too [3]. The Weissenberg pattern of the monomer reveals a new oriented crystalline phase [2]. This new crystalline phase also appears in the powder X-ray diffractograms at different conversions. The cell dimensions of the crystalline polymer are $a = 11.02$, $b = 9.39$ and $c = 4.2$ Å. We have assumed that the b axis has a 3_1 helix structure (systematic absence of OkO reflections if $k \neq 3n$).

The precipitated polymer was found to be amorphous. The X-ray pattern of this polymer shows two broad peaks with $d_1 = 4.04$ Å and $d_2 = 3.25$ Å.

In the present work we make an attempt at establishing the most probable structure of the polymeric chain, using IR data and the results of conformational energy calculations [4, 5].

Experimental and calculations

The polymers were prepared by the methods described previously [1, 2].

The IR spectra were recorded on a UR 10 spectrograph in KBr pellets with 3 mg polymer in 1 g KBr.

Computation of conformational energies

The atomic coordinates (Table I) of *threo-* and *erythro*-dimethylethylene carbonate were computed by minimizing the strain energies, using the

Table I

Atomic coordinates of threo and erythro-dimethylethylene carbonates with minimal strain energy (in Å) and the polar coordinates of atoms in threo and erythro poly(vinylene carbonate) monomeric units

Atom	X (Å)	Y (Å)	Z (Å)	L (Å)	Θ (deg)	Φ (deg)	Type
	Erythro-dimethylethylene carbonate			*Erythro*-poly(vinylene carbonate)			
1	−0.7434	−0.0093	1.5390	1.5460	125.928	178.063	5
2	0.7821	−0.0317	1.5419	1.5256	125.190	0.000	5
3	−1.1473	0.0307	0.1546	1.4427	108.996	−127.430	2
4	0.0285	0.0358	−0.4884	1.3402	102.406	− 42.282	3
5	1.2190	−0.0057	0.1557	1.4557	107.366	51.567	2
6	−1.0481	0.9685	1.9367	1.0987	103.406	122.169	1
7	−0.0171	−0.0007	−1.7013	1.2143	116.497	3.613	4
8	1.0785	0.9508	1.9252	1.0955	105.956	− 58.295	1
9	−1.6510	−1.0046	2.2997	—	—	—	6
10	1.6728	−1.0169	2.3315	—	—	—	6
	Threo-dimethylethylene carbonate			*Threo*-poly(vinylene carbonate)			
1	−0.7506	−0.0461	1.5349	1.5460	120.226	− 73.058	5
2	0.7842	0.0244	1.5419	1.5365	120.209	0.000	5
3	−1.1473	−0.0006	0.1540	1.4375	108.864	120.800	2
4	0.0285	0.0218	−0.4884	1.3400	102.642	46.559	3
5	1.2190	0.0009	0.1557	1.4529	107.088	− 51.618	2
6	−1.0935	−1.0209	1.9019	1.0965	104.833	−124.100	1
7	−0.0176	0.0032	−1.7013	1.2139	116.448	− 3.102	4
8	1.1155	0.9981	1.9213	1.0963	110.134	−164.937	1
9	−1.5807	0.9898	2.3279	—	—	—	6
10	1.6066	−1.0124	2.3387	—	—	—	6

WESTHEIMER—HENDRICKSON—WIBERG* method. The potential functions and its parameters used for minimization are presented in Table II.

For computing the Coulomb energies, the partial charges originating from the inductive effect were determined by the DEL RE method [6], applying the modified γ values given by NAGY and PÁRKÁNYI [7] (Table III). The conformation of the polymer was calculated by a computer program (POLYMER) based on the method of DE SANTIS *et al.* [4]. Atomic coordinates are present-

*For details of the method, *cf.*: F. H. WESTHEIMER: Calculation of the Magnitude of Steric Effects. in *Steric Effects in Organic Chemistry*, Ed. M. S. Newmann, John Wiley and Sons Inc., New York, 1963, p. 523; WIBERG, K. B.: J. Amer. Chem. Soc., **87,** 1070 (1961); ALLINGER, N. L., SPRAQUE, J. T.: J. Amer. Chem. Soc., **94,** 5734 (1972); ALTONA, C., SUNDERALINGAM, H.: J. Amer. Chem. Soc., **92,** 1955 (1970); Tetrahedron, **26,** 2135 (1970); GREGORY, C. C., NIN, N. G.: Macromolecules, **6,** 91 (1973); ERNER, O., LIFSON, S.: J. Amer. Chem. Soc., **94,** 4121 (1972), and references therein.

Table II

Potential function used for minimizing the strain energies of monomeric units (E_{mon}) and for calculating the conformational energies of polymers (E_{tot}) together with their parameters

$$E_{mon} = 1/2 \sum' k^l_{ij} (L_{ij} - l^0_{ij})^2 + 1/2 \sum' k^{th}_{ijk} (\Theta_{ijk} - th^0_{ijk})^2 + 1/2 \sum' f(V^0_{jk}, \Phi_{jk}) +$$

$$+ \sum' e_{ij} \left[\left(\frac{R^0_{ij}}{R_{ij}} \right)^{12} - 2 \left(\frac{R^0_{ij}}{R_{ij}} \right)^6 \right] + \sum' \frac{1387}{\varepsilon_0} \frac{q_i q_j}{R_{ij}}$$

$$E_{tot} = E_{mon} + \sum_{s=1}^{6}{}' \left\{ \sum' e_{ij} \left[\left(\frac{R^0_{ij}}{R_{ij}} \right)^{12} - 2 \left(\frac{R^0_{ij}}{R_{ij}} \right)^6 \right] + \sum' \frac{1387}{\varepsilon_0} \frac{q_i q_j}{R_{ij}} \right\}_s$$

$$R^0_{ij} = 1/2 (R^0_{ii} + R^0_{jj}), \quad e_{ij} = -\frac{e_{ii} \times e_{jj}}{2(e_{ii} + e_{jj})}, \quad \varepsilon_0 = 4$$

Atom	Type	R^0_{ii} [Å]	e_{ii} [kJ/mol]
HYDROGEN	1	2.40	0.0365
OXYGEN (sp^3)	2	3.08	0.6600
CARBON (sp^2)	3	3.70	0.3679
OXYGEN (sp^2)	4	3.08	0.6600
CARBON (sp^3)	5	3.70	0.3679
METHYL	6	3.60	0.0440

Bond type	k^l_{ij} [mdyn/Å]	l^0_{ij} [Å]	V^0_{jk} [kJ/mol] $f(V^0_{jk}, \Phi_{jk})$
6—5	4.4	1.512	— —
5—1	4.6	1.094	— —
5—2	5.0	1.416	11.564 V° [1—cos (3Φ)] + V°/10 [1—cos (2Φ)]
5—5	4.4	1.512	5.204 V° [1—cos (3Φ)]
4—3	11.0	1.221	— —
3—2	5.0	1.316	3.687 V° [1—sin (2Φ)]

Angle type	k^{th}_{ijk} [mdyn Å/rad²]	th^0_{ijk} [deg]
6—5—5	0.40	109.46
6—5—2	0.98	109.46
5—6—1	0.24	109.46
5—5—2	0.98	109.46
5—5—1	0.24	109.46
2—5—1	0.50	107.20
4—3—2	0.65	125.00
2—3—2	0.65	121.60
5—2—3	1.10	90.00

Table III

Partial charges of atoms in the monomeric units

CARBON-S	0.0545	CARBON-D	0.3029	HYDROGEN	0.0633
OXYGEN-S	−0.2124	OXYGEN-D	−0.1139	METHYL	0.0000

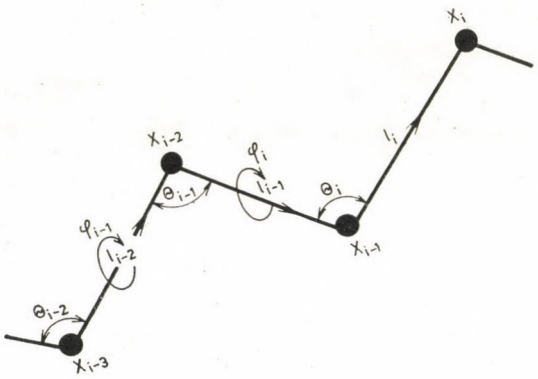

Fig. 1. Polar coordinate system of the polymer chain

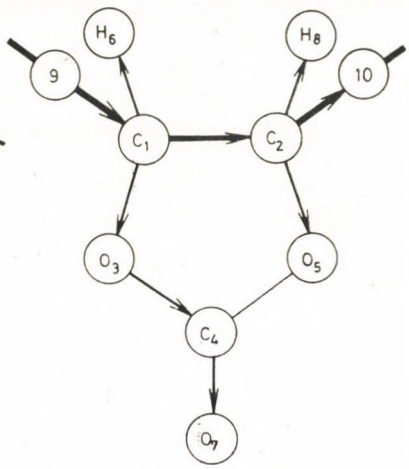

Fig. 2. Numbering of the vinylene carbonate monomeric unit and the corresponding polar coordinate system

ed in a polar coordinate system related to the preceding atoms according to the pattern of Fig. 1. L_i is a vector (valence) pointing from the $i-1$-th atom to i-th atom; Θ_i is the valence angle between L_{i-1} and L_i; φ_i is the dihedral angle between the $L_{i-2}-L_{i-1}$ and the $L_{i-1}-L_i$ planes (*trans* position = 0°).

The numbering of atoms and the construction of the polar coordinate system are illustrated in Fig. 2.

The monomer units characterized in this way were incorporated into 6-membered chains $(C_1-C_2-C_1'-C_2'-)_3$ and changes in the energy corresponding to a monomer unit were determined as a function of the dihedral angle for the C_2-C_1' bond.

The monomer units were assumed to be rigid and their energy of rotation about the bond, the repulsion, attraction and electrostatic energies within the molecule and between the chain segments were calculated. The individual energies were calculated from the following equation:

$$E_{\text{poly}} = \frac{1}{2} \sum V_{ij}^0 \{1 - \cos[n_{ij}(\varphi_{ij} - \varphi_{ij}^0)]\} +$$

$$+ \sum e_{ij} \left(\frac{R_{ij}^0}{R_{ij}}\right)^{12} - 2 \sum e_{ij} \left(\frac{R_{ij}^0}{R_{ij}}\right)^{6} + \sum \frac{1387}{\varepsilon^0} \cdot \frac{q_i q_j}{R_{ij}}$$

where V_{ij}^0 potential barrier of rotation about the $C_2—C_1'$ bond (kJ/mol),
n_{ij} = 3 for the $C_2—C_1'$ bond,
φ_{ij} dihedral angle,
φ_{ij}^0 dihedral angle at the minimum-energy state,
R_{ij} distance between the atoms i and j (Å),
R_{ij}^0 sum of van der Waals radii of atoms i and j (Å),
e_{ij} potential corresponding to the distance of minimum-energy (R_{ij}^0) between atoms i and j (kJ/mol),
q_i, q_j electric charge of the atoms calculated by the method of Del Re [6] in electrons,
ε° dielectric constant.

Each chain segment consists of one monomer unit in the isotactic model and a pair of monomer units which are mirror images of each other (the φ coordinates have opposite signs) in the syndiotactic model.

The computation was performed for five different chains, *viz. threo-* and *erythro-iso*tactic, *threo-* and *erythro-sindio*tactic as well as *threo-erythro*, where the conformational energies were computed as functions of the dihedral angles between monomer units. In *iso*tactic chains the dihedral angle of the 2nd chain atom, in the other cases those of the 2nd and 4th atoms were changed in increments of 10 degrees as a first approximation. In the vicinity of minima the increments were decreased to 1 degree.

Results and discussion

The sections of the IR spectra characteristic of the polymer conformation are shown in Figs 3 and 4. In the spectrum of the polymer obtained by solid state polymerization (Fig. 3) two broad peaks could be separated by graphical methods after subtracting the base line. The integrated area of the peak at 3000 cm^{-1} is three times larger than that of the peak at 2937 cm^{-1}. In the spectrum of the polymer obtained by liquid state polymerization (Fig. 4) five peaks appear at 2855, 2870, 2930, 2975 and 3000 cm^{-1}, respectively. The sum of the integrated peak area at the two higher wavenumbers is equal to the sum of the remaining three. The half widths of peaks in the latter part of the spectrum are smaller than in the former one. The only exception is the peak at 3000 cm^{-1} which is practically identical in both sections.

A comparison of the corresponding spectra of poly(vinylene carbonate) and polyacenaphthylene [5, 8, 9] shows that the wavenumbers are increased in poly(vinylene carbonate). The wavenumber of the peak at 3000 cm^{-1} is higher than the highest wavenumber observed in *cis*-decaline [8, 9] and/or polyacenaphthylene [5, 8] found to be characteristic of equatorial anellation of hydrogen atoms at the H—C(C—H) bond frequencies. This increase in the

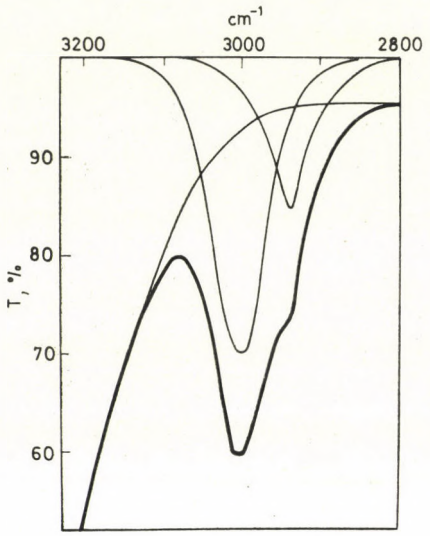

Fig. 3. IR spectrum of poly(vinylene carbonate) obtained by γ-irradiation in the solid state

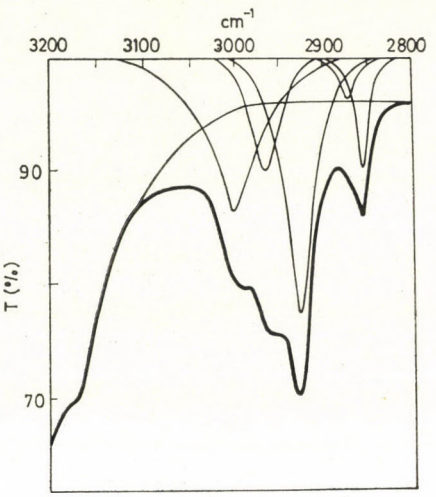

Fig. 4. IR spectrum of poly(vinylene carbonate) obtained by γ-irradiation in the liquid state

frequency can be explained by the large inductive effect of oxygen atoms in a five- membered ring. It can be assumed that this line corresponds to an *e*-anellation, *e.g. erythro* segments in the polymer chains.

Since the monomeric units are chemically symmetrical and the partial charge distributions on the C–H bonds are equivalent, it can be concluded that the integrated peak area is proportional to the number of H atoms with identical anellation. This could mean that in the polymer obtained by a solid state reaction three H atoms have the same anellation corresponding to a dihedral angle of 180° (*erythro*) and one H atom has a different relative position. This could be characteristic for an *erythro-syndio*tactic chain. On the basis of the spectrum of poly(vinylene carbonate) obtained in the liquid state, the peak at 2975 cm^{-1} can be assigned to the *threo* monomeric units. The bands from 2855 to 2937 cm^{-1} probably show an approximately axial anellation of hydrogen atoms along the main chains.

Result of energy computations

Figures 5 and 6 show the energy as a function of the dihedral angle of the monomer units in the *threo-* and *erythro-iso*tactic chain. Table IV summarizes the data on the helices corresponding to the minima marked by numbers. The broken lines give the energy function of dimers, whereas the dotted lines represent the differences in the energy functions which approximately correspond to the attractive intraction arising along the helix chain.

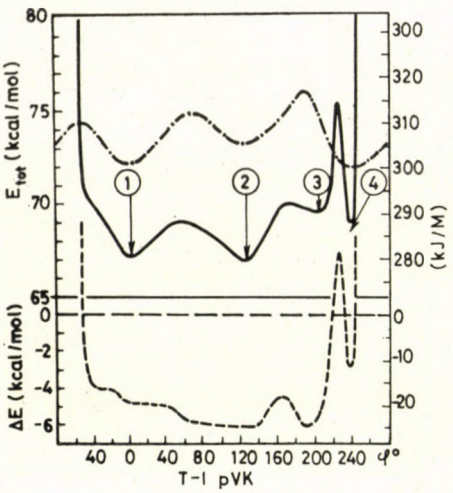

Fig. 5. Energy function of *threo-iso*tactic poly (vinylene carbonate) chains (solid line) and of dimers (broken line), and the attractive potential between monomeric units (dotted line) as a function of the dihedral angle φ_2. Numbers in circle refer to the data of Table IV

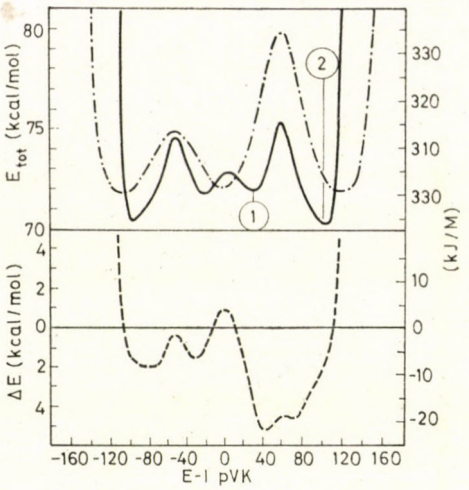

Fig. 6. Energy function of *erythro-iso*tactic poly(vinylene carbonate) chains as a function of the dihedral angle φ_2 (see Fig. 5)

As the energy barrier is remarkably low between the individual minima (20 kJ/mol), the chain may assume all minimum positions, thus the chains are flexible.

The energy function of the *erythro-iso*tactic chain is symmetrical for the *trans* conformation, however, that of the *threo-iso*tactic chain is not. The translational periods of all six different polymer chains are smaller than is to be expected from X-ray measurements.

The energy functions of the *threo-syndio*tactic chain depending on the dihedral angles of the 2nd and 4th chain atoms, respectively, are demonstrated in Fig. 7. Table IV also includes the data of the nonequivalent minima positions. The energies of these two positions differ only slightly, the barrier between them is also small (5 kJ/mol), also indicating a flexible chain. The translational periods of the chains differ to a great extent from those observed by X-ray diffraction.

The energy function of *erythro-syndio*tactic chains depending on two dihedral angles is presented in Fig. 8. Of five helices with local energy minima, two have translational periods corresponding to the X-ray results (*cf.* Table IV). The helical chain marked No. 4 is shown in Fig. 9. This is a 3_1 helix with a chain period (D = 3.12 Å) identical with that observed in the polymer single-crystal pattern (3.13 Å [2]). Therefore, the unidentified third crystal axis could be identical with the first axis (*i.e.* 11.02 Å), owing to a trigonal unit cell.

In Fig. 10 the helical chain marked No. 2 corresponds to the absolute minimum of the energy function. The translational period of this chain is

Table IV

Data of helices corresponding to the local minima of the potential functions. R, Φ and D defined in Ref. [4]

Number	φ_1	φ_2	E_{tot} [kJ/mol]	R [Å]	Φ [deg]	D [Å]	N	Helix	Type
				*threo-iso*tactic chains					
1	2	—	281.38	1.065	76.147	2.330	4.727	19_4	(5_1)
2	130	—	280.51	0.890	80.380	2.416	4.480	9_2	
3	208	—	291.12	1.333	113.761	1.472	3.164	3_1	
4	240	—	288.85	1.588	98.923	1.154	3.639	11_3	(7_2)
				*erythro-iso*tactic chains					
1	32	—	301.59	0.710	160.038	2.341	2.250	9_4	
2	102	—	294.71	1.208	125.970	1.675	2.858	3_1	
				*threo-syndio*tactic chains					
1	0	0	281.77	0.450	180.000	2.540	2.000	2_1	
2	2	120	281.63	0.682	120.185	3.710	2.995	3_1	
				*erythro-syndio*tactic chains					
1	10	−10	299.86	—	—	4.840	—		
2	10	90	291.28	1.929	87.154	3.135	4.130	4_1	
3	50	120	301.66	0.886	93.168	3.751	3.864	4_1	
4	130	−20	296.96	1.938	129.680	3.117	2.776	11_3	(3_1)
5	120	30	301.52	2.312	131.548	2.187	2.737	11_3	
				threo-erythro chains					
1	− 10	90	289.24	2.000	163.549	3.230	2.201	9_4	(2_1)
2	− 40	90	289.61	2.344	113.642	3.178	3.167	3_1	
3	−120	−20	287.84	2.783	97.323	2.662	3.699	15_4	
4	− 50	−90	296.30	1.687	177.090	3.247	2.032	2_1	
5	100	−90	297.21	2.016	161.563	2.838	2.228	9_4	
6	100	−10	290.68	3.009	92.604	2.228	3.888	4_1	
7	0	0	288.10	0.987	107.386	4.852	3.333	10_3	
8	120	120	292.43	2.363	92.321	2.737	3.899	4_1	

practically the same as that of the previous one (3.14 Å); the helix is of the 4_1 type. The energy difference of these two helices is small, the barrier between them is 6 kJ/mol, also indicating a flexible polymer chain.

In Fig. 11 the energies of the *threo-erythro* polymer chains are presented as a function of the dihedral angles of 2nd and 4th chain atoms. Eight helical chains are on the energy minimum. Table IV includes the data of these too. Three of these helices have chain periods similar to those observed by X-ray

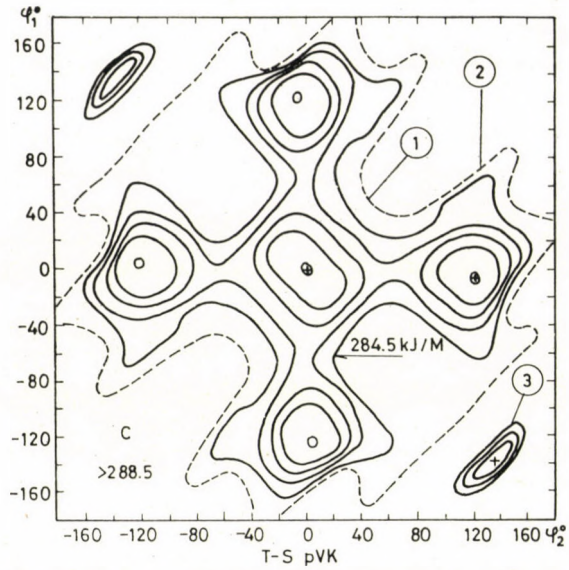

Fig. 7. Energy function of *threo-syndio*tactic poly(vinylene carbonate) chains as a function of dihedral angles φ_2 and φ_4. The lines connect sites with differences of 1 kJ/mol

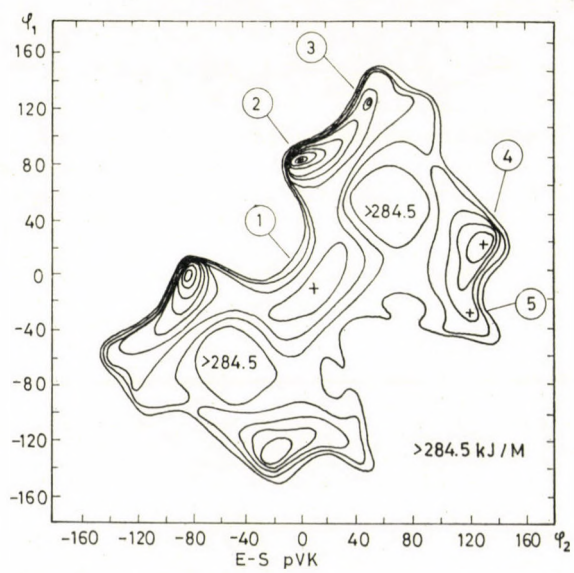

Fig. 8. Energy functions of *erythro-syndio*tactic poly(vinylene carbonate) chains as a function of dihedral angles φ_2 and φ_4 (see Fig. 7)

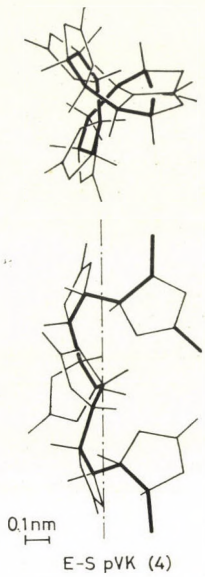

Fig. 9. Helical structure of *erythro-syndiotactic* poly(vinylene carbonate) chain No. 4. The double line represents the main chain

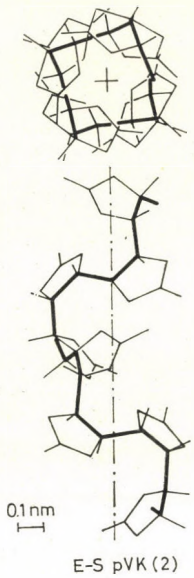

Fig. 10. Helical structure of *erythro-syndiotactic* poly(vinylene carbonate) chain No. 2 (see Fig. 9)

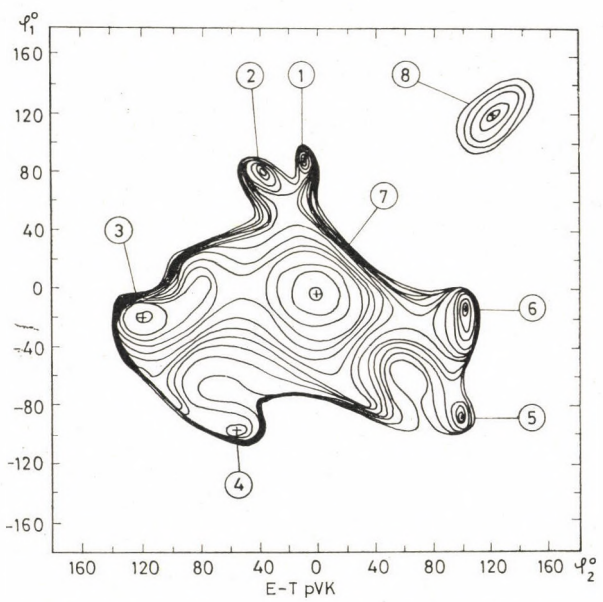

Fig. 11. Energy function of *threo-erythro* poly(vinylene carbonate) chains as a function of dihedral angles φ_2 and φ_1 (see Fig. 7)

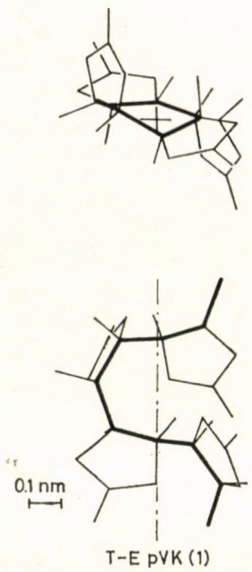

Fig. 12. Helical structure of *threo-erythro* poly(vinylene carbonate) chain No. 2 (see Fig. 9)

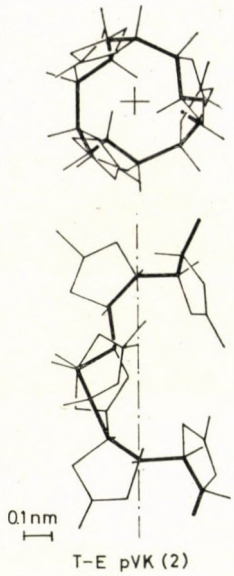

Fig. 13. Helical structure of *threo-erythro* poly(vinylene carbonate) chain No. 2 (see Fig. 9)

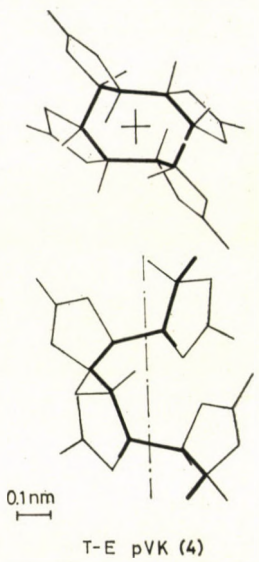

Fig. 14. Helical structure of *threo-erythro* poly(vinylene carbonate) chain No. 4 (see Fig. 9)

diffraction. These are shown in Figs 12 (No. 1), 13 (No. 2) and 14 (No. 4). Helix No. 2 is a 3_1 helix of minimum position. However, the structure of the chains with the absolute minimum differs substantially from the expected chain period. As in this case all the energy barriers are small, the transitions between minimum sites are practiclly free. No. 8 is the only chain with a high energy barrier (>100 kJ/mol), however, its chain period is substantially smaller than the measured value.

According to energy calculations, the regular chains can be either *ertyhro-syndio*tactic or *threo-erythro* chains. The powder- or single-crystal X-ray data [2, 3] are consistent only with *erythro-syndio*tactic chains. The anellation of H atoms depending on the dihedral angles of helices at the minimum-energy position of the *threo-erythro* chain implies smaller wavenumbers in the IR spectra than those observed in the polymer formed by a solid state reaction. The IR spectra of the polymer obtained by a liquid state reaction is characteristic of a polymer chain with *erythro* and *threo* segments, representing different helical structures of the chain.

The phenomena observed in solid state polymerization [1—3] are in good agreement with the occurrence of *erythro-syndio*tactic chains and helices.

If the axis of the helix shown in Fig. 8 is parallel to the axis of the monomer crystal, the positions of monomeric units along the helix can be correlated with their original positions in the crystal lattice. This geometrical similarity

also suggests an *erythro-syndio*tactic chain formation. On the basis of the calculated energy function, our observation that the primarily formed chain is transformed into a chain of different geometrical structure seems reasonable.

The translational period of this secondary structure should be identical with that in the structure formed primarily; this can only be observed in *erythro-syndio*-tactic chains.

The calculated density of the polymer based on a trigonal unit cell with $a = b = 11.02$ and $c = 9.39$ Å [2] is 1.733 g cm^{-3}. The estimated density of amorphous polymer is 1.583 g cm^{-3}, 1.439 g cm^{-3} and 1.504 g cm^{-3}, according to VAN KREVELEN and HOFTYZER [10], KITAYGORODSKII [11] and BONDI [12]. The mean value of the estimated density is 1.509 g cm^{-3}, in good agreement with the value calculated from the density of the crystalline polymer, using the relationship of VAN KREVELEN and HOFTYZER [10] (1.5077 g cm^{-3}). The best estimated value is that of BONDI [12]. Accordingly, the degree of crystallinity of the precipitated polymer is ca. 50%.

The measured and calculated data are not in contradiction. In summary, the following conclusions can be drawn.

a) All polymer chains formed either from *erythro* or *threo* segments are flexible. Thus the expected segment lengths are small.

b) The conformational energies of the different geometrical types of polymer chains differ only slightly. The energy functions have broad small minima, the energy values of these minima do not differ much from each other, therefore, several different types of helices can be present even though the chain structure is identical. The packing of the chains determines their helical arrangements.

c) The polymer formed in heterogeneous, topotactic solid state polymerization is crystalline, probably an *erythro-syndio*tactic 3_1 helix with high density. There is no forced isomorphism between the polymer formed and the monomer, in contrast to the phenomenon observed in acenaphthylene [5]. In parallel to the increasing conversion, high-density sites accumulate inhomogeneously, as they only form around polymerization centres, therefore, the oriented eutectic-like polymer–monomer system becomes more and more unstable until it becomes stabilized by a structural transformation. Finally, a polymer plastified by its monomer is formed, which can be observed through a polarizing microscope [1].

d) In the precipitated polymer the length of segments with identical conformation is small (30—50 Å) and the degree of crystallinity is low because of the different types of helices in the same polymer chain.

e) The probabilities of formation of *threo-* and *erythro* segments are approximately identical in liquid state polymerization. The degree of regularity of this polymer is lower than that in polymers obtained in the solid state.

*

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INFRARED STUDIES OF SOLVENT EFFECT; COMPLEXING OF THE CARBONYL GROUP WITH PHENOL

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The influence of the hydroxyl group in phenol on the carbonyl vibration has been studied with a view of analyzing the hydrogen-bonding ability of several esters with phenol. The rate of change of bond moment with bond distance, $d\mu/dr$, for the free and H-bonded C=O bonds has been determined from infrared intensity measurements. The existence of 1:1 and 1:2 complexes is confirmed; the structure of the complexes formed is discussed on the basis of the observed frequency shifts.

Introduction

The manifestation of molecular interactions — both intra- and intermolecular — in various physical properties has been studied in great detail [1]. Of the polar groups that have been studied by spectroscopic, cryoscopic, magnetic and dielectric methods, the O—H group is of particular interest because of its polar attraction. It is of great interest to know the relative strengths of hydrogen bonds and the specific structures that are formed by such bonding between proton acceptors such as esters, ketones, nitriles and amines. By dielectric measurement, GILES *et al.* [2] have shown the possibility of formation of a hydrogen-bonded complex between phenols and several ketones and amines. Studies of the infrared carbonyl absorption bands of representative esters, ketones and aldehydes in phenol by several workers [3—7] also confirmed the existence of one or more specific complexes. The spectroscopic method, in particular the infrared study of hydroxyl and carbonyl absorption bands, provides information about the stretching and deformation vibrations of X—H bonds and acceptor groups. The shift in the stretching vibration of a group to lower frequencies may be regarded as a measure of the energy of intermolecular interaction. In the present investigation, the behaviour of the carbonyl bands of several esters in mixtures of phenol and carbon tetrachloride is studied, in order to elicit information about the interaction between the hydroxyl and carbonyl groups and examine the relative contributions of the bulk dielectric effect and other types of local effects.

Experimental

A Hilger H 800 spectrophotometer equipped with a sodium chloride optical system was used in a double beam operation. The samples were contained in H 890 Hilger variable path length precision micrometer cells with sodium chloride end plates. Approximately 0.04 *M* solutions of the esters were studied. The cell thickness used was 0.0234 cm. The temperature of the cell was maintained at 298 K. AnalaR samples of CCl_4 and phenol and distilled pure samples of esters were used.

Results and discussion

The carbonyl absorptions by 0.04 *M* ester solutions in CCl_4, containing various amounts of phenol were determined. In the pure solvent a single sharp band is found at a characteristic frequency (Table I).

Upon the addition of phenol, new bands appear with a frequency shift, and the intensity of the original band decreases. As the concentration of phenol is increased, the low-frequency band intensity continues to increase at the expense of the higher-frequency shift and the positions of the individual bands are constant within one wavenumber. This behaviour indicates the formation of @ 1 : 1 complex. As the concentration of phenol is further increased beyond 0.1 *M*, a new band appears at a still lower frequency. The asymmetry on the low-frequency side is now replaced by an asymmetry on the higher-frequency side and the original $\nu(C=O)$ band intensity decreases further. A further increase in phenol concentration results in only a small decrease in the intensity of the 1 : 1 complex, whereas the new band lying at a still lower frequency continues to increase in intensity, with the simultaneous disappearance of the free $\nu(C=O)$ band; it becomes predominant at higher concentrations, indicating the formation of @ 1 : 2 complex (Fig. 1).

Using the integrated intensity values calculated from the relation given by FREEMAN [8] and assuming that the carbonyl vibration is a pure stretching mode, the change in bond moment upon stretching can be calculated from the

Table I

Acceptor	Frequencies [cm^{-1}]			$(d\mu/dr)_{mean}$ 1 : 1	$(d\mu/dr)_{mean}$ 1 : 2
	free $\nu C=O$	1 : 1 $\nu C=O$	1 : 2 $\nu C=O$	(esu cm^{-1})	
Methyl acetate	1757	1735	1713	8.865	6.503
Ethyl acetate	1749	1731	1714	5.447	4.063
iso-Butyl acetate	1753	1726	1715	7.677	1.781
n-Amyl acetate	1750	1728	1718	7.706	4.518
Benzyl acetate	1756	1731	1720	8.013	4.199
Phenyl acetate	1778	1754	1748	8.395	5.913

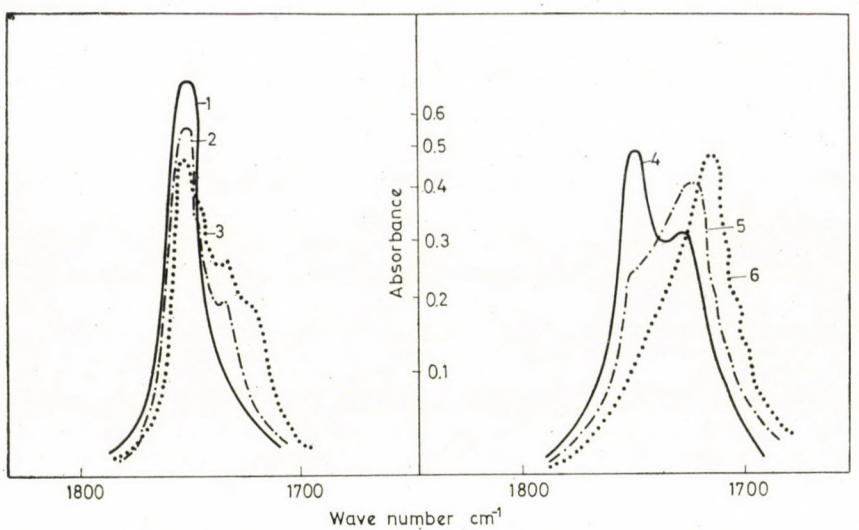

Fig. 1. Spectra of 0.04 *M* ethyl acetate in mixtures of phenol and CCl_4. (1) Pure ethyl acetate, (2) with 0.03 *M* phenol, (3) with 0.08 *M* phenol, (4) with 0.14 *M* phenol, (5) with 0.4 *M* phenol, (6) with 1.2 *M* phenol

relations [9]

$$\frac{d\mu}{dr} = \left(\frac{1}{m_c} + \frac{1}{m_0}\right)^{1/2} \frac{d\mu}{dQ}$$

and

$$\frac{d\mu}{dQ} = \pm\left(\frac{3c'}{\pi} A_s\right)^{1/2}$$

where m_c and m_0 are the masses of carbon and oxygen atoms, c' is the velocity of light and A_s represents the integrated intensity of the band of the complex. In Tables II—VII are given the integrated intensities and the changes in dipole moment for various donor concentrations, referred to the values of pure carbonyl stretching in CCl_4 as a standard.

The concentrations of free and self-associated phenol species are obtained from the peak intensities of the free $\nu C=O$ band in CCl_4 and at various concentrations of phenol in CCl_4. The integrated intensity and hence $(d\mu/dr)$ of the $\nu C=O$ bond increase owing to bond formation and apparently reaches a maximum at about 0.4 *M* phenol, indicating that the complex formation is probably complete at this concentration. These results can be readily explained in terms of the pulsed charge cloud model of BOOBYER and ORVILLE-THOMAS [10].

In all esters except phenyl acetate there is complete disappearance of the free $\nu C=O$ band at phenol concentrations around 1.0 *M*, which indicates the full formation of the C=O complex with phenol. In the case of phenyl acetate the free $\nu C=O$ band does not disappear even at 1.0 *M* phenol, indicating

Table II

νC=O vibration of methyl acetate (concentration 0.04.M)

Phenol concentration in CCl_4 (mol/l)	1 : 1 complex		1 : 2 complex	
	$A_s \times 10^7$ ($cm^2 mol^{-1} cm^{-1}$)	$d\mu/dr \times 10^{10}$ (esu cm^{-1})	$A_s \times 10^7$ ($cm^2 mol^{-1} cm^{-1}$)	$d\mu/dr \times 10^{10}$ (esu cm^{-1})
0.00	4.88	6.535	....	.....
0.03	14.95	8.409	....	.....
0.05	18.66	8.700	....	.....
0.08	19.45	8.755	....	.....
0.10	20.18	8.800	3.88	6.030
0.20	20.73	8.833	4.86	6.528
0.40	25.89	9.099	5.00	6.587
0.80	26.34	9.119	5.03	6.596

Table III

νC=O vibration of ethyl acetate (concentration 0.04 M)

Phenol concentration in CCl_4 (mol/l)	1 : 1 complex		1 : 2 complex	
	$A_s \times 10^7$ ($cm^2 mol^{-1} cm^{-1}$)	$d\mu/dr \times 10^{10}$ (esu cm^{-1})	$A_s \times 10^7$ ($cm^2 mol^{-1} cm^{-1}$)	$d\mu/dr \times 10^{10}$ (esu cm^{-1})
0.00	6.84	3.339	....	.....
0.05	14.18	4.806	....	.....
0.08	16.58	5.198	....	.....
0.14	16.77	5.232	....	.....
0.20	23.07	6.139	9.66	3.968
0.40	23.70	6.207	10.77	4.190
0.80	17.24	5.300	12.40	4.495
1.20	16.89	5.247	12.89	4.583

Table IV

νC=O vibration of iso-butyl acetate (concentration 0.04 M)

Phenol concentration in CCl_4 (mol/l)	1 : 1 complex		1 : 2 complex	
	$A_s \times 10^7$ ($cm^2 mol^{-1} cm^{-1}$)	$d\mu/dr \times 10^{10}$ (esu cm^{-1})	$A_s \times 10^7$ ($cm^2 mol^{-1} cm^{-1}$)	$d\mu/dr \times 10^{10}$ (esu cm^{-1})
0.00	7.78	3.561	....	.....
0.08	25.94	6.501	....	.....
0.10	31.20	7.122	....	.....
0.20	43.00	8.381	1.73	1.677
0.40	46.47	8.702	1.90	1.761
0.80	.....	.....	2.19	1.887

Table V

νC=O vibration of amyl acetate (concentration 00.4 M)

Phenol concentration in CCl_4 (mol/l)	1 : 1 complex		1 : 2 complex	
	$A_g \times 10^7$ ($cm^2 mol^{-1} cm^{-1}$)	$d\mu/dr \times 10^{10}$ (esu cm^{-1})	$A_g \times 10^7$ ($cm^2 mol^{-1} cm^{-1}$)	$d\mu/dr \times 10^{10}$ (esu cm^{-1})
0.00	12.67	4.546	....	.....
0.03	28.46	6.803	....	.....
0.05	28.92	6.845	....	.....
0.08	33.78	7.435	....	.....
0.10	44.00	8.468	9.79	3.995
0.20	49.50	8.980	10.21	4.078
0.40	.....	.....	14.91	4.930
0.80	.....	.....	15.85	5.070

Table VI

νC=O vibration of benzyl acetate (concentration 0.04 M)

Phenol concentration in CCl_4 (mol/l)	1 : 1 complex		1 : 2 complex	
	$A_g \times 10^7$ ($cm^2 mol^{-1} cm^{-1}$)	$d\mu/dr \times 10^{10}$ (esu cm^{-1})	$A_g \times 10^7$ ($cm^2 mol^{-1} cm^{-1}$)	$d\mu/dr \times 10^{10}$ (esu cm^{-1})
0.00	12.69	4.494	....	.....
0.05	30.96	7.186	....	.....
0.08	33.58	7.398	....	.....
0.10	34.38	7.484	....	.....
0.20	43.50	8.420	....	.....
0.40	55.43	9.504	8.84	3.794
0.80	40.14	8.087	13.01	4.605

that the complexation of phenol with phenyl acetate is not complete, as supposed to other esters. In general, in the case of esters, two bands are obtained even at comparatively low concentrations.

The mean dipole moment derivatives of the carbonyl bond characteristic of the 1:1 and 2:2 complexes are also reported for all the esters studied. $(d\mu/dr)$ for the O – H bonds should naturally be higher. However, it is not possible to calculate the exact values from the O – H band intensities, because of the overlapping bands arising from self-association effects because of two other symmetrical bands resulting from H-bridge isomerism as explained by FRITZCHE [11]. However, the magnitude of $\overrightarrow{\Delta\mu}$, the interaction moment along the O – H ... O bond, can be estimated from the $(d\mu/dr)$ value for the C = O bonds reported here for the 1 : 1 complexes.

Table VII

νC=O vibration of phenyl acetate (concentration 0.04 M)

Phenol concentration in CCl_4 (mol/l)	1 : 1 complex		1 : 2 complex	
	$A_s \times 10^7$ ($cm^2 mol^{-1} cm^{-1}$)	$d\mu/dr \times 10^{10}$ (esu cm^{-1})	$A_s \times 10^7$ ($cm^2 mol^{-1} cm^{-1}$)	$d\mu/dr \times 10^{10}$ (esu cm^{-1})
0.00	9.09	7.674	....	.....
0.05	13.06	8.222	....	.....
0.08	13.61	8.281	....	.....
0.10	14.10	8.352	....	.....
0.14	14.50	8.357	....	.....
0.20	15.24	8.433	....	.....
0.40	19.03	8.726	....	.....
0.80	.....	.....	3.38	5.746
1.20	.....	.....	3.92	6.080

The value of $(d\mu/dr)$ for 1 : 1 complexes of the carbonyl systems studied here varies from about 5×10^{-10} esu cm^{-1} to 8×10^{-10} esu cm^{-1}. If one of the oxygen sp^2-hybrid orbitals is almost collinear with the O – H ... O axis, it will be in a most favourable position for maximum interaction between the O – H bond and the lone pair forming an atomic dipole. Using minimized distances of 1.03 Å and 1.04 Å for free and H-bonded O – H [12–14], and a maximum displacement of 0.025 Å [15], along the O ..... O distance, one obtains a $\overrightarrow{\Delta\mu}$ of about 0.10—0.15 D, owing to the polarization of the C = O bond. A similar or slightly higher value would also be expected for the induced moment for the O – H bond. So a total $\overrightarrow{\Delta\mu}$ of about 0.3—0.4 D may be explained by considering the vibrations of the lone pair of electrons together with the vibrations of the O – H bond.

From a qualitative study of the complex formation between the carbonyl group and phenol, conclusions can be drawn on the various possible structures of the molecular complexes.

a) If one molecule of phenol is directly attached to the C = O group, a 1 : 1 complex is formed with a large frequency shift.

b) There are two possible structures for the 1 : 2 complex: (i) the two phenol molecules are attached directly to the C = O group with a large frequency shift, (ii) one phenol molecule is attached to the carbonyl group and the other is H-bonded to this phenol molecule, causing an unresolvable frequency shift. The large frequency shift in the case of esters favours the structure in which two phenol molecules are directly attached to the C = O group.

*

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CARBOHYDRATE METHYL ETHERS, VIII*

THIN-LAYER CHROMATOGRAPHIC SEPARATION OF ISOMERIC GLUCOSE METHYL ETHERS AND THEIR DETERMINATION WITH ANTHRONE

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The thin-layer chromatographic separation of all di-, tri- and tetra-O-methyl-D-glucoses has been achieved. Solvent systems III—IV have been found suitable for the separation of the dimethyl ethers, the trimethyl ethers and the tetramethyl ether. The individual structural isomers could be separated in system IV and in the combined systems III—VII, in the case of the trimethyl and dimethyl ethers, respectively. The methyl ethers separated are determined by the use of the anthrone reaction in the 10—70 μg range.

In the course of investigations on the bond types in polysaccharides, the separation of partially methylated monomers and their quantitative determination has become necessary. Several paper chromatographic systems and measurement procedures have been described [1] for this purpose. Although thin-layer chromatography has been widely applied in studies of the hydrolysis products of methylated polysaccharides, no procedure has been suggested in the literature providing reliable separation of, for instance, the different isomeric methyl ethers of a single hexose.

Of the trimethylglucose, TSCHESCHE and BALLE [2] achieved the separation of the 2,4,6- and 3,4,6-isomers. TSCHESCHE and WULFF [3] also reported the separation of all the four possible tri-O-methyl-D-glucoses, however, the R_f values were only slightly different. Such a degree of separation is not sufficient for quantitative work. The system recommended by HAY *et al.* [4] also provides only limited separation. The system developed by LIPTÁK and JODÁL [5] ensures good separation of the 2,3,4,6-tetra-O-methyl-, 2,3,4-tri-O-methyl-, 2,3-di-O-methyl- and the 2,4-di-O-methyl-D-glucoses. For quantitative determination the phenol-sulfuric acid procedure [4] or the aniline hydrogen phthalate procedure [5] has been applied.

Results

In the course of investigating the structure of glucans, we attempted separation of all possible isomeric glucopyranose methyl ethers. Previous results indicated that the separation of glucose methyl ethers methylated to different

*Part VII: L. KISS, A. LIPTÁK, P. NÁNÁSI: Acta Chim. (Budapest), **83**, 201 (1974)

extent could easily be realized. The difficulties arise in the separation of the various structural isomers of identical degree of substitution. In all separation experiments, Kieselgel G adsorbent was applied; when organic solvents were used, the plates were activated for 1 hr. at 110°C, while in the case of aqueous solvent systems the activation step was omitted. The following solvent systems were used in our experiments:

I. Chloroform–methanol 9 : 1
II. Benzene–acetone 1 : 1
III. Methyl ethyl ketone–water (azeotropic system)
IV. Water
V. Benzene–acetone 3 : 7
VI. Butan-1-ol–ethyl acetate–water 6 : 4 : 3 (upper phase)
VII. Butan-1-ol saturated with water.

The R_{TMG} values are summarized in Table I.

Table I

Methyl-D-glucose	Solvent system						
	I	II	III	IV	V	VI	VII
2,3,4,6-tetra-O-	100	100	100	100	100	100	100
2,4,6-tri-O-	65	62	75	131	—	—	—
2,3,4-tri-O-	60	63	86	137	—	—	—
2,3,6-tri-O-	67	70	85	148	—	—	—
3,4,6-tri-O-	65	65	86	121	—	—	—
2,4-di-O-	—	—	54	163	57	83	84
2,6-di-O-	—	—	58	163	55	83	84
3,4-di-O-	—	—	65	152	55	89	87
3,6-di-O-	—	—	60	161	55	83	82
4,6-di-O-	—	—	50	142	46	78	79
2,3-di-O-	—	—	66	158	53	91	91

In the case of the tri-O-methyl-D-glucoses the best, practically complete, separation was achieved in water (IV). They could be separated from one another, as well as from tetra-O-methyl-D-glucose and the di-O-methyl-D-glucoses. Of the di-O-methyl-D-glucoses, only the 2,4-derivative appears near the 2,3,4- and 2,3,6-tri-O-methyl-D-glucose isomers.

Solvent systems I—II—III did not give satisfactory separation for the tri-O-methyl-D-glucoses, yet all the three systems are of importance, since in

systems I and II the 2,3,6-substituted isomer, and in system III the 2,4,6-isomer can be separated from the three other trimethyl ethers.

In the case of dimethylglucoses the best separation has been achieved in system III, although this separation was by far not so good as that of the trimethyl ethers, the greatest disadvantage being that the 2,3- and 3,4-isomers ran practically together, and also the separation of the 2,6- and 3,6-isomers was poor.

Systems IV—VII are reported for the dimethylglucoses because the 4,6- and 3,4-isomers can be separated from each other and from the rest of the methyl ethers in system IV; furthermore, this system is suitable for the separation of the 2,3- and 3,4-substituted isomers, which migrate together in system III. In system V, it is the 4,6-isomer which can be completely separated from the other five isomers. The same performance has also been obtained with system VII. It is worth noting that 4,6-di-O-methyl-D-glucose migrates with the lowest R_f value in all systems examined by us, and can be always completely separated from the other five dimethylglucose isomers.

Quantitative determination of the glucose methyl ethers separated has been successfully accomplished with anthrone [6] in the following way: after developing the chromatogram, the compounds separated were located by means of aniline hydrogen phthalate in one layer of a parallel chromatogram, then the substances in 1.5×1.5 cm areas were removed together with the adsorbent from the other layer, suspended in water and the colour was developed with anthrone. After separation of the adsorbent by centrifuging, the light absorption of the supernatant was measured at 625 nm. The reference solution was prepared by treating the adsorbent scraped off from carbohydrate-free 1.5×1.5 cm area of the layer in the same way.

The calibration curves were directly constructed with anthrone for each compound covering the 10—70 μg range; the curves perfectly agreed with the absorbance values of similar amounts obtained after chromatographic develop-

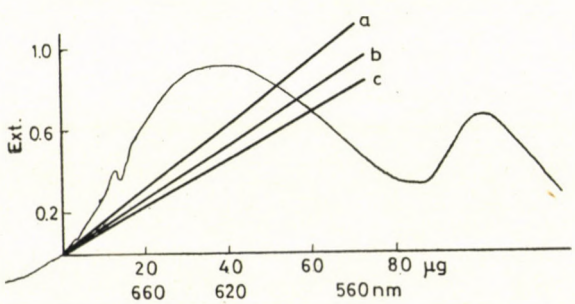

Fig. 1. Spectrum and calibration curve of the complex of 2,4-di-O-methyl-D-glucose formed with anthrone. (a) 2,4-di-O-methyl-D-glucose, (b) 2,3,4-tri-O-methyl-D-glucose, (c) 2,3,4,6-tetra-O-methyl-D-glucose

ment and removal from the layer; the only exeption was 2,3-di-O-methyl-D-glucose, where the quantities determined on the layer were 5—8% lower.

The chromophores of the glucose methyl ethers formed with anthrone are identical; their spectra agree with that shown in Fig. 1.

The calibration curves for the individual methyl ethers are also shown in Fig. 1. There is no significant difference between the individual isomers, in fact, the calibration curves for the 2,3,6- and 3,4,6-tri-O-methyl-D-glucoses are perfectly identical, and the situation is the same for the 3,4-di-O-, 3,6-di-O- and 2,4-di-O-methyl-D-glucoses. The calibration curve obtained for 2,3-di-O- and 2,6-di-O-methyl-D-glucoses was identical but lower than that of other four dimethylglucoses. The method is suitable for the determination of these glucose methyl ethers with 2—3% accuracy.

Experimental

One-per cent alcoholic solutions of the glucose methyl ethers [7—10] were prepared and known volumes of the solutions were applied onto Kieselgel-G layers of 20×20 cm area by means of a Terumo microsyringe of 25 μl capacity. The chromatogram was developed in methyl ethyl ketone–water azeotropic mixture up to a height of 15 cm. After drying, the spots at the side of the plates were detected with aniline hydrogen phthalate at 105°C. On this basis, the positions of the spots in the parallel chromatogram were marked and the substances were removed together with an adsorbent layer of 1.5×1.5 cm area each. The adsorbent containing the substance was suspended in 1 ml of distilled water and 2 ml of anthrone reagent was added.

The chromophore was developed by treatment at 100°C for 15 min; after cooling, the solution was subjected to centrifuging at 7000 rpm for 10 min. The supernatants were transferred directly into the spectrophotometric cells and measured photometrically.

The reference solution was prepared by identical treatment of the adsorbent scraped off from a carbohydrate-free part of the layer having 1.5×1.5 cm area.

The calibration curves were constructed for each glucose methyl ether in the 10—70 μg range.

*

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STUDY OF THE REACTION OF GRIGNARD REAGENTS WITH 4-(3H)-QUINAZOLINONES AND 4H-3,1-BENZOXAZIN-4-ONES

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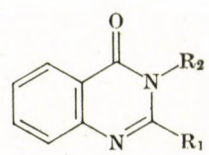
2,3-Diaryl-4(3H)-quinazolinones (**Id**–g) reacted with Grignard reagents to give 2,3-diaryl-4-(methyl or phenyl)-4-hydroxy-3,4-dihydroquinolines (**V**). 2-Aryl-4(3H)-quinazolinones (**Ih**–j) yielded the corresponding substituted carbinols (**VI**). Similarly, 2-aryl-4H-3,1-benzoxazin-4-ones (**VII**) afforded the substituted carbinols (**VIII**), which, on cyclization, gave 4,4-disubstituted-2-aryl-4H-benzoxazines (**IX**).

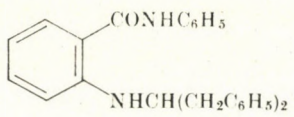
The action of Grignard reagents on 4(3H)-quinazolinones (**Ia**—*j*) has been previously investigated [1—5].



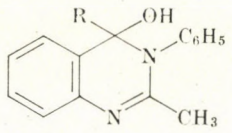
I

	R_1	R_2
a:	H	C_6H_5
b:	CH_3	C_6H_5
c:	C_6H_5	C_6H_5
d:	C_6H_5	$C_{10}H_7-1$
e:	C_6H_5	C_6H_4Cl-p
f:	C_6H_5	$C_6H_4CH_3-p$
g:	C_6H_4Cl-p	C_6H_4Cl-p
h:	C_6H_5	H
i:	C_6H_4Cl-p	H
j:	$C_6H_4CH_3-p$	H

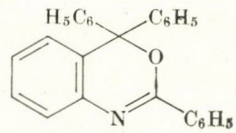
KOELSCH [1] reported the reaction of **Ia** with benzylmagnesium chloride to give N-(β,β'-diphenylisopropyl)- anthranilanilide (**II**) as the chief product. KOELSCH also found that when the quinazolone had a substituent in the 2-position, attack by the Grignard reagent apparently occurred at the carbonyl group in 4-position. HAMER *et al.* [2] treated 1,2-dimethyl-4(3H)-quinazolone with Grignard reagent and reported that addition to the carbonyl group took place. SEN [3] observed the attack of the Grignard reagent on the carbonyl group of 2-methyl-3-phenyl-4(3H)-quinazolinone to give **III**. On the other hand, MUSTAFA *et al.* [5] and NOSSEIR [6] reported the formation of 2,4,4-triphenyl-4H-3,1-benzoxazine (**IV**) from 2,3-diphenyl-4(3H)-quinazolinone (**1c**).



II

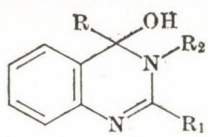


III



IV

In the present investigation the reaction of Grignard reagents with 4(3H)-quinazolinones has been explored. It has been found that the Grignard reagents react with 2,3-diaryl-4(3H)-quinazolinones (**Id—g**) to give products in agreement with the results obtained by KOELSCH [1] and SEN [3]. The Grignard reagents attacked the carbonyl group in the 4-position yielding 2,3-diaryl-4-(methyl or phenyl)-4-hydroxy-3,4-dihydroquinazolines (**Va—e**).



V

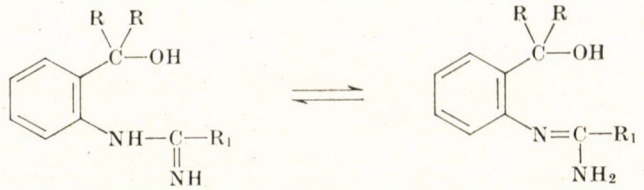
	R	R_1	R_2
a:	C_6H_5	C_6H_5	$C_{10}H_7-1$
b:	CH_3	C_6H_5	C_6H_4Cl-p
c:	C_6H_5	C_6H_5	C_6H_4Cl-p
d:	C_6H_5	C_6H_5	$C_6H_4CH_3-p$
e:	CH_3	C_6H_4Cl-p	C_6H_4Cl-p

It is worth mentioning that the Grignard reaction of quinazolones containing a *p*-nitro-substituted phenyl group in the 3-position gave resinous material which could not be purified.

Similarly, Grignard reagents attack the carbonyl group in the compounds bearing an aryl substituent in position 2 only. In this case, the reaction proceeds further, resulting in compound **VI** produced by ring opening. Cleavage of the ring, like in the formation of **VI**, can be observed when 2-aryl-3,1-benzoxazin-4-ones (**VII**) are allowed to react with Grignard reagents to give the expected 2-benzamidoaryldiphenyl- (or dimethyl-) carbinols (**VIII**), which cyclize to 2-aryl-4,4-diphenyl- (or dimethyl-) 4H-3,1-benzoxazines (**IX**) on treatment with a mixture of sodium acetate and acetic anhydride.

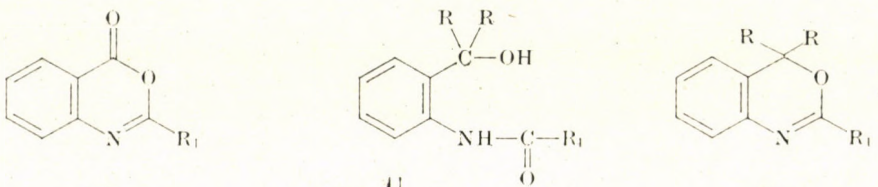
Structures, **V**, **VI**, **VII** and **IX** have been confirmed, besides the correct analytical data, by IR spectroscopy.

The IR spectra of compounds **V** show a broad band located at 3350 cm^{-1}, which corresponds to the stretching vibrations of the OH group. It is to be noted that the two characteristic bands due to the asymmetric and symmetric stretching vibrations of the lactone ring are absent in these compounds.



VI

	R	R_1
a:	CH_3	$C_6H_4CH_3-p$
b:	C_6H_5	C_6H_4Cl-p
c:	CH_3	C_6H_5
d:	C_6H_5	C_6H_5



VII VIII IX

		R	R_1
VIII and **IX**	**a:**	C_6H_5	$C_6H_4CH_3-p$
	b:	CH_3	$C_6H_4CH_3-p$
	c:	C_6H_5	C_6H_4Cl-p
	d:	CH_3	C_6H_4Cl-p

The IR spectra of compounds **VI** are characterized by two strong bands at 1655 and 1635 cm^{-1}, which can be attributed to the two C=N groups. This is due to amine-imine tautomerism. A broad band at 3350 cm^{-1} and 3325 cm^{-1} can be assigned to the asymmetric and symmetric stretching vibrations of the NH_2 group overlapped with NH stretching vibrations.

The IR spectra of compounds **VIII** are characterized by a strong broad band at 3340 cm^{-1} with a shoulder at 3260 cm^{-1} corresponding to the stretching vibrations of the OH group overlapped with NH stretching vibrations. Compounds **VIII** also show the presence of C=O group at 1660 cm^{-1}. The carbonyl band is shown in case of the original benzoxazone (**VII**) at 1775 cm^{-1}. It is clear that the two characteristic bands due to the asymmetric and symmetric stretching vibrations of the lactone ring are absent in compound **VIII**.

The IR spectra of compounds **IX**, on the other hand, exhibit no band corresponding to the stretching vibrations of a carbonyl group. Moreover, these compounds show two strong bands located at 1265 and 1035 cm^{-1}, corresponding to the asymmetric and symmetric vibrations of the lactone ring.

Experimental

The IR spectra were obtained using a Perkin Elmer Model 137 infrared spectrophotometer. The KBr pellet technique was used. All m.p.'s are uncorrected.

Table I

Products from the reaction of Grignard reagents with **I** *and* **VII**

Compound	M.p., °C	Solvent	Formula (Mol. wt.)	Analysis Calcd./Found			
				%C	%H	%N	%Cl
Va	107	P	$C_{30}H_{22}N_2O$	84.48	5.20	6.57	—
			(426.50)	84.09	5.15	6.55	—
Vb	205	E/P	$C_{21}H_{17}ClN_2O$	72.30	4.91	8.03	10.16
			(248.83)	72.51	5.00	7.99	10.30
Vc	247	E/P	$C_{26}H_{19}ClN_2O$	76.00	4.66	6.82	8.63
			(410.89)	76.10	4.30	7.00	8.93
Vd	223	B/P	$C_{21}H_{16}Cl_2N_2O$	65.81	4.20	7.31	
			(383.39)	65.49	4.33	7.11	
VIa	208	B	$C_{17}H_{20}N_2O$	76.08	7.51	10.44	
			(268.36)	76.31	7.72	10.39	
VIb	190	B/P	$C_{26}H_{21}ClN_2O$	75.60	5.13	6.78	
			(412.97)	75.13	4.67	6.92	
VIc	203	B	$C_{16}H_{18}N_2O$	75.56	7.13	11.02	
			(254.34)	75.19	7.60	11.41	
VId	227	B	$C_{26}H_{22}N_2O$	82.47	5.86	7.39	
			(378.66)	82.71	6.30	7.62	
VIIIa	174	B	$C_{27}H_{23}NO_2$	82.42	5.89	3.56	
			(393.49)	82.67	5.94	3.54	
VIIIb	117	B/P	$C_{17}H_{19}NO_2$	75.80	7.11	5.20	
			(269.36)	75.66	7.32	5.18	
VIIIc	187	B	$C_{26}H_{20}ClNO_2$	75.18	4.87	3.38	
			(413.96)	75.44	5.20	3.42	
VIIId	123	B/P	$C_{16}H_{16}ClNO_2$	66.31	5.56	4.83	
			(289.81)	66.08	5.26	4.72	

B = benzene; P = petroleum spirit; E = ethyl acetate.

Reaction of I and VII with Grignard reagents

A solution of **I** or **VII** [7—10] (0.01 mole) in 50 ml dry benzene was added dropwise to a solution of the Grignard reagent (phenylmagnesium bromide or methylmagnesium iodide) (0.03 mole) in dry ether. The ether was evaporated and the reaction mixture heated under reflux for 5 hrs, and then left to stand overnight. The reaction mixture was worked up as usual. The yellow solid residue was crystallized from an appropriate solvent to give **V, VI,** and **VIII,** respectively, in 60—65% yield. The results are listed in Table I.

Table II

4H-3,1-Benzoxazines **(IX)**

Compound	M.p., °C	Formula (Mol. wt.)	Analysis Calcd./Found %C	%H	%N
IXa	208	$C_{27}H_{21}NO$	86.37	5.64	3.73
		(375.48)	85.89	5.74	3.39
IXb	157	$C_{17}H_{17}NO$	81.24	6.80	5.50
		(251.33)	81.60	6.56	5.12
IXc	218	$C_{26}H_{18}ClNO$	78.88	4.58	3.54
		(395.88)	79.20	4.91	3.83
IXd	181	$C_{16}H_{14}ClNO$	70.70	5.19	5.15
		(271.80)	70.29	5.40	5.31

Cyclization of VIII with acetic anhydride

To a mixture of **VIII** (1 g) anhydrous sodium acetate and 30 ml acetic anhydride were added, and the reaction mixture was heated under reflux for 3 hrs. After concentration and cooling the solid product obtained was crystallized from a mixture of benzene and petroleum spirit (b.p. 40—60 °C). The yield was 65%. The results are listed in Table II.

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THE ACID-CATALYZED REARRANGEMENT OF N-NITRO-DERIVATIVES OF 2-AMINOTHIAZOLE, I

KINETICS, SOLVENT AND SUBSTRATE ISOTOPE EFFECTS IN THE ACID-CATALYZED REARRANGEMENT OF 2-THIAZOLYLNITRAMINES

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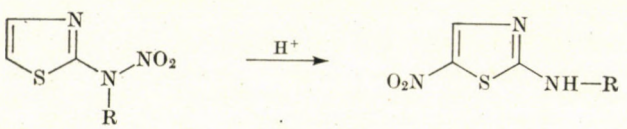
The kinetics of the acid-catalyzed rearrangement of three 2-(N—R)-nitraminothiazoles (R = H, CH_3, C_2H_5) have been measured over the acidity range of 88—96% sulfuric acid. It has been established that the rearrangement is subject to general acid catalysis by (1) the influence of the isotopic composition of the solvent on the rate of reaction of the same substrate, and (2) the acidity function correlation of the reaction rates. The reactivity of the 5-deuterated 2-(N-methyl)-nitraminothiazole was examined, where primary deuterium isotope effect was found. Spectroscopic evidence was obtained for the formation of a reactive intermediate. The kinetic results can be interpreted by a five-step mechanism, in which the slow steps are second protonation of the nitramine and proton-loss from the σ complex.

The acid-catalyzed rearrangement of 2-nitraminothiazole derivatives (Chart 1) was described by DICKEY *et al.* [1]. The study of this process led to the conclusion that the reaction was analogous to the well-known aromatic nitramine rearrangement [2], the reaction mechanism of which has recently been the subject of intensive studies [3, 4], whereas the above-mentioned rearrangement, except for another qualitative investigation [5], has not been examined in detail.



I

II

1 R = H
2 R = CH_3
3 R = C_2H_5

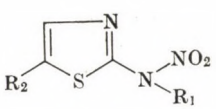
Compounds **II** (R = H, $COCH_3$, or $CONHC_2H_5$) are important chemotherapeutics [6], thus the rearrangement of 2-thiazolylnitramines is of considerable theoretical and practical interest. The objective of this work was the thorough investigation of the rearrangement, shown in Chart 1. Further information about the mechanism of the rearrangement should be available from the kinetics of the process and from the influence of substrate structural modifications on its rate. As the first problem, characterization of the nature of

acid intervention — its general or specific nature — is of primary importance. If the rearrangement is subject to specific acid catalysis, the rate-determining step follows a reversible protonation, so that the rates will reflect not only the ease of protonation, but also the facility of later bond-breaking or -making processes. The aromatic nitramine rearrangement involves such a mechanism [4]. On the other hand, if the reaction is subject to general acid catalysis, the proton transfer is rate-limiting.

In this investigation, we studied the influence of acid catalysts of different isotopic compositions and concentrations on the rearrangement rates of 2-nitraminothiazole and its N-substituted derivatives. To clarify also the role of proton loss, we replaced the hydrogen by deuterium in the 5 position of the 2-(N-methyl)-nitraminothiazole. The materials used are listed in Table I.

Table I

Chemical shifts of 2-nitraminothiazole derivatives in 96% sulfuric acid solutions at 23 °C



Compound	R_1	R_2	δ (CH)	δ (CH_3)
(1)	H	H	6.30 (s)	—
(2)	CH_3	H	6.38 (q)	3.42
(3)	C_2H_5	H	6.27 (s)	—
(4)	CH_3	D	6.38 (s)	3.42

Experimental

Preparation of materials

2-Nitraminothiazole was prepared by nitration of 2-aminothiazole at 0°C; m.p. 202°C (lit. [5] m.p. 204°C).

2-(N-methyl)-nitraminothiazole was obtained by methylation of the sodium salt of the above compound; m.p. 269°C (lit. [1] m.p. 269°C).

2-(N-ethyl)-nitraminothiazole. A solution consisting of 7.25 g (0.05 mol) of 2-nitraminothiazole, 200 ml of water and 10.6 g (0.1 mol) of sodium bicarbonate was mixed with 7.7 g (0.05 mol; 6.6 ml) of diethyl sulfate. The mixture was stirred for 2 hrs at room temperature and 2 hrs at 50°C. The separated material was filtered off with suction, washed with water, and dried at 60°C to obtain 3.3 g white crystals, m.p. 182—183°C (from dimethylformamide–ethanol).

$C_5H_7N_3O_2S$. Calcd. C 34.56; H 6.06; N 24.33; S 18.50. Found C 34.52; H 6.09; N 24.29; S 18.50%.

5-Deuterio-2-(N-methyl)-nitroaminothiazole. 4 g of 2-aminothiazole was dissolved in 10 ml of 50% D_2SO_4, and the solution was kept for 2 hrs at 80°C. The water was distilled off, then twice 5 ml of deuterium oxide was added, followed by repeating the distillation. The

residue was treated with 4 g of KNO_3 in 10 ml of D_2O; the mixture was heated to 80°C, then chilled. The crystals of 5-deuterio-2-amino-(d_2)-thiazole · DNO_3 which separated were filtered off with suction, and dried at 60°C to obtain 4.5 g of the product, m.p. 156 °C. NMR analysis showed about 95% deuterium content in position 5.

2.50 g of 5-deuterio-2-amino-(d_2)-thiazole · DNO_3 was dissolved in 3 ml of 96% D_2SO_4 at −10°C, stirred for 20 min at 0°C, then poured onto 10 g of ice. The 5-deuterio-2-nitraminothiazole which separated was filtered off and washed with water and ethanol to obtain 0.7 g, m.p. 200°C. According to NMR analysis, the deuterium content in position 5 was ca. 95%.

0.4 g 5-deuterio-2-nitraminothiazole was dissolved in 10 ml water containing 0.47 g $NaHCO_3$, then 0.4 ml dimethyl sulfate was added dropwise, and the mixture was stirred for 2 hrs. Crytals of 5-deuterio-2-(N-methyl)-nitraminothiazole separated, which were filtered off with suction and washed with water and ethanol to obtain 0.30 g, m.p. 268—270°C. NMR analysis showed that the substance contained 96% 5-deuterio compound, without any detectable 4-deuteration.

Isolation of the rearrangement product of 2-(N-methyl)-nitraminothiazole. 0.48 g of nitramine was dissolved in 1.5 ml of 96% H_2SO_4 and stirred for 1 hr. at room temperature. The reaction mixture was poured onto 10 g of ice. After adjustment of the pH to ca. 5.5 with ammonium hydroxide, the mixture was chilled and the yellow crystals which separated were filtered off, washed with water and dried at 60°C, to obtain 0.35 g of 2-methylamino-5-nitrothiazole, m.p. 220—222°C (ethanol) (lit. [1] m.p. 220—222°C).

Acid solutions. The required sulfuric and deuteriosulfuric acid concentrations were adjusted by dilution with water and deuterium oxide, respectively. The acid content was determined by titration against standard alkali.

Kinetic measurements. The kinetic measurements were carried out with VARIAN A-60 D and JEOL C-60 HL instruments. The substrate (0.001 mol) was dissolved in 0.5 ml sulfuric acid at 0°C, transferred to the NMR tube, sealed, and the NMR spectra were run at 1—5 min intervals, thermostated at a given temperature. 3-Trimethylsilylpropane-sulfuric acid was used as external standard. At least two runs were made with each compound at every given acid concentration and temperature. The first-order rate constants were determined graphically from plots of $\ln c^0/c$ against time.

Results and discussion

The kinetics of the rearrangement can be well followed by the change of NMR spectra in time. Thus the spectrum of a solution of 2-(N-methyl)-nitraminothiazole in 96% sulfuric acid at 23°C has two signals: the AB signal of the thiazole protons at $\delta = 6.38$ and the methyl signal at 3.42. As the reaction advances, these are gradually replaced by the peaks of the final product, the C-4 proton signal at 8.35, and the methyl signal at 3.88. The chemical shifts of the 2-(N-alkyl)-nitraminothiazoles observed in 96% sulfuric acid solution are recorded in Table I, and those of the final products in Table II.*

Table II

Chemical shifts of 2-amino-5-nitrothiazole derivatives in concentrated sulfuric acid solutions

II, R	δ (CH)	δ (CH_3)
H	8.20	—
CH_3	8.35	3.88
C_2H_5	8.38	—

*Hydrogen-deuterium exchange was not observable in the ring protons of 2-nitraminothiazole derivatives.

The reaction was found to follow pseudo-first-order kinetics, as shown by the excellent linear first-order plots. As examples, the plots for 2-nitraminothiazole measured in 96% H_2SO_4 and D_2SO_4 at 23°C are shown in Fig. 1.

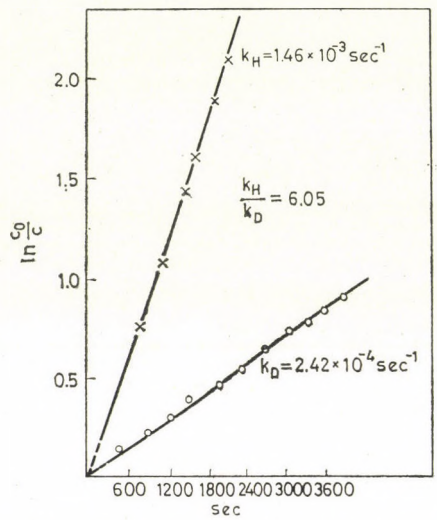


Fig. 1. Pseudo-first-order plots for the rearrangement of 2-nitraminothiazole in 96% sulfuric acid and deuteriosulfuric acid at 23°C

The first-order rate constants, determined graphically, are recorded in Table III. As shown by the first three data, the effect of N-alkyl substituents is an increase of the reaction rate. Further, a significant solvent isotope effect was observed; the reaction rate is slower in deuteriosulfuric acid. Thus, for 2-nitraminothiazole in 96% acid at 23°C $k_{H_2SO_4}$: $k_{D_2SO_4} = 6.0$, and for the N-methyl derivative $k_{H_2SO_4}$: $k_{D_2SO_4} = 8.0$.

Table III

First-order rate constants of the acid-catalyzed rearrangement of 2-nitraminothiazole derivatives in H_2SO_4 and D_2SO_4

Starting compound	Catalyzing acid (96%)	Temperature, °C	Concentration, mole/lit.	$k_{obs} \cdot 10^4$ sec^{-1}
(1)	D_2SO_4	23	1.8	2.4
(2)	D_2SO_4	23	1.8	4.0
(3)	D_2SO_4	23	1.8	10.3
(2)	D_2SO_4	13	1.8	1.66
(2)	D_2SO_4	36	1.8	38.0
(1)	H_2SO_4	23	1.8	14.6
(2)	H_2SO_4	23	1.8	31.9
(2)	H_2SO_4	13	1.8	21.4

The nature of acid catalysis may be ascertained from the rate effect produced by changes in the solvent isotopic composition [7—9]. Specific acid-catalyzed reactions usually proceed faster in deuterated than in normal solvents, whereas, for general acid-catalyzed processes the opposite is true. Our results are those anticipated for a general acid-catalyzed reaction.

The rate of a general acid-catalyzed reaction depends on the concentration of the acid catalyst, whereas the velocity of a specific acid-catalyzed process is determined by the pH of the medium only [4a].

The acid-catalyzed rearrangement of 2-thiazolylnitramines takes place within a fairly narrow acidity range. As DICKEY *et al.* [1] have shown, the rearrangement proceeds rapidly in 96% sulfuric acid at 20°C, but in 85% sulfuric acid it is very slow, and below this concentration there is no rearrangement. According to our results, in 99—100% sulfuric acid the rearrangement takes place instantaneously. Investigations in solutions below 96% sulfuric acid gave further information about the rearrangement. In 50% sulfuric acid at 36°C, or in 96% sulfuric acid at 0°C, where no rearrangement occurs, the chemical shifts of the ring protons of 2-nitraminothiazole derivatives do not differ essentially from those recorded in an indifferent solvent, *e.g.*, dimethyl sulfoxide, while in 96% sulfuric acid solution at 36°C they appear at 1.5—1.6 ppm upfield as compared with the original signals.

The shift of the CH resonance in concentrated sulfuric acid may be attributed to the formation of a reactive intermediate possessing a considerably altered electronic structure, in comparison with the original N-nitro compound (Table IV).

The formation of the reactive intermediate in 94—96% sulfuric acid at 23—36°C is so rapid that right after dissolution the nitramine can only be observed as an intermediate in the spectra. Decreasing the sulfuric acid concentration, the initial transformation of nitramine into the intermediate appears as a new reaction, and in about 90% sulfuric acid it can be well measured in the first minutes of the rearrangement process.

Table IV

Chemical shifts of 2-nitraminothiazole derivatives in dimethyl sulfoxide and in dilute and concentrated sulfuric acid solutions at 36 °C

Starting compound	δ_1 (CH) (DMSO)	δ_2 (CH) (50% H_2SO_4, 90% H_2SO_4, first minutes)	$\delta_2-\delta_1$	δ_3 (CH) (96% and 90% H_2SO_4, intermediate)	$\delta_2-\delta_3$
(1)	7.84 (q)	7.90 (q)	0.06	6.30 (s)	1.60
(2)	7.85 (q)	7.92 (s)	0.07	6.38 (q)	1.54
(3)	7.75 (q)	7.82 (s)	0.07	6.27 (s)	1.55
(4)	7.85 (s)	7.92 (s)	0.07	6.38 (s)	1.54

For example, the spectrum of 2-(N-methyl)-nitraminothiazole in 90% deuteriosulfuric acid recorded in the first minute at 36°C contains the peak of the thiazole protons as a single sharp line at $\delta = 7.9$ and the ring proton doublets of the intermediate at 6.38, while the two signals at 4.18 and 3.42 are due to the $N-CH_3$ groups in the starting material and the intermediate, respectively. (A small peak from an unidentified product was observed in all experiments at 7.10 in the first minutes.) The spectrum recorded in the 45th minute of the rearrangement consists, besides the peaks of the intermediate, of the CH signal at 8.35 ppm and the methyl signal at 3.88 ppm of the final product (Fig. 2).

Similar results have been obtained for the other 2-nitraminothiazole derivatives. The chemical shifts of the ring protons measured in the first minutes in 90% sulfuric acid solution and those of the intermediates are recorded in Table IV.

Both the formation and the decomposition of the intermediate were found to be pseudo-first-order processes. The kinetics of the first stage were followed by observing the disappearance of the starting material in the NMR spectra; the second step was studied similarly by following the formation of the 5-

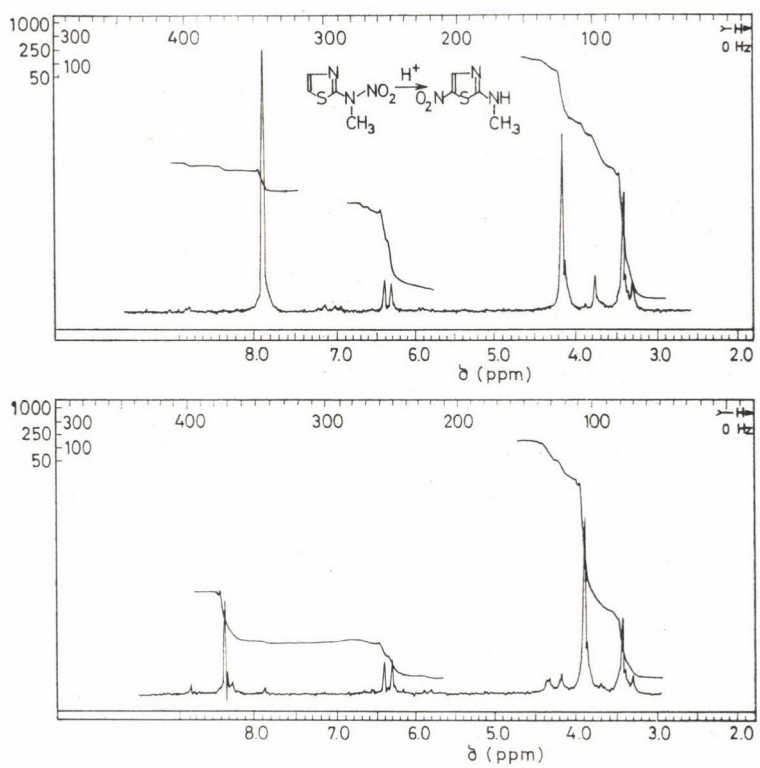


Fig. 2. NMR spectra of the acid-catalyzed rearrangement of 2-(N-methyl)-nitraminothiazole in 90% deuteriosulfuric acid at 36°C

nitrothiazole compound. The k'_{obs} rate constants of the pre-equilibrium are larger by an order of magnitude than the k''_{obs} rate constants of the formation of the final product.

A characteristic kinetic shape can be obtained by plotting the concentration change of the starting nitramine, the reactive intermediate, and the final product against time. The variation of the concentration values with time for 2-(N-methyl)-nitraminothiazole in 90% sulfuric acid and deuteriosulfuric acid at 36°C is shown in Fig. 3.

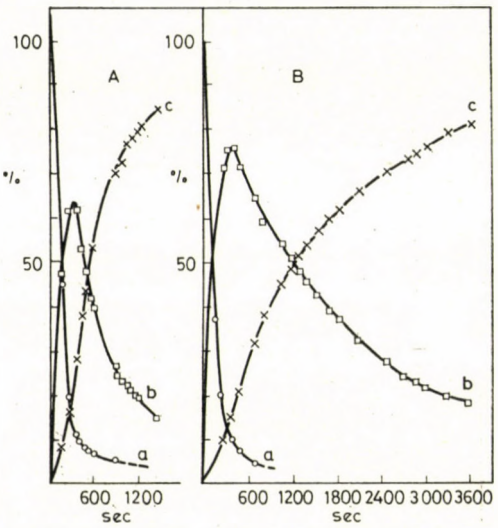


Fig. 3. Kinetic diagram of the rearrangement of 2-(N-methyl)-nitraminothiazole in 90% sulfuric acid at 36°C; (*a*) starting N-nitro compound, (*b*) intermediate, (*c*) final 5-nitro compound. Starting material: A: (2); B: (2). Acid catalyst: A: H_2SO_4(90%); B: D_2SO_4(90%)

Table V shows the graphically determined rate constants of various rearrangement reactions in 90% acid at 36°C. A solvent isotope effect was observed for both stages of the reaction. Thus for 2-(N-methyl)-nitraminothiazole $k'_{obs,\ H_2SO_4}$: $k'_{obs,\ D_2SO_4} = 1.7$ and $k''_{obs,\ H_2SO_4}$: $k''_{obs,\ D_2SO_4} = 1.9$ (in 90% acid, at 36°C).

For the N-ethyl derivative the solvent isotope effect of the first stage was less significant. For the second step a primary isotope effect $k''_H : k''_D = 3.9$ was observed on the rate coefficient when the rates of 2-(N-methyl)-nitraminothiazole and its 5-deuterated analogue were compared. On rearrangement of the 5-deuterated derivative in deuteriosulfuric acid, the solvent and substrate isotope effects were superimposed.

Both the lifetime of the starting nitramine and that of the intermediate decreased with increasing acidity. Kinetic results for the rearrangement of 2-(N-methyl)-nitraminothiazole in deuteriosulfuric acid at 36°C are given in Table VI.

Table V

First-order rate constants of the rearrangement of 2-nitraminothiazole derivatives in 90% sulfuric acid at 36 °C

Starting nitramine	90% acid	C mole/lit.	$k'_{obs} \cdot 10^3$ sec^{-1}	$k''_{obs} \cdot 10^4$ sec^{-1}
(1)	H_2SO_4	2	3.7	6.1
(2)	H_2SO_4	2	6.5	8.7
(2)	D_2SO_4	2	3.8	4.6
(3)	H_2SO_4	2	2.5	15.6
(3)	D_2SO_4	2	2.1	7.7
(4)	H_2SO_4	2	6.6	2.2
(4)	D_2SO_4	2	3.3	1.1

Table VI

Rearrangement of 2-(N-methyl)-nitraminothiazole in D_2SO_4 at 36 °C

D_2SO_4 %	$-D°$ (25°)	$-D°$ (36°)	$\log k'_{obs} + 4$	$\log k''_{obs} + 4$
88.6	8.86	8.57	1.3927	0.4472
89.9	9.03	8.73	1.5798	0.6628
91.4	9.24	8.94	1.7634	0.9494
96.0	9.85	9.53	—	1.5798

The D° scale of SIERRA and OJEDA [10] was used for the calculations; the D° values have been corrected for temperature using the data of JOHNSON *et al.* [11], as D° has been assumed to equal H° [10].

The plots of $\log k'_{obs}$ and $\log k''_{obs}$ *vs.* $-D°$ (Fig. 4) are good straight

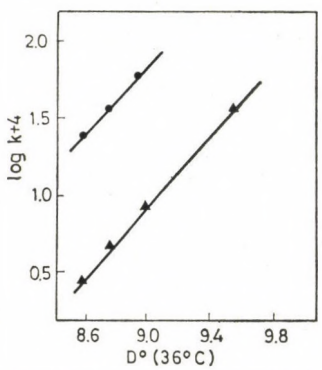
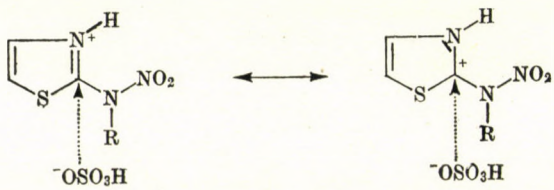


Fig. 4. Rate profiles ($\log k_{abs}$) for the rearrangement of 2-(N-methyl)-nitraminothiazole in deuteriosulfuric acid at 36°C. ●: formation of the intermediate; ▲: formation of 2-methylamino-5-nitrothiazole

lines. The slope of the plots is 0.87 and 1.18, respectively, showing a first-order dependence of both stages upon D°.

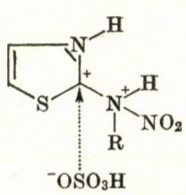
These kinetic results of the rearrangement studies reveal that the reaction is subject to general acid catalysis, where the proton has an important role in two or more steps of the isomerization. The influence of the proton has already been demonstrated in the first protonation step, when the observed intermediate was formed. The large upfield shift (1.5—1.6 ppm) of the ring proton peaks may be attributed to the break of the aromatic character of the thiazole ring. We postulate that this is due to the formation of a complex between the protonated thiazole ring and the hydrogen sulfate anion. Thus a possible structure for the reactive intermediate is **III**.



III

Attempts at isolating **III** as a crystalline derivative remained unsuccessful. No spectroscopic evidence was obtained for the existence of a similar intermediate in studies of concentrated sulfuric acid solutions of the simple 2-alkylaminothiazoles.

N-alkyl substitution increases the reaction rate by its $+I$ effect. This influence is effective in the second, slow stage of the reaction (Table V), which shows that the amino nitrogen in this stage is electron-deficient. The observed results suggest that this electron deficiency is due to a second protonation in a slow, reversible step, which occurs on the exocyclic nitrogen of the reactive intermediate, and the unstable double-protonated intermediate **IV** may be stabilized by the loss of proton, or by cleavage of the N–N bond.

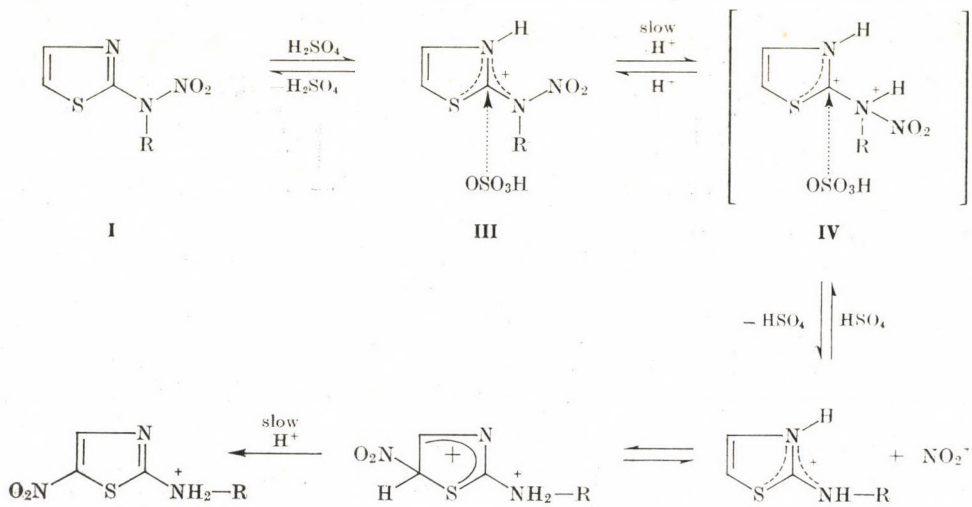


IV

We postulate that the cleavage of the nitro group is accompanied by the decomposition of the complex **IV**, the stability of which was due to the polarizing, electron-withdrawing effect of the nitro group. Further, the separated nitronium ion and the protonated 2-aminothiazole fragments can recombine

into an N-nitro compound. However, the nitration of the thiazole ring results in the progress of the reaction by which these fragments recombine into 5-nitrothiazolyl compound. This is well compatible with recent studies of BURTON *et al.* [12], according to whom in concentrated sulfuric acid five-membered N-heterocycles are nitrated on the conjugate form of the basic hetero rings. The decomposition of the σ-complex formed in the course of the nitration is a relatively slow, kinetically significant step.

Fitting all the above pieces of evidence together, we propose that the mechanism of the acid-catalyzed rearrangement of 2-nitraminothiazole derivatives in concentrated sulfuric acid can be represented as shown in Chart 2.



It follows that the acid-catalyzed rearrangement of 2-nitraminothiazole derivatives is not completely analogous to the aromatic nitramine rearrangement.* The participation of a basic hetero atom in the ring alters the character of the reaction, and the first protonation occurs on the ring nitrogen. Thus N–N bond cleavage is initiated only by a second protonation, which changes the character of the acid catalysis and the rate-determining step, too.

The determination of the intra- or intermolecular character of the reaction requires special studies [13]. We hope to present the results of such an investigation shortly.

*No spectroscopic evidence for radical intermediates has been obtained in the ESR spectrum recorded in the course of the rearrangement.

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SYNTHESIS OF N-ACYL-OLIGOPEPTIDES OF POTENTIAL ANTITUBERCULOTIC ACTIVITY

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N-Acyl-oligopeptides of potential antituberculotic activity have been prepared from simple basic materials. In the first type the peptides, acylated with a fatty acid, were built up from valine, phenylalanine and lysine, and in the second type from leucine, phenylalanine and lysine. For elucidation of the structure–activity relationships, the effect of the number, character and sequence of the amino acids and that of the individual fatty acids were studied. The compound of highest potency, N^{α}-palmitoyl-L-lysyl-D-phenylalanyl-L-leucyl-L-lysine amide, exhibited an activity of 3 μg/ml against *Mycobacterium tuberculosis* $H_{37}R_v$, *in vitro*.

Despite a large amount of research performed in the field of peptide antibiotics, few attempts have been made to synthesize oligopeptides from simple, easily available sources. French [1] and Japanese [2] scientists prepared a number of acyl-oligopeptides of mediocre antimicrobial potency. PAULAY and BAJUSZ obtained, in an attempt to synthesize structures abstracted from gramicidin S, a series of substances exhibiting considerable antituberculotic activity *in vitro* (D-phenylalanyl-L-leucyl-L-lysyl-D-phenylalanyl-L-lysyl-L-leucine amide — 6 μg/ml) [3].

In continuation of this work, we tried to elucidate how acylation affects the antimicrobial potency of peptides. Acyclic compounds were built up from simple aromatic (phenylalanine), basic (lysine) and aliphatic amino acids, the first type of substances containing L-valine, the second type L-leucine. For elucidation of the structure–activity relationships, the effect of the number, character and sequence of amino acids and that of individual fatty acids was studied.

The compounds synthesized, together with their respective potencies against *Mycobacterium tuberculosis* $H_{37}R_v$, are summarized in Table I. It is apparent that as a result of acylation by fatty acids, the size of the peptide may be significantly reduced; while in the earlier paper [3] six-membered, acyclic hexapeptides were the smallest exhibiting antituberculotic activity, here even acyl-dipeptides might be considered active molecules (**3**, **4**, and **31**). Compound **57**, inactive as a free peptide, represents in the acylated form (**61**, **65** and **69**) the peak of activity in the second type of substances, palmitic acid [or(—)-6-methyloctanoic and(—)-6-methylheptanoic acids] easily replacing the D-phenylalanyl-L-leucyl sequence of **81a**.

Table I

	L-Valine-containing peptides	Min. inhib. concn. *M. tub.* $H_{37}R_v$ μg/ml
3	palmitoyl ..... phe-Val ..... OMe	25
4	palmitoyl ..... phe-Val ..... N_2H_3	25
8	palmitoyl ..... phe-Val-Lys-amide	25
18	Lys-phe-Val-Lys-amide	>100
11	palmitoyl ..... Lys-phe-Val-Lys-amide	100
13	6-MOA ..... Lys-phe-Val-Lys-amide	100
15	6-MHA ..... Lys-phe-Val-Lys-amide	100
17	oleoyl ..... Lys-phe-Val-Lys-amide	100
26	phe-Val-Lys-phe-Val-Lys-amide	25
21	palmitoyl-phe-Val-Lys-phe-Val-Lys-amide	100
23	6-MOA...phe-Val-Lys-phe-Val-Lys-amide	100
25	oleoyl....phe-Val-Lys-phe-Val-Lys-amide	100
	monopalmitoyl-dicyclohexylurea	>100
	dicyclohexylurea	>100
	palmitic acid	>100
	6-MOA—OH = (—)-6-methyloctanoic acid	>100
	6-MHA—OH = (—)-6-methylheptanoic acid	>100
	oleic acid	>100

Of the three types of fatty acids (unbranched or branched chain, and unsaturated), acylation with palmitic acid, (—)-6-methyloctanoic acid or (—)-6-methylheptanoic acid resulted in highly active agents (**61**, **65** and **69**), while the corresponding oleoyl-tetrapeptide (**71**) proved to be less satisfactory. In

	L-Leucine-containing peptides and homologues	Minc. inhib. concn. *M. tub.* $H_{37}R_v$ μg/ml
31	palmitoyl ..... phe-Leu ... OMe	25
32	palmitoyl ..... phe-Leu ... N_2H_3	100
36	palmitoyl ..... Lys-phe ..... N_2H_3	>100
39	palmitoyl ..... phe-Lys ... amide	>100
42	palmitoyl ..... Lys-Lys ... amide	50
45	palmitoyl ..... phe-Leu-Lys-amide	100
47	oleoyl ..... phe-Leu-Lys-amide	25
53	palmitoyl ..... Lys-Leu-phe ... N_2H_3	25
57	Lys-phe-Leu-Lys-amide	>100
58	Lys-Phe-Leu-Lys-amide	>100
61	palmitoyl ..... Lys-phe-Leu-Lys-amide	3
62	palmitoyl ..... Lys-phe(*t*-Bu)-Leu-Lys-amide	>100
63	palmitoyl..... Lys-Phe-Leu-Lys-amide	>100
65	6-MOA ..... Lys-phe-Leu-Lys-amide	> 65
67	6-MOA ..... Lys-Phe-Leu-Lys-amide	>100
69	6-MHA ..... Lys-phe-Leu-Lys-amide	6
71	oleoyl ..... Lys-phe-Leu-Lys-amide	25
73	oleoyl ..... Lys-Phe-Leu-Lys-amide	>100
78	Lys-Leu-phe ... Lys-amide	>100
77	palmitoyl ..... Lys-Leu-phe ... Lys-amide	100
81a	phe-Leu-Lys-phe-Leu-Lys-amide	25
81	palmitoyl-....phe-Leu-Lys-phe-Leu-Lys-amide	25
83	6-MOA ..... phe-Leu-Lys-phe-Leu-Lys-amide	25
85	oleoyl ..... phe-Leu-Lys-phe-Leu-Lys-amide	25
91	Lys-phe-Leu-Lys-phe.....Lys-amide	25
90	palmitoyl-Lys-phe-Leu-Lys-phe.....Lys-amide	25

addition, branched-chain fatty acids broaden the antimicrobial range of tetrapeptides: while all N-acyl-peptides in this study exhibited antimicrobial activity solely against *Myrobacterium tuberculosis* $H_{37}R_v$, these show activity against Gram positive microorganisms and fungi as well.

The fatty acid plays a specific role in the character of the molecule. It may promote, similarly to polymyxins [4, 5], the transfer of the molecule through the lipophilic cell membrane. Branched-chain fatty acids must especially be taken into consideration, as several natural antobiotics contain these residues (polymyxins, aspartocin, amphomycin, glumamycin, stendomycin, etc.).

Comparing the potencies of the two types of substances, it is evident that, up to acyl-tripeptides, valine-containing substances (**3**, **4** and **8**) are more active than leucine-containing ones (**32**, **36**, **39**, **42** and **45**). From tetrapeptides on, however, the activity pattern is changed, and leucine-containing peptides become more potent; acyl-tetrapeptides (**61**, **65** and **69**) represent the peak of activity, with minimal inhibitory concentrations of 3—6 μg/ml, as compared to the corresponding valine analogues (**11**, **13** and **15**) having a negligible potency of 100 μg/ml. This seems to be all the more striking as the difference is just a single methylene group between the two series. Most probably, the size of the branched side chain of the peptide plays a fundamental role in its biological properties. In gramicidin S analogues, the 1,1'-L-valine unit of the molecule [cyclo(L-valyl-L-ornithyl-L-leucyl-D-phenylalanyl-L-prolyl)$_2$] could easily be exchanged for leucine, as well as for alanine, but substitution by glycine, devoid of any side chain, led to complete loss of the activity [6, 7]. In our case the limits appear to be even narrower. With the lack of one methylene group in valine, the adsorption of the molecule to the active surface is no longer assured, whereas *t*-butyl substitution of D-phenylalanine in **62** prevents adsorption due to its bulkiness.

Peptide elongation either at the C- (**90**) or the N-terminal (**81** and **83**) of the molecule resulted in less potent substances.

In accordance with literature data, the configuration of amino acids plays a fundamental role. Only substances containing D-phenylalanine represent potent molecules, those having L-phenylalanine are devoid of antimicrobial activity, either in the acylated form (**63**, **67** and **73**) or as the free peptide (**58**).

As regards the sequence of amino acids in tripeptide **53**, L-lysyl-L-leucyl-D-phenylalanine appeared to be a favourable one. Changing this sequence to D-phenylalanyl-L-leucyl-L-lysine led to significant loss of activity (**45**). Reversing the D-phenylalanyl-L-leucyl sequence in the most potent tetrapeptide (**61**) to L-leucyl-D-phenylalanyl (**77**) equally resulted in diminished potency. In leucine-containing hexapeptides, however, sequence modification did not affect the activity (**81a** and **91**, or **81** and **90**). While amino acid sequence studies of the earlier paper [3] suggested that the N-terminal D-phenylalanyl-L-leucyl-L-lysyl-D-phenylalanine represented the active core of the molecule responsible for biological potency, in our acyl-peptides this core appears to be rather the C-terminal L-lysyl-D-phenylalanyl-L-leucyl-L-lysine.

In the course of preparing the oligopeptides, the α-amino groups were protected by carbobenzoxy groups, which were removed by catalytic hydrogenation, and the ε-amino goup of lysine by *t*-butyloxycarbonyl group, which was cleaved with trifluoroacetic acid. In the case of deblocking of **60** on the 100 mmole scale, the *t*-butyl group alkylated, according to NMR data, the aromatic nucleus of phenylalanine (**62**) in a ratio of 4 : 9, similarly to the experiences of ALAKHOV, KIRYUSHKIN and LIPKIN [8], who found that the *t*-butyl group alkylated the indole nucleus of tryptophan. This side-reaction could not be suppressed by the addition of H_2O. In the NMR spectrum of **61**, the signal of the *t*-butyl protons (1.9 ppm) was not manifest, as compared with the signal of the CH_2 protons (1.3 ppm), while in the spectrum of **62** there was a ratio of 1 : 4 between the two signals.

The carboxyl group was protected in the form of methyl ester or amide.

The molecules were built up either by stepwise elongation of the chain using DCC condensation, by the active ester method, or by fragment condensation applying azide coupling; the active ester method furnished the most satisfactory results, especially in the coupling of fatty acids.

In the course of the parallel syntheses of both types of peptides, the reduced reactivity of the first type of substances, due to steric hindrance from valine, was always manifest. Furthermore, both amino acids and oligopeptides containing fatty acid residues equally possessed reduced reactivity in the coupling steps, as well as in the preparation of certain derivatives. No amides could be made from such methyl esters, and the preparation of hydrazides always met with difficulties. Consequently, the original layout of the syntheses had to be revised, leaving the acylation step to the end of the peptide synthesis.

Experimental

Thin-layer chromatograms were run on "Silica Gel for TLC According to Stahl" or on "Kieselgel $HF_{524+366}$ nach Stahl für Dünnschicht" plates, with chloroform–methanol 9 : 1 (R_{FI}), chloroform–methanol 1 : 1 (R_{FII}), chloroform–methanol 95 : 5 (R_{FIII}), chloroform–acetone 8 : 2 (R_{FIV}) and ethyl acetate–pyridine–acetic acid–water 30 : 20 : 6 : 11 (R_{FV}). The spots were detected with ninhydrine, chlorine–tolidine, or in UV light (by incorporating a fluorescent indicator in the thin-layer).

Silica gel chromatographies were carried out on "Kieselgel Reanal 1/14 for Chromatography".

Organic extracts were dried over anhydrous sodium sulfate and evaporations were carried out under reduced pressure in a rotary evaporator.

Acid hydrolysates of peptide derivatives were prepared, using 6*N* HCl (110°C, 16 hrs) and the amino acid composition of the hydrolysates was determined either qualitatively or quantitatively by gas chromatography or using an amino acid analyser.

Starting materials. Carbobenzoxyamino acids and amino acid methyl esters were prepared according to the general procedures; the protected and activated lysine derivatives were obtained as described by STURM, GEIGER and SIEDEL [11] and WÜNSCH and TRINKL [12].

Intermediates and end products were purified by chromatography, recrystallization and repeated precipitation.

Microbiological assays (Table I) were carried out by serial dilution and the agar diffusion method on the following test organisms: *Mycobacterium tuberculosis* $H_{37}R_v$ (Dubos' medium),

Table II

Physico-chemical data of valine-

	Formula	Method	Yield,* %	M.p., °C	$[\alpha]_D^{20}$
1	Z-phe-Val-OMe	[9]	59.80	140[c]	−7.3 c = 1 MeOH
2	Z-phe-Val-hydrazide	[10]	83.80	227[a]	−7.4 c = 0.1 MeOH
3	palm-phe-Val-OMe	F+C	39.80	105[a]	−13.0 c = 0.1 MeOH
4	palm-phe-Val-hydrazide	E	50.30	193[a]	−13.4 c = 0.1 MeOH
5	Z-phe-Val-Lys(BOC)-OMe	A	83.30	132[b]	−18.6 c = 1 MeOH
6	Z-phe-Val-Lys(BOC)-amide	D	94.80	217[a]	−5.4 c = 1 DMFA
7	palm-phe-Val-Lys(BOC)-amide	F+B	45.80	184–185[c]	−28.4 c = 0.1 $CHCl_3$
8	palm-phe-Val-Lys-amide	G	81.00	148[b]	
9	Z-Lys(BOC)-phe-Lys(BOC)-amide	F+B	85.50	196[d]	−4.8 c = 1 DMFA
10	palm-Lys(BOC)-phe-Val-Lys(BOC)-amide	F+B	66.40	178[c]	−3.6 c = 0.1 DMFA
11	palm-Lys-phe-Val-Lys-amide	G	76.00	192[d]	−32.3 c = 0.1 1*N* HCl
12	MOA-Lys(BOC)-phe-Val-Lys(BOC)-amide	F+C	50.50	174[c]	−23.4 c = 0.1 MeOH
13	MOA-Lys-phe-Val-Lys-amide · 2HCl	G	60.80	95[b]	
14	MHA-Lys(BOC)-phe-Val-Lys(BOC)-amide	F+C	47.50	178[c]	−23.9 c = 0.1 MeOH
15	MHA-Lys-phe-Val-Lys-amide · 2HCl	G	86.00	97[b]	
16	Ol-Lys(BOC)-phe-Val-Lys(BOC)-amide	F+C		oil	
17	Ol-Lys-phe-Val-Lys-amide · 2TFA	G	79.10	156[b]	
18	Lys-phe-Val-Lys-amide · 3TFA	F+G	80.00	89[b]	
19	Z-phe-Val-Lys(BOC)-phe-Val-Lys(BOC)-amide	F+A	77.40	238[a]	−3.7 c = 1 DMFA
20	palm-phe-Val-Lys(BOC)-phe-Val-Lys(BOC)-amide	F+B	95.00	151[c]	
21	palm-phe-Val-Lys-phe-Val-Lys-amide	G	88.00	195[c]	
22	MOA-phe-Val-Lys(BOC)-phe-Val-Lys(BOC)-amide	F+C	73.00	148[c]	
23	MOA-phe-Val-Lys-phe-Val-Lys-amide · 2TFA	G	58.50	187[b]	
24	Ol-phe-Val-Lys(BOC)-phe-Val-Lys(BOC)-amide	F+C	69.00	144[c]	
25	Ol-phe-Val-Lys-phe-Val-Lys-amide	G	50.00	222[c]	
26	phe-Val-Lys-phe-Val-Lys-amide · 3HCl	F+G	89.00	190[l]	

containing peptides

R_F					Analysis						
					Found, %			Formula	Required, %		
I	II	III	IV	V	C	H	N		C	H	N
			0.8		67.09	7.23	6.92	$C_{23}H_{28}N_2O_5$	67.10	6.86	6.79
			0.3		63.87	6.91	13.90	$C_{22}H_{28}N_4O_4$	64.10	6.86	13.60
			0.7		71.82	10.05	5.66	$C_{31}H_{52}N_2O_4$	72.01	10.08	5.42
			0.3				10.99	$C_{30}H_{52}N_4O_3$			10.82
			0.5	1.0	63.33	7.58	8.66	$C_{34}H_{48}N_4O_8$	63.72	7.55	8.75
0.1			0.1				11.42	$C_{33}H_{47}N_5O_7$			11.21
			0.6		67.31	9.89	9.23	$C_{41}H_{71}N_5O_6$	67.50	9.82	9.60
0.0			0.0	1.0			10.81	$C_{36}H_{63}N_5O_4$			11.15
0.6					62.01	7.94	11.40	$C_{44}H_{67}N_7O_{10}$	62.00	7.91	11.47
0.6					65.96	9.61	10.20	$C_{52}H_{91}N_7O_9$	65.20	9.56	10.25
0.0				0.6			12.50	$C_{42}H_{75}N_7O_5$			12.93
0.7					62.52	8.75	11.25	$C_{45}H_{77}N_7O_9$	62.81	8.98	11.41
0.1				0.8			12.50	$C_{35}H_{61}N_7O_5 \cdot 2HCl$			13.43
0.7					62.30	8.73	11.38	$C_{44}H_{75}N_7O_9$	62.44	8.88	11.60
0.1				0.8			12.83	$C_{34}H_{59}N_7O_5 \cdot 2HCl$			13.65
0.7											
0.0				0.8			9.20	$C_{44}H_{77}N_7O_5 \cdot 2TFA$			9.70
0.0				0.8			11.40	$C_{26}H_{45}N_7O_4 \cdot 3TFA$			11.35
0.6					63.63	7.65	11.21	$C_{58}H_{85}N_9O_{12}$	63.30	7.79	11.45
0.9							9.95	$C_{66}H_{109}N_9O_{11}$			10.51
0.0				0.8			9.80	$C_{56}H_{93}N_9O_7$			10.23
0.9							11.43	$C_{59}H_{95}N_9O_{11}$			11.41
0.0				0.7			10.84	$C_{49}H_{79}N_9O_7 \cdot 2TFA$			11.10
0.9							9.61	$C_{68}H_{111}N_9O_{11}$			10.25
0.0				0.7			9.80	$C_{58}H_{95}N_9O_7$			10.03
0.0				0.6			13.92	$C_{40}H_{62}N_9O_6 \cdot 3HCl$			14.41

Table III

Physico-chemical data of leucine-

	Formula	Method	Yield,* %	M.p., °C	$[\alpha]_D^{20}$
27	Z-Phe-Leu-OMe	[9]	53.40	110[e]	−24.8 c = 2.8 MeOH
28	Z-Phe-Leu-hydrazide	[10]	97.30	196[a]	−25.9 c = 0.5 MeOH
29	Z-phe-Leu-OMe	[9]	66.30	126—127[c]	−19.0 c = 2 MeOH
30	Z-phe-Leu-hydrazide	[10]	98.00	188[a]	−49.8 c = 0.54 MeOH
31	palm-phe-Leu-OMe	F+C	49.30	74—75[a]	+4.93 c = 1 $CHCl_3$
32	palm-phe-Leu-hydrazide	E	75.10	174[a]	−42.5 c = 0.1 MeOH
33	Z-Lys(BOC)-phe-OMe	B	83.30	145—148[f]	0.0 c = 0.5 MeOH
34	palm-Lys(BOC)-phe-OMe	F+B	58.30	97—98[b]	
35	Palm-Lys(BOC)-phe-hydrazide	E	76.00	167[a]	−78.0 c = 0.1 MeOH
36	palm-Lys-phe-hydrazide · TFA	G	62.00	105[f]	−78.0 c = 0.1 MeOH
37	Z-phe-Lys(BOC)-amide	C	73.30	187[a]	−26.3 c = 0.1 MeOH
38	palm-phe-Lys(BOC)-amide	F+B	79.30	184[b]	−18.5 c = 0.1 MeOH
39	palm-phe-Lys-amide · TFA	G	96.70	104[g]	−18.5 c = 0.1 MeOH
40	Z-Lys(BOC)-Lys(BOC)-amide	B	76.20	155[a]	−10.1 c = 1 MeOH
41	palm-Lys(BOC)-Lys(BOC)-amide	F+B	60.80	147—150[g]	−8.97 c = 0.5 MeOH
42	palm-Lys-Lys-amide sulfate	G	43.80	244[h]	−15.6 c = 2 H_2O
43	Z-phe-Leu-Lys(BOC)-amide	A	79.20	188[b]	−13.6 c = 0.5 DMFA
44	palm-phe-Leu-Lys(BOC)-amide	F+C	42.90	180—182[d]	
45	palm-phe-Leu-Lys-amide · HCl	G	79.10	189—190[b]	
46	Ol-phe-Leu-Lys(BOC)-amide	F+C	70.50	168—180[d]	
47	Ol-phe-Leu-Lys-amide · HCl	G	79.30	178—184[b]	
48	Z-Lys(BOC)-Leu-OMe	B	69.20	114[e]	−11.9 c = 1 $CHCl_3$
49	Z-Lys(BOC)-Leu-hydrazide	E	93.00	155[b]	
50	Z-Lys(BOC)-Leu-phe-OMe	A	43.10	132[b]	−40.5 c = 1 $CHCl_3$
51	palm-Lys(BOC)-Leu-phe-OMe	F+B	53.80	135[b]	
52	palm-Lys(BOC)-Leu-phe-hydazide	E	89.70	210[b]	−35.2 c = 1 $CHCl_3$
53	palm-Lys-Leu-phe-hydrazide · HCl	G	54.20	165—167[b]	
54	Z-Lys(BOC)-phe-Leu-Lys(BOC)-amide	F+B	85.00	192[b]	−12.9 c = 1 DMFA
55	Z-Phe-Leu-Lys(BOC)-amide	A	79.20	188[b]	−13.6 c = 0.5 DMFA

containing peptides

R_F					Analysis						
					Found, %			Formula	Required, %		
I	II	III	IV	V	C	H	N		C	H	N
			0.8								
			0.5		64.60	7.54	13.39	$C_{23}H_{30}N_4O_4$	64.80	7.10	13.22
			0.8								
			0.5								
			0.8		72.40	10.33	5.28	$C_{32}H_{54}N_2O_4$	72.41	10.25	5.28
			0.5		70.01	10.12	10.58	$C_{31}H_{54}N_4O_3$	70.20	10.10	10.55
			0.7		64.78	7.39	7.81	$C_{29}H_{39}N_3O_7$	64.41	7.28	7.76
			0.7		68.76	10.08	6.73	$C_{37}H_{63}N_3O_6$	68.90	9.85	6.52
0.8			0.7		67.10	9.86	10.60	$C_{36}H_{63}N_5O_5$	67.20	9.84	10.85
0.0	0.6			0.9	60.77	9.03	10.32	$C_{31}H_{55}N_5O_3 \cdot TFA$	60.10	8.57	10.63
0.5					63.74	6.94	10.52	$C_{28}H_{38}N_4O_6$	63.91	7.28	10.65
0.6					68.39	10.06	9.06	$C_{36}H_{62}N_4O_5$	68.60	9.91	8.89
0.0				0.9	61.39	8.66	9.06	$C_{31}H_{54}N_4O_3 \cdot TFA$	61.60	8.62	8.70
0.5			0.2		59.88	8.48	11.65	$C_{30}H_{49}N_5O_8$	59.51	8.14	11.52
0.7					64.31	10.37	9.94	$C_{38}H_{73}N_5O_7$	64.10	10.34	9.83
	0.0			0.7			10.75	$C_{28}H_{57}N_5O_3 \cdot H_2SO_4$			11.51
0.6					63.34	7.84	10.91	$C_{39}H_{49}N_5O_7$	63.83	7.72	10.95
0.5					67.75	9.82	9.42	$C_{42}H_{73}N_5O_6$	67.75	9.88	9.40
0.1	0.7						9.96	$C_{37}H_{65}N_5O_4 \cdot HCl$			10.30
0.5					68.95	9.87	9.35	$C_{44}H_{75}N_5O_6$	68.70	9.81	9.09
	0.8	0.1					9.15	$C_{39}H_{67}N_5O_4 \cdot HCl$			9.93
			0.6		61.38	8.22	8.03	$C_{26}H_{41}N_3O_7$	61.71	8.16	8.28
			0.1				14.22	$C_{25}H_{41}N_5O_6$			13.80
			0.5		63.83	7.93	8.62	$C_{35}H_{50}N_4O_8$	64.15	7.71	8.56
			0.5				7.02	$C_{43}H_{74}N_4O_7$			7.37
			0.3				11.52	$C_{42}H_{74}N_6O_6$			11.13
				0.8			12.55	$C_{37}H_{66}N_6O_4 \cdot HCl$			12.11
		0.4			62.47	8.20	11.20	$C_{45}H_{69}N_7O_{10}$	62.26	8.01	11.30
0.6					63.34	8.84	10.91	$C_{34}H_{49}N_5O_7$	63.84	7.72	10.95

Table III

	Formula	Method	Yield,* %	M.p., °C	$[\alpha]_D^{25}$
56	Z-Lys(BOC)-Phe-Leu-Lys(BOC)-amide	F+B	99.00	198[b]	−18.5 c = 0.1 MeOH
57	Lys-phe-Leu-Lys-amide · 3TFA	F+G	65.00	85[b]	
58	Lys-Phe-Leu-Lys-amide · 3TFA	F+G	65.70	81[b]	−2.2 c = 0.5 MeOH
59	palm-Lys(BOC)-phe-Leu-Lys(BOC)-amide	F+B	68.60	165[i]	−22.8 c = 0.1 MeOH
		F+C	28.20	165[k]	−22.9 c = 1 MeOH
60	palm-Lys(BOC)-Phe-Leu-Lys(BOC)-amide	F+B	77.00	159[k]	−20.2 c = 0.1 MeOH
61	palm-Lys-phe-Leu-Lys-amide	G	69.00	66[b]	−23.6 c = 0.5 MeOH
62	palm-Lys-phe(*t*-Bu)-Leu-Lys-amide	G		76[b]	−25.4 c = 0.5 MeOH
63	palm-Lys-Phe-Leu-Lys-amide · 2TFA	G	93.40	158[b]	−16.9 c = 0.1 H_2O
64	MOA-Lys(BOC)-phe-Leu-Lys(BOC)-amide	F+C	31.00	165—169[i]	−21.2 c = 0.1 MeOH
65	MOA-Lys-phe-Leu-Lys-amide · 2HCl	G	58.60	85[b]	
66	MOA-Lys(BOC)-Phe-Leu-Lys(BOC)-amide	F+C	63.00	205[i]	−12.1 c = 0.1 MeOH
67	MOA-Lys-Phe-Leu-Lys-amide · 2TFA	G	40.00	195[b]	−14.27c = 0.5 MeOH
68	MHA-Lys(BOC)-phe-Leu-Lys (BOC)-amide	F+C	20.90	168[i]	−22.2 c = 0.1 MeOH
69	MHA-Lys-phe-Leu-Lys-amide · 2HCl	G	87.00	82[b]	
70	Ol-Lys(BOC)-phe-Leu-Lys(BOC)-amide	F+C		oil	
71	Ol-Lys-phe-Leu-Lys-amide · 2TFA	G	19.00	141[b]	
72	Ol-Lys(BOC)-Phe-Leu-Lys(BOC)-amide	F+C		oil	
73	Ol-Lys-Phe-Leu-Lys-amide · 2TFA	G	39.00	149[b]	−19.1 c = 0.1 MeOH
74	Z-Lys(BOC)-Leu-phe-hydrazide	E	65.40	214[a]	
75	Z-Lys(BOC)-Leu-phe-Lys(BOC)-amide	A	41.40	156[b]	−52.73c = 0.1 DMFA
76	palm-Lys(BOC)-Leu-phe-Lys(BOC)-amide	F+B	70.00	172[i]	−23.0 c = 0.1 MeOH
77	palm-Lys-Leu-phe-Lys-amide	G	43.30	71[b]	−24.2 c = 0.5 MeOH
78	Lys-Leu-phe-Lys-amide · 3HCl	F+G	39.70		
79	Z-phe-Leu-Lys(BOC)-phe-Leu-Lys(BOC)-amide	F+A	75.20	207[b]	−27.0 c = 1 DMFA
80	palm-phe-Leu-Lys(BOC)-phe-Leu-Lys(BOC)-amide	F+B	89.00	145[b]	

(cont.)

R_F					Analysis						
					Found, %			Formula	Required, %		
I	II	III	IV	V	C	H	N		C	H	N
0.7					62.32	8.14	11.26	$C_{45}H_{69}N_7O_{10}$	62.30	8.00	11.30
0.0				0.8			11.00	$C_{27}H_{47}N_7O_4 \cdot 3TFA$			11.22
0.0				0.8			10.96	$C_{27}H_{47}N_7O_4 \cdot 3TFA$			11.22
0.8					65.47	9.59	10.08	$C_{53}H_{93}N_7O_9$	65.50	9.64	10.10
0.8					66.30	9.70	9.66				
0.7					65.26	9.81	9.80	$C_{53}H_{93}N_7O_9$	65.50	9.64	10.10
0.0				0.6			12.34	$C_{43}H_{77}N_7O_5$			12.70
				0.8							
0.0				0.9	56.80	8.13	10.27	$C_{43}H_{77}N_7O_5 \cdot 2TFA$	56.41	7.96	9.80
0.8					63.00	9.13	11.36	$C_{46}H_{79}N_7O_9$	63.30	8.75	11.20
0.1				0.9			12.70	$C_{36}H_{63}N_7O_5 \cdot 2HCl$			13.10
0.7					63.10	9.03	11.00	$C_{46}H_{79}N_7O_9$	63.30	8.75	11.20
				0.8			10.53	$C_{36}H_{63}N_7O_5 \cdot 2TFA$			10.85
0.7					62.54	9.28	11.10	$C_{45}H_{77}N_7O_9$	62.70	9.01	11.40
0.04				0.8			13.00	$C_{35}H_{61}N_7O_5 \cdot 2HCl$			13.40
0.7											
0.0				0.8			9.0	$C_{45}H_{79}N_7O_5 \cdot 2TFA$			9.50
0.7											
0.0				0.8			8.9	$C_{45}H_{79}N_7O_5 \cdot 2TFA$			9.50
			0.3				12.98	$C_{34}H_{50}N_6O_7$			12.85
0.7							11.10	$C_{45}H_{69}N_7O_{10}$			11.30
0.7					65.12	9.34	9.50	$C_{53}H_{93}N_7O_9$	65.50	9.64	10.10
				0.7			12.41	$C_{43}H_{77}N_7O_5$			12.71
0.0				0.2			14.91	$C_{27}H_{47}N_7O_4 \cdot 3HCl$			15.25
0.7					63.75	7.80	10.90	$C_{60}H_{89}N_9O_{12}$	63.87	7.95	11.18
0.9							9.85	$C_{68}H_{113}N_9O_{11}$			10.20

Table II

	Formula	Method	Yield,* %	M.p., °C	$[\alpha]_D^{25}$
81	palm-phe-Leu-Lys-phe-Leu-Lys-amide·2TFA	G	89.10	200[l]	
	↓				
82	MOA-phe-Leu-Lys(BOC)-phe-Leu-Lys(BOC)-amide	F+C	68.00	141[e]	
83	MOA-phe-Leu-Lys-phe-Leu-Lys-amide·2TFA	G	74.10	184[b]	
	↓				
84	Ol-phe-Leu-Lys(BOC)-phe-Leu-Lys(BOC)-amide	F+C	64.00	141[e]	
85	Ol-phe-Leu-Lys-phe-Leu-Lys-amide·2TFA	G	71.50	215[b]	
	↓				
86	Z-Lys(BOC)-phe-Lys(BOC)-amide	F+B	78.40	172[b]	
	↓				
87	Z-phe-Leu-Lys(BOC)-phe-Lys(BOC)-amide	F+A	90.50	197[a]	−34.0 c = 0.5 MeOH
	↓				
88	Z-Lys(BOC)-phe-Leu-Lys(BOC)-phe-Lys(BOC)-amide	F+B	80.00	178[b]	−39.4 c = 0.1 MeOH
	↓				
89	palm-Lys(BOC)-phe-Leu-Lys(BOC)-phe-Lys(BOC)-amide	F+B	89.00	155[c]	
90	palm-Lys-phe-Leu-Lys-phe-Lys-amide·3TFA	G	23.60	160[b]	
91	Lys-phe-Leu-Lys-phe-Lys-amide·4TFA	F+G	26.40		

Solvents: [a] MeOH; [b] MeOH–ether; [c] MeOH–petr. ether; [d] ethyl acetate; [e] MeOH–acetone; [f] ethyl acetate–petr. ether; [g] ethyl acetate–ether; [h] MeOH–ethyl acetate; [i] MeOH–water; [k] ethyl acetate–MeOH; [l] TFA–ether

*Yield relates to reaction indicated by arrow.

apathogenic *Mycobacteria*, *Bendo pyogenes*, *Escherichia coli GR*, *Shigella sonnei*, *Sarcina lutea*, *Staphylococcus Duncan*, *Streptococcus faecalis*, *Bacillus subtilis*, *Haemophilus* group, pathogenic and apathogenic fungi and *Candida albicans*.

Description of the general procedures (Tables II and III)

Method A: Azide coupling

The appropriate protected peptide hydrazide (15 mmoles) in dimethylformamide (82 ml) and 6*N* HCl (7.4 ml) was treated at −10°C with 5*M* sodium azide (3.3 ml). The reaction mixture was stirred for 15 min at −5°C, then neutralized with 6.6 ml of triethylamine and the methyl amino acid or methyl peptide (15 mmoles) in dimethylformamide (41 ml) was added at −10°C. The resulting mixture was stirred at −10°C for 1 hr and at room temperature for 24 hrs, then it was evaporated to dryness at reduced pressure. The residue was washed with 1*N* citric acid, 5% $NaHCO_3$ solution and water, dried and washed with ether.

Dipeptides **2, 28** and **30** were always coupled by this method.

c ont.)

R_F					Analysis						
					Found, %			Formula	Required, %		
I	II	III	IV	V	C	H	N		C	H	N
0.0				0.9			9.76	$C_{58}H_{97}N_9O_7 \cdot 2TFA$			10.00
0.8							11.90	$C_{61}H_{99}N_9O_{11}$			11.10
0.0				0.7			10.75	$C_{51}H_{83}N_9O_7 \cdot 2TFA$			10.23
0.8							9.70	$C_{70}H_{115}N_9O_{11}$			10.00
0.0				0.7			9.71	$C_{60}H_{99}N_9O_7 \cdot 2TFA$			9.78
0.5					61.78	7.41	10.85	$C_{39}H_{58}N_6O_9$	62.15	7.74	11.14
0.5					63.74	7.80	11.18	$C_{54}H_{78}N_8O_{11}$	63.90	7.74	11.20
0.8					62.20	8.02	11.11	$C_{65}H_{98}N_{10}O_{14}$	62.70	7.94	11.25
0.8							10.50	$C_{73}H_{122}N_{10}O_{13}$			10.40
0.0				0.6			9.85	$C_{58}H_{98}N_{10}O_7 \cdot 3TFA$			10.10
0.0				0.2			10.62	$C_{42}H_{68}N_{10}O_6 \cdot 4TFA$			11.05

Method B: Active ester procedure

The appropriate amino acid amide or partially deblocked peptide amide (2 mmoles) in pyridine (5 ml) was coupled either with Z-Lys(BOC)-ON*p* or with palm-ON*p* (2 mmoles) for 72 hrs at room temperature. In the latter case an additional 1 ml of triethylamine had to be added to the solution to trigger the reaction. The reaction mixture was precipitated with 1*N* citric acid (50 ml), the filtered precipitate washed with 5% $NaHCO_3$ solution and water, dried and precipitated from methanol–petroleum ether.

Method C: DCC coupling

The appropriate methyl amino acid and or methyl peptide hydrochloride (10 mmoles) in dichloromethane (100 ml) and triethylamine (10 mmoles) was coupled at 0°C for 12 hrs with a protected amino acid, a protected peptide or a fatty acid, respectively (10 mmoles), in the presence of DCC (10 mmoles). The precipitated DCU was filtered off and the filtrate diluted with dichloromethane (100 ml). The solution was washed with 1*N* HCl, 5% $NaHCO_3$ solution and water, dried over Na_2SO_4 and evaporated to dryness at reduced pressure.

Method D: Ammonolysis

The appropriate protected oligopeptide methyl ester (10 mmoles) was kept for 4 days at room temperature in 150 ml methanol, saturated with ammonia at 0°C in a sealed tube. The amide crystallized from the solution. No amide was obtained from methyl peptides acylated with a fatty acid.

Method E: Hydrazide formation

The appropriate protected oligopeptide methyl ester (2 mmoles) was refluxed for 2 hrs in a mixture of 72% hydrazine hydrate (5 ml) and methanol (5 ml). The reaction mixture was allowed to stand at room temperature overnight. The crystals which separated were filtered off and washed with cold methanol and ether.

In the case of methyl peptides acylated with a fatty acid, this reaction was raher slow. Consequently, the reaction time had to be prolonged to 6 hrs and the procedure eventually repeated to achieve full conversion.

Method F: Hydrogenolysis

A solution of Z-peptide-OMe (10 mmoles) in methanol (100 ml) and HCl (10 mmoles) was hydrogenated at room temperature over 10% palladized charcoal. The filtered solution was evaporated to dryness under reduced pressure and worked up without further purification.

Method G: Cleavage with trifluoroacetic acid

The appropriate oligopeptide containing a BOC-protected lysine residue (5 mmoles) was treated for 2 hrs at room temperature with trifluoroacetic acid (5 ml). The reaction mixture was evaporated below 30°C under reduced pressure and the residue collected in ether. The product was eventually converted into the base, hydrochloride, or sulfate.

Symbols

BOC	*t*-butyloxycarbonyl-
DCC	dicyclohexylcarbodiimide
DCU	dicyclohexylurea
DMFA	dimethylformamide
MeOH	methanol
MHA	(−)-6-methylheptanoyl-
MOA	(−)-6-methyloctanoyl-
Ol	oleoyl-
ON*p*	*p*-nitrophenyl ester
palm	palmitoyl-
t-Bu	*t*-butyl-
TFA	trifluoroacetic acid
Z	carbobenzoxy-

The abbreviations for L-amino acid residues and their derivatives, as well as their mode of use are in accordance with the suggestions of the Committee on Nomenclature adopted by IUPAC [J. Biol. Chem. **247,** 977 (1972)]. D-amino acids are abbreviated in small letters, e. g.: D-Phe = phe; L-Phe = Phe.

*

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STEREOCHEMICAL STUDIES, XXIV*
t-BUTYLCYCLOPENTANE DERIVATIVES, III**

IR AND NMR INVESTIGATION OF *CIS* AND *TRANS*-4-*t*-BUTYLCYCLOPENTANE-1,2-OXIDE

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The steric structure of *cis*- and *trans*-4-*t*-butylcyclopentane-1,2-oxide (**1, 2**) supposed earlier was confirmed by IR and PMR investigation. IR and PMR spectra are both suitable for identification of the isomers. The functional groups can be identified by the IR spectra, the steric structure follows from the relative shift of the PMR signals. The *cis* or *trans* position of the functional groups was also confirmed by applying tris(dipivalomethanato)europium as shift reagent.

Cis- and *trans*-4-*t*-butylcyclopentane-1,2-oxides (**1**, **2**) are suitable starting materials for the synthesis of mono- and disubstituted *t*-butylcyclopentane derivatives and have been used as key compounds in the synthesis of the four stereoisomeric 2-amino-4-*t*-butylcyclopentanols [1] as well as of *cis*- and *trans*-3-*t*-butylcyclopentanol [2]. The steric structures of compounds



1



2



3

1 and **2** follow from their way of preparation. Treating 4-*t*-butylcyclopent-1-ene (**3**) with perphthalic acid, the ratio of the stereoisomeric 4-*t*-butylcyclopentane-1,2-oxides formed was about 11 : 1. Taking into consideration the steric course of the epoxidation of analogous 4-substituted cyclopent-1-enes leading to *trans* epoxides as the main product [3—5], it is obvious that the compound formed in 92.1% yield must be *trans*-4-*t*-butylcyclopentane-1,2-oxide. On the other hand,

*Part XXIII: G. BERNÁTH, K. L. LÁNG, M. TICHÝ, M. PÁNKOVÁ: Acta Chim. (Budapest). In the press.

Part II: G. BERNÁTH, L. GRUBER, I. TÖMÖSKÖZI: Acta Phys. et Chem. Szeged **18, 217 (1972).

it is worth mentioning that, while the steric course of the epoxidation of related 4-substituted cyclopent-1-enes is straightforward, in the case of 3-methylcyclopent-1-ene an unexpected conformational effect has been recently observed [6]; the reaction of 3-methylcyclopent-1-ene with *m*-chloroperphthalic acid furnished more *cis* than *trans* epoxide.

The preparation of the title compounds (**1**, **2**) could be successfully achieved also in other, independent ways [1], and the reactions and spectroscopic characteristics of the aminoalcohols [1] and other compounds [2, 7] prepared from the above epoxides were in good accordance with our configurational assignments. Nevertheless, in order to prove the structure beyond any doubt, it appeared necessary to study the IR and PMR spectra of these compounds.

The IR spectra of 1 and **2** (Figs 1 and 2), though showing some characteristic differences, are essentially very similar, and thus cannot be used as evidence for the above structures; yet the spectra are suitable to distinguish between the pure isomers. The presence of the *t*-butyl group and of the *cis*-1,2-substituted oxirane ring follows unequivocally from the spectra. The νCH and the skeletal vibration, found at 3020 and 840 cm^{-1} in both spectra, are characteristic of the oxirane function [8—9]. The 840 cm^{-1} band is the most intense and also supports the *a priori cis* fusion of the oxirane and cyclopen-

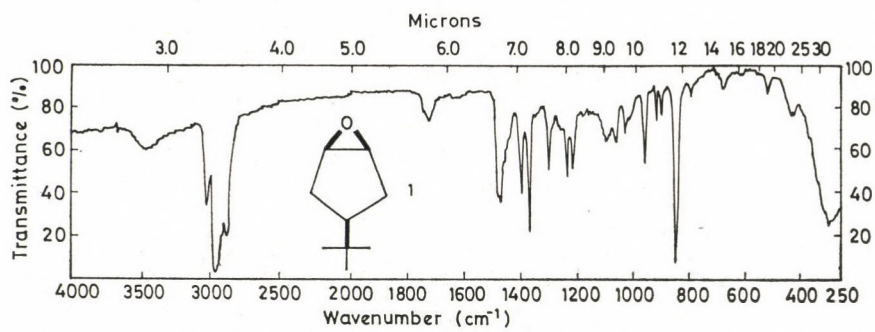


Fig. 1. IR spectrum of *cis*-4-*t*-butylcyclopentane-1,2-oxide **(1)** in KBr pellet

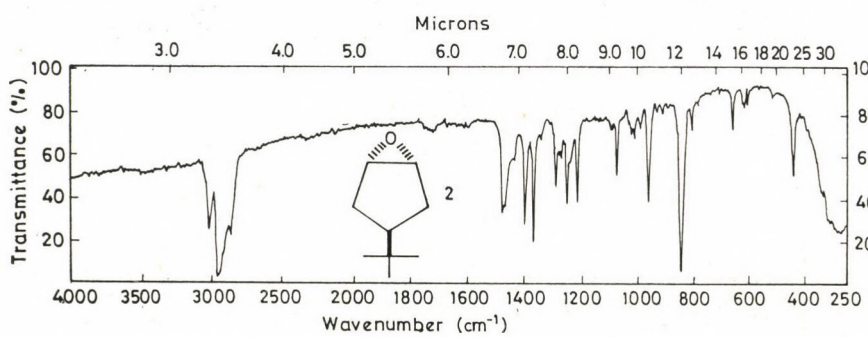


Fig. 2. IR spectrum of *trans*-4-*t*-butylcyclopentane-1,2-oxide **(2)** in KBr pellet

tane rings [10]. The asymmetrical bending vibrations of the methyl groups ($\delta_{as}^{+}CH_3$) and the plane symmetrical (scissoring) bending vibration of the ring methylene groups ($\beta_s^{\square}CH_2$) appear merged near 1470 cm^{-1} in both spectra. The $\delta_s CH_3$ doublets are found at 1395 and 1365 cm^{-1} and at 1398 and 1361 cm^{-1}, respectively (splitting and different intensities of the two maxima are together characteristic of the *t*-butyl group [11]). The skeletal vibrations of the carbon-carbon bonds, also characteristic of the *t*-butyl group, are found at 1230 and 1215 cm^{-1}, and at 1248 and 1212 cm^{-1}, respectively [12].

The PMR spectra (Figs 3, 4), beyond permitting the identification of **1** and **2**, make possible the determination of their configuration; a significant difference in the position of the methyl singlet of the *t*-butyl group can be seen. The signal at 0.85 ppm in the spectrum of the main product is shifted diamagnetically in the case of the minor product (see Fig. 3), and is found at 0.77 ppm. As known, the anisotropic effect of three-membered rings increases the shielding of the protons 'above' the plane of the ring causing thereby a diamagnetic shift [13]. The minor product of epoxidation must be therefore the *cis* isomer (**1**) because the methyl protons of the *t*-butyl group are all shielded by the oxirane ring due to the rotation of the substituent. The higher δ value (0.85 ppm) of the *trans* isomer can be explained by the similar shielding of 4-*t*-butylcyclopentene (**3**) ($\delta = 0.88$ ppm).

The steric structures are also confirmed by further details of the PMR spectra. The identical signals of the annellated protons of C-1 and C-2 appear at practically the same δ values (3.30 and 3.29 ppm, respectively), however, with different widths (3 Hz and 2 Hz, respectively). The singlet is usually charac-

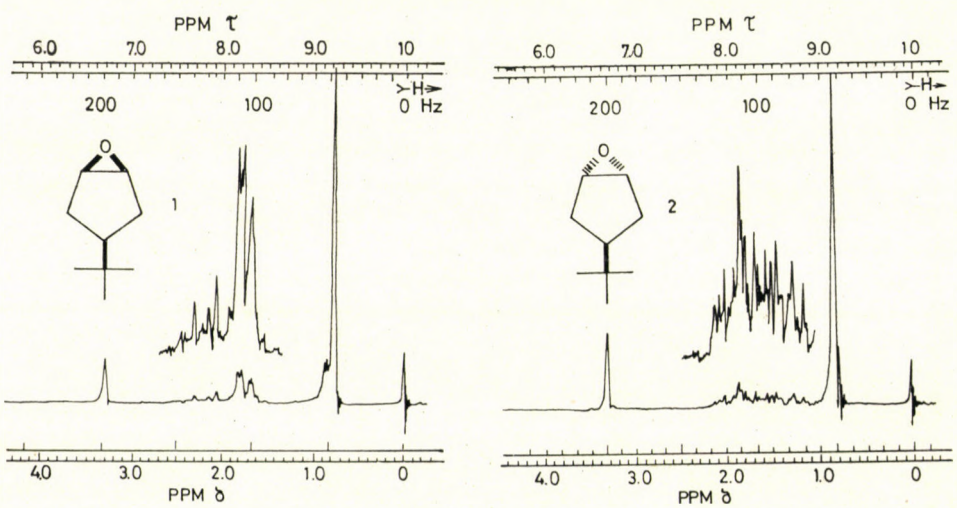
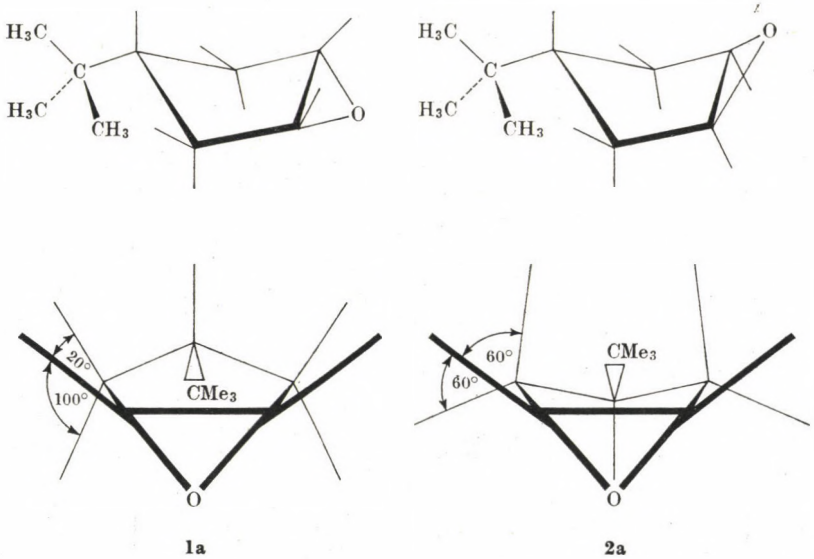


Fig. 3 and 4. PMR spectrum of *cis*- (**1**) and *trans*- 4-*t*-butylcyclopentane-1,2-oxide (**2**) in carbon tetrachloride

teristic of bridgehead protons of oxiranes condensed with rings. The coupling constant with vicinal protons is small, due partly to the small dihedral angle (about 90°), partly to the $-I$ effect of the oxygen atom [14, 15].

From the circumstance that the signal width is greater in the *cis* isomer (**1**) than in the *trans* isomer (**2**), it may be inferred that the coupling between ring protons C-2 and C-3, and between C-1 and C-5 must be greater, though they show no splitting. Taking into consideration that the cyclopentane ring is forced into envelope conformation by the condensed oxirane ring, it is clear that the most probable conformation is the one in which the C-4 atom is not in the plane of the other four carbon atoms, and the *t*-butyl group is *quasi-equatorial* (**1a**, **2a**). In these conformations the dihedral angles between the annellated hydrogens and the neighbouring methylene protons are ~20° and ~100° (**1a**), or ~60° and ~60° (**2a**). According to the KARPLUS relation [16], the greater coupling constant has to be expected for the *cis* isomer.



1a **2a**

The complex multiplet of the ring protons C-3, C-4, and C-5 furnishes a further supporting piece of evidence for the steric structures. Namely, in the case of the *trans* isomer (**2**) the multiplet is broader and partly considerably shifted towards lower δ values. The diamagnetic shift is caused by the anisotropic effect of the oxirane ring, which increases the shielding of the *cis* hydrogens in positions 3 and 5, and even in position 4. This explains the fact that in the spectrum of the *cis* isomer the signal of the C-4 proton appears separately at higher δ values (between 130 and 150 Hz, *i.e.* at about 2.2 ppm), whereas the chemical shifts of the methylene protons (about 1.7 ppm) are identical, the multiplet being between 90 and 120 Hz. In contrast, in the case of the *trans*

isomer the methine and the methylene protons give an overlapping, diamagnetically shifted multiplet in the region 65—130 Hz, their bands covering a much wider range; *i.e.* the chemical shifts of the protons in *cis* and *trans* position to the oxirane ring are considerably different.

Though the PMR characteristics discussed were in accordance with the assumed structures, as the differences of the spectra are rather small and their interpretation involves a supposition concerning the preferred conformation, further investigation was necessary to prove the *cis* and *trans* configurations. Therefore, the PMR spectra of both isomers were measured in the presence of different quantities of a shift reagent [tris(dipivalomethanato)europium].

The complex, by forming a bond with the oxygen atom of the epoxide, will increase chiefly the chemical shift of the nearest protons [17]. Observing the most intense and simplest signal, namely that of the methyl singlet, it can be expected that the chemical shift of the *cis* isomer, found originally at a lower δ value, will be more markedly shifted than that of the *trans* isomer, *i.e.*, gradually increasing the concentration of the shift reagent in the sample, the difference of the shifts will first diminish, then shifts of the two isomers become equal, and finally the difference will increase again when the relation of the shift values is reversed in comparison with the original relation; *i.e.*

$$\delta CH_3(cis) < \delta CH_3(trans)$$

The experimental results were in good agreement with these expectations. Plotting the changes in chemical shift as a function of the shift reagent concentration, a straight line was obtained; the slope was greater in the case of the *cis* isomer (Fig. 5). In order to obtain rigorously identical experimental condi-

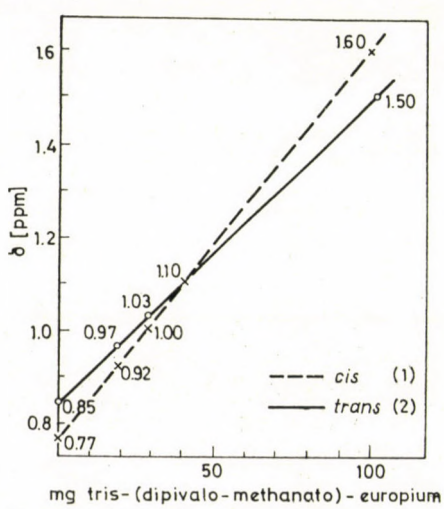


Fig. 5. Chemical shifts of the methyl signals of the *t*-butyl group of compounds **1** and **2** in carbon tetrachloride solution, after the addition of tris(dipivalomethanato)europium of various concentrations as shift reagent

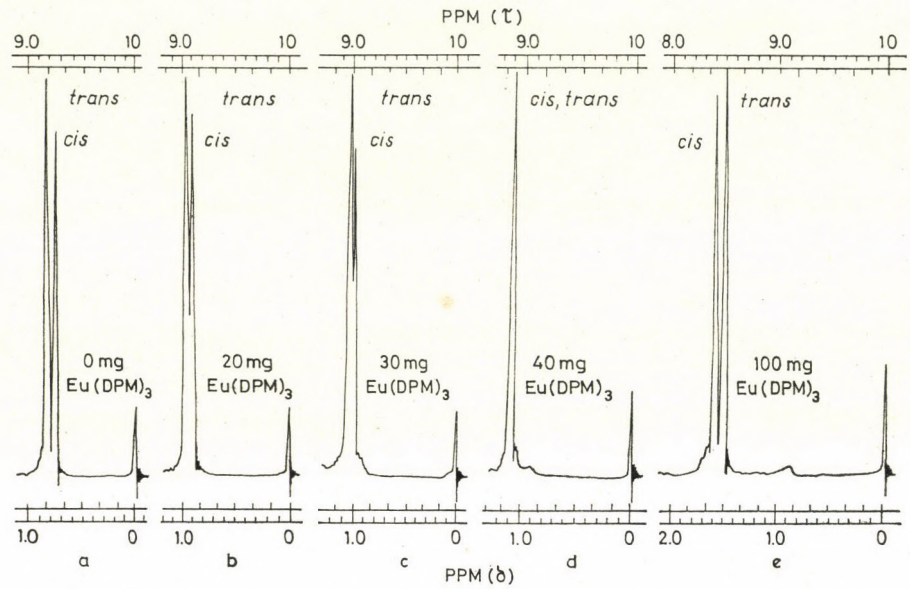


Fig. 6. Part of the PMR spectrum of a 1 : 1 mixture of compounds **1** and **2** with the methyl signals of the *t*-butyl group after the addition of 20, 30, 40 and 100 mg of tris(dipivalomethanato)europium as shift reagent

tions and clear-cut results, the experiments were made with a nearly 1 : 1 mixture of the isomers instead of examining the pure isomers separately. The sample contained somewhat less *cis* isomer in order to permit a clear distinction of the signals. Thus the signal of the *cis* isomer, of lower δ value, was somewhat weaker in the spectrum of the mixture (Fig. 6a). The original difference of the δ values (0.08 ppm) gradually decreases on adding the shift reagent (Figs 6b, 6c), and completely disappears after the addition of 40 mg of the complex; *i.e.* the two signals coalesce (Fig. 6d). Adding further shift reagent, the signals separate again, but now the weaker signal of the *cis* isomer is found at the higher δ values. In the presence of 100 mg complex the shift difference becomes 0.10 ppm (Fig. 6e).

Experimental

IR spectra were recorded in KBr pellets, using a Perkin–Elmer 457 spectrometer. PMR spectra were obtained at room temperature in carbon tetrachloride solution at 60 MHz, with a Varian A-60D instrument, using TMS as internal standard. Tris(dipivalomethanato)europium for PMR (Merck) was applied as shift reagent.

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INVESTIGATION OF THE INTERACTION OF TRYPTOPHAN-CONTAINING DIPEPTIDES WITH NUCLEIC ACIDS BY FLUORESCENCE SPECTROSCOPY

(SHORT COMMUNICATION)

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A great deal of interest in the past decade was centered on the recognition process between nucleic acids and protein systems. Our laboratory followed a simplified approach to the problem which involves the analysis of the interaction specificities of small peptides with nucleic acids. Recently we reported the scanning of melting temperature of complexes of DNA and dipeptide esters containing Tyr and Trp [1]. Interaction of model peptides containing basic amino acids resulted in all cases in a rise of the melting temperature of DNA, suggesting a stabilization of the helical structure during binding, while a much smaller effect could be observed with Glu-TrpOMe · HCl ($\Delta T_m = +8°C$) under identical experimental conditions. Model peptides containing Ser instead of basic amino acids seemed to have not much value in stabilizing the ordered double-stranded structure of DNA ($\Delta T_m < \pm 3°C$) [1]. Experimental data indicated a similar behaviour also for the following aromatic amino acid containing peptides: Glu(OMe)-TyrOMe · HCl [3], Glu(OMe)-PheOMe · HCl [3] and Glu-His-Phe (a gift from Mrs. H. MEDZIHRADSZKY; prepared by saponification of Glu-His-PheOMe [2]). NOVAK and DOHNAI also reported that no stabilization of calf thymus DNA could be demonstrated by Tyr-Glu-Tyr-Glu-Tyr on the basis of melting temperature studies [4]. The failure to observe a change in the T_m of the complexes is not necessarily an indication for the lack of interaction, but may be the result of an equal affinity of the helical and coil states of the polynucleotide for the peptide. The technique of fluorescence spectroscopy seemed a more suitable method to investigate the binding process [5].

Experimental

The ultraviolet absorption spectra were obtained with Unicam SP 700 and Specord UV Vis recording spectrophotometers. Melting transitions were monitored with a Beckman DU (G 2400) spectrophotometer, fitted with water-jacketed cell compartments and with a thermocouple inserted into the liquid. Fluorescence spectra were taken with a Farrand spectrophotofluorometer, using 10 mm cells. All measurements were carried out at room temperature, in pH 6.35 buffer solutions. The Trp-containing dipeptide esters selected for the spectrofluorometric studies and prepared in our laboratory were as follows:Ser-Trp-OMe · HCl [6], D-Ser-TrpOMe · HCl [6], Lys-TrpOMe · HCl [1],

Orn-TrpOMe · HCl [1] and Glu-TrpOMe · HCl (amino acids are of L-configuration unless otherwise stated). The last peptide was obtained by coupling Z-Glu (OBz) and TrpOMe, using the mixed anhydride method, followed by removal of the protecting groups by catalytic hydrogenation. The hydrochloride was isolated as a hygroscopic solid and checked for purity by microanalysis and TLC. Trp-GlcN was also included in this series as a model of glycopeptide, since it has been suggested [7] that the significance of the glycosyl residues is to impart a discrete recognitional role to glycoproteins. The synthesis could be achieved by an adaptation of the method of LIEFLÄNDER [8]. Z-Trp was coupled with unprotected D-glucosamine in dioxane-tetrahydrofuran, using the mixed anhydride method, followed by removal of the N-protecting group by catalytic hydrogenation. Analytical: $C_{17}H_{22}N_3O_6 \cdot HCl + H_2O$. Calcd. C 48.4; H 6.45; N 9.96; Cl 8.4. Found C 48.85; H 6.52; N 9.5; Cl 8.2%. $[\alpha]_{546}^{20} = +42°$ (c = 1, water).

All Trp-containing peptides were excited at 295 nm and the fluorescence intensity was measured at 355 nm. All readings were adjusted to a constant relative emission for the quinine sulfate reference solution (1 μg/ml). The advantage of choosing Trp-peptides as models was that the overlapping of absorption and emission spectra was small, and a correction for reabsorption effect could be neglected (Fig. 1a). No shift was found in the fluorescence spectra of the peptides in the presence of DNA, and no alteration of the absorption spectra was noted. Fluorescence was measured in a concentration range where fluorescence intensity increases linearly with peptide concentration in the absence of DNA, and in the presence of DNA only the slope is reduced (Fig. 1b).

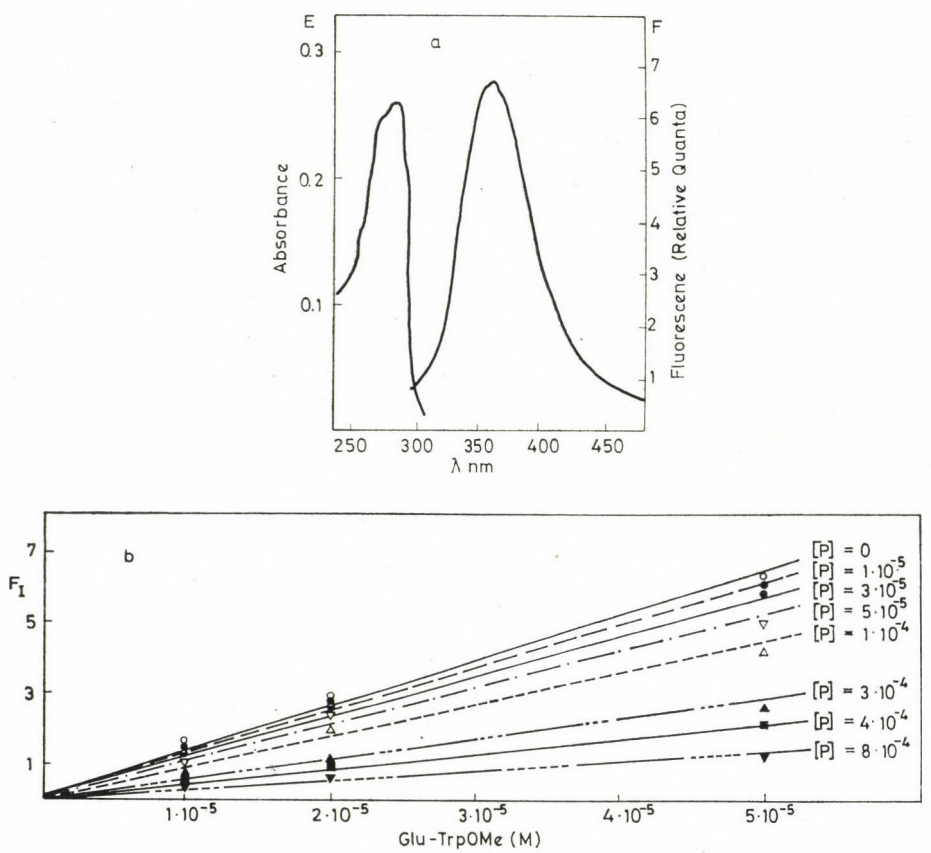

Fig. 1. (a) UV absorption (left-hand curve) and fluorescence emission spectra (right-hand curve) of Glu-TrpOMe ($c = 5 \cdot 10^{-5} M$; pH 6.35). (b) Concentration dependence of the relative fluorescence intensity of Glu-TrpOMe solutions in the absence ([P] = 0) and in the presence of DNA at different concentrations

The following nucleic acid preparations were used: Chicken blood DNA (Reanal, Budapest); P 6.9% N 10.9%. $\varepsilon(P)_{260nm}$: 7000 (pH: 6.35). *M. lysodeikticus* DNA (Miles Laboratories Inc.); $\varepsilon(P)_{260nm}$: 7800 (pH: 7). Poly(A) (Koch-Light); MW 100,000, P 5.35%.

Results and discussion

The fluorescence of the indole ring of the peptides is quenched in the presence of DNA. The percentage decreases in fluorescence intensity for Lys-TrpOMe, D-Ser-TrpOMe and Trp-GlcN complexes, as plotted against the molar ratio of DNA(P)/peptide, are depicted in Fig. 2a. The change of relative fluorescence intensity in the presence of increasing amounts of added DNA follows a linear relationship as illustrated by the straight-line plots in Fig. 2b. A plot of F/F_0 against 1/[P] should give a straight line, whose Y-axis intercept could be used to obtain the values of C_f (concentration of free ligand) and r [the mean number of moles of compound bound per base (mole P)] [9]. By correlating these parameters, binding data could be treated according to the equation developed by SCATCHARD [10]; straight-line plots were obtained (Fig. 2c).

At high peptide concentrations ($4 \cdot 10^{-5}$—$5 \cdot 10^{-5} M$) and low ionic strength ($I = 0.0036$), the Scatchard plots show some 'secondary site' binding (presumably due to an aggregation of the ligand), but 'primary site' binding does occur first and is much stronger. This is demonstrated in Fig. 2d by the Scatchard plots obtained for Orn-TrpOMe, Glu-TrpOMe and Ser-TrpOMe complexes. It has previously been shown [11] that the concentration of the ligand has an effect on the results.

Estimations of the values of n (available binding sites) and K (association constant) are summarized in Table I. It should be noted that the derivation of these values is based on the assumption that fluorescence loss is due only to binding, whereas several other factors might be involved, and also bound molecules could still fluoresce feebly. More reliable values can be expected from equilibrium dialysis studies, which we hope to accomplish in the next future. At the same time it seems justified to regard our present data as relative indices suitable to reflect differences in binding affinity.

No significant changes could be observed in binding of the various peptides to native DNA when the ionic strength was increased (Table II). Electrostatic forces might play therefore only a secondary part in the interaction.

The most important factors inherent in the structure of the DNA molecule which could contribute to the specificity of interaction are the base composition, base order and macromolecular configuration. To investigate the influence of the base composition, DNA samples with different GC contents were examined (Table II). Only the binding of Orn-TrpOMe seems to be influenced by an increase of the GC content (72%) of the nucleic acid. We have to emphasize that these experiments were carried out at higher ionic strength ($I = 0.126$); differences in binding might be therefore less pronounced.

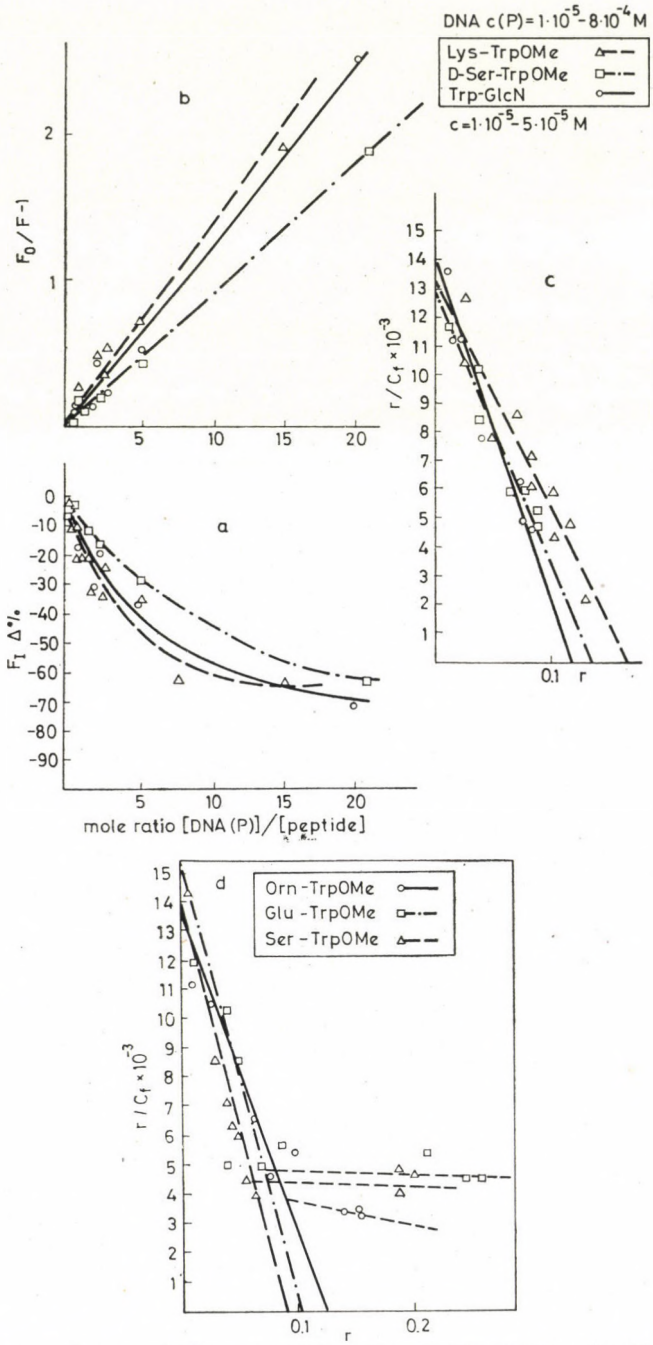

Fig. 2. (a) Percentage decrease in fluorescence intensity for Trp-GlcN, D-Ser-TrpOMe and Lys-TrpOMe on interaction with DNA as plotted against the molar ratio DNA(P)/peptide (pH 6.35; $I = 0.0036$). (b) Quenching curves for DNA; F_0 and F are the observed intensities of fluorescence in the absence of DNA and in the presence of varying amounts of added DNA, respectively. (c) Scatchard plots for the binding of Trp-GlcN, D-Ser-TrpOMe and Lys-TrpOMe ($c = 1 \cdot 10^{-5} - 5 \cdot 10^{-5}$ *M*) to DNA (pH 6.35, $I = 0.0036$). (d) Scatchard plots for the binding of Orn-TrpOMe, Ser-TrpOMe and Glu-TrpOMe ($c = 1 \cdot 10^{-5} - 5 \cdot 10^{-5} M$) to DNA (pH 6.35; $I = 0.0036$)

Table I

Number of binding sites per phosphate and association constants for the interaction of various Trp-containing model peptides with native and denatured chicken blood DNA and Poly(A) (pH 6.35; 0.002 *M* phosphate buffer containing 0.001*M* NaCl). The values have been obtained from Scatchard plots

Peptide	DNA chicken blood				Poly(A)	
	native		denatured			
	n	$K(M^{-1}\times10^{-5})$	n	$K(M^{-1}\times10^{-5})$	n	$K(M^{-1}\times10^{-5})$
Trp-GlcN	0.12	1.21	—	—	—	—
D-Ser-TrpOMe	0.135	0.96	—	—	—	—
Lys-TrpOMe	0.17	0.79	—	—	—	—
Orn-TrpOMe	0.125	1.08	0.2	0.77	0.13	1.15
Ser-Trp-OMe	0.095	1.53	0.15	1.13	0.1	1.3
Glu-TrpOMe	0.105	1.47	0.14	1.28	0.12	1.0

Table II

Number of binding sites per phosphate and association constants for the interaction of Ser-TrpOMe Orn-TrpOMe and Glu-TrpOMe with chicken blood DNA and M. lysodeikticus DNA (pH 6.35; 0.02*M* phosphate buffer containing 0.1*M* NaCl). The values have been obtained from Scatchard plots

Peptide $c = 2\cdot10^{-5}\,M$	DNA $c_{(p)} = 2\cdot10^{-5}$—$8\cdot10^{-4}\,M$	n	$K(M^{-1}\times10^{-5})$
Ser-TrpOMe	CB	0.1	1.7
	ML	0.1	1.7
Orn-TrpOMe	CB	0.12	1.28
	ML	0.1	1.4
Glu-TrpOMe	CB	0.11	1.45
	ML	0.11	1.59

CB = chicken blood; GC content 42%
ML = M. lysodeikticus; GC content 72%

To investigate the influence of the macromolecular configuration on the binding process, experiments were carried out with denatured DNA (heated at 100°C for 10 minutes, followed by quick cooling in ice; ΔE=30%) and with

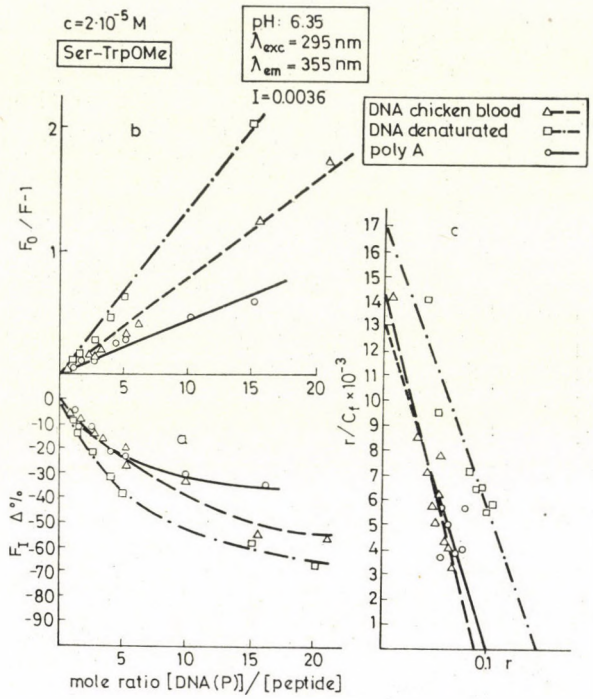

Fig. 3. Interaction of Ser-TrpOMe with native and denatured DNA and Poly(A). (a) Percentage decrease in relative fluorescence intensity plotted against the molar ratio [P]/peptide (pH 6.35; $I = 0.0036$). (b) Changes in fluorescence intensity demonstrated as the plot of $F_0/F-1$ *vs.* the molar ratio of [P]/peptide. (c) Scatchard plots for the binding of Ser-TrpOMe ($c = 2 \cdot 10^{-5}$ *M*). Values of unbound ligand concentration (C_f) calculated from the results of fluorescence measurements

Poly(A). The experimental results are demonstrated in Figs 3a, b, c for Ser-TrpOMe, and in Figs 4a, b for Glu-TrpOMe and Orn-TrpOMe, respectively. The interaction followed the same pattern for all three peptides. In the case of denatured DNA (low ionic strength) the product Kn is increased compared to values obtained with native DNA, but the Scatchard plots suggest that this is rather the result of an increase of n, while the values of K are showing a tendency of decrease (Table I). Considerable binding could be observed also with Poly(A) (Table I).

It has been reported that the indole ring intercalates between bases and forms stacked complexes both in single-stranded Poly(A) [12] and in double-stranded DNA [13, 14]. Tryptamine binds almost as well to single-stranded polynucleotides or denatured DNA as to native double-stranded DNA [12]. Our present results seem to be consistent with these findings.

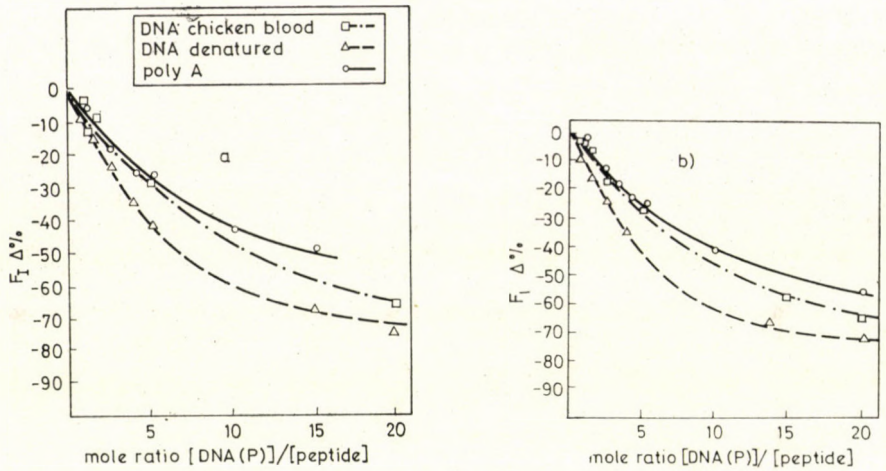

Fig. 4. Interaction of native and denatured DNA and Poly(A) with (a) Orn-TrpOMe, (b) Glu-TrpOMe ($c = 2 \cdot 10^{-5} M$). Percentage decrease in relative fluorescence intensity plotted against the molar ratio [P]/peptide (pH 6.35; $I = 0.0036$)

Conclusions

The results of the fluorescence spectral studies indicate that the lack of changes of T_m in the case of some Trp-containing peptide–DNA complexes is due to stabilization of denatured DNA relative to native DNA. Probably the exposure of the hydrophobic bases in denatured DNA enhances the binding by hydrogen bonds, especially for Ser and Glu derivatives. In fact, all Trp peptides show strong interaction with nucleic acids. There is only one type of strong binding site and its characteristics suggest that the driving force of the interaction might be intercalation of the indole ring between the bases, as it has been postulated for other indole derivatives [14]. Although insufficient data have been obtained to characterize fully the binding curves for each compound, some conclusions can be drawn about their relative ability to be bound to DNA. There are differences to some extent between the various peptides in the strength of binding, although the value of K is of the same order for each peptide. More significant seems to be the difference in the number of available binding sites. There is about one site per five nucleotides for the Lys derivative, but only one site per ten nucleotides for the Ser and Glu derivatives on native DNA. The interaction of the side-chain of the second amino acid and spatial fitting of the molecule seem to influence the arrangement of the peptides along the nucleotide chain and the number of bound molecules.

Evidence for a direct side-chain-base interaction and a 'preferential' scheme for interactions between amino acids and nucleotides on the monomer

level was reported by SAXINGER *et al.* [15]. Studies with a wider choice of model peptides might provide more information about this kind of interaction specificity and on the role of functional relationships.

*

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THE STEREOCHEMISTRY OF THE CAROTENOID VIOLEOXANTHIN

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The ^{1}H–n.m.r., ^{13}C–n.m.r., o.r.d. and c.d. spectra of violeoxanthin were examined. Violeoxanthin was shown to be the 9-*cis* isomer of violaxanthin, with the same absolute stereochemistry at all chiral centres. The full assignment of the ^{13}C–n.m.r. spectrum of violeoxanthin was made by comparison with spectra of related carotenoid and vitamin A acetate models.

Violeoxanthin was reported by STRAIN [1] as a constituent of pansy flowers *(Viola tricolor)*. He showed [2] that it was similar to violaxanthin (**I**), and that when treated with acid both carotenoids appeared to give the same auroxanthin (**II**).

SZABOLCS and TÓTH, in a preliminary publication [3], reported that violeoxanthin is a *cis* isomer of violaxanthin. On the basis of physical properties, interconversion, and formation of zeaxanthin (**III**) and auroxanthin from both pigments, it was proposed that violeoxanthin is the 9-*cis* isomer of violaxanthin. These studies have been extended and now provide proof of the 9-*cis* formulation. Various *cis* isomers of violaxanthin, sometimes called neoviolaxanthin U or V, have been reported [1—16]. Some of these pigments clearly refer to violeoxanthin.

The shift (4—5 nm) in λ_{max} of violeoxanthin, compared with that of violaxanthin, indicates that the form is a mono-*cis* isomer with a 'sterically unhindered' *cis* bond [17]. This excludes an 11-*cis* double bond as this 'sterically hindered' structure would have a degraded spectrum. The weak *cis* peak observed with violeoxanthin (see Fig. 2) suggests that the *cis*-double bond is peripheral [18]. Thus the 9-*cis* formulation is more likely than either the 13-*cis* or the 15-*cis* structure. A 7-*cis* structure would not be expected to exhibit a *cis* peak. It would be highly hindered and unlikely to be formed on iodine-catalysed isomerization [19], though the interconversion of (all-*trans*) violaxanthin and violeoxanthin occurs readily under these conditions.

The ^{1}H-n.m.r. spectrum of violeoxanthin shows one set of methyl signals which correspond to those of violaxanthin, and an additional set from the *cis* end group (Table I). The small difference in the two sets excludes a 7-*cis* double bond [19]. A similar slight shift is also observed when the n.m.r. spectrum of the common *cis* neoxanthin (**IV**) is compared with that of all-*trans* neoxanthin

Table I

^1H–n.m.r. spectra in $CDCl_3$ of the epoxide end groups of neoxanthin, violaxanthin and their cis isomers

	1-Me	5-Me	9-Me	13-Me
Violeoxanthin (*cis* end)	0.98, 1.16	1.21	1.91	1.93
Violaxanthin (all *trans*)	0.95, 1.12	1.16	1.89	1.92
Neoxanthin (9-*cis*)	1.00, 1.16	1.20	1.92	1.94
Neoxanthin X (all-*trans*)	0.96, 1.14	1.17	1.91	1.94

(neoxanthin X). Unfortunately the chemical shifts of the methyl signals are not sufficiently characteristic to assign unambiguously the position of the *cis* double bond. Attention was therefore directed to the ^{13}C–n.m.r. spectrum.

The ^{13}C–n.m.r. spectra of violaxanthin and violeoxanthin (Fig. 1) show that the *cis* double bond changes significantly the sp^2 region, and, with one notable exception, has little effect on the sp^3 signals. (These results also support the exclusion of a 7-*cis* structure since there is little doubt that this would be

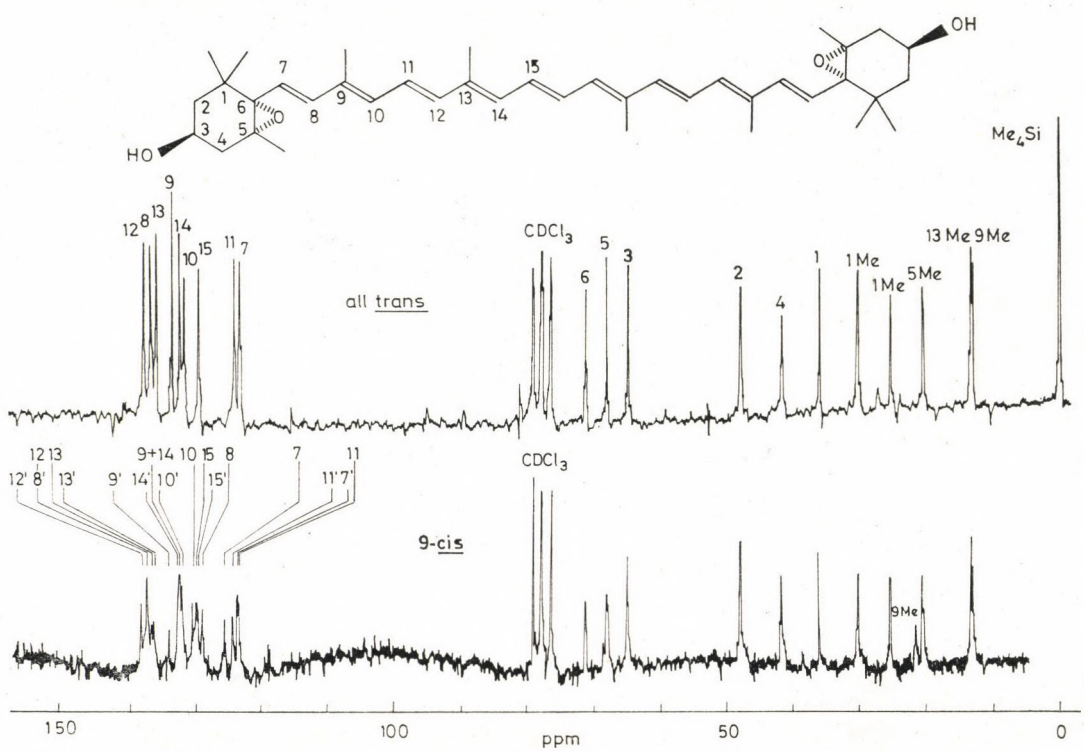
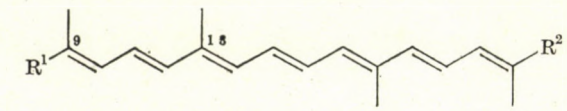


Fig. 1. ^{13}C-n.m.r. spectrum of violaxanthin (upper curve) and violeoxanthin (lower curve), in $CDCl_3$ at 22.63 MHz

associated with other marked changes in the sp^3 region.) However, an interpretation of the differences observed requires a full assignment of the ^{13}C–n.m.r. spectrum.

ROBERTS *et al.* [20] suggested an assignment of the ^{13}C–n.m.r. spectra of β-carotene (V) and several related compounds. Extensive studies have confirmed [21] the conclusions regarding the sp^3 signals. The study of [15,15'—$^2H_2$] β-carotene by VETTER *et al.* [22] unambiguously located the signal due to C-15 in the β-carotene spectrum, but showed that the interpretation of the other sp^2 signals needs revision. This problem must first be resolved before attempting the full analysis of the ^{13}C–n.m.r. spectra of violeoxanthin and violaxanthin



I $R^1 = R^2 = a$

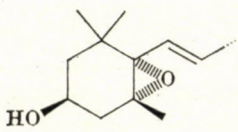
II $R^1 = R^2 = b$

III $R^1 = R^2 = c$

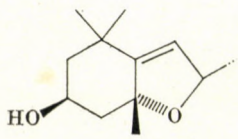
IV $R^1 = a$, $R^2 = d$ (9-*cis*)

V $R^1 = R^2 = e$

VI $R^1 = R^2 = f$



a



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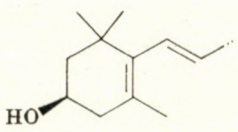

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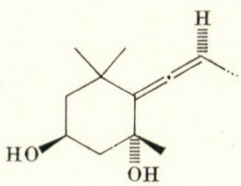

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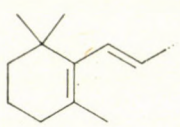

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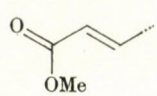

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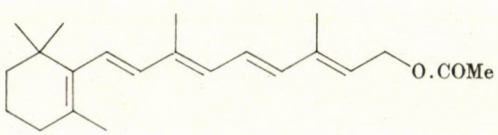

VII

Our assignment for β-carotene was made using a combination of single frequency off resonance (SFOR) data [23], specific deuteration (with [11,12—

$^2H_2$] vitamin A acetate), the polarization effect of a carbonyl group (with methylbixin), and the effect of *cis* double bonds. The spectrum of all-*trans* methylbixin (**VI**) comprises twelve out of the thirteen possible signals (see Table II). Characteristic chemical shift values identify the carbonyl group (C-6),* ester methyl, and inchain methyl signals (9-Me and 13-Me), and show that the latter are fortuitously coincident. Polarization of the polyene chain by the carbonyl group clearly results in strong shielding of the α-position and deshielding of the β-position; the signals due to C-7 and C-8 are therefore readily identified. The absence of $^1H-{}^{13}C$ spin–spin coupling under SFOR conditions distinguishes C-9 and C-13 from the other sp^2 signals, and combined with polarization effects, the signals due to these two carbons can be recognized. Comparison of the spectrum of all-*trans* methylbixin with that of 9-*cis* methylbixin shows clearly the influence of the *cis* double bond on the 9-methyl signal, which is shielded by -7.7 ppm, and the complementary, but equally pronounced, shielding of C-8 by $+8.5$ ppm (see Table III).

The sp^3 signals in the spectrum of all-*trans* vitamin A acetate (**VII**) were assigned by ROBERTS *et al.* [20], but subsequent SFOR studies by BREMSER *et al.* [23] showed the need for revision of the sp^2 carbon signals. We therefore compared the spectrum of vitamin A acetate with that of the [11,12$-{}^2H_2$] analogue. The two signals absent in the latter spectrum are clearly due to C-11 and C-12; slight isotope effects (0.04 to 0.10 ppm) were also observed on C-9, C-10, C-13 and C-14. Comparison of the spectra of 9-*cis* and 13-*cis* vitamin A acetate with the all-*trans* case, together with the knowledge derived from the methylbixin studies of the influence of a *cis* double bond on neighbouring sp^2 carbons, enables a full assignment to be made of the vitamin A acetate spectrum, and hence of the spectra of β-carotene and methylbixin. Confirmation of the β-carotene assignment was obtained by a study of a series of apo esters from 11-apo to 2'-apo [21]. A similar conclusion has recently been derived by BREMSER and PAUST [24] based on a limited study of apo aldehydes and ketones. With these data it is straightforward to deal with the spectra of zeaxanthin and violaxanthin (see Table II).

A 9—10 or 13—14 *cis* double bond is most clearly seen by the effect on the signal associated with the methyl group attached to it (Table III). Although a complementary shift is observed with C-8 or C-12, respectively, this sp^2 signal is difficult to recognize unambiguously among the many similar signals in this region of the spectrum. The spectrum of violeoxanthin has a diagnostic signal at δ 21.1 which must be due to either the 9- or 13-methyl carbon. This represents a shift of 8.3 ppm which clearly indicates that either the 9—10 or 13—14 double bond is *cis*. An 11—12 *cis* double bond would give a shift of only 4.9 ppm at the 13-methyl [25, 26]. A similar small shift at the 9-methyl might also be associat-

* carotenoid numbering

Table II

^{13}C–n.m.r. chemical shifts ($\delta_{TMS} = 0$) in $CDCl_3$

	1	2	3	4	5	6	7	8	9	10	11	12
All-*trans* methylbixin	—	—	—	—	—	167.9	115.9	149.0	133.5	139.4	124.4	141.7
Methylbixin {*trans* end	—	—	—	—	—	167.9	115.9	149.1	133.5	139.5	124.3	141.9
Methylbixin {*cis* end	—	—	—	—	—	168.1	117.6	140.5	131.6	138.0	123.3	140.5
All-*trans* vitamin A acetate	34.3	39.7	19.3	33.1	129.4	137.9	127.0	137.7	136.6	130.0	125.8	135.8
9-*cis*-vitamin A acetate	34.2	39.7	19.4	33.1	129.4	138.2	128.9	130.1	134.9	128.5	124.8	135.3
13-*cis* vitamin A acetate	34.3	39.7	19.3	33.1	129.6	137.9	128.1	137.6	138.2	130.2	127.4	127.8
β-carotene	34.3	39.7	19.3	33.2	129.3	138.0	126.7	137.8	136.0	130.8	125.0	137.3
Zeaxanthin	37.1	48.2	65.1	42.4	125.5	142.3	126.1	138.5	135.7	131.3	124.9	137.6
Violaxanthin	35.4	47.1	64.1	40.9	67.3*	70.4*	123.9	137.2	134.2	132.4	124.6	138.2
Violeoxanthin {*trans* end	35.4	47.3	64.2	41.0	67.2*	70.3*	123.9	137.3	134.2	132.3	124.6	138.2
Violeoxanthin {*cis* end	35.4	47.3	64.2	41.0	67.8*	70.6*	126.0	129.2	132.6	130.8	123.6	137.3

*Assignments marked with an asterisk may be reversed.

	13	14	15	1-Me's	5-Me	9-Me	13-Me	Other signals
All *trans* methylbixin	136.8	134.7	131.1	—	—	12.6	12.6	MeO 51.5
Methylbixin {*trans* end	136.6*	135.0	131.3	—	—	12.6	12.8	MeO 51.5
Methylbixin {*cis* end	137.0*	134.3	130.8	—	—	20.3	13.1	MeO 51.7
All *trans* vitamin A acetate	139.2	124.5	61.3	29.0	21.7	12.7	12.7	MeCO . O 20.9 170.9
9-*cis*- vitamin A acetate	138.7	124.6	61.2	29.0	21.9	20.7	12.7	MeCO . O 20.7 170.4
13-*cis* vitamin A acetate	137.3	122.7	60.3	29.0	21.8	12.7	21.0	MeCO . O 20.5 171.0
β-carotene	136.4	132.4	130.0	29.0	21.7	12.7	12.7	
Zeaxanthin	136.5	132.6	130.0	28.7 30.2	21.7	12.8	12.8	
Violaxanthin	136.4	132.9	130.2	24.7 29.7	20.0	12.8	13.1	
Violeoxanthin {*trans* end	136.3	132.8	130.7*	24.9 28.7	20.0	12.8	13.1	
Violeoxanthin {*cis* end	136.7	132.6	130.0*	24.9 29.7	20.0	21.1	13.1	

Table III

*Effect of cis double bond on ^{13}C–n.m.r. chemical shifts ($\Delta\delta = \delta_{cis} - \delta_{trans}$)**

	6	7	8	9	10	11	12	13	9-Me
9-*cis* methylbixin (cis end)	0.2	1.7	−8.5	−1.8	−1.4	−1.1	−1.2	0.2	7.7
9-*cis* vitamin A acetate	0.3	2.1	−7.6	−1.6	−1.6	−1.0	−0.5	0.3	8.0
13-*cis* vitamin A acetate	0.2**	1.6**	−8.0**	−1.8**	−1.8**	−1.0**	−**	−**	8.3**
Violeoxanthin (*cis* end)	0.1	2.2	−8.0	−1.6	−1.6	−1.0	−0.9	0.3	8.3

*For similar data on 9-*cis* and 13-*cis* retinal in acetone, dioxane or cyclohexane see references [25] and [26].

**Values displaced one isoprenoid unit to facilitate direct comparison with the other data.

ed with a 7—8 *cis* double bond. Although a central 15—15' *cis* double bond has been excluded, the observed shift confirms this conclusion; the 13-methyl signal of 15—15' *cis* β-carotene [20] and phytoene [27] only shows a shift of −0.2 ppm.

Using the data from the other *cis* isomers (Table III), the spectrum of 9-*cis* or 13-*cis* violaxanthin can be predicted. It is clear that only the former assignment fits the experimentally observed spectrum of violeoxanthin (Table II). This conclusion is the first use of ^{13}C–n.m.r. for the determination of the geometrical configuration of a carotenoid, and shows that, when the assignment problem is overcome, it represents an extremely powerful technique for such studies. The present results, when coupled with the ^{1}H–n.m.r. data mentioned earlier (Table I), also provide strong support for the corresponding 9-*cis* formulation of the common *cis* neoxanthin [28].

We turn now to the question of the absolute configuration. Violaxanthin (**I**) is readily isomerized to a mixture of auroxanthins (**II**) when treated with acid. These 5,8-epoxides only differ in their stereochemistry at C-8 and C-8'. A ^{1}H–n.m.r. study [29] showed that the epoxide oxygen atom is *trans* to the 3-hydroxyl group. Treatment of violaxanthin with lithium aluminium hydride gave zeaxanthin (**III**) [30] with the same absolute stereochemistry as natural zeaxanthin [31, 32]. Thus the absolute stereochemistry of violaxanthin is as shown (**I**). Isomerization of violeoxanthin with iodine [33] gave violaxanthin indistinguishable from the natural carotenoid. Both samples of violaxanthin have the same absolute stereochemistry as shown by their o.r.d. [31] and c.d. spectra (Table IV). It follows that violeoxanthin must have the same 3S, 5R, 6S, 3'S, 5'R, 6'S configuration as violaxanthin.

The c.d. spectra of violaxanthin and violeoxanthin (Fig. 2 and Table IV) in the ultraviolet region show the same characteristic inversion observed with

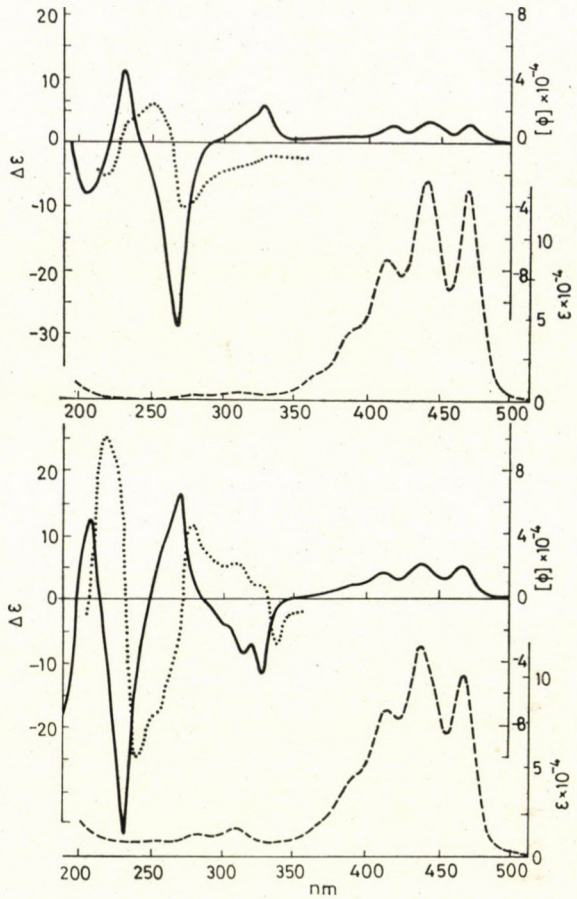

Fig. 2. O.r.d.-in dioxan (·····), c. d. in ethanol (———), and electronic spectra in ethano (— — —) of violaxanthin (above) and violeoxanthin (below)

Table IV

C.d. spectra Δε (λ_{max} in nm) in ethanol

Violaxanthin	Violaxanthin ex violeoxanthin	Violeoxanthin	Neoxanthin X	Neoxanthin
— 8.03 (205)	—10.8 (210)	13.45 (208)		— 7.72 (204)
11.60 (230)	13.7 (233)	—37.15 (231)	— 2.04 (222)	—15.45 (229)
—29.40 (266)	—37.6 (268)	18.20 (268)	— 5.90 (265)	6.84 (267)
		— 5.21 (303)	— 0.49 (299)	— 1.40 (302)
3.57 (316)		— 9.97 (314)	— 0.49 (311)	— 2.92 (315)
5.80 (328)		—13.45 (328)	— 0.07 (328)	— 3.86 (328)
0.89 (395)		2.17 (391)	0.64 (393)	1.12 (388)
2.14 (420)		4.34 (412)	1.27 (420)	2.24 (416)
3.39 (444)		6.95 (438)	1.83 (444)	2.99 (438)
2.68 (471)		5.64 (465)	2.00 (475)	2.43 (467)

their o.r.d. spectra [31]. However, both carotenoids have positive maxima corresponding to the principal light absorption maxima. Calculation [34] of the o.r.d. spectra from the much more accurate c.d. spectra show close similarities with the experimental results. The o.r.d. spectra of heterodichiral carotenoids may be predicted with reasonable accuracy by addition of the spectra corresponding to each chiral end group [31]. Limited tests suggest that similar additivity is possible with c.d. spectra [35]. This indicates that the end group in violeoxanthin with the *cis* double bond contributes a component substantially stronger than that of the end group in the all-*trans* isomer. A similar inversion effect is observed with the o.r.d. [28] and c.d. spectra of 9-*cis*-neoxanthin (**IV**) and its all-*trans* isomer (Table IV), as well as with *cis* isomers of fucoxanthin [36]. The necessity for stereochemical purity in c.d. studies is clearly demonstrated by these spectra.

*

We thank the Science Research Council for a research grant, Dr. G. M. CLARKE for samples of 9-*cis* and 13-*cis* vitamin A acetate, Dr. O. ISLER for a sample of [11,12-$^2H_2$] vitamin A acetate, and Mr. J. F. HAGEL for some of the ^{13}C-n.m.r. spectra. Dr. G. ENGLERT has kindly informed us of similar ^{13}C-n.m.r. studies with vitamin A acetate and β-carotene.

This paper is regarded as Part XXXI in the series 'Carotenoids and Related Compounds'; for Part XXX see reference [37].

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RECENSIONES

L. ERDEY and G. SVEHLA: *Ascorbinometric Titrations*

Akadémiai Kiadó, Budapest, 1973 (184 pages, 28 figures, 21 tables)

This monograph offers a comprehensive treatment of the analytical method introduced by Professor ERDEY as early as 1950 and developed further with his co-workers for nearly two decades. The book has been divided into five chapters: Introduction, Ascorbic acid standard solutions, End-point detection in ascorbinometric titrations, Direct titrations with ascorbic acid, Indirect determinations. The monograph contains 170 references, giving a full literature survey of the field and is completed with detailed author and subject indexes.

The Introduction gives information about the discovery of vitamin C, *i.e.* ascorbic acid, about its production, synthesis, structure determination as well as its acidic and redox properties, with literature references. It deals in a detailed manner with the oxidation—reduction potential of the ascorbic acid–dehydroascorbic acid system as a function of the pH. It concludes that ascorbinometric titrations are practicable in the pH range between 0 and 8.

The next chapter describes the preparation of ascorbic acid standard solutions, their standardization with potassium hexacyanoferrate(III), potassium dichromate, potassium bromate, potassium iodate and potassium hydrogen iodate. (Iodometry has been used in the last three cases.) The problems of decomposition and stabilization are also discussed.

Chapter 3 summarizes the possibilities of end-point detection in ascorbinometric titrations. In particular, results obtained by Professor ERDEY and co-workers in applying 4-amino-4'-methoxy-diphenylamine (Variamine Blue) as a redox indicator have obtained a detailed treatment. The book gives also a survey on the instrumental end-point detection methods (potentiometry, amperometry, 'dead-stop' method, radiofrequency methods) which can be used in ascorbinometric titrations.

Chapters 4 and 5 deal with practical applications of ascorbinometry. Among others, detailed descriptions are given for the determination of iron, hexacyanoferrate (III), iodine, chlorate, bromate, iodate, silver, mercury, thallium, copper, gold and vanadium. Having described some direct titrations which can be carried out in non-aqueous media (e. g. acetic acid), the authors give a survey of the indirect methods of determination, based upon the titration of iodine, hexacyanoferrate(III), iron(III), thallium(III).

It is the merit of Dr. Gyula SVEHLA that the monograph has been compiled after the death of Professor László ERDEY. The book gives a high-level and comprehensive description of this important research field of the school of this early deceased world-famous analyst.

The work of the Publishing House of the Hungarian Academy of Sciences (Akadémiai Kiadó) has to be appreciated since the attractive and careful publishing of this volume certainly contributes to the spreading of this rather generally applicable reductometric analytical method developed in Hungary.

E. BODOR

R. Stendel (Prof. Dr. rer. nat.: Institut für Anorganische und Analytische Chemie, Technische Universität Berlin): *Chemie der Nichtmetalle* (mit einer Einführung in die Theorie der Atomstruktur und der chemischen Bindung)

Walter de Gruyter, Berlin — New York 1974 (472 pages, 123 figures, 52 tables)

The first part of this textbook deals with the fundamentals of the atomic structure and chemical bonding; the subject given in the title is treated only in the second part, from page 175.

The first part consists of the following chapters: Einführung (1 page), Elementarteilchen (2 pages), Masseinheiten und Umrechnungsfaktoren (2 pages), Atommodelle (42 pages) Theorie der chemischen Bindung (114 pages).

The chapter on atomic models describes the structure and properties of the electronic orbitals and the atomic nucleus. The treatment of electronic structure begins with Bohr's model of the hydrogen atom. Subsequently, the wave-mechanical model of the hydrogen atom, the orbitals of polyelectronic atoms as well as the "Aufbau" principle and the periodic system are discussed. The chapter on chemical bonding is divided into five sections: Ionic bond; Covalent bond; van der Waals bond; Geometry of molecules; Bond properties.

This first part of the textbook containing a good summary of the fundamental knowledge of the structure of elements and compounds using well-selected and clear examples, provides suitable basis for the treatment of nonmetals and their compounds.

The second part of the book begins with hydrogen, followed by oxygen and the sulfur group (S, Se, Te, Po), subsequently, halogens, noble gases, nitrogen, phosphorus and arsenic, carbon and silicon are treated; the series ends with boron. Although this order has some practical advantages (primarily, the treatment of oxygen at the beginning), still oxygen fluorides and sulfur halides precede the general description of halogens.

The author explains first of all problems concerning structure and bonding in his book, but gives profound and sufficient data for descriptive chemical knowledge, too. Especially valuable information is provided for a general picture of the structure of nonmetal compounds by sections preceding or following the treatment of elements or groups of elements. These enable the reader to find direct connections between structural data determined experimentally and the electronic structure of atoms and molecules.

This book summarizing a part of inorganic chemistry as taught at universities, contains also several important new results (*e.g.* noble-gas compounds, nitrogen molecule as complex ligand, etc.). It may prove useful not only for undergraduate students but also for research chemists, chemical engineers, and biochemists by providing up-to-date information on nonmetals and their compounds.

E. Bodor

C. Richard and P. Granger: *Chemically Induced Dynamic Nuclear and Electron Polarizations — CIDNP and CIDEP*

Volume 8 of "NMR Basic Principles and Progress (Grundlagen und Fortschritte)", editors P. Diehl, E. Fluck and R. Kosfeld

Springer Verlag, Berlin — Heidelberg — New York, 1974 (123 pages and 26 figures)

Chemically Induced Dynamic Nuclear Polarization (CIDNP) was first observed in 1967. Since that time several papers have been published in this field. A theoretical review of these publications is given in this book and simultaneously a survey is offered of those practical areas where the method can be used in order to obtain basic information.

The book consists of four chapters. The first chapter is an introduction to the concepts of CIDNP. The ideas of the radical-pair theory of CIDNP are presented with the aid of an "effective field" model. The second chapter deals with the theoretical developments of the radical-pair theory and is especially interesting to NMR spectroscopists. From a purely practical point of view, Chapter 3 seems to be the most interesting. It deals with applications of the method to the study of chemical reactions and magnetic properties. The following types of radical reactions

can be investigated: thermal or photochemical decomposition of peroxides, reduction of diazonium salts with $NaBH_4$, NaOH, etc., rearrangements, reactions of carbenes, free-radical attacks on aromatic molecules, photochemical reactions of aldehydes, reactions of azo-compounds, biradical reactions, reactions of organometallic compounds with alkyl and aromatic, halides, decomposition reactions, radical ions (nucleophilic and electrophilic substitutions),other nuclei (^{13}C, ^{19}F, ^{31}P, ^{15}N, ^{2}H), first-order, competitive, consecutive, bimolecular and zero-order reactions in chemical kinetics, determination of the magnetic properties of radicals and molecules, sign determination, hyperfine coupling constant A, spectroscopic splitting factor g or Δg, $J_{determination}$, relaxation times.

The last chapter discusses the so far less known CIDEP effect interesting for scientists involved in ESR studies.

The book is well edited and made up. Though more details dealing with the practical applications would be desirable, the book is very useful, especially to scientists having a sound knowledge in the theory of ESR and NMR investigations.

P. HAJDU

F. BRESCIA, S. MEHLMAN, C. PELLEGRINI and S. STAMBLER: Chemistry (a modern introduction)

W. B. Saunders Company, Philadelphia—London—Toronto, 1974 (XVIII + 644 + XXII pages, 163 numbered figures, 41 tables, 8 coloured illustrations)

The authors treat chemistry divided into the following 24 chapters: (1) Introduction (35 pp.), (2) Gases (35 pp.), (3) Liquids and Solids (20 pp.), (4) Atoms and Molecules (37 pp.), (5) Nomenclature–Chemical Arithmetic (17 pp.), (6) Electricity and Atomic Structure (43 pp.), (7) Regularities in the Properties of Elements (18 pp.), (8) Chemical Bonding: Forces between Atoms and Molecules (37 pp.), (9) The Covalent Bond: the Shape of Molecules (35 pp.), (10) Energy Changes in Chemical Reactions (29 pp.), (11) Chemical Equilibrium (27 pp.), (12) Solutions (31 pp.), (13) Ionic Solutions, Oxidation and Reduction (9 pp.), (14) Acids and Bases (17 pp.), (15) Ionic Equilibrium (25 pp.), (16) Electrochemistry (31 pp.), (17) Chemical Kinetics (21 pp.), (18) Nuclear Chemistry (27 pp.), (19) The Chemistry of *Several* Common Nonmetallic Elements (28 pp.), (20) The Chemistry of Some Representative Metals (25 pp.), (21) The Transition Metals (15 pp.), (22) The Chemistry of Carbon Compounds (32 pp.), (23) Polymers and Proteins (20 pp.), (24) Instrumental Analysis (16 pp.). Six Appendixes containthe values of basic constants symbols and abbreviations, conversion factors, the electronic structure of the elements, general solubility rules and four-place ten-base logarithms. The book is concluded with a 22 page subject index. The colour-printed book contains several unnumbered figures in the text providing a good help for better and deeper understanding together with more than seven hundred Additional Problems.

The authors undertook the task of developing such a view in the reader based on the simple explanation of elementary concepts, without assuming any previous mathematical or physical knowledge, that enables him to understand and master basic up-to-date chemistry. This has been done, in addition to a logical sequence of the material, by clear and simple composition, descriptive figures and a good typography.

Several problems — and their detailed solution — have been included into the text for illustrating the practical application of basic concepts. Although this breaks sometimes the continuity of the treatment, and the too detailed explanation of solutions is not always necessary, nevertheless, it undoubtedly gives useful help to beginners to acquire chemical knowledge without any difficulties.

Inorganic chemistry is dealt with in Chapters 7, 19, 20 and 21. The aim of the authors was to include the minimum amount of lexical knowledge only. Data burdening memory are dealt with on the basis of analogies derived from the periodic system, electronic structure and the structure of matter. It has to be noted by the way that — similarly to most books on inorganic chemistry published recently — this book also breaks earlier traditions: elements with new electrons on sub-orbitals s or p are classed into subgroups A, whereas transition metals into subgroups B.

E. BODOR

Topics in Current Chemistry, Vol. 45
Dynamic Chemistry

Springer-Verlag, Berlin, Heidelberg, New York, 1974, 221 pages

Volume 45 of the series, dealing with the most topical questions in chemistry, contains five independent studies under the comprehensive title of "Dynamic Chemistry". Three of these deal with dynamic stereochemistry, and in fact treat fairly closely related problems at various depths of generalization and discussion and from different aspects. The two remaining articles examine questions of dynamic chemistry which are quite different from the other three and also from each other. It is reasonable, therefore, to discuss the three stereochemical papers first, although these do not follow one another directly in the volume.

Experimental Force Field Calculations (pp. 1→38) by C. ALTONA and D. H. FABER provides a detailed and comprehensive review of the method initiated by Westheimer and developed mainly by Hendrickson, Wiberg and Allinger, which involves calculation of the geometry and energy content of molecules not by quantum-chemical means, but by the application of classical mechanical models. This computer procedure, known as molecular mechanics or the force field method, is nowadays extensively used in the study of the conformation of cyclic compounds, and can be regarded as a higher-potential development of the molecular models, which is able to give even quantitative data. As regards the possible conformations of a molecule, it provides information not only on the geometry, but also on the energy conditions. The article thus deals with a field which is frequently reviewed and which is treated even in stereochemistry textbooks, but which today is definitely of topical interest. It is not so much an introductory account as a comparison and critical evaluation of the various methods. It discusses questions of principle and practical difficulties (parameterization and calculation technique) in the energy computation "from inside", *i.e.* from the aspect of the specialist dealing with them. It is therefore addressed primarily to those readers who are to a certain extent already acquainted with this field. The tabulated summary of the literature at the end of the article is unquestionably of great value.

J. E. ANDERSON: *Chair-Chair Interconversion of Six-Membered Rings* (pp. 139—168). This second stereochemical article reviews the literature connected with the dynamics of the most thoroughly studied conformational change, the chair-chair interconversion of the cyclohexane ring. A study is primarily made of the question of how the energy barrier of the conformational change is affected by the various strain-inducing factors (torsional or Pitzer strain, named 1,2-interaction in the article, angular or Baeyer strain, van der Waals interaction and dipole-dipole interaction). The paper collects the results of the considerable experimental material, and also the relevant calculations, relating to substituted cyclohexane derivatives, and to others containing heteroatoms, but definite and clear-cut conclusions are drawn only rarely. The many questions of detail are not successfully welded into a uniform picture. The article without doubt contains many useful data, but it does not provide a unified view of the dynamics of conformational changes. Nevertheless, it may serve as a good illustration for the previous article, in so far as it presents a wider sphere of application of conformational energy calculations.

F. A. L. ANET: *Dynamics of Eight-Membered Rings in the Cyclooctane Class* (pp. 169—220). The third stereochemical article is quite outstanding. It is a detailed and deep analysis of a question which at first sight may perhaps appear not to be of great significance: the dynamics of the conformational changes of cyclooctane and some of the simple cyclooctane derivatives. A closer reading of the article, however, gives a somewhat striking revelation of the fineness of detail of the molecular dynamics which may be discovered by application of the temperature-dependent dynamic NMR technique (H and ^{19}F NMR). Although the essence of the experimental method too may be learned from the article, the greatest experience is provided by the rationality of the logic of the stereochemical considerations. If the reader does not begrudge the time and trouble, and studies the article thoroughly with Dreiding models in his hand (for only thus is it worthwhile), he may become acquainted to the maximum with the performance of modern stereochemistry, and may acquire a completely new view of the symmetry of molecular structure, and the geometric and energetic conditions of structural changes, *i.e.* of dynamic stereochemistry. This excellent article certainly presents many useful novelties, even for specialists in this field, but it may also provide an instructive experience for all chemists interested in this most modern area of stereochemistry and its results only from a little more distance. Almost half of the 79 references dealt with in the article are papers of the author. Throughout the article it can be felt that the author is the greatest authority in this field; not

only has he collected the results of others, but a considerable proportion of them stem from his own work.

The remaining two articles study aspects of dynamic chemistry relating to the electronic structure. A particularly great experience is provided by *The Removal of Orbital Symmetry Restrictions to Organic Reactions* (pp. 39—91) by *F. D.* MANGO, which is perhaps the finest gem of the entire volume. In its clarity and its simple and understandable style it surpasses the pedagogic level of many good textbooks. Again it can only be said that this article not only reports an interesting chemical question, but also thereby deepens the reader's general chemical attitude. The theme of the article is the catalytic effect of transition metal ions on symmetry-forbidden reactions. In fact, it treats cycloaddition processes of type [2 + 2] only, but in this it presents the basic principles so clearly that the reader can readily follow the examples relating to the more complex processes too. The essence of the catalytic effect of the metal ion is as follows. The bond between the ligand and the metal ion develops by the partial transfer of an electron pair from the highest occupied molecular orbital (HOMO) of the donor ligand (*e.g.* an olefin) to an empty d-orbital of the metal ion, with the same symmetry as the HOMO; at the same time, however, by means of back-donation from one of the occupied d-orbitals of the metal ion an electron passes into the lowest unoccupied molecular orbital (LUMO) of the ligand. The electronic structure of the ligand bound in the complex thus lies between the ground state and the excited state, and therefore [2 + 2] cycloaddition, which is forbidden in the ground state, but allowed in the excited state, may take place within the complex (*via* an electron-flow brought about by the metal ion), *i.e.* the symmetry-forbidden state is resolved. The author terms this a forbidden-to-allowed process. The substance of this fairly involved process is presented in very simple and clear figures and is described with admirable pedagogic skill. A close study of the article is of value not only for coordination chemists, but also for those organic chemists who have become disaccustomed to thinking of the symmetry of the d-orbitals.

R. C. DOUGHERTY: *The Relationship between Mass Spectrometric, Thermolytic and Photolytic Reactivity* (pp. 93—138). The relationship mentioned in the title, between the fragmentation to be observed in the mass spectrometer and the reactivity displayed under the conditions of thermolysis or photolysis, stems from the fact that a molecular ion formed as a result of electronic bombardment can be regarded as analogous with the ground-state molecule from the point of view of the highest occupied molecular orbital, and with the excited state as a consequence of its radical character. As compared with the two electrically neutral molecular states, however, there is a fundamental difference in reactivity as a result of the electric charge of the fragmenting molecular ion and the high energy available for its formation. The author first examines on many interesting examples the assertion of the general structural viewpoints (charge, energy content, presence of heteroatoms, steric effects), and then systematizes the rich experimental material in groups of compounds. (The article includes 139 literature references.) It is stated as a conclusion that, although the reactivities displayed under the different experimental conditions show many differences quantitatively, there is a characteristic relationship between them; this makes mass spectrometry a well-applicable means for the study of thermolytic and photochemical reactions. The article primarily lays stress on questions of detail. The many examples are especially interesting for those engaged in one or other of the special fields; evaluation of the more general principles of the topic is at times too limited, though the author himself confesses that this is deliberate.

With its rich and varied contents, Volume 45 of Topics in Current Chemistry provides useful and interesting reading for all chemists interested in the results of the latest fields of chemistry.

M. KAJTÁR

C. A. MEAD: Symmetry and Chirality
Topics in Current Chemistry, Vol. 49

Springer-Verlag, Berlin, Heidelberg, New York, 1974, 88 pages

A study is made of the chiral properties of a molecular family in which various substituents are linked to a given molecular skeleton. One parameter is ascribed to each of the substituents, and with the aid of group theory chiral functions are constructed from the parameters. The chiral functions are characterized in that they are insensitive to the orientation of the

molecule, but there is a change in sign if the substituents are exchanged so as to produce a mirror image of the original molecule. The fields of application of the chiral functions are not detailed; it is merely pointed out that they are of importance, for example, in the interpretation of optical activity. A number of interesting correlations are derived from considerations involved in the derivation of the chiral functions. For instance, in the case of a given molecular skeleton and allowing chiral or achiral ligands, it is possible to establish the greatest number of identical ligands for which the molecule is still chiral. Criteria are given with regard to when the members of a given molecular family may definitely be classified as of right or left type (shoe-like molecules), and when not (potato-like molecules).

The author assumes the reader to have as much understanding of group theory as a graduate chemist. In fact, without a certain grounding in group theory the book would be difficult to understand. At any event, the author presents the chiral functions relating to the most important molecular skeletons; these may naturally be utilized even if the details of their derivation are not known.

F. TÖRÖK

William A. PRYOR: *Einführung in die Radikalchemie*

Verlag Chemie, Weinheim, 1974 (118 pp., 10 figures, 23 tables)

This book is the German translation of the English original published in the United States in 1966. Similarly to other volumes published so far in the "Chemie Paperback" series of the publishers, this volume also offers a concise but clear and well-arranged picture of the subject. The book consists of 13 chapters. The first of these deals with definitions and the theoretical basis of radical reactions and radical chemistry including spectra, reactivities and problems concerning the corresponding dissociation energies. Configurational problems of radicals, as well as some important processes of radical formation (thermal, photochemical and redox reactions leading to radicals) are treated in the subsequent chapters. The remaining parts give a detailed description of various radical reactions. Separate chapters have been devoted to hydrogen migration reactions, halogenation, addition processes, radical polymerization, aromatic substitution, bond rearrangements and different isomerization processes.

Very well selected descriptive illustrations help the better understanding of each chapter and, whenever necessary, the author adds data in tabulated form, too. No particular mathematical qualification is necessary for understanding the chapter on reaction kinetics. In order to check the understanding of each subject group, 5—7 control exercises have been included after each chapter. Although the English original was published in 1966, the book can still be regarded as up-to-date.

B. LOSONCZI

G. FÖLDIÁK, Gy. CSERÉP, I. GYÖRGY, M. RODER and L. WOJNÁROVITS: *Advances in chemistry* Vol. 20

Relationship between the radiation-chemical reactions of hydrocarbons and their molecular structure. Akadémiai Kiadó, Budapest 1974. 232 pages

The book, published in the series "Advances in chemistry", reports on 232 pages on recent results concerning the radiolysis of hydrocarbons. The 331 references convince the reader that the authors have indeed summarized in this monograph "recent" results in the field of the radiation-chemical reactions of hydrocarbons. The predominant part of this literature was published after the mid-1960's. The references include nearly all works that can be considered of merit in this sphere of theme.

The monograph consists of six parts. The first part summarizes knowledge concerning the fundamental processes of hydrocarbon radiolysis. The reader becomes acquainted with the absorption of radiating energy, the reactions of excited molecules, ions, free radicals, radical ions, and with the effect of the conditions of irradiation (dose, dose rate, temperature, etc.) on the yield. Next, the authors describe physical and chemical methods making possible the determination of the yield and mechanism of radiation-chemical processes.

The 5 subsequent chapters deal with the radiation chemistry of various hydrocarbons (aliphatic alkanes, cycloalkanes, aliphatic alkenes, cycloalkenes and aromatics).

All chapters are easy to survey, tables and figures illustrate and make comparable the data of the different chapters. Where known, the reaction mechanism or the presumed reaction mechanism is given. The monograph gives a general picture of the "weak" points of various molecules in radiation chemistry, and of the kind of C–H and C–C bonds whose rupture is to be expected for a given molecule.

Regrettably, the monograph does not include the valuable results attained in solid phase and graft polimerization, among others, by Hungarian scientists *e. g.* in the Research Institute for Plastics Industry and the Central Research Institute for Chemistry of the Hungarian Academy of Sciences.

The book deserves a place on the book-shelf of all experts dealing with, or interested in, radiation chemistry.

L. SÜMEGI

COLBERT, J. C.: *Sugar Esters, Preparation and Applications* Chemical Technology Reviews, Vol. 32

Noyes Data Corp., Park Ridge, New Jersey, London 1974. 310 pages

The book is a compilation for practical purposes, in which 149 US and 2 British patents have been worked up. The application of the preparation and the use of the individual sugar esters is facilitated by a recipe-like description of patent examples for those interested in the subject. Among the sugar esters, saccharose esters are treated at the greatest length, which can be explained by the ion like compilation, a great merit of the book is that the preparations of the individual esters are described by grouping the solvents according to the catalyst, on the basis of the acid component.

The author discusses over 114 pages the preparation and application of alkyl and fatty acid esters. Ester formation via transesterification, with acid anhydrides, acid chlorides and ketenes are dealt with in detail. Examples are given concerning the use of heterocyclic amines, alkylamides and sulfoxides as solvents and on transesterification in emulsion and without solvent. In the processes using acid anhydrides and acid chlorides, dextrine, dextrane and lactose are also used besides saccharose as hydroxyl component, particularly in the preparation of mixed esters. After the discussion of the preparation procedures, a separate chapter deals with the recovery and purification of fatty acid esters (by precipitation, extraction, distillation, washing), with the fractionation of mono- and diesters and their application. Examples are given of the use of fatty acid esters in petroleum products as inhibitors of sediment formation, as flowing point depressors, and of their use as coating materials of drug tablets, as plasticizers in the plastics industry, and as antioxidants in the food industry.

Among other organic esters, the preparation and application of polymerizable sugar acrylates and methacrylates, aromatic esters, dibasic carboxylic acid esters, nucleoside esters, urea esters etc., are also discussed.

Sugar esters formed with inorganic acids are discussed over more than 100 pages. Phosphate esters are treated most extensively, *i. e.* saccharose mono- and polyphosphates, phosphites, phosphonates and their salts. The salts of glucose-1-phosphate and of other amino acids with antibiotics are of importance in the pharmaceutical industry, while the salts of saccharose phosphates with trace elements in the fodder industry. Certain phosphate esters (*e. g.* phosphomannane) can be prepared also by fermentation methods. The sulfate esters of various sugars can be used as surfactants, emulsifiers, wetting agents, the sulfate esters of polysaccharides (*e. g.* dextrane, dextrine) as pharmazeuticals (anticoagulant, tablet coating materials), while glucose hydrocarbon sulfonates can be used as biodegradable ingredients of detergents.

E. LÁSZLÓ

E. J. Slowinski, W. C. Wolsey and W. L. Masterton: *Chemical Principles in the Laboratory, with Qualitative Analysis*

W. B. Saunders Co. Philadelphia—London—Toronto 1974. 343 pp.

In the preface of the book the authors note that chemistry has always been an experimental science and, in spite of the very good results obtained on the basis of theoretical considerations, it will remain essentially an experimental science also in the future. This is naturally meant in the sense that measured experimental results recorded in the research laboratories must be followed by modern theoretical interpretation, but the basis of the results is the experiment, the measurement. In the spirit of this basic principle, the authors attempted in this book to acquaint the beginner chemist through experiments with as many chemical principles as possible.

The experiments described in this book were partly selected from the literature, partly developed by the authors in the laboratories of the University of Connecticut and Macalester College, Minnesota, and are first published here. Laudably, the aim of the authors was to give a wider selection of experiments than that encountered during average courses in chemistry. Classical qualitative analysis and the reactions of ions have not been included in the program for their own sake, but to make the students acquainted with the properties and basic reactions of inorganic substances.

The book of 343 pages, complemented by 6 tables and 15 figures, was published in 1974 by W. B. Saunders Co., and is divided into 15 chapters. Fourteen among these contain fundamental chemical operations, while the fifteenth discusses the reactions of the classical system of anions and cations.

The predominant part of the tasks is from many aspects similar to the practical work performed during the first years at our universities: determination of the molecular weight based on the depression of the freezing point and the elevation of the boiling point; works of preparativ character (*e. g.* the preparation of CuCl); some tasks in titrimetric analysis (chelatometric measurement of water hardness). Some of the laboratory work (preparation of salicylic acid, bromination of acetone, preparation of resins) concerns organic chemistry.

A novelty thought recommendable by the reviewer is that a fairly large number of energetic calculations and some tasks of special character (measurement of the half-life of radioactive isotopes, construction of molecular models) are also included in the book.

In summary, the book introduces the beginner to chemistry in a modern way, stimulating thinking but it does not differ essentially from methods customary in other countries. The study of the book can be recommended to colleagues teaching chemistry to freshmen at universities and colleges.

I. Pais

J. L. Clouser: *Keller plan for self-paced study using Masterton and Slowinski's Chemical Principles*

W. B. Saunders Co. Philadelphia—London—Toronto, 1974, 164 pages

After first reading, it could seem that this publication is intended for facilitating the learning of the book reviewed above. However, it becomes clear from the titles of the chapters that the authors of the former book have written several variants of a basic curriculum for chemistry freshmen. This had to be mentioned in advance, because the reviewing of this publication is not as easy task in view of the considerable number of references, and, at the same time, the unavailability of the reference sources. It would have been suitable if the reviewer had been acquainted with the problems whose solution forms an important part of Clouser's book.

The 164-page publication, which appeared in 1974, gives explanatory notes on 23 subjects together with the solutions of the problems mentioned. In the reviewer's opinion, the author has done very much to stimulate logical thinking, but the book does not give new approaches which could be recommended with emphasis to the reader.

Nevertheless, it should be pointed out as a merit of the book that after 4—5 subjects the author gives "Reviews", where many questions are raised to teach the students how to see the essence and how to solve problems. The following excerpt illustrates the point:

"Imagine that you have to analyse a substance originating from the Moon. You assume on the basis of the investigations that the substance is the new metal of atomic number 114, "eka-lead". Describe those methods, which are suitable to decide that the substance in question is an element and not a compound. Indicate also the measuring accuracy of the instruments needed for the investigation. Expound in which way mass spectrography is suitable for the determination of the atomic mass and the ratio of the single isotopes."

In connection with other parts of the curriculum the author also raises questions, which presume familiarity of the students with modern experimental methods (x-ray diffraction, etc.) and instruments.

In summary, the study of the book can be recommended to colleagues on the educational staff who wish to modernize teaching.

I. PAIS

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Erratum

From the paper of SWAMI, M. P., JAIN, P. C., RANA, V. B., SAHNI, S. K. and SRIVASTAVA, entitled o-Hydroxy-4-benzamidothiosemicarbazide as a Chelating Reagent, IV., published in Vol. 85, pages 409—415 of our journal, Table III has been omitted by mistake, and is now supplemented.

Table III

I. R. Spectral data and its tentative assignments

(OH – BTSC)	$[Ti(O-BTSC)_2]Cl_2$	$[(VO)_2(O-BTSC)_2(OH)_2]$ H_2O	$[Fe(O-BTSC)_2]$ $3H_2O$	$[Pd(O-BTSC)(OH]$ $4H_2O$	$[Ce(O-BTSC)_2(NO_3)H_2O$	$[UO_2(O-BTSC)(NO_3)]$ $2H_2O$	Assignments
—	—	3630 (sh)	3648 (m)	3650 (m)	3609 (m)	3615 (m)	ν(OH) of H_2O
3560 (s)	—	—	—	—	—	—	ν(OH) of phenol
3230 (m)	3270 (s)	3270 (s)	3330 (s)	3332 (s)	3270 (s)	3335 (s)	ν(NH) and (NH_2)
1630 (m)	1612 (s)	1601 (s)	1607 (s)	1632 (ssh,	—	1607 (s)	Amide & NH_2 bend +H—OH bend
1585 (m)	1580 (s)	1514 (s)	1530 (m)	1536 (m)	1549 (s)	1536 (m)	NH rock + CN
1547 (s)	1542 (m)						
1497 (s)	1496 (s)	1485 (s)	1491 (m)	1451 (s)	1463—1433 (mb)	1490 (m)	ν(CN) & (NH) rock
			1470 (m)			1468 (m)	
1309 (s)	1316 (s)	1309 (s)	1295 (m)	1294 (s)	1290 (s)	1283 (m)	ν(CN) and ν(CS)
	1283 (s)	1283 (s)					
1242 (s)	1229 (s)	1219 (s)	1236 (s)	1230 (s)	1235 (s)	1229 (m)	NH_2 rock +
1158 (m)	1160 (s)	1160 (s)	1162 (m)	1145 (m)	1150 (m)	1158 (m)	NCS bend + δNH_2
1136 (w)	1145 (w)						
1110 (w)	1110 (s)	1116 (ssh)	—	1112 (m)	1115 (m)	1111 (m)	
	1082 (m)	1074 (ssh)					
1066 (w)			1064 (w)		1058 (m)		$\delta(NO_3)$ in cerium complex and ν(NO) in uranium complex
1042 (wsh)	1031 (s)				1057 (w)	1027 (s)	
1021 (m)	—	—	—	—	—	—	
		1000 (m)	1000 (m)	999 (m)	998 (m)	990 (m)	δ(OH)
955 (m)	949 (w)	—	—	976 (m)	—	—	ν(V=O)
873 (m)	860 (w)	870 (w)	850 (m)	854 (m)	862 (wsh)	840 (m)	δ(NN)
830 (w)	834 (w)	834 (w)			832 (m)	834 (w)	
771 (m)	765 (s)	770 (ssh)	777 (m)	760 (m)	764 (m)	762 (m)	δ(NCO) + ν(CS) + ν(CN)
747 (m)	748 (s)						
	700 (m)	713 (m)	713 (m)			715 (m)	
694 (s)							

ACTA CHIMICA

ТОМ 87 – ВЫП. 3

РЕЗЮМЕ

Кинетический анализ кривых ТГ

Й. ШИМОН, Е. БУЗАГ-ГЕРЕ и Ш. ГАЛ

После краткого обзора теоретических возможностей, а также экспериментальных трудностей, возникающих при получении кинетических параметров на основе кривых ТГ обсуждаются эффекты экспериментальных условий на форму кривых ТГ. Данные ТГ представлены для реакции термической дегидратации моногидрата оксалата кальция, полученного на образцах весом $\sim$ 1 мг в воздухе и вакууме. Сравниваются результаты, полученные на различных микровесах и приводятся вполне допустимые рассуждения для минимализации влияния экспериментальных условий.

Зависимость анионообменных равновесий от концентрации смоляной фазы

А. МАРТОН, П. ХАЛМОШ и Й. ИНЦЕДИ

Техника равновесной колонны была использована для определения зависимости констант ионообменных развновесий моно- и бивалентных ионов органических кислот от состава смоляной фазы. Были определены изотермы ионного обмена для моно- и бивалентных анионов малеиновой и фумаровой кислот при различных суммарных нормальностях растворов. Коэффициент селективности с поправкой значительно изменяется с изменением концентраций смоляной фазы во всех изученных случаях. При повышенных загрузках смолы во всех случаях наблюдалось обращение селективности, что указывает на значительные различия в состояниях гидратации смолы в вдух различных ионных формах. Был использован хлорид Dovex 1X4 (100—200 меш), образующий анионообменную смолу. Все измерения проводились на системах при 25°С в водных средах.

Молярная поляризация нитробензола в полярных растворителях

Й. ЛИСИ

Были исследованы бинарные смеси нитробензола с полярными жидкостями. Было найдено, что в исследованных системах молярная поляризация нитробензола определяется, с изменением пространственной поляризации, молярной поляризацией чистого нитробензола, а также согласно уравнению

$$P_n^* = -P_{ir}\left(\frac{\varepsilon - 1}{\varepsilon + 2} - 1\right).$$

Предел увеличения P_u определяется уравнением Сугдена, справедливым для аполярных растворителей. Нижний предел уменьшения P_u означает поляризацию смещения. Была найдена зависимость между относительной пермитивностью полярной жидкости и взаимной растворимостью с нитробензолом.

Исследование строения цепочки поливиниленкарбоната, образующегося в твердой фазе

Ф. ЧЕР

Сравнивались ИК спектры поливиниленкарбонатов, полученных в твердой и жидкой фазах и инициированных γ-облучением. Были расчитаны конформационные энергии полимерной цепочки, построенной из эритро- и трео-сегментов, соединенных изо- и синдиотактической связью. В расчетах использовали атомные координаты, полученные минимализацией внутренней энергии напряжения трео- и эритро-диметилэтиленкарбоната. Результаты, полученные для геликса, сравнивали с рентгенодиффракционными данными. Было установлено, что в твердофазной полимеризации первоначально образуются эритросиндикатические геликсы 3_1, которые при высаждении превращаются в геликсы 4_1. Полимер, образующийся в жидкой фазе, представляет собой трео-эритро-атактическую цепочку.

ИК исследования эффекта растворителя; комплексообразование карбонильной группы с фенолом

В. ШАНМУГАСУНДАРАМ и С. Р. М. МЕЙЯПАН

Влияние гидроксильной группы фенола на колебания карбонила было исследовано с точки зрения анализа способности к образованию водородной связи между некоторыми эфирами и фенолом. Скорость изменения момента связи с длиной связи $d\mu/dr$ для свободных и Н-связанных C=O была определена на основе измерения интенсивности ИК полос системы. Подтверждается существование комплексов с составом 1 : 1 и 1 : 2 и, исходя из наблюдаемых смещений частот, обсуждается структура образующихся комплексов.

Метиловые эфиры углеводов, VIII

Разделение изомеров метиловых эфиров глюкозы тонкослойной хроматографией и определение их с помощью антрона

А. ЛИПТАК и Л. БЕРКИ

Было осуществлено разделение ди-, три- и тетра-О-метил-О-глюкопираноз с помощью ТСХ. Системы растворителей III—IV пригодны для разделения диметильных, триметильных и тетраметильных эфиров. Для разделения некоторых структурных изомеров в случае триметильных эфиров следует использовать систему IV, а в случае диметильных эфиров комбинацию систем III—VII. Разделенные метиловые эфиры были определены с помощью антрона (в области содержания 10—70 мг).

Исследование реакции реагентов Гриньяра с 4-хиназолонами и 3,1,4-бензоксазонами

Т. ЗИМАИТИ, М. АНВАР, Ф. И. АБДЕЛЬ-ХАЙ и М. Ф. АБДЕЛЬ-МЕГИД

2,3-Диарил-4-хиназолоны (Id—g) взаимодействуют с реагентами Гриньяра, давая 2,3-диарил-4-(метил или фенил)-4-гидроксихиназолины (V). 2-Арил-4-хиназолоны (Ic—j) дают соотвествующие замещенные карбинолы (VI). Подобным образом 2-арил-3,1,4-бензоксазоны (VII) приводят к образованию соотвествующих замещенных карбинолов (VIII), которые циклизуются в 4,4-дизамещенные 2-арилбензоксазины (IX).

Кислотно-кализированная перегруппировка N-нитропроизводных 2-аминотиазоля, I

Кинетика и изотопный эффект растворителя и субстрата в кислотно-катализированной перегруппировке 2-тиазолилнитраминов

А. НЕМЕШ и Г. ТОТ

Кинетика кислотно-катализированной перегруппировки трех 2-(N—R)-нитроаминотиазолей (R = H, CH_3, C_2H_5 была измерена в интервале кислотности 88—96%-ой серной кислоты. Было найдено, что перегруппировка подвергается общему кислотному катализу через 1. влияние изотопного состава растворителя на скорость реакции того же субстрата и 2. корреляцию кислотной функции со скоростью реакции. Это было найдено проверкой реактивности 5-дейтерированного 2-(N-метил)-нитроаминотиазоля, где был обнаружен первичный изотопный эффект. Были получены явные спектроскопические доказательства образования реактивного промежуточного продукта. Кинетические результаты интерпретируются на основе пяти-ступенчатого механизма, в котором медленными ступенями были второе протонирование нитроамина и потеря протона σ-комплексом.

Синтез N-ацилолигопептидов с потенциальной антитуберкулезной активностью

Ю. ШТВЕРТЕЦКИ, И. ХОЛЛОШИ и Ш. БАЮС

N-Ацилолигопептиды с потенциальной антитуберкулезной активностью были приготовлены из простых основных материалов. В первом случае пептиды, ацилированные жирной кислотой, были построены из валина, фенилаланина и лизина, а во втором случае из леуцина, фенилеланина и лизина. Для выявления зависимости структура — активность, был исследован эффект числа, характера и последовательности аминокислот, а также последовательности индивидуальных жирных кислот. Соединение наивысшей активности N^{α}-пальмитоил-L-лизил-D-фенилаланил-L-леуцил-L-лизинамид обладает активностью 3μг/мл против Mycobacterium tuberculocis $H_{37}R_v$ in vitro.

Стереохимические исследования, XXIV
Производные третбутилциклопентана, III

Исследование цис- и транс-4-трет-бутилциклопентан-1,2-оксида с помощью ИК и ЯМР спектроскопии

П. ШОХАР и Г. БЕРНАТ

Стерическая структура *цис-* и *транс*-4-*трет*-бутилциклопентан-1,2-оксида (**1**, **2**), предложенная ранее, была подтверждена на основе ИК и ЯМР исследований. Как ИК так и ЯМР спектры пригодны для идентификации изомеров. Функциональные группы могут быть идентифицированы на основе ИК спектров, а стерическая структура на основе относительных сдвигов сигналов ЯМР. *Цис-* и *транс*-положения функциональных групп подтверждались, применяя трис- (дипивало-метанато)-европий, как реагент сдвига.

Стереохимия каротиноидного виолеоксантина

Г. П. МОСС, Й. САБОЛЬЧ, Й. ТОТ и Б. Ц. ВИДОН

Были сняты H^1— ЯМР, C^{13}— ЯМР, ОРД и ЦД спектры виолеоксантина. На основе спектров было установлено, что виолеоксантин является 9-*цис*-изомером виолаксантина с той же самой абсолютной конфигурацией всех хиральных центров. Полная интерпретация C^{13}— ЯМР спектров виолеоксантина была произведена на основе сравнения со спектрами подобных каротиноидов и ацетата витамина А.

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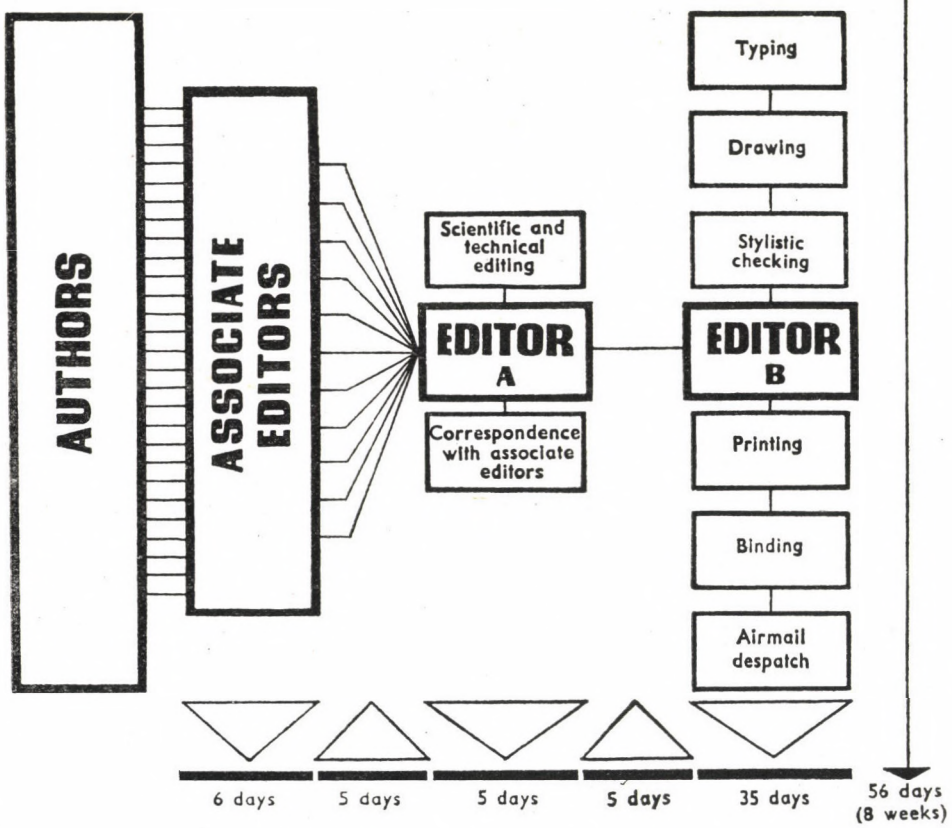

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LIGAND SUBSTITUTION AND COMPLEX STRUCTURE, XI

NICKEL(II) COMPLEXES OF SCHIFF-BASES FORMED FROM AMINOPYRIDINES AND SALICYL ALDEHYDE

J. CSÁSZÁR and J. BALOG

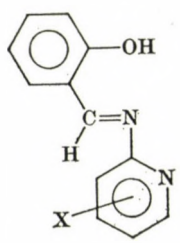
(Department of General and Physical Chemistry, József A. University, Szeged)

Received November 23, 1974

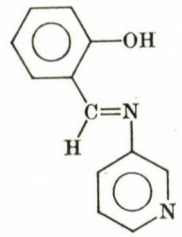
Schiff-bases (SB) formed from $C_6H_4(OH)CHO$ and 2-NH_2-C_5H_4N, 3-$NH_2C_5H_4N$, 2-NH_2-3-CH_3-C_5H_3N, 2-NH_2-4-CH_3-C_5H_3N, 2-NH_2-5-CH_3-C_5H_3N, and 2-NH_2-6-CH_3-C_5H_3N, and their nickel(II) complexes have been studied. With the 6-CH_3-derivative a $[Ni(SB)_2]$ complex, with the others $[Ni(SB)_2 \cdot 2H_2O]$ type complexes are formed. The molecules are strongly distorted. The 6-CH_3 derivative acts as a tridentate, the other Schiff-bases act as bidentate ligands in the formation of the complexes.

In former papers [1, 2, 3] we discussed the properties of Ni[HSAI-N-Y-Aryl]$_2$ type complexes. We have found that the substituents of the aromatic ring bound to the azomethine nitrogen greatly affect the magnetic, dielectric, spectral and other properties of these complexes.

As an extension of these studies, we have prepared the Schiff-bases (SB) (a and b) of salicylaldehyde (HSA), aminopyridines (n-NH_2-py) and substituted aminopyridines, and their nickel(II) complexes. These studies were aimed at obtaining information on



(a)



(b)

I X = H
V = 3-CH_3
VII = 4-CH_3
IX = 5-CH_3
XI = 6-CH_3

(1) bonding type of the potentially tridentate ligands, and
(2) the effect of methyl substituents in the pyridine ring.

Experimental

The Schiff-bases were prepared by mixing stoichiometric amounts of analytically pure salicylaldehyde with pyridine derivatives dissolved in ethanol. The crude products were recrystallized from ethanol. The complexes were prepared either by the reaction of the Schiff-bases with nickel acetate, or by that of the bis(salycilaldehyde)nickel(II) · $2H_2O$ with the amine, in acetone or in chloroform solution. The analytical data of the compounds are shown in Table I.

The solution and reflection spectra were recorded with a Beckman DU instrument, and the infrared spectra* with a Zeiss UR—10 spectrophotometer. Proton resonance spectra were recorded on a Varian A—60 instrument, with samples dissolved in carbon tetrachloride, using TMS as internal standard. Magnetic measurements were carried out at a field strength of about 7500 gauss, at room temperature. A $Ni(en)_3S_2O_3$ standard was used for the calibration of the instrument; data from the literature [4] were taken for calculating the diamagnetic correction.

Table I

Melting points (°C) and analysis data of the Schiff-bases and complexes studied

No.	Amines and chelates	M. p. °C	C%		H%		N%	
			Calcd.	Found	Calcd.	Found	Calcd.	Found
I	2-NH_2-py	64.1	72.71	72.76	5.08	5.11	14.13	14.11
II	$Ni(SB)_2 \cdot 2H_2O$						11.45	11.52
III	3-NH_2-py	57.0	72.71	72.73	5.08	5.15	14.13	14.15
IV	$Ni(SB)_2 \cdot 2H_2O$						11.45	11.57
V	2-NH_2-3-CH_3-py	80.3	73.57	73.60	5.70	5.72	13.20	13.21
VI	$Ni(SB)_2 \cdot 2H_2O$						10.83	10.91
VII	2-NH_2-4-CH_3-py	99.4	73.57	73.61	5.70	5.72	13.20	13.16
VIII	$Ni(SB)_2 \cdot 2H_2O$						10.83	11.01
IX	2-NH_2-5-CH_3-py	100.5	73.57	73.61	5.70	5.76	13.20	13.21
X	$Ni(SB)_2 \cdot 2H_2O$						10.83	10.96
XI	2-NH_2-6-CH_3-py	65.8	73.57	73.58	5.70	5.75	13.20	13.24
XII	$Ni(SB)_2$						11.64	11.57

Results

Study of the Schiff-base ligands

The ligands can be easily prepared from their components; their ultraviolet spectra were recorded in methanol and benzene; the maxima are listed in Table II. These data, together with Figs 1, 2 and 3 show that the absorp-

* For the spectra, our thanks are due to Dr. N. MAREK, Department of Medical Chemistry, Medical University, Szeged.

Table II

Spectral data of Schiff-bases in methanol and benzene

No.	Solvent	Band maxima (nm and lg ε)				
I	CH_3OH	~450 (2.10)	345 (4.02)	303 (4.07)	270 (4.03)	~222
	C_6H_6	—	352 (4.04)	307 (4.07)	270 (4.00)	—
III	CH_3OH	—	340 (3.88)	—	276 (4.06)	~220
	C_6H_6	—	343 (3.92)	—	281 (4.04)	—
V	CH_3OH	~445 (2.47)	346 (4.08)	315 (4.06)	271 (4.04)	~220
	C_6H_6	—	356 (4.22)	320 (4.18)	270 (4.12)	—
VII	CH_3OH	~440 (2.20)	345 (4.01)	302 (4.06)	272 (4.04)	~224
	C_6H_6	—	353 (4.06)	305 (4.10)	272 (3.95)	—
IX	CH_3OH	~450 (2.20)	347 (4.06)	310 (4.08)	269 (4.04)	~226
	C_6H_6	—	355 (4.13)	315 (4.09)	273 (4.07)	—
XI	CH_3OH	~444 (2.30)	343 (4.09)	310 (4.10)	269 (4.07)	~222
	C_6H_6	—	353 (4.10)	312 (4.06)	275 (3.94)	—

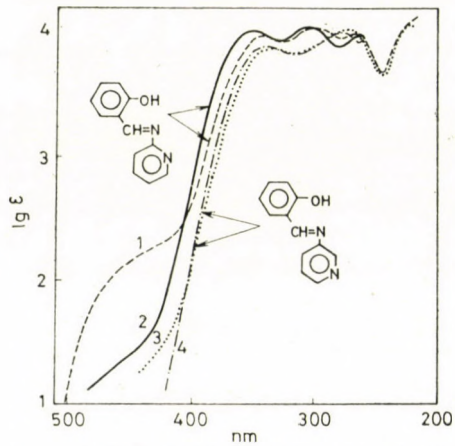


Fig. 1. Absorption spectra of HSA-2-NH_2-C_5H_4N and HSA-3-NH_2-C_5H_4N in methanol (Curves 1 and 3) and in benzene (Curves 2 and 4)

tion spectra are similar to those other Schiff-bases of salicylaldehyde and aromatic amines [5, 6]. The characteristic advance band in methanol, ascribed formerly [4, 6] to a benzenoid–quinonoid equlibrium, emerges between 430 and 450 nm.

A different behaviour can be observed for the 3-NH_2-py derivative: the advance band has a very low intensity (Fig. 1). The nitrogen in *meta* position decreases the charge density at the azomethine nitrogen nearly to

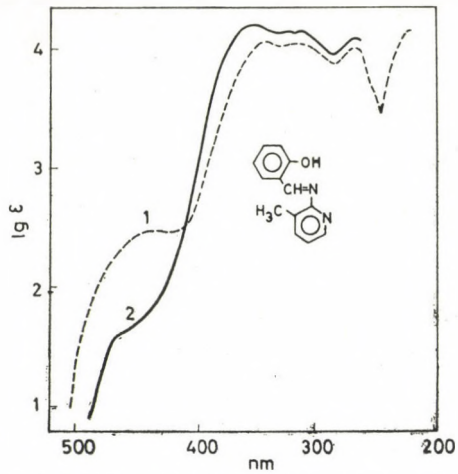


Fig. 2. Spectrum of HSA-2-NH_2-3-CH_3-C_5H_3N in methanol (1) and in benzene (2)

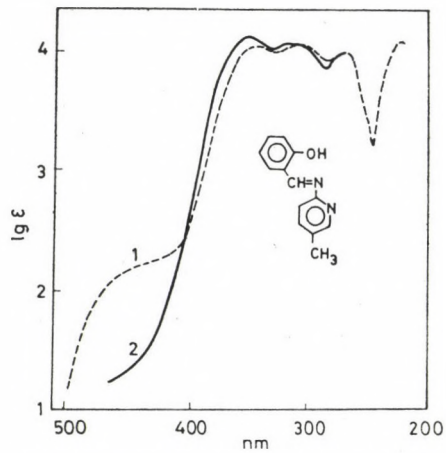


Fig. 3. Spectrum of HSA-2-NH_2-5-CH_3-C_5H_3N in methanol (1) and in benzene (2)

the same extent as a nitro group, therefore, the probability of the above equilibrium is very small.

The equilibrium constants at 25°C in methanol-benzene are for compounds **I**, **III**, **V**, **VII**, **IX**, and **XI** 4.6, 0.5, 2.0, 5.7, 8.6 and 4.6, respectively. Apparently, the nitrogen in *meta* position has a very strong effect. On the other hand, as a result of the opposite effects of the *ortho*-nitrogen and the methyl group, the equilibrium constant increases in the order $2 < 6 < 4 < 5$ of the methyl position. This sequence is understandable if we consider that the 2-CH_3 group, owing to its steric effect, forces the pyridine ring out of the plane and thus hinders the quinonoid structure to extend over the entire

molecule. With the *ortho-* and *para*-directing effect of the CH_3 group in mind, the $6 < 4 < 5$ sequence is acceptable as a resultant effect of the pyridine nitrogen and the CH_3 group.

In Table III the principal characteristics of the proton resonance spectra of the Schiff-bases studied are shown; a typical spectrum is recorded in Fig. 4.

The OH proton signals are between 12.46 and 13.69 ppm; this assignment has been verified by deuterium exchange. The lowest value is found for **III**; according to what we have mentioned earlier, here a benzenoid/quinonoid equilibrium is not be expected. We find that the ppm values and the intensities of the advance band in alcoholic solutions change in parallel.

Table III

PMR characteristics of Schiff-bases (ppm)

No.	OH	CH=N	CH_3
I	13.11	9.47	—
III	12.46	8.60	—
V	13.69	9.46	2.49
VII	13.23	9.50	2.38
IX	13.19	9.43	2.33
XI	13.26	9.47	2.55

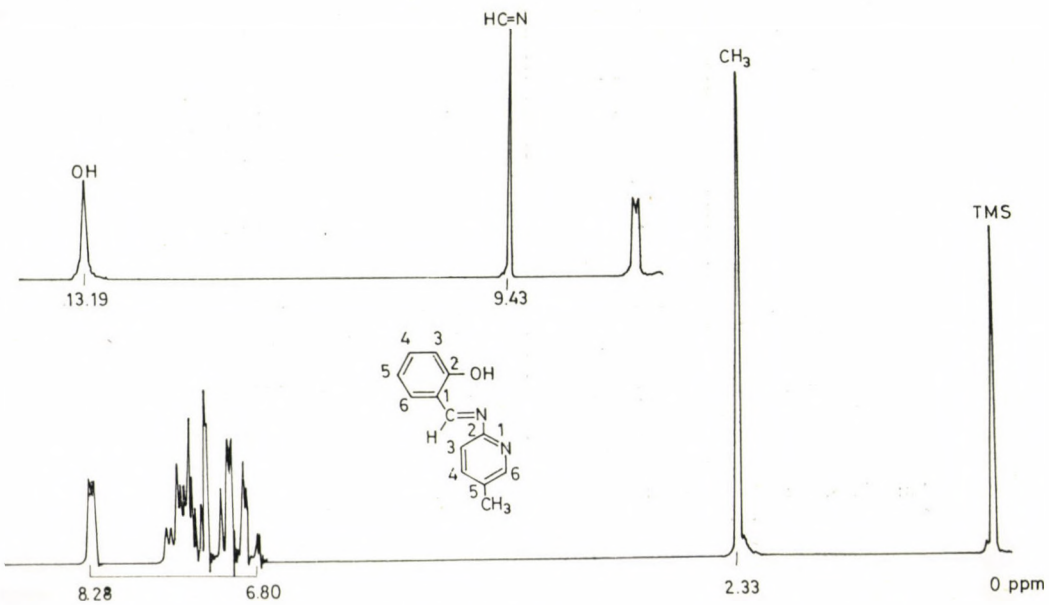


Fig. 4. PMR spectrum of HSA-2-NH_2-5-CH_3-C_5H_3N in carbon tetrachloride

Table IV

Some characteristic frequencies of ligands and their complexes[a]

No.	γ = CH	ν C—O	ν C=N
I	742—767 s	1287 s	1618 s
			1559 s
II	750 s	1334 s	1571 s
			1542 s
	767 s	1289 s	1626 s
III	820 s		
	859 v		
IV	761 s	1331 s	1618 s
	820 m		
V	755* s	1287 s	1620 s
	802 m		
VI	760 s	1316 s	1614 s
	782 m		1568 s
	769 s	1272 s	1603 s
VII	840 s		1552 s
	872 s		
	754 s	1282 s	1570 s
VIII	812 m		1526 s
	836 m		
	778 s	1285 s	1619 s
IX	850 s		1577 s
	874 m		
X	763 m	1323 m	1614 s
			1566 s
XI	768 s	1289 s	1619 s
	806 s		1560 s
XII	759 s	1330 s	1610 s
	788 m		1558 s

[a] s: high-, m: medium-, v: low-intensity band
* broad, complex band

The sharp singlet of the azomethine proton appears between 8.60 and 9.50 ppm. The methyl proton in compounds **V**—**XI** gives signals in the range between 2.33 and 2.55 ppm. The high value of the azomethine proton signal is remarkable; in compounds of a similar structure (type = N-Y-C_6H_4). the corresponding values are 8.4—8.6 ppm. The region between 6.5 and 8.5 ppm is extremely complicated, where the signals of the aldehyde and pyridine ring protons appear with significant couplings.

In the infrared spectra of the ligands the frequencies of salicylaldehyde and the hetero-aromatic parts of the molecule are readily identified. In Table IV are shown the data of the main νC=N, νC—O and γ=CH vibrations.

Study of the complexes

The complex is easily prepared by the reaction of the Schiff-base with the nickel salt, or by the reaction of the bis(salicylaldehyde)nickel(II) · $2H_2O$ and the corresponding amine. In contrast to earlier findings [7], well-defined final products can be obtained also in the cases of 2-NH_2-py and 3-NH_2-py. The analyses of the complexes are listed in Table I. With the exception of the 2-NH_2-6-CH_3-py derivative, all the complexes contain two molecules of

Table V

Magnetic moments and spectral data of the complexes

	II	IV	VI	VIII	X	XII
	3.40	3.07	3.16	3.18	3.30	3.28
	9.30	10.20	9.10	9.30	10.10	~ 8.00
Reflection spectrum	13.20	17.40	~13.20	~13.00	~13.20	12.5
	15.20		16.30	16.90	~15.50	14.70
			~17.70		~16.90	
ν_2/ν_1	1.63	1.71	1.79	1.82	1.67	1.84
Spectrum in chloroform	9.50	[a]	9.00	9.40	[a]	8.70
	15.50		15.50	15.90		~15.80
ν_2/ν_1	1.63		1.72	1.69		1.82
Spectrum in pyridine	10.20	10.30	10.00	10.20	10.00	10.40
	16.90	17.10	16.50	16.90	16.50	~17.30
ν_2/ν_1	1.66	1.66	1.65	1.66	1.65	1.66
B (cm^{-1})	1071	1102	1011	1071	1011	1134

[a] insoluble

water of crystallization; the presence of water is apparent also from the infrared spectra. Further study is needed to explain why the colour of complexes **II** and **X** turns yellow at temperature around 300°C without decomposition.

The magnetic moments of the solids are listed in Table V. The complexes show paramagnetism correspondings to 3.0—3.4 BM, *i.e.* to two unpaired electrons. Owing to the slight solubility of the complexes, the magnetic moments of their solutions could not be measured. Reflexion and absorption spectra of all the complexes (*cf.* Table V, and Fig. 5) point to hexa-coordination. Beer's law is obeyed: thus association can be excluded. From the composition of these compounds a great decrease of symmetry can be deduced; this is suggested also by the inflexions and sub-maxima found in the spectra, by the very high values of parameter B calculated [8] from the wavenumbers of the first two bands and by the relatively high magnetic moment. The pattern of the spectra is significantly altered by the solvent used (Fig. 6).

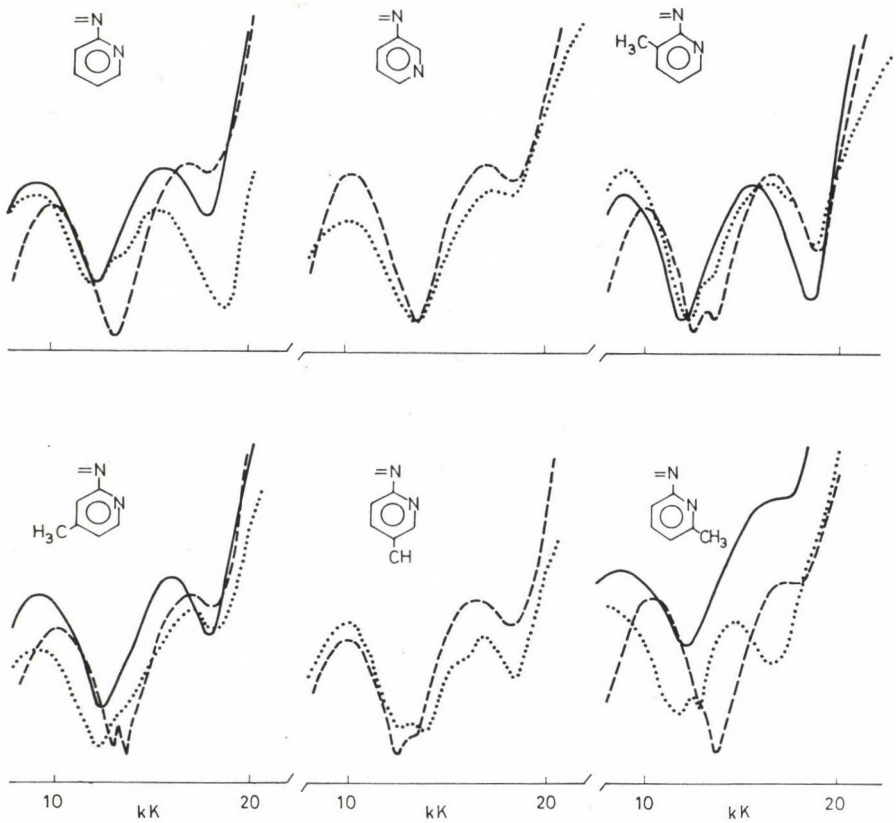


Fig. 5. Spectra of the complexes of the types $[Ni(SB)_2]$ and $[Ni(SB)_2 \cdot 2H_2O]$ Reflection spectrum (.....), in chloroform (———), and in pyridine (– – – –)

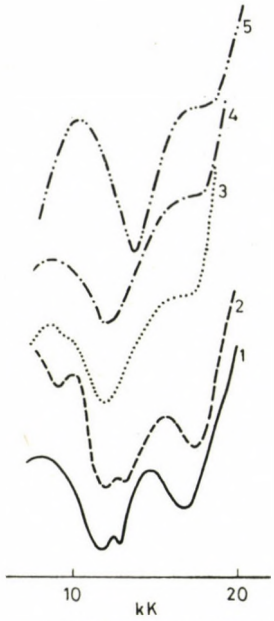


Fig. 6. Spectrum of the complex of HSA-2-NH_2-6-CH_3-C_5H_3N. 1: Reflection curve; 2: in methanol; 3: in methylene chloride; 4: in chloroform; 5: in pyridine

The compounds are soluble in pyridine; from these solutions bis-pyridine adducts can be recovered. The solutions in pyridine and the isolated adducts are paramagnetic (3.10—3.20 BM) and their spectra are more similar to those of octahedral structures.

Selected infrared frequencies are shown in Table IV. A comparison of the frequencies of Schiff-bases and their complexes demonstrates a tendency similar to that found in the case of other mononuclear complexes [9, 10, 11].

Conclusions

On the basis of the experimental results, the following can be established concerning the structure of these complexes.

(1) All the compounds, except **XII**, have the composition $Ni(SB)_2 \cdot 2H_2O$;

(2) The water of crystallization is very strongly bonded to the central ion thus forming a hexa-coordinate molecule;

(3) A very high degree of distortion of the molecules is suggested by the high magnetic moments of the compounds, by the pattern of their spectra and by the B parameters calculated;

(4) Ligands **I**, **III**, **V**, **VII** and **IX** participate in the formation of the complex as bidentate and as a tridentate ligand.

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LIGAND SUBSTITUTION AND COMPLEX STRUCTURE, XII

COMPLEXES OF SCHIFF-BASES OF THE TYPE $C_6H_4(OH)CH=B=CH(OH)C_6H_4$

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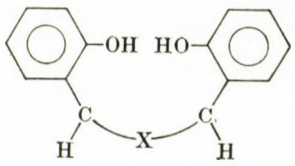
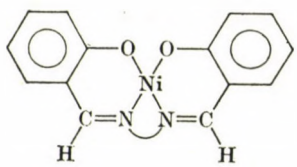
From ultraviolet, visible, infrared and PMR data and from the magnetic behaviour, conclusions have been drawn on the structure of the Schiff-bases formed from salicylaldehyde and hydrazine, ethylenediamine, 1,3-propylenediamine and 1,4-butylenediamine, and of the nickel(II) complexes of these ligands.

It is well known that square planar nickel(II)-complexes are diamagnetic [1—5] and that some of them show partial paramagnetism when dissolved [6—10]. Compounds of the type $Ni–O_4$ are paramagnetic, whereas the types $Ni–S_4$ and $Ni–S_2N_2$ are diamagnetic [11]; compounds of the types $Ni–N_4$ and $Ni–N_2O_2$ may be dia- or paramagnetic, depending on the nature of the ligand and the solvent, and on the temperature.

Complexes of bidentate Schiff-base ligands are well known. We have studied the Schiff-bases (A) formed from salicylaldehyde (HSA) with hydrazine (HN) ethylenediamine (ED), 1,3-propylenediamine (PD) and 1,4-butylenediamine (BD) and the complexes (B) of these.



A



B

X= =N—N= (HSAIHN)

=N—$(CH_2)_2$—N= (HSAIED)

=N—$(CH_2)_3$—N= (HSAIPD)

=N—$(CH_2)_4$—N= (HSAIBD)

Experimental

The Schiff-bases were prepared by the reaction of salicylaldehyde with hydrazine or the diamines in ethanolic solutions at appropriate mole ratios. Table I shows the melting points and analyses of the compounds after two recrystallizations. The complexes were obtained from $Ni(HSA)_2 \cdot 2H_2O$ and the diamine, mixed in a 1 : 1.2 ratio in chloroform or in acetone [12, 13]. HSAIHN was prepared by the reaction of the Schiff-base with $NiAc_2$ in acetone. The crude product was filtered and washed with ethanol and ether.

Ultraviolet and visible reflection and transmission spectra were recorded with a Beckman DU spectrophotometer. The solvents were purified according to known procedures [14];

Table I

Analyses of Schiff-bases and their complexes

No.	Compound	M.p. (°C)	Analysis					
			% C		% H		% N	
			Calcd.	Found	Calcd.	Found	Calcd.	Found
I	$C_{14}H_{12}O_2N_2$	216.8	69.99	69.91	5.03	5.00	11.66	11.61
II	$NiK \cdot 4\,H_2O$		45.44	45.78	5.16	5.46	—	—
III	$C_{16}H_{16}O_2N_2$	125.6	71.62	71.60	6.01	6.06	10.44	10.42
IV	NiK		59.13	59.05	4.34	4.25	—	—
V	$C_{17}H_{18}O_2N_2$	51.6	72.32	72.24	6.43	6.40	9.92	9.87
VI	$NiK \cdot 2\,H_2O$		54.44	54.47	5.37	5.56	—	—
VII	$C_{18}H_{20}O_2N_2$	90.2	72.95	72.91	6.80	6.71	9.45	9.40
VIII	$NiK \cdot 2\,H_2O$		55.42	56.61	5.63	5.76	—	—

reflection curves were measured without dilution against an analytically pure MgO standard. Infrared spectra were recorded in KBr pellets with a Perkin—Elmer 200 instrument.

Proton resonance spectra were recorded on a JEOL 60 MHz instrument at 25°C ir $CDCl_3$ with TMS as internal standard.

Results

Study of the ligands

Ultraviolet spectra. Figures 1 and 2 show the spectra of HSAIHN and HSAIBD; the spectral data obtained in ethanol, hexane and/or benzene are listed in Table II.

The spectra of HSAIHN are the same in polar and nonpolar solvents. The structure, $C_6H_4(OH)CH{=}N{-}N{=}CH(OH)C_6H_4$, of the Schiff-base was verified by mass spectrometry.* In the case of compounds **III**, **V** and **VII**,

* For the mass-spectroscopic measurements our thanks are due to Dr. István SZILÁGYI.

an advance band appears between 400 and 440 nm; in a previous paper, this has been attributed to a benzenoid/quinonoid equlibrium [16]. The equilibrium constants measured in a methanol–benzene mixture [17] for the three

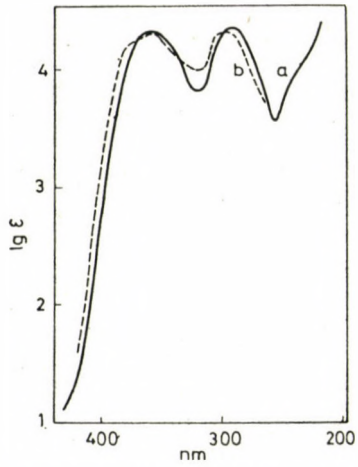


Fig. 1. Spectrum of HSAIHN in ethanol (a) and benzene (b)

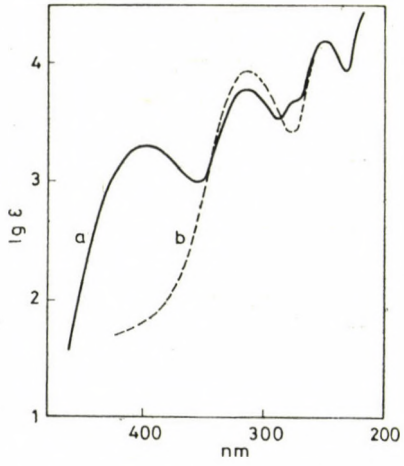


Fig. 2. Spectrum of HSAIBD in ethanol (a) and benzene (b)

compounds mentioned are $K = 1.22$, 1.35, and 1.38, respectively. The bands below 360 nm can be assigned to the azomethine group and to the aromatic system [18, 19].



C

Infrared spectra. Figures 3, 4 and 5 show the infrared spectra of ligands **I, V** and **VII**; the νC=N and νC–O frequencies are listed in Table II. Besides these frequencies (cf. [20]) the sharp γ = CH band emerges between 750 and 755 nm; the frequencies characteristic of the aromatic are above 1200 cm^{-1},

Table II

Ultraviolet, infrared and PMR spectra of the ligands

No.	Ultraviolet spectral data					K	Infrared frequencies		PMR data (δ ppm)			
	Solvent	nm and lg ε					ν C=N	ν C–O	OH	CH=N	α CH_2	β CH_2
I	C_2H_5OH	—	358	293	—	—	1628	1278	11.58	8.94	—	—
			4.33	4.38								
	C_6H_6	—	360	300	—							
			4.30	4.33								
III	C_2H_5OH	408	319	286	257	1.22	1638	1288	13.23	8.45	3.97	—
		3.22	3.88		4.33							
	C_6H_{12}	—	323	—	259							
			3.98	4.37								
V	C_2H_5OH	404	318	286	257	1.35	1639	1285	13.45	8.48	3.64	1.91
		3.35	3.88		4.37						3.76	2.02
	C_6H_{12}	—	322	—	259						3.87	2.13
			3.99		4.41							2.25
												2.36
VII	C_2H_5OH	400	317	284	255	1.38	1633	1285	13.58	8.43	3.58	1.71
		3.30	3.80		4.22						.	.
		—	317	—	—						.	
			3.96								3.68	1.81
											.	.
											.	.
											3.77	1.97

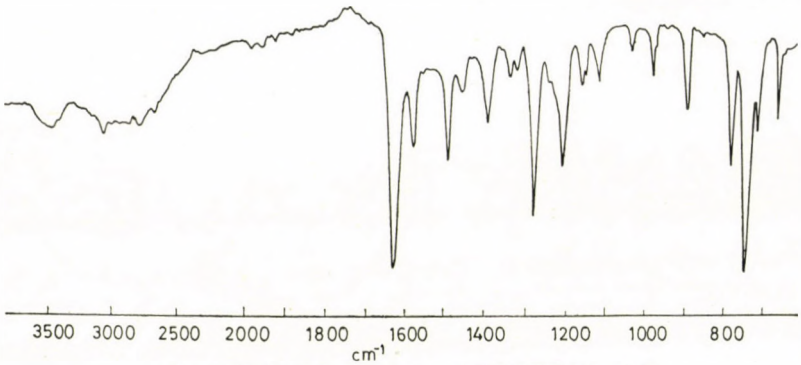


Fig. 3. Infrared spectrum of HSAIHN in KBr

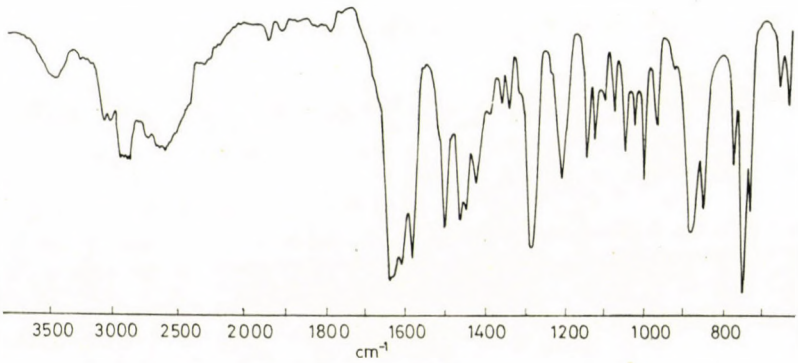


Fig. 4. Infrared spectrum of HSAIPD in KBr

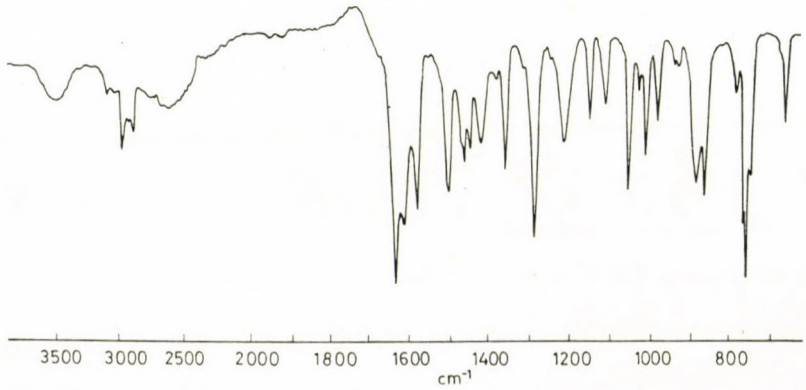


Fig. 5. Infrared spectrum of HSAIBD in KBr

the aliphatic $\nu_{as}\,CH_2$ and $\nu_s\,CH_2$ bands, the aromatic CH vibrations appear between 2500—3000 cm^{-1}.

PMR spectra. The signals can be accurately identified in the PMR spectra recorded for the four ligands in $CDCl_3$. Table II shows the chemical shifts of the protons in OH, CH=N, α-CH_2 and β-CH_2.

In I the signal of the OH-proton is extremely sharp; this — considered together with the ultraviolet spectrum — suggests that no hydrogen bond

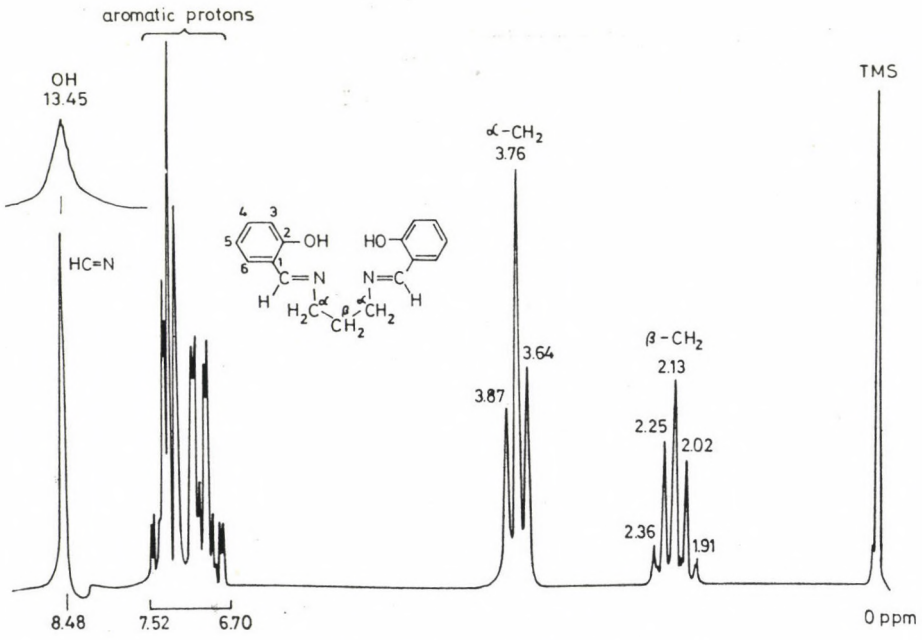


Fig. 6. PMR spectrum of HSAIPD in $CDCl_3$

is formed, or that there is but a very slight probability of its formation. The OH-proton signal for ligands **III**, **V** and **VII** appears at substantially higher ppm values as a broad band.

The signal of the CH=N proton [20—23] is a sharp singlet. The α-CH_2 signal in **III** is a single sharp peak, but in **V** this is split into three equidistant signals (Fig. 6); while in **VII** several coalescent signals indicate the coupling of vicinal protons. The same can be said about the β-CH_2 signals of **VII**, while the β-CH_2 group of **V** indicates the number of components exactly as expected. The distance between the individual peaks is 0.11 ppm.

In the 6.8—7.5 ppm range we find the signals of the aromatic protons in two groups of bands; the group at lower ppm corresponds to the 3-H and 5-H, that at higher ppm to the 4-H and 6-H protons.

Study of the complexes

Magnetic properties

The magnetic moments of the solid compounds are shown in Table III.

The Ni(HSAIED) complex is diamagnetic [24, 25], its ground state is a singlet (S=O) and this indicates, without doubt, that the chelate molecule,

Table III

Magnetic moments, visible and infrared spectra of the complexes

No.	B.M.	Spectral data (kK)			Infrared frequencies	
		reflection spectrum	in pyridine	reflection spectrum of pyridine adduct	ν C=N	ν C–O
II	3.25	9.30; 15.30; 18.10; 22.40; ~26.00	9.30; 16.50; ~19.30; ~27.50; 31.90		1600	1357
IV	Dia	18.7	~18.50; 24.00; 29.50	12.20; 18.30	1626	1348
VI	3.28	10.30; 16.90; ~26.00	11.00; 18.00; 16.40; 30.50	11.00; 17.90; ~25.00	1632	1348
VIII	3.30	9.90; 16.30; ~25.00	10.50; 17.30; 26.30; 31.30	10.20; 16.90; ~24.50	1628	1350

more exactly: the NiO_2N_2 group, is square planar. It remains diamagnetic in inert solvents, no adduct is formed even in pyridine [25]. Here, obviously, it is not steric hindrance that prevents the bonding of pyridine molecules. The strong square planar ligand field increases the difference in energy between the $d_{x^2-y^2}$ and the next orbital to such an extent that the $d_{x^2-y^2}$ orbital becomes unit for bond formation.

The other three compounds are paramagnetic. The values measured correspond to two unpaired electrons and indicate a strongly distorted, hexacoordinate nickel(II) ion. According to some authors, complex **VI** is diamagnetic [26], according to others it is paramagnetic [27]. Our findings support the conclusion drawn by BERKELEW. In pyridine, and in other non-coordinating solvents the magnetic moment is practically the same. This suggests that there is only a single species in solution thus no equilibrium system similar to that with Ni(HSAI-R)$_2$ type complexes is formed.

It is remarkable that the magnetic properties of complexes **IV**, and **VI** and **VIII** are different. Considering the structure of the ligands, this may be ascribed to electronic rather than to steric effects.

Visible spectra. Table III contains spectral data for the chelates and their pyridine adducts; the spectra of complexes **II**, **VI** and **VIII** are shown in Figs 7, 8 and 9.

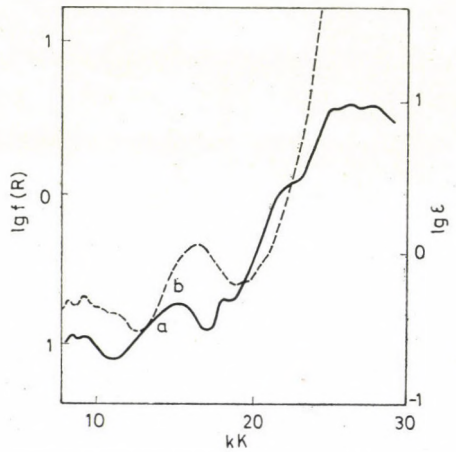


Fig. 7. Spectrum of Ni(HSAIHN); (a); reflection curve (b) in pyridine

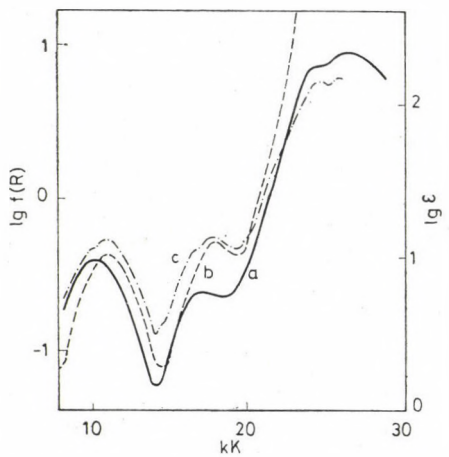


Fig. 8. Spectrum of Ni(HSAIPD); (a): reflection curve, (b): in pyridine, (c): reflection curve of the product crystallized from pyridine

The structure of the complex of HSAIHN poses some problems. Spectra indicate a very strongly distorted, hexacoordinate Ni(II) ion. Earlier, SACCONI [28] studied complexes of the Schiff-bases of salicylaldehyde and R–CO–

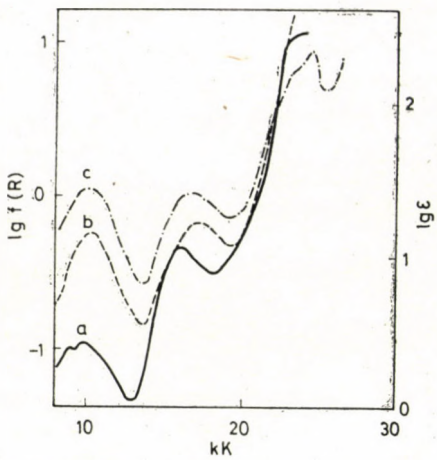
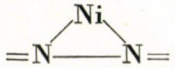
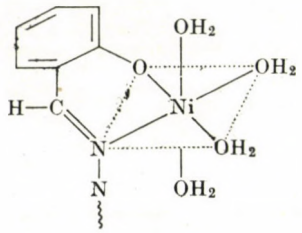


Fig. 9. Spectrum of Ni(HSAIBD); (a): reflection curve, (b): in pyridine, (c): reflection curve of the product crystallized from pyridine

$NHNH_2$ type hydrazides. Depending on R, either tetrahedral or square planar complexes are formed. If HSAIHN were a quadridentate ligand, a three-membered  ring would form; however, this is unlikely for steric reasons. Presumably, only one half of the quadridentate ligand molecule participates in the formation of the chelate, the remaining coordination sites being occupied by water molecules (D). This view is supported also by infrared spectra.



D

The ligand in Ni(HSAIED) is quadridentate; the chelate molecule has a cis square planar geometry [29]. The reflection and absorption spectra of samples in an inert solvent are practically the same [25, 30]. In the visible spectrum only one band emerges: this is characteristic of square planar diamagnetic chelates. This band can be assigned to the $^1A_1(F) \rightarrow {}^1B_1(G)$ transition [30].

There is no doubt that the spectra of the Ni(HSAIPD) · $2H_2O$ and Ni(HSAIBD) · $2H_2O$ complexes indicate hexa-coordination. The different behaviour of these ligands from that of HSAIED, and the differences in the chelates formed, can be ascribed mainly to electronic effects.

In pyridine the bands are shifted to higher frequencies. These spectra are exactly the same as those of the products crystallized from pyridine. In pyridine the characteristic bands shift to lower energies with increasing length of the alkyl bridge; a similar phenomenon has been observed by HOLM [13] in chloroform solution. This means that an increase in the number of methylene groups decreases the field strength of the ligand.

The four chelates behave differently also in pyridine. In the solution of **II** a very complicated system is produced: molecular species of the type $[Ni(HSAIHN)(H_2O)_npy_{4-n}]$ are formed. If **II** dissolved in hot pyridine and is then allowed to crystallize, no single product is obtained, and the complex seems to decompose.

According to the literature [31, 32], Ni(HSAIED) does not form an adduct with pyridine though the spectrum of the product isolated from pyridine shows a low intensity band at 12—13 kk. Chelates **VI** and **VIII** give bis-pyridine adducts as evidenced by the spectra. The RACAH B parameters calculated from the reflection spectra of chelates **IV**, **VI**, **VIII** crystallized from pyridine are 678, 992 and 1071 cm^{-1} thus the ionic character becomes stronger in the ethyl, propyl, butyl sequence.

Infrared spectra. Table III presents the νC=N and the νC–O frequencies.

Views on the behaviour of the νC=N frequency differ. Some authors maintain [33] that its position remains practically unchanged when upon complex formation, others find it shifted to higher [34] or lower [35] wavenumbers. In our earlier studies [36] we have found in agreement with THORNTON and PERCY [37], that the νC=N band shifts to lower wavenumbers relative to the free ligand. A comparison of the data in Tables II and III shows that this shift for complexes **II**, **VI** and **VIII** is 28, 10, 7 and 5 cm^{-1}, respectively.

The νC–O band of the ligands in the chelates is shifted higher wavenumbers. This shift is quite considerable, being the greatest in the HSAIHN complex. These findings are in good agreement with literature data on the Al(III) [39], Ni(II) [39] and Mn(III) [40] complexes of HSAIED-type ligands.

The infrared spectra of all complexes show five low intensity bands at 420—460, 450—520, 500—530, 540—570 and 580—600 cm^{-1}. Generally, this range corresponds to the Me-ligand vibrations. In metal complexes of HSAIED, UENO *et al.* [41] has found the Me–O and Me–N stretching bands between 430 and 610 cm^{-1}. Most probably, the two bands at higher frequencies can be assigned to the Ni–O, whereas those at the lower frequencies to the Ni–N vibrations, which combine with the vibrations of the aromatic rings.

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MÖSSBAUER, INFRARED AND NMR SPECTROSCOPIC STUDIES ON THE SOLUTIONS OF SOME ALKALI AND PHOSPHONIUM CYANOFERRATES

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Some alkali and phosphonium cyanoferrates have been investigated by Mössbauer, infrared, and ^{1}H-NMR spectroscopic methods.

The Mössbauer parameters of the frozen aqueous solutions of alkali cyanoferrates indicate that, upon freezing, Na^+ ions do not, but K^+ ions do associate with cyanoferrate anions. This segregation process can be suppressed by adding glycerol or a quaternary phosphonium salt to the solution. In the former case the viscosity of the solution increases, and in the latter presumably the stronger interaction of cyanoferrate anion and phosphonium cation plays role.

The ν_{CN} and ν_{NO} frequencies of $[Fe(CN)_5NO]^{2-}$ decrease with the increasing donicity of the solvent. The NO stretching frequency is much more decreased, indicating that upon solvation a strong interaction occurs between the donor solvent molecule and the π^* acceptor orbital of the NO ligand. The Mössbauer parameters are, in similar solutions, independent of the donicity of the solvent. The line positions in the NMR spectrum of tris-(tributylbenzylphosphonium)-hexacyanoferrate(III) depend on the concentration and on the donicity of the solvent.

It is known that the replacement of the alkali cations of cyanoferrates by bulky organic cations, such as quaternary phosphonium cations, strongly affects the properties of cyanoferrates [1]. The infrared ν_{CN} frequencies and the Mössbauer parameters also show substantial changes [1, 2]. In order to reveal the properties of these compounds, we performed Mössbauer, infrared and NMR spectroscopic investigations, expecting to gain further information on the nature of the interactions between the cyanoferrate anion and the quaternary phosphonium cation by studying the solutions of complexes.

Mössbauer-spectroscopic studies on alkali cyanoferrate solutions

The Mössbauer spectra of frozen aqueous solutions of alkali cyanoferrates were studied by DOMINQUES and DANON [3]. It has been found that the quadrupole splitting of $\Delta E = 0.80$ mm/s of $Li_3Fe(CN)_6 \cdot 4H_2O$ decreases

to a value of 0.25 mm/s at room temperature as a result of hygroscopic water incorporation. The quadrupole splitting of solid $Na_3Fe(CN)_6 \cdot 6H_2O$ measured at the temperature of liquid nitrogen was 0.958 mm/s, but it was almost zero in aqueous solutions. The quadrupole splitting of $K_3Fe(CN)_6$ was found to be 0.445 mm/s in both crystalline form and frozen solution (at 77 K). The above authors suggest that the freezing of sodium cyanoferrate solutions produces crystal hydrate segregates in which the electric field gradient (EFG) induced by the Na^+ ions compensates the EFG due to the bonding electrons, whereas in frozen aqueous solutions of $K_3Fe(CN)_6$ segregates of $K_3Fe(CN)_6$ are formed.

The Mössbauer parameters obtained by the fast freezing technique employed in our experiments (see Table I) are different from the cited results. In frozen solutions also containing 10—50% of glycerol segregation can be neglected, and the structure of the fast-frozen solutions is presumably the

Table I

The Mössbauer parameters of frozen aqueous solutions of alkali cyanoferrates at the temperature of liquid nitrogen

Rapid freezing was performed dropwise. Radiation source ^{57}Co-Pt.
Error of measurements: ± 0.06 mm/s

Solute and its concentration	δ mm/s	ΔE, mm/s
0.44 *M* Na_3A*	−0.44	0.97
0.43 *M* Na_3A + 9.3 w% glycerol	−0.48	1.08
0.44 *M* Na_3A + 0.91 *M* Fo**	−0.44	1.10
0.5 *M* K_3A	−0.41	0.62
0.44 *M* K_3A + 10 w% glycerol	−0.40	0.96
0.5 *M* K_3A + 50 w% glycerol	−0.41	1.07
0.5 *M* K_3A + 0.25 *M* Fo	−0.46	0.62
0.5 *M* K_3A + 0.5 *M* Fo	−0.41	0.80
0.2 *M* K_3A + 0.4 *M* Fo	−0.50	1.04

* $A = [Fe(CN)_6]^{3-}$ ** $Fo = [(C_4H_9)_3PCH_2C_6H_5]Cl$

same as that of the liquid solution. The Mössbauer parameters obtained in such solutions for Na^+ and K^+ ions agree within the experimental error. Consequently, the nature of the cation has no appreciable effect on the results of the measurement, indicating that in aqueous solutions the inner solvation sphere of the overwhelming majority (90%) of the $[Fe(CN)_6]^{3-}$ anions contains only H_2O molecules. (This result is in agreement with the equilibrium constant, pK = 1.3, of the $[KFe(CN)_6]^{2-}$ ion [4].)

Assuming that in the frozen glycerol-containing solutions the quadrupole splitting of about 1 mm/s arises mostly from the bonding electrons, we obtain for the mean radius of the unpaired electron of the $3d_{xy}$ orbital $\langle r^{-3}\rangle^{-1/3} = 0.48$ Å, because the Jahn—Teller contribution of cyanide ligands to the quadrupole splitting can be neglected in comparison with the value of 1 mm/s. (The details of the calculation are given in Appendix I.) This value is in good agreement with the mean radii of Fe^{3+} $3d^5$ electrons, given by JØRGENSEN [5] as $\langle r\rangle = 0.49$ Å, and therefore the value of $\Delta E \approx 1$ mm/s can be attributed, with a high probability, to the effect of bonding electrons.

In solutions of no glycerol content the presence of Na^+ and phosphonium cations does not cause segregation which would decrease ΔE, but the quadrupole splitting values characteristic of frozen solutions containing K^+ ions indicate the formation of crystal hydrate segregates. Regarding that in glycerol-containing solutions the quadrupole splitting is due only to the bonding electrons, it can be assumed on the basis of the EFG contribution of the K^+ ions, estimated from the point charge model (see Appendix II), that in the segregate there are most probably two K^+ ions in the inner sphere of the $[Fe(CN)_6]^{3-}$ ion, since the effect of the potassium ions is the highest in this case. (Assuming that the EFG induced by the K^+ ions in the place of the iron nucleus is opposite in sense to that of the bonding electrons.)

An increase in the concentration of phosphonium chloride decreases the K^+ association. This effect may be attributed to the interaction of phosphonium and cyanoferrate, but it cannot be excluded either that the addition of phosphonium chloride to the solution promotes, similarly to glycerol, the glass formation under freezing, thereby suppressing segregation.

Mössbauer and infrared spectroscopic investigations of pentacyano nitrosylferrate solutions

On the nature of the interaction between the pentacyano nitrosylferrate anion and bulky organic cations (quaternary ammonium or phosphonium cations) only few data can be found in the literature. According to the infrared studies of GANS, SABATINI and SACCONI [6] on some derivatives with quaternary ammonium cations, the NO stretching frequency, measured in solid phase, is characteristically different from that of the alkali derivatives. Furthermore, according to our measurements, the ν_{NO} frequency of pentacyano nitrosylferrate also depends on the solvent.

In order to study more closely the role of solvent, we have determined the infrared ν_{CN} and ν_{NO} frequencies of sodium pentacyano nitrosylferrate,

Table II

The ν_{NO} and ν_{CN} frequemcies of $[Fe(CN)_5NO]^{2-}$ complexes with different cations, measured in solution

Solvent (DN)		$[(C_4H_9)_4P^+]$			Na^+		H^+	
		ν_{NO}	ν_{CN}		ν_{NO}	ν_{CN}	ν_{NO}	ν_{CN}
Solid complex		1888	2134	2145	1939	2142	1940	2145
						2159		2176
						2173		2202
Acetil chloride	0.7	1921 b	2147					
Nitromethane	2.7	1905	2140					
Acetonitrile	14.1	1895	2139					
Benzyl cyanide	15.1	1891	2136					
Acetone	17.0	1884	2137					
Tetrahydrofurane	20.0	1887	2137					
Dimethylformamide	26.6	1882	2136		1884	2133	1884	2133
Dimethylsulfoxide	29.8	1887	2137		1885	2132	1885	2132
Pyridine	33.1	1886	2135					

hydrogen pentacyano nitrosylferrate and bis(tetrabutyl-phosphonium) pentacyano nitrosylferrate (Table II, [8]), in solvents with various donicities [7].

The data of the table indicate that the CN and NO stretching frequencies decrease with the increasing donicity of the solvent (the variation of the latter frequency is more expressed), and in solvents with the highest donicities the frequencies are the same as in the solid phosphonium complex. This suggests the conclusion that the frequencies measured in the solutions are independent of the nature of the cation, and vary only with the donicity of the solvent.

The probable explanation for the solvent-dependence is that the NO group is solvated and the donor solvent molecule and the empty π^* acceptor orbital of the NO ligand interact [9]. The NO group is known to be a good π^* acceptor; this property is even more expressed in pentacyano nitrosylferrate, and thus the interaction becomes stronger as the donicity of the solvent increases. (The NO ligand reacts with the solvent molecule in the form of NO^+ groups.) The increasing occupancy of the π^* orbital involves a decrease in the N–O bond order, and, consequently, a shift in the NO stretching frequency towards lower wavenumbers. The smaller shift in the ν_{CN} frequencies is due to the much weaker π^* acceptor behaviour of the cyano ligands.

Unlike the infrared frequencies, the Mössbauer parameters measured in solvents with different donicities do not vary with the solvent (Table III), *i.e.* the isomeric shifts and quadrupole splittings are the same whithin the experimental error. The latter parameters agree, however, with the higher

Table III

The Mössbauer parameters of the frozen solutions of $[(C_4H_9)_4P]_2[Fe(CN)_5NO]$ in solvents with different donicities (concentration 0.5 M)

Radiation source ^{57}Co-Pt. Error of measurements: ± 0.05 mm/s.
During the measurement of the spectra the temperature of the absorbents: 80 K

Solvent	Donicity,* DN	δ mm/s	ΔE, mm/s
Acetyl chloride	0.7	−0.518	1.943
Nitrobenzene	4.4	−0.524	1.946
Acetonitrile	14.1	−0.562	1.991
Acetone	17.0	−0.601	1.972
Dimethylformamide	26.6	−0.541	1.961
Pyridine	33.1	−0.569	1.972

* Donicities are given in GUTTMANN's donor number [7]

quadrupole splitting measured in the phosphonium complexes, and not in the alkali compound. This clearly indicates that in sodium pentacyano nitrosylferrate the quadrupole splitting is lower owing to the strong polarization of the alkali cation. Under such conditions, however, the solvent effect, which strongly decreases the ν_{CN} and ν_{NO} frequencies as a function of the donicity, does not prevail on the central atom, *i.e.* it has no measurable effect on the extent of back-coordination between iron(III) and its ligands.

NMR investigations of phosphonium hexacyanoferrate(III) solutions

It is known that as a result of interactions between paramagnetic anions and bulky, diamagnetic organic cations the ^{1}H-NMR spectrum of the latter undergoes substantial changes [10]. This is also indicated *e.g.* by the NMR spectra of hexacyanoferrate(III) complexes with various quaternary ammonium cations [11].

We have recorded the ^{1}H-NMR spectra of $[(C_4H_9)_3PCH_2C_6H_5]_3 \cdot [Fe(CN)_6]$ in $CDCl_3$ and DMSO-d_6 solutions of various concentrations. The NMR data are given in Table IV. (The data given in Table IV are frequency differences in cps related to the corresponding signals of $[(C_4H_9)_3PCH_2C_6H_5]Cl$. In the measurements TMS standard was used.)

The data of the table indicate that in the phosphonium hexacyanoferrate(III) complex the NMR signals of the cation are strongly shifted upon the effect of the paramagnetic anion. The shifts are greater in more concentrated solutions, which can be attributed to a higher degree of association at these concentrations. The shift is the greatest for the protons of the benzyl

Table IV

The NMR signals of the protons of $(C_4H_9)_3P^+CH_2C_6H_5$ cation in the complex $[(C_4H_9)_3PCH_2C_6H_5]_3[Fe(CN)_6]$

Solvent	Concentration mol/1000 g of solvent	$-CH_3$	$-(CH_2)_2-$	$-CH_2-P$	$>CH_2-P$	$-C_6H_5$
$CDCl_3$	0.01	12	10	44	76	10
	0.1	22	18	78	88	18
	0.2	38	36	94	94	34
D_6-DMSO	0.05	4	4	12	16	6
	0.1	10	10	18	22	12
	0.2	20	20	28	32	20

group in α position with respect to the phosphorous atom, these protons of the cation being the most electron-deficient, *i.e.* the most acidic. It is striking that the shifts measured in DMSO-d_6 are smaller, which can be explained by the fact that in $CDCl_3$ solutions of identical concentrations the extent of association is higher owing to the very low donicity of the solvent, and therefore the anion–cation interaction is much stronger.

Experimental

In the Mössbauer measurements a ^{57}Co source (diffused into Pt) with an acitivity of 5 mCi was used. The fast freezing was accomplished by adding the solution dropwise to liquid nitrogen. The absorbent was prepared from the resulting 'beads'.

The NMR spectra were recorded on a VARIAN 60 MHz equipment, the infrared spectra were taken on a ZEISS UR—10 spectrophotometer.

Appendix

I. *The quadrupole splitting due to the bonding electrons* can be expressed as

$$\Delta E_{el} = \frac{1}{2} e^2 q_{el} (1 - R) Q \left(1 + \frac{\eta^2}{3}\right)^{1/2}$$

where e is the charge of an electron, eq_{el} is the z component of the electric field gradient (EFG), V_{zz} arising from the bonding electrons, R is the Sternheimer factor, Q is the quadrupole moment of nucleus ^{57}Fe, and η is the asymmetry factor of EFG.

In the low-spin iron(III) compound the $3d^5$ electrons are on the t_{2g} level, and the unpaired electron can be assigned to the d_{xy} orbital. (When the octahedral symmetry around the iron(III) ion is distorted, the t_{2g} orbital splits in a manner that the d_{xy} level is higher than d_{yz} and d_{xz}, and thus the

d_{xy} orbital remains unfilled [12]. The distortion of the octahedron in solid phase has been proved by x-ray diffraction measurements [13], and this distortion is not completely eliminated, presumably, in solution phase, either.)

By means of the point charge model [14] can be determined from the parameters of the d_{xy} orbital:

$$q_{el} = \langle 3\cos^2\Theta - 1\rangle \langle r^{-3}\rangle = +\frac{4}{7}\langle r^{-3}\rangle,$$

where Θ is the angle between the z axis and the position vector of the d_{xy} electron, and r is the radius belonging to the d_{xy} orbital. The x and y components of the EFG induced by the bonding electrons are only slightly different (the distortion manifests itself primarily along the z axis), hence $\left(1+\frac{\eta^2}{3}\right)^{1/2} \approx 1$.

Consequently,

$$\Delta E_{el} = \frac{1}{2} e^2 \frac{4}{7} \langle r^{-3}\rangle \langle 1 - R\rangle Q$$

The ΔE [mm/s] ≈ 1 mm/s quadrupole splitting measured in the glycerol solutions and expressed in terms of Doppler velocity can be converted into energy by the equation

$$E_{el} = E\frac{\Delta E[mm/s]}{c}$$

where E is the energy of the photon ($E = 14.4$ keV $= 2.3 \cdot 10^{-8}$ erg). Thus we obtain

$$\langle r^{-3}\rangle^{-1/3} = \left(\frac{e^2\, 4\,(1-R)\,Qc}{2.7\,E\,\Delta E}\right)^{1/3}$$

From the values $Q = 0.19$ barn and $(1 - R) = 0.68$, taken from the literature [15], $r = 0.48$ Å can be obtained.

II. To calculate the *EFG tensor due to the ligands* let us regard the CN^- and K^+ ions as point charges

If the coordinate system is chosen so that the EFG tensor is diagonal, the contribution of the ligands to the quadrupole splitting can be written as

$$\Delta E_{lig} = \frac{1}{2} e^2 (1 - \gamma_\infty) Q q_{lig} \sqrt{1 + \eta^{2/3}}$$

where $1 - \gamma_\infty = 10.0$, the STERNHEIMER factor [15]. If the EFG tensor is

not diagonal, it must be diagonalized, and its eigenvalue largest in absolute value will be V_{zz}. The two remaining eigenvalues are V_{xx} and V_{yy}.

Let us compress the negative charge of CN^- into the mid-point of the C–N bond. Then, from Coulomb's law, the EFG tensor components in point (0; 0; 0), where the ^{57}Fe nucleus is placed, of a charge Ze located in point $(x; y; z)$ can be given as

$$EFG_{ii} = -(3i^2 - r^2)r^{-5}Ze$$

$$EFG_{ij} = -3ij\, r^{-5}Ze \qquad (i \neq j)$$

where i and j represent coordinates x, y and z, and $r = \sqrt{x^2 + y^2 + z^2}$. Furthermore: $EFG_{ij} = -Zet_{ij}$.

On the basis of the x-ray diffraction data of $K_3[Fe(CN)_6]$ measured at 95 K [13], the atomic coordinates are expressed in a rectangular coordinate system attached to Fe(III) (Table V):

Table V

Atomic coordinates from X-ray diffraction measurements [13]

	x_1	y_1	z_1	xÅ	yÅ	zÅ
K1	0.4982	0.2303	0.3745	3.344	2.374	2.092
K2	0	0	0.5000	0	0	4.175
C1	0.1250	0.1737	0.0309	0.838	1.791	−0.002
C2	0.1861	−0.0523	0.2080	1.249	−0.539	1.350
C3	0.1874	−0.0508	−0.1148	1.259	−0.524	−1.445
N1	0.1998	0.2680	0.0502	1.342	2.764	0.003
N2	0.3080	−0.0771	0.3319	2.068	−0.795	2.131
N3	0.2866	−0.0935	−0.1858	1.925	−0.964	−2.247
F1				1.090	2.278	0.000
F2				1.659	−0.667	1.741
F3				1.592	−0.744	−1.846

$$r = x_1a + y_1b + z_1c = xi + yj + zk$$

where $a = 7.03$ Å $(i \sin 107.2° + k \cos 107.2°)$

$b = 10.31$ Å $\cdot\, j$

$c = 8.35$ Å $\cdot\, k$

F1, F2 and F3 are mid-points.

As the octahedron is centro-symmetric, charges of $-2e$ can be comprised in points F1, F2 and F3, to yield

$$EFG_{ij} = +2et_{ij}$$

Assume that one of the K^+ ions remains on the $[Fe(CN)_6]^{3-}$ ion. Let it be K2 (see Table V), since it is closer to Fe(III). Assume that the second K^+ is located opposite to the first.

The intermediate and final results of the calculation based on these assumptions are given in Tables VI and VII.

Table VI/a

Calculation of EFG without K^+ (assuming the solid structure)

	t_{xx}	t_{yy}	t_{zz}	t_{xy}	t_{yz}	t_{xz}
atom Z	10^{-2} Å^{-3}					
F1 −2	−0.688	8.956	−6.218	7.268	0.000	0.000
F2 −2	2.092	−5.048	2.956	−3.424	−8.937	3.593
F3 −2	1.029	−4.495	3.466	−3.305	8.198	−3.832
	2.433	−0.587	0.204	0.539	−0.739	−0.239
$\frac{EFG}{e}$	4.866	−1.174	0.408	1.078	−1.478	−0.478

Table VI/b

The EFG components in the case of one or two K^+ ions

$\frac{EFG}{e}$	*xx*	*yy*	*zz*	*xy*	*yz*	*zx*
$1K^+$	1.374	1.374	−2.748	0	0	0
$1K^+ + 6CN^-$	6.240	0.200	−2.340	1.078	−1.478	−0.478
$2K^+ + 6CN^-$	7.614	1.574	−5.088	1.078	−1.478	−0.478

Table VII

The eigenvalues of the EFG tensor (λ_i, $i = 1, 2, 3$)

K^+	λ_1/e	λ_2/e	λ_3/e	q_{lig}	$\sqrt{1+\frac{\eta^2}{3}}$	ΔE
	10^{-2} Å^{-3}	10^{-2} Å^{-3}	10^{-2} Å^{-3}	10^{-2} Å^{-3}		mm s^{-1}
0	5.18	−2.13	1.06	5.18	1.061	0.154
1	0.63	6.49	−3.02	6.49	1.051	0.191
2	7.83	5.41	1.68	7.83	1.037	0.228

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INVESTIGATION OF THE ELECTRIC CONDUCTIVITY OF METAL CHLORIDE–H_2O AND METAL CHLORIDE–HCl–H_2O SOLUTION SYSTEMS, I

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The results of comparative investigations concerning the conductivity and molar conductivity of metal chloride (particularly alkali metal and earth alkali metal chloride)–HCl–H_2O ternary systems and of their component binary systems are discussed. From the course of the electric conductivity — concentration curves of the single aqueous binary systems, from the measure and direction of the changes produced in the electric conductivity of binary systems by the addition of a third component — salt or acid —, and from phenomena found generally valid for the corresponding systems (inversion HCl concentration, inversion salt concentration, shifting of the binary $\varkappa$-maximum in ternary systems, etc.), the author concludes on the structural conditions of the binary systems and of the ternary systems formed, and on the dependence of structure on concentration.

In accordance with our concept on the investigation of solution structure, expounded in the introduction of our previous communication [1], a general investigation was made on the temperature and binary and ternary concentration dependence of the electric conduction of systems of the type alkali metal chloride (or alkali earth metal chloride and manganese chloride)–H_2O, and alkali metal chloride (or alkali earth metal chloride)–HCl–H_2O. These investigations are based on our experimental results published earlier [2a—2h] and on other data in the literature [2i—2m], under consideration of the conclusions of our own earlier review articles [3a—3c] and those of other works [3d—3e], but partly over and above these consideration, examining the phenomena from another aspect. Part I of our present communication deals with general conclusions on solution structure, drawn from these comparative investigations.

Investigation of the electric conductivity of binary solution systems metal chloride–H_2O and HCl–H_2O

1. It can be seen from the comparative figures 1/a and 1/b that the course of both the electric conductivity–molality ($\varkappa - m$) and the molar conductivity–molality ($\lambda - m$) curves depends strongly on the nature of the cation. Phenomena observed can be interpreted similarly as has been

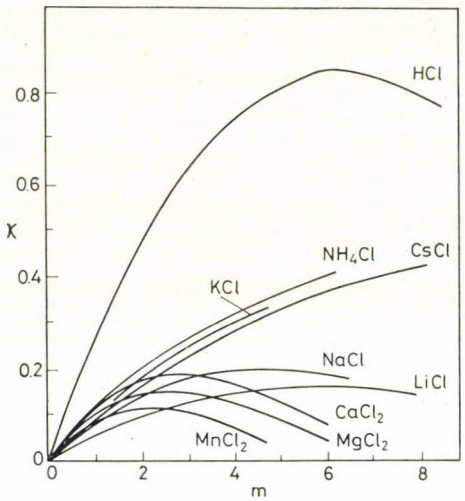

Fig. 1a

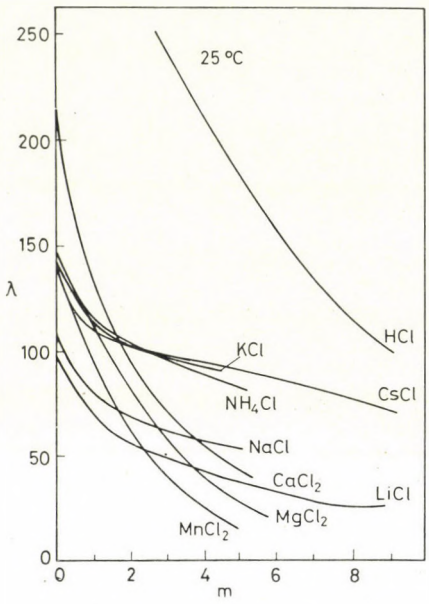

Fig. 1b

done in our preceding communication [1] in the case of the viscosity–concentration curves, naturally with the exception of proton conducting HCl and in certain instances of the case of the transition metal ions, and their effect on conduction.

In the case of HCl, as contrary to its curve characteristic of the dependence of viscosity on concentration, the curve of the concentration dependence of molar conductivity does not lie in the range corresponding to monovalent metal chlorides, but owing to its proton conducting property, it deviates very strongly from the course of the conductivity curves of these chlorides in the case of lower concentrations, and the range of conduction is only at high acid concentrations. This latter decrease in electric conductivity can be interpreted by the continuous decrease at such high acid concentrations of the possibility of proton conduction, existing in more dilute HCl solutions. This is due on the one hand to the fact that owing to hydration, the ratio of free water molecules is completely eliminated up to the limit of total hydration, and on the other hand, on a further increase of concentration, the hydrate sheath around the H_3O^+ and OH^- ions becomes less complete, so that the contacting ratio of the water molecules bound in the hydrate sheath decreases also with increasing concentration. At the same time, the ion–ion interaction is increasing considerably. All this results that at high concentrations even the hydrodynamic migration of H_3O^+ and OH^- must decrease.

Moreover, the comparative investigation of the electric conductivity–concentration curves of aqueous metal salt solutions shows that in spite of the fact that the concentration dependence of conductivity is determined by factors influencing also the concentration dependence of viscosity (ionic charge, ion dimension, electron configuration, and the same properties of the accompanying anion), the single factors, and particularly the electron configuration of the ion, act in a different way and to a different measure on the conduction of electrolyte solutions, than on viscosity.

This can be best documented by the behaviour of Mn^{2+}. The ionic radius ($r = 0.80$ Å) of Mn^{2+} ion of [Ar] $3d^5$ configuration falls between that of Ca^{2+} ($r = 0.99$ Å) of [Ar] configuration and of Mg^{2+} ($r = 0.65$ Å) of [Ne] configuration. Accordingly, the $\eta - m$ curve of $MnCl_2$, even if not in a proportion corresponding completely to the ionic radius, still lies between those of $CaCl_2$ and $MgCl_2$ [1]. However, as can be seen from Fig. 1/b, the $\lambda - m$ curve of $MnCl_2$ does not lie anymore between those of $CaCl_2$ and $MgCl_2$, but below both. This shows that the electron configuration has a stronger effect on conduction than on viscosity, and quasi 'carries out' the $\lambda - m$ curve of $MnCl_2$ from between those of $MgCl_2$ and $CaCl_2$ in the direction of lower conductivities.

It seems, therefore, that the effect of the non-complete electron shell on conductivity is large in the case of the ion of non noble gas configuration, and acts in the same direction, as the decrease in ionic dimension in the case of ions of noble gas configuration with the same charge number. This latter means an increase in hydration or rather hydration energy, which can then lead in the case of ions of non noble gas configuration already to the formation of aqua complexes, and indeed, as has been proved also experimentally, leads in the case of Mn^{2+} [4] to $[Mn(H_2O)_6]^{2+}$.

Similarly as has been found in the investigation of viscosity, the order of succession of the curves of the concentration dependence of electric conductivity for the single aqueous salt solutions, or the order of electric conductivity of the single aqueous salt solution at a given concentration does not change practically with temperature. This supports also the opinion [5] that the measure of the hydration of the ions, at least in dilute solutions, does not change with temperature, or if so, only slightly.

The course of the $\varkappa - m$ and naturally of the $\lambda - m$ curves clearly show that the main factor determining the concentration dependence in the case of a given cationic charge and the same anions (*i.e.* in the case of each metal chloride, chosing identical concentrations, and considering as identical the pure electrostatic ion–ion interaction) is the ion–solvent interaction, that is to say, the cation dimension influencing the hydration effect, characteristic of the measure of this interaction. The larger is the dimension of the cation, the smaller is the hydration effect and the smaller is the dimension of the

ion-hydrate complex, the so called moving unit, moving under the action of the electric field, and consequently, the higher will be the values of $\varkappa$ and λ for given salt concentrations, and the higher the concentration at which the maximum value of conductivity is exhibited on the $\varkappa$—m curve, if exhibited at all.

With respect to the latter, HCl behaves again differently, insofar as due to its protonic conduction property, the value of $\varkappa$, at least in not too concentrated solutions, is at every concentration much higher, than in the case of single metal chlorides conducting by hydrodynamic migration. However, at the same time the maximum value of conductivity practically occurs in the same concentration range as in the case of metal chlorides, that is to say, at considerably lower concentrations than would be expected on account of protonic conduction. This indicates that protonic conduction must be suppressed in this concentration range, which is over the limit of total hydration also with respect to HCl [6], due mainly to the absence of free water and the hindered rotation of all the water molecules, bound already in the hydration sphere. Thus, with increasing HCl concentration, migration or conduction by pure hydrodynamic way comes more and more to the fore. *I.e.* the mechanism of conduction of the other metal chlorides. The ion hydrate complex, formed on account of the relatively strong positive hydration character of the H_3O^+ ion, begins thus to behave also from the point of view of conduction, as if H_3O^+ would be already a common metal ion. This is well documented by the course of the λ—m curves, according to which the order of magnitude of the λ values of hydrochloric acid solutions of $m_{HCl} \approx$ $\approx$ 10—12 concentration, and even its value is already the same as those of CsCl.

Evidently, in the case of bivalent cations, due to the considerably higher degree of hydration, the dimension of the moving unit is considerably larger than in the case of a monovalent cation of identical dimension. Indeed, particularly in the case of cations of smaller dimension, such as *e.g.* Mg^{2+}, Mn^{2+}, etc., there is nothing to prevent the existence of even two complete hydrate spheres of geometrically maximal number. Therefore, with these metal chlorides, the decrease in conductivity, as compared to monovalent metal ions, on increasing the concentration exceeds the increase in conductivity, arising from the twofold charge transportation capacity of the bivalent metal introduced. Therefore, at lower concentrations, the $\varkappa$—m curve of the chloride of the Mg^{2+} ion of about the same dimension as Li^+, lies above the curve of LiCl. However, at higher concentrations, due to the double charge, considerably stronger ion–ion interactions are operative than in the case of monovalent ions, so that $\varkappa$-maxima occur already at considerably lower concentrations, than in the case of the chlorides of monovalent, positively hydrating metal ions.

It can be seen, therefore, that also in the case of bivalent cations of noble gas configuration, taking at identical solution concentrations identical ion–ion interactions into consideration, only the effect of the dimension of the ion-hydrate complex remains as predominant factor, in the same way as has been found in the case of the chlorides of monovalent ions of noble gas configuration. Therefore, on the basis of the comparison of the conduction of cations of noble gas configuration with identical charge, the system and the degree of hydratation of the cations and anions forming the system, as well as its dependence on concentration can be evaluated for a given concentration.

Starting from this concept, in Fig. 2/a the ratio of the conductivity of the binary aqueous solutions of each of two different salts has been plotted as a function of the salt concentration. It can be seen from the figure that the corresponding $\varkappa_{MeCl}/\varkappa_{Me'Cl}$ values lie in good approximation along straight

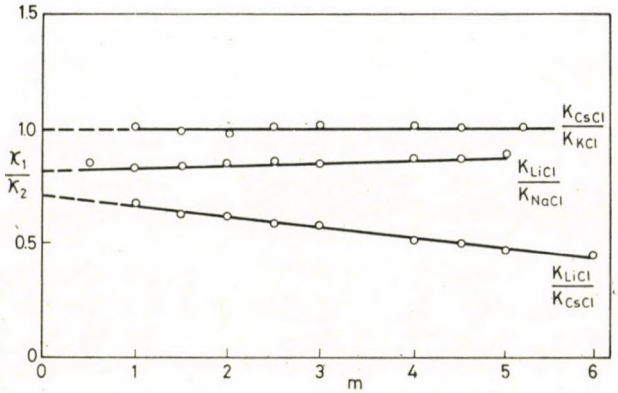

Fig. 2a

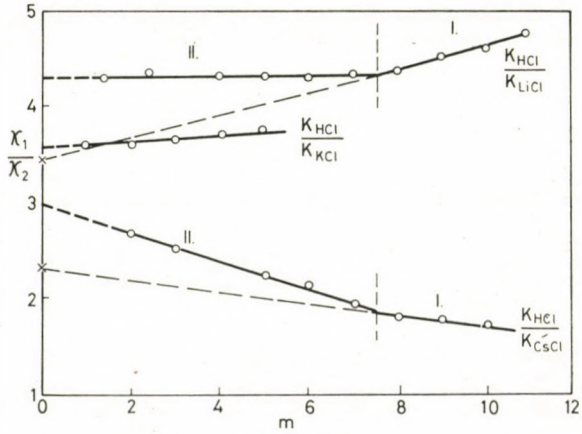

Fig. 2b

lines, the end points of which extrapolated to 0 concentration are practically the same as the corresponding conductivity ratio of solutions of infinite dilution!

Thus, it is in general valid that

$$\frac{\varkappa_{\mathrm{MeCl}}}{\varkappa_{\mathrm{Me'Cl}}} = \alpha + \beta_m \tag{1}$$

and

$$\alpha = \left[\frac{\varkappa_{\mathrm{MeCl}}}{\varkappa_{\mathrm{Me'Cl}}}\right]_{m=0} = \frac{\lambda_{\mathrm{MeCl},\infty}}{\lambda_{\mathrm{Me'Cl},\infty}} \tag{2}$$

Let us investigate now the $\frac{\varkappa_{\mathrm{MeCl}}}{\varkappa_{\mathrm{Me'Cl}}}$ ratio not only for the metal chlorides of identical conduction mechanism, but to include also the at least in not too concentrated solution indubitably protonic conducting HCl–H_2O solutions. This gives the $\frac{\varkappa_{\mathrm{HCl}}}{\varkappa_{\mathrm{Me'Cl}}}$ isothermal diagram shown in Fig. 2/b, from which it can be clearly seen that for CsCl and LiCl solutions, realizable also in higher concentrations, the concentration dependence of the value of the $\frac{\varkappa_{\mathrm{HCl}}}{\varkappa_{\mathrm{MeCl}}}$ ratio gives two linear sections, differing from each other rather strongly with respect to slope. In the case of KCl and NaCl solutions, unsaturated only up to 4—5 moles, only one linear section occurs.

Since the $\frac{\varkappa_{\mathrm{MeCl}}}{\varkappa_{\mathrm{Me'Cl}}}$ straight lines of metal chlorides, containing ions conducting with an identical mechanism are according to our opinion straight lines for the very reason that the migration mechanism of the ions is the same, and the ion–ion interactions increase in the same measure for the two salts with increasing concentration, because both cations are of the same value, it must be followed from the two slopes of the $\frac{\varkappa_{\mathrm{HC!}}}{\varkappa_{\mathrm{MeCl}}}$ straight lines that this is indicative of the presence of two kinds of mechanisms, or rather of the disappearance of one of them, with only the other remaining. This is supported also by the fact that when the $\frac{\varkappa_{\mathrm{HCl}}}{\varkappa_{\mathrm{MeCl}}}$ straight line in the concentrated solution interval is extrapolated to lower concentrations, the ratio

$$\left[\frac{\varkappa_{\mathrm{HCl}}}{\varkappa_{\mathrm{MeCl}}}\right]_{m=0} = \frac{\lambda_{\mathrm{HCl},\infty}}{\lambda_{\mathrm{MeCl},\infty}}$$

is obtained.

On the other hand, this supports the conclusion drawn already by LENGYEL *et al.* [7] from the measurement of the transport number that in

more concentrated HCl–H_2O solutions the protonic conduction mechanism practically stops or is at least very strongly repressed, and only when the solution is diluted, at medium concentrations, it begins again to increase steadily. The magnitude of the difference determined by lines I and II

$$\frac{\varkappa_{HCl}^{proton}}{\varkappa_{MeCl}^{hydrod.}} - \frac{\varkappa_{HCl}^{hydrod.}}{\varkappa_{MeCl}^{hydrod.}}$$

serves as measure of this increase.

Since the breaking point is at the concentration value $m_{HCl} \approx 7$, and since the higher protonic conduction can be actually interpreted only if free water is also present, the concentration corresponding to the breaking point indicates at the same time the complete hydration in the HCl–H_2O system, or at least its near concentration range and its limit. This means that at this concentration $\sim$8 molecules of water are bound to one HCl molecule, and taking into account that according to our earlier consideration [8] $\sim$3 molecules of water are presumed to be in the hydrate sheath around Cl^-, it follows that at this concentration, corresponding to complete hydration, $\sim$5 water molecules are bound around each H^+ ion. Therefore, this is the hydration number of the H^+ ion, which corresponds also to the tetrahedral structure of water.

It is therefore evident that according to this concept only a single straight line is possible in the diagrams $\frac{\varkappa_{KCl}}{\varkappa_{NaCl}} - m$ and $\frac{\varkappa_{HCl}}{\varkappa_{NaCl}} - m$, since KCl and NaCl attain already before the limit concentration of the complete hydration of the H^+ ion their saturation concentration.

Investigation of the electric conductivity of ternary solution systems: metal chloride–HCl–H_2O

1. The electric conductivity–concentration diagrams of systems of metal chloride–HCl–H_2O type, but in general, also those of other solutions of Me_xA_y–H_zA_v–H_2O type (see *e.g.* [9]) can be classed into two types (Fig. 3). In the case of systems belonging to type I, the specific conduction of the electrolyte at higher acid and salt concentrations does not change practically, or if so, only slightly, on a further increase of the acid concentration. Such behaviour is exhibited by the hydrochloric acid solutions of the chlorides of water structure breaking metal ions of dynamic, positive hydration (LiCl, $MgCl_2$, $CaCl_2$, etc.). In the case of systems belonging to type II, this phenomenon does not occur even at high salt and acid concentrations. Such behaviour is shown by the hydrochloric acid solutions of the chlorides of metal ions of less positive or negative hydration (NaCl, KCl, NH_4Cl, CsCl).

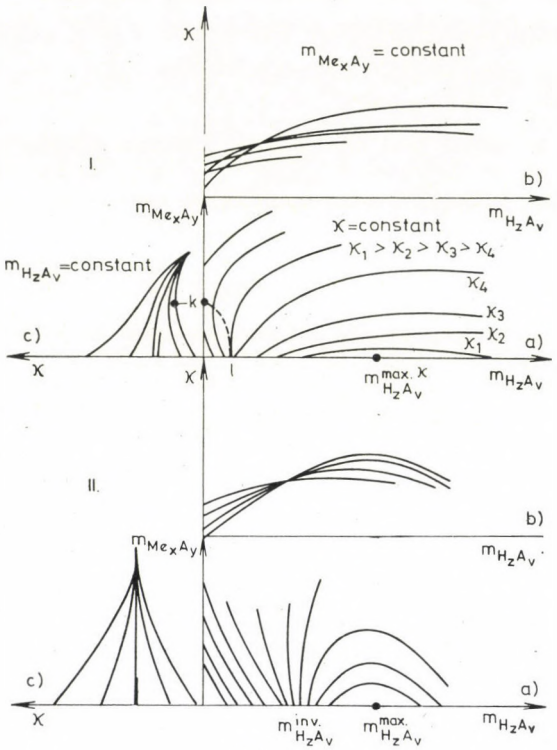

Fig. 3

Similarly, the isothermal molar conductivity concentration diagrams of the corresponding electrolyte systems can also be classed into two types (Fig. 4). Those systems belong to type I, in which the change in molar conductivity on the addition of HCl to the binary salt solution may be positive, negative and even zero, depending on the concentration of the binary salt solution. Systems of this kind are metal chloride–HCl–H_2O systems containing a metal cation of very positive hydration. On the other hand, those systems belong to type II, in which HCl added to the salt solution causes always an increase in molar conductivity, independently of the salt concentration, and begins to decrease only at higher hydrochloric acid concentrations. Systems of this kind are metal chloride–HCl–H_2O systems containing a metal cation of negative hydration.

It can be seen from the conductivity–concentration diagrams plotted for ternary systems [2], and particularly for metal chloride–HCl–H_2O systems containing a metal cation of strong positive hydration (Li^+, Mg^{2+}, Ca^{2+}) that the marked maximum character of the $[\varkappa - m_{HCl}]_{m_{salt}}$ curves, belonging to the various m_{salt} = const. values, diminishes with increasing m_{salt}, the curves become gradually flatter, and at high m_{salt} = const. concentrations

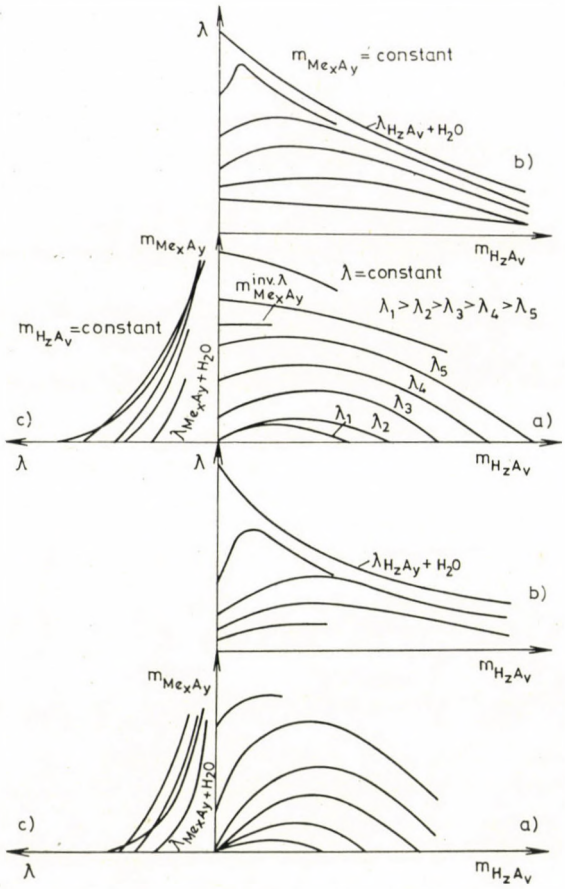

Fig. 4

become even practically parallel to the HCl–H_2O axis, *i.e.* hydrochloric acid does not influence practically the conductivity of such very concentrated salt solutions. Here, the change in conductivity is determined practically only by the salt concentration. The same is supported by the course of the ternary $[\lambda - m_{HCl}]_{m_{MgCl_2}}$ curves [2h], which document perhaps even more clearly that at high salt concentrations, hydrochloric acid added does not practically change the magnitude of molar conductivity. Indeed, this fact observed is considered as a further prove that HCl introduced into such concentrated salt solutions seems to dissociate only very slightly, and is dissolved only physically [1].

2. It has been found in our earlier investigations [2] that in metal chloride–HCl–H_2O systems (but according to our opinion, in every system of Me_xA_y–H_zA_v–H_2O type, where the conductivity–concentration curve of

the binary aqueous solution shows a maximum, thus *e.g.* also in the $MnSO_4$–H_2SO_4–H_2O system investigated by us [10]), the addition of HCl or H_zA_v acid to the binary aqueous metal chloride or Me_xA_y solutions of any concentration always increases the initial conductivity, even if in a decreasing measure with increasing salt concentration, or possibly does scarcely change it, and begins to decrease it in a measure depending on the nature of the salt and its concentration only after the addition of a further quantity of acid. On the other hand, the sign of the change in conductivity, produced by the addition of the salt to the binary hydrochloric acid solution, will depend on the concentration of the initial binary acid solution. Therefore, similarly as in the case of viscosity (see Eqs. 11 and 12 in [1]), if the ***isothermal salt concentration coefficient*** is defined also for the electric conductivity of the binary aqueous H_zA_v solution, at low salt concentrations

$$\alpha_\varkappa = \left(\frac{\partial \varkappa}{\partial m_{Me_xA_y}}\right)_{m_{H_zA_v},t} \begin{Bmatrix} \geqq \\ < \end{Bmatrix} 0, \text{ if } m_{H_zA_v} \begin{Bmatrix} \leqq \\ > \end{Bmatrix} m_{H_zA_v}^{inv,\varkappa} \tag{3}$$

and at higher salt concentrations, at a value depending on the type of hydration of the cation, it is

$$\alpha_\varkappa = \left(\frac{\partial \varkappa}{\partial m_{Me_xA_v}}\right)_{m_{H_zA_v},t} < 0 \tag{4}$$

Thus, for each Me_xA_y–H_zA_v–H_2O system a $m_{H_zA_v}^{inv.\varkappa}$ so called inversion acid concentration can be given. When salt is added at this concentration, the conductivity of the solution does not change within a certain salt concentration range (see Fig. 3).

At acid concentrations lower than the inversion acid concentration — $m_{HCl} < m_{HCl}^{inv.\varkappa}$ — the salt added increases the conductivity of the solution. This is evidently in connection with the fact that due to the dissociation of the salt added to the hydrochloric acid of relatively low concentration, the number of ions per unit volume increases. In the case, when a small amount of salt is added to a dilute hydrochloric acid concentration, the complete quantity of the salt introduced will be completely hydrated, and free water still be present, so that the relatively not too large increase in viscosity [1] does not yet considerably diminish ionic mobility. At the same time, neither is ion–ion interaction so large that the decrease in ionic mobility arising from it could compensate the increase in conductivity, due to the increase in number of the charge carriers.

However, the further addition of salt increases to such a measure the number of ions that a complete hydrate sheath can not be developed around the ions. Thus also in the ternary solution the limit of complete hydration is exceeded. Ion–ion interaction steadily increases, mobility decreases, and

the decrease in conductivity caused by it can already surpass also the increase in conductivity arising from the increase in the number of ions.

If we start from a hydrochloric acid solution of a higher concentration than the inversion concentration — $m_{HCl} > m_{HCl}^{inv,x}$ — the number of ions is already initially so large that, owing on the one hand to the initially high ion–ion interaction, and on the other hand to the increase in viscosity by uncomplete hydratation, the addition of salt produces an effect, which is immediately manifested in a decrease in conductivity.

Thus, between the two hydrochloric acid concentration ranges there should exist a hydrochloric acid concentration to which the addition of a salt up to a certain concentration increases the conductivity due to an increase in the number of ions just compensates the decrease in mobility of the ions. This concentration is the *inversion HCl concentration.*

The correctness of the interpretation of the phenomenon is supported also by the fact that on the basis of our investigations of various metal chloride–HCl–H_2O systems [2] the inversion HCl–concentration depends on the nature of the metal chloride component of the ternary system, and within this, at given cation valency, on the cation dimension. With increasing cation dimension at identical cation charges $m_{HCl}^{inv,x}$ increases (see Fig. 5). Therefore, the higher is the hydration effect, *i.e.* the smaller is the cation dimension and the higher the cation charge, the sooner occurs that state, in which the increase in conductivity due to the increase in the number of ions is already just compensated by the decrease in mobility of the ions, caused by ion–ion interaction and by the increase in viscosity.

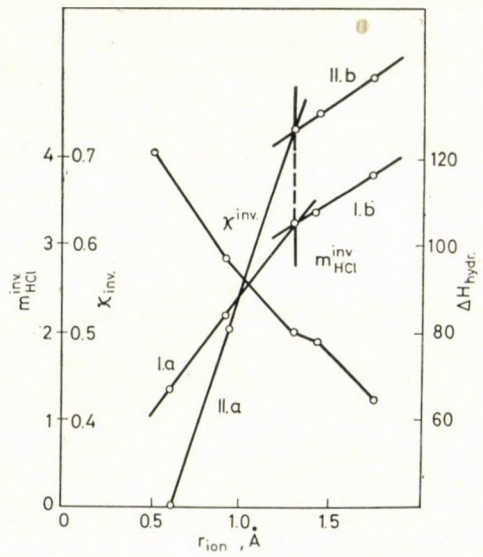

Fig. 5

Thus, according to our experiences, the $m_{HCl}^{inv,\varkappa}$ inversion value of conductivity, established in HCl–H_2O systems on the addition of salt, can give information in the case of identical anions also on the relative hydration power of the cations of the salt. This is documented also by the fact that the hydration energies of the single alkali and earth alkali metal ions [11] increase with decreasing cation radius in the same order and in about the same ratio, as the value of $m_{HCl}^{inv,\varkappa}$ (see Fig. 5).

That hydration effects occuring in the ternary solutions of the chlorides of cations with identical charge have a dominating character in influencing conductivity is still more convincingly indicated by the results of the analysis of the dependence of the $m_{HCl}^{inv,\varkappa}$ values of various alkali metal chlorides on the cation radius. It has been found that in the case of these metal chlorides the dependence of the inversion acid concentration on the cation radius can be practically divided into two linear section (straight lines I/a and I/b of Fig. 5). Out of these, one is characteristic of cations with positive hydration, and can be described by the following equation

$$[m_{HCl}^{inv,\varkappa}]_{pos.hydr.} = -0.96 + 3.22\, r_{cation} \tag{5}$$

The other linear section is characteristic of cations with negative hydration, and can be described by the following equation

$$[m_{HCl}^{inv,\varkappa}]_{neg.hydr.} = 1.95 + 1.07 r_{cation} \tag{6}$$

The intersection of the two straight lines is at 1.3 Å. It has been shown on the basis of viscosity measurements [1] that in the case of monovalent ions this is the cation dimension limit of positive and negative hydratation.

Moreover, $\varkappa_{inv}$ values belonging to the $m_{HCl}^{inv,\varkappa}$ inversion concentration of chlorides with various alkali metal cations are also linear functions of the ionic radius of cations with positive and negative hydration:

$$[\varkappa_{inv}]_{pos.\,hydr.} = -0.04 + 0.59\, r_{cation} \tag{7}$$

$$[\varkappa_{inv}]_{neg.\,hydr.} = 0.572 + 0.11\, r_{cation} \tag{8}$$

and the two corresponding straight lines (straight lines II/a and II/b in Fig. 5) similarly intersect each other at an ion radius value of 1.3 Å.

At the same time, according to our experimental data, the value of the inversion HCl–concentrations in the single metal chloride–HCl–H_2O systems practically does not change with the temperature. On the other hand, inversion conductivity belonging to it increases with increasing temperature.

The dependence of $m_{HCl}^{inv,\varkappa}$ on the nature of the substance and on temperature seems also to support the fact that in addition to the increase in the

number of charge carriers, the development of inversion is essentially influenced by the hydration conditions. This concept is consistent with the experience of Mishchenko [11] according to which hydration conditions are only very slightly temperature dependent below the so-called limit of complete hydratation, and the single $m_{HCl}^{inv,\varkappa}$ values are certainly below this limit, so that $m_{HCl}^{inv,\varkappa}$ is also practically independent of the temperature.

Let us now investigate more extensively the dependence of molar conductivity on ternary concentration, and the conclusions which can be drawn from it for the ternary solutions of the chlorides of metal ions with strong positive hydration — Li^+, Ca^{2+}, Mg^{2+} — creating conditions corresponding to diagram I in Fig. 4.

The system of curves in Fig. 4 clearly shows that though the molar conductivity of the single binary HCl solution is higher than that of the binary aqueous metal chloride solutions of the same concentration [2] (*e.g.* in the case of $MgCl_2$ about 2.5-fold), this difference is manifested under ternary conditions only in metal chloride solutions of relatively lower salt concentrations. In this range of salt concentration, HCl added to the binary salt concentration increases molar conductivity, in more dilute salt solutions stronger, in more concentrated less.

However, HCl added even in larger quantities to more concentrated binary salt solution will not be able anymore to increase the initial molar conductivity of the binary salt solution: HCl added to such binary salt solution will already decrease the molar conductivity. This means that while in each metal chloride solution containing ions with positive or negative hydration, an isothermal inversion acid concentration is developed in the case of conductivity, whereas in the case of molar conductivity an isothermal inversion salt concentration is established in the solution of metal chlorides containing cations with strong positive hydration, for which the β_λ *isothermal acid concentration coefficient* is

$$\beta_\Lambda = \left(\frac{\partial \Lambda}{\partial m_{HCl}}\right)_{m_{MeCl_2},t} \gtreqless 0, \text{ if } m_{MeCl_2} \lesseqgtr m_{MeCl_2}^{inv,\varkappa} \tag{9}$$

This phenomenon is indicative of the fact that in the solution of metal chlorides containing metal ions which are hydrated strongly, protonic conduction caused by HCl introduced above the inversion salt concentration evidently is strongly repressed. This is due on the one hand to the fact that at such concentrations there is already no free water in the original metal chloride solution proper (the limit of complete hydration has been exceeded; *e.g.* for $MgCl_2$ $m_{MgCl_2}^{limit} \approx 1.5$), and even if HCl introduced can still dissociate here, according to our opinion, owing to the relatively small amount of water molecules available for the ions in the solution and thus to the small ratio

of contacting water molecules, further to the hindered rotation due to strong orientation, the possibilities of protonic conduction are much more restricted. On the other hand, as a consequence of the introduction of the third component, ion–ion interactions become more and more pronounced, so that the possibility of hydrodynamical migration is also decreased.

Indeed, in the binary concentrated salt solution region the molar conductivity decreases even more strongly on the addition of HCl. However, in this region, as has been seen also in the investigation of viscosity [1], viscosity too is already decreasing on the addition of HCl. All this can be possible only, and this supports also our findings concerning viscosity, that in salt solutions of such high concentration HCl can dissociate only slightly. As an uncharged species it is dissolved physically, and it decreases simultaneously both viscosity and molar conductivity.

On the other hand, the addition of single metal chlorides to the binary HCl solution, due to the fact that the mobility of the ions formed from them is lower than that of the proton, causes a decrease in conductivity, as compared to the molar conductivity of the initial binary HCl solution, even in the case of the most dilute HCl solutions, where relatively many water molecules are present, and the dissociation of both HCl and the added metal chloride may be complete. It seems, therefore, that in spite of the fact that the number of ions is increased by the introduction of the single metal cations with strong positive hydration and by the Cl^- ions, the increasing effect of the increase of ion number on molar conductivity is surpassed already in such dilute solutions by the decreasing effect of increasing ion–ion interaction on conductivity. Eventually, the Me^+ or Me^{2+} and Cl^- ions of not very high mobility decrease more strongly the protonic conduction of H_3O^+ ions, than their contribution in increasing conduction. This is the reason why molar conductivity may decrease even in dilute HCl solution as an effect of the addition of chlorides containing metal cations with strong positive hydration. This can be observed particularly distinctly in the case of the $MgCl_2$–HCl–H_2O system, containing the Mg^{2+} ion, which is most strongly hydrated among the cations investigated [2h].

3. On the structural relations developed in ternary solutions and determined decisively by ion–ion and ion–solvent interactions, and on the changes of these relations as a function of concentration, a certain information may be obtained from the measure and direction of the shift of $\varkappa_{max}$ the maximum conductivity value found for binary HCl–H_2O solutions, caused in ternary solution by the action of various salt components, and from the shape and structuring of the curves, representing the course of the $\varkappa$-maximum in ternary systems.

Figure 6 shows on the ternary concentration net the course and the path of the shift of the HCl concentration corresponding to the $\varkappa$-maxima of the

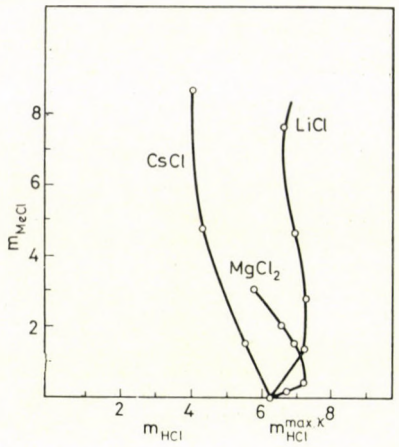

Fig. 6

binary HCl–H_2O solution, caused by the effect of CsCl, LiCl and $MgCl_2$. It is evident from the curves that both the shape and direction of the course of the curves, corresponding to cations with different hydration character, are very different. Moreover, the curve is sectioned, similarly as has been found already in the investigation of the concentration dependence of various properties of the corresponding binary salt solutions (as *e.g.* β_η) discussed already [1], further thermodynamic functions of activation to be investigated summarily in our following communications, or discussed already in some of our earlier communications in the course of the investigation of the single metal chloride–HCl–H_2O systems [2], and molar volume, $\lambda\eta$ [12].* All this indicates that the dominant solution structure relations, occuring in certain definite and separable concentration ranges of the binary salt solutions forming the ternary system, are preserved also in the ternary system, even if influenced to a larger or slighter measure by HCl.

The curves of the diagram pertinent to chlorides of cations with strong hydration clearly show that the acid concentration corresponding to the $\varkappa$-maximum of the HCl–H_2O system is shifted by the action of salt towards higher HCl concentrations. In the first moment, this seems remarkable, because if the ion strength is higher, it were to be expected that the maximum of conductivity occurs at an acid concentration lower than the initial, since ion–ion interactions are higher, as there is a greater number of ions in a given volume, so that the average distance between the ions is smaller. Indeed,

* In the latter case, the comparison is the more interesting, as becomes evident from a comparison with Fig. 1 in [12], as the course and direction of the so-called *M*-curves, characteristic of the concentration dependence of the combined effect of changes in temperature and concentration, and the course and direction of the corresponding curves in Fig. 6 of the present communication have a completely similar character for the single types of salts.

the phenomenon cannot be explained by a simple increase of the ion–ion interactions alone. According to our opinion, it can have only a structural reason, that is to say a reason arising from structural changes. If, for example, HCl is added to the binary aqueous 0.5 *M* $MgCl_2$ solution, which leaves the original molarity of $MgCl_2$ unchanged, *i.e.* we proceed along the straight line corresponding to $m_{MgCl_2} = 0.5$ constant, parallel to the abscisse axis of diagrams of the type shown in Fig. 3, then the salt in the solution begins to repress the dissociation of HCl introduced already in larger concentrations. This can occur either directly, or by producing possibly after the primary complete dissociation of HCl secondary H_3O^+–solvent–Cl^- complexes without charge,* resulting in the same final effect. Decreasing thus the number of charge carriers, the ion–ion interaction is decreased (will be lower than the value calculated from complete dissociation at the given ionic strength), and will become only at a HCl concentration higher than the concentration corresponding to the $\varkappa$-maximum of the binary hydrochloric solution of such magnitude that it can decrease already in its resultant effect $\varkappa$ as a function of its concentration, that is to say to push it over the corresponding ternary $\varkappa$-maximum.

Since the concentration shift corresponding to the $\varkappa$-maximum of the HCl–H_2O system is of just the opposite direction in the case of CsCl, it is to be presumed that CsCl does not repress, or if so only slightly, the dissociation of HCl, *i.e.* it does not force HCl to form uncharged species. Therefore, the addition of HCl to binary CsCl solution, due to its practically complete dissociation, increases monotonously the number of ions and thus also ion–ion interaction. Owing to this, $\varkappa$ begins to decrease already at HCl concentrations lower than that corresponding to the $\varkappa$-maximum of the binary hydrochloric acid solution, and similarly, its $\varkappa$-maximum occurs also at a lower concentration. This tendency does not change even towards higher CsCl concentrations, though the measure of the shift of the HCl concentrations corresponding to $\varkappa$-maximum towards lower and lower HCl values decreases somewhat. All this indicates that in HCl solutions containing Cs^+ and Cl^- ions of lower hydration power, a supression of the dissociation of HCl or the development of possible secondary uncharged species is not to be expected, or only to a very slight degree, even in the case of high ternary ionic strengths.

In the case of CsCl, the curves exhibit in good approximation two sections. However, it can be seen from the diagram that the curves of LiCl and $MgCl_2$ have decisively and sharply at least two, but *e.g.* in the case of LiCl practically three sections. In these cases, adding appropriately HCl to salt solutions of higher concentration than the binary salt concentrations $m_{LiCl} \approx 1.8$ and $m_{MgCl_2} \approx 0.7$, resp., the HCl concentration corresponding to

* The investigation of the latter assumption and the possibility of the phenomenon will be discussed in detail in our subsequent communications.

the development of the $\varkappa$-maxima begins again to decrease, the curve turns toward left, and can even become at higher salt concentrations lower than the HCl concentration corresponding to the binary $\varkappa$-maximum. However, with these salts this does not mean according to our opinion that HCl dissociation or possibly the probability of the appearance of certain secondary complexes is smaller in the solution. (The existence of complexes of this character and its proves will be discussed in our subsequent communications, dealing with the investigation of other properties, *e.g.* thermodynamical functions of activation, solubility, etc.). We think that the introduction into the solution of the Mg^{2+} ion of very high field strength and of the $2\ Cl^-$ ion, equivalent to it, increase very strongly the ion–ion interactions, and this causes the earlier occurance, at already lower HCl concentration, of the newer decrease of $\varkappa$, that is to say, the appearance of the $\varkappa$-maximum.

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INVESTIGATION OF THE ELECTRIC CONDUCTIVITY OF METAL CHLORIDE–H_2O AND METHAL CHLORIDE–HCl–H_2O SOLUTION SYSTEMS, II

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Relationships are given for the binary and ternary isothermal concentration dependence of the electric conductivity of metal chloride–H_2O and metal chloride–HCl–H_2O systems, and for possible modes of its calculation. The constants of the equations and the accurary of their calculations are analysed, and conclusions are drawn on the interactions occuring in the solvent systems investigated and on the dependence of these interactions on concentration.

As a continuation of the preceding communication [1], summarizing the results of investigations on the electric conductance in metal chloride–H_2O and metal chloride–HCl–H_2O systems, with a view to solution structure, the present paper summarizes investigations carried out with the aim to find relationships, suitable for the description and calculation of the binary and ternary concentration dependence of the electric conduction in the above systems.

Investigation of an equation, suitable for the description and calculation of the binary concentration dependence of electric conduction.

The concentration dependence of electric conduction in binary salt solution systems has been extensively investigated for a broad concentration range by Falkenhagen, Wishaw and Stokes [2], who gave also a quantitative description, starting from Debye—Hückel's theory. However, these equations are in essence $\lambda - \eta - c$ equations, which contain in addition to the constants obtained theoretically also explicitly the viscosity, so that essentially they give information on the mutual relationship of electric conduction and viscosity and its concentration dependence. At the same time, for the ternary systems of the type investigated, there are no solutions giving good results in the full concentration range.

The present work attempts to find and investigate a conductivity-molarity equation of similar type and accurary as found by us [3] for the viscosity–concentration relationship, which describes well the relationship in the *full* binary and ternary concentration range. Moreover, starting from the consideration that the mechanisms of viscous flow and hydrodynamical conduction can be taken as identical (essentially as a conutinuous process of the

transition of the moving unit through appropriate energy barriers under the action of electric field or gravitational or mechanical field of force), it was hoped that a better understanding of the conduction mechanism in solutions and its dependence on concentration and structure can be reached by the investigation of the constants contained in the equation and by their comparison with the constants of the viscosity–concentration equation, discussed in [3].

According to our investigations, the concentration dependence of the conductivity of aqueous binary alkali and alkali earth metal chloride solutions or of HCl solutions under isothermal conditions is described with good approximation by the equation

$$\varkappa = (a + b\sqrt{m} + cm)\, m\,, \tag{1}$$

where

$$b = b' + b''m \tag{2}$$

and

$$c = c' + c''m \tag{3}$$

and from where the so-called *molal conductivity* is

$$\Lambda' = \frac{\varkappa}{m} = a + b\sqrt{m} + cm \tag{4/a}$$

and

$$\Lambda' = \frac{\varkappa}{m} = a + (b' + b''m)\sqrt{m} + (c' + c''m)\, m \tag{4/b}$$

The constants of Eqs (1) and (4) for 25°C are given in Table I, while the documentation of the accuracy of the equations is contained in Table II.

The seemingly simple Eq. (4) involves actually considerable more complicated interactions, than those met in the case of the calculation of viscosity [3], permitting eventually the derivation of a simple equation of calculation, which can be solved also graphically and is practically valid for the whole concentration range.

For the formulation of such conduction equation, describing well the relationships in the whole concentration range, the consideration of five constants is indispensable. However, it should not be forgotten that this is *only one constant more*, than e.g. the number of constants of Eq.

$$\Lambda = \Lambda_\infty - A\sqrt{c} - Dc\sqrt{c} - Bc$$

valid only up to a limit concentration of 0.1 mole/dm^3 [2b].

Table I

Compound	Cation radius Å	$a \cdot 10^3$	$b' \cdot 10^3$	$b'' \cdot 10^3$	$c' \cdot 10^3$	$c'' \cdot 10^3$
LiCl	0.60	114.89	— 57.102	— 5.750	19.357	0.696
NaCl	0.95	126.38	— 65.646	—16.007	36.950	2.503
KCl	1.33	149.66	— 49.66	20.874	— 7.779	—6.359
NH_4Cl	1.43 (1.35)	151.86	— 49.800	20.000	— 7.500	—6.000
CsCl	1.69	154.46	— 72.476	—14.495	40.636	1.736
HCl	1.12	425.60	— 82.187	7.813	—31.406	—0.219
$MgCl_2$	0.65	148.26	37.612	25.159	—93.915	—0.943
$CaCl_2$	0.99	270.95	—237.437	—64.874	150.142	10.619

Among these five constants, the constant a is evidently related to Λ_∞ or can be simply calculated from it,[1] while exact physical interpretation of the other four constants is a difficult task, as can be seen from the course of the curves shown in Fig. 1, giving the atomic ion cation radius dependence of the single constants for the case of compounds of MeCl type. *From the mutual relationship of the shape of the curves* for the single constants, at the most, certain probable assumptions can be made. The diagram shows namely the following:

1. The inflection of the constant a occurs just at the cation radius ($\sim$1.3 Å) corresponding to the boundary of positive hydratation and negative hydratation. The maxima of b' and b'' and the minima of c' and c'' occur at the same place. The physical meaning of the constant a is known. Since according to (5) $a = \Lambda_\infty \varrho_{\text{water}}$, practically a is also the sum of the molar conductivities relative mobilities of the dissolved ions, which is determined by the dimensions of the moving unit having a hydrate sheath, produced around the single ions by *ion–solvent interactions.*

2. The constants of HCl and H_3O^+ do not lie along the corresponding curves of the atomic ions, but, owing to the different nature of conduction mechanism, they deviate even much stronger, than was found in the case of viscosity [3]. At the same time, the constants of NH_4Cl or NH_4^+ *lie only*

[1] Since the m–c conversion equation is

$$m = \frac{1}{\frac{\varrho}{c} \frac{M_{\text{salt}}}{1000}}$$

if $c \to 0$, then $\varrho \to \varrho_{\text{water}}$ and $\frac{\varrho}{c} \to \infty$; so that the constant $\frac{M_{\text{salt}}}{1000}$ becomes more and

Table II

m	Compound	LiCl	NaCl	KCl	NH_4Cl	CsCl	HCl	$MgCl_2$	$CaCl_2$
	meas.	0.0721	0.0842	0.1070	0.1075	0.1100	0.3200	0.1160	0.1294
1	calc.	0.0721	0.0842	0.1070	0.1086	0.1099	0.3196	0.1162	0.1294
	Δ%	0.00	0.00	0.00	1.02	−0.09	−0.12	0.17	0.00
	meas.	0.1190	0.1446	0.1957	0.1970	0.2000	0.5450	0.1610	0.1894
2	calc.	0.1187	0.1444	0.1957	0.1980	0.1984	0.5356	0.1620	0.1888
	Δ%	−0.25	−0.14	0.00	0.51	−0.18	−1.72	0.62	−0.32
	meas.	0.1522	0.1890	0.2760	0.2750	0.2740	0.7000	0.1617	0.2058
3	calc.	0.1513	0.1886	0.2760	0.2791	0.2734	0.6830	0.1617	0.2058
	Δ%	−0.59	−0.21	0.00	1.48	−0.22	−2.43	0.00	0.00
	meas.	0.1730	0.2200	0.3400	0.3420	0.3358	0.7820	0.1360	0.1875
4	calc.	0.1730	0.2195	0.3400	0.3450	0.3355	0.7784	0.1360	0.1902
	Δ%	0.00	−0.23	0.00	0.88	−0.09	−0.46	0.00	1.44
	meas.	0.1855	0.2400		0.3950	0.3844	0.8250	0.1030	0.1545
5	calc.	0.1855	0.2398		0.3830	0.3846	0.8334	0.1025	0.1544
	Δ%	0.00	−0.08		−3.02	0.05	1.02	−0.49	−0.06
	meas.	0.1896				0.4220	0.8400		0.1200
6	calc.	0.1903				0.4213	0.8567		0.1143
	Δ%	0.37				−0.17	1.99		−4.75
	meas.	0.1820				0.4611	0.8270		
8	calc.	0.1814				0.4614	0.8373		
	Δ%	−0.60				0.07	1.25		
	meas.	0.1580				0.4686	0.7850		
10	calc.	0.1566				0.4680	0.7681		
	Δ%	−0.89				0.00	−2.15		

then exactly on the corresponding curves (points marked with ○ in Fig. 1), *if not the generally accepted cation radius of 1.43 Å* [4], *but the effective ionic radius of 1.35 Å, introduced in the course of the discussion of viscosity* [3] *is used for the calculations.* Thus, data obtained from electric conduction support also our opinion on the behaviour of the NH_4^+ ion, expounded in connection with viscosity.

3. The course of the curves representing the cation radius dependence of the constants b' and b'', and c' and c'', respectively, is identical with respect to b' and b'', and c' and c'', respectively. However, with respect to b' and c',

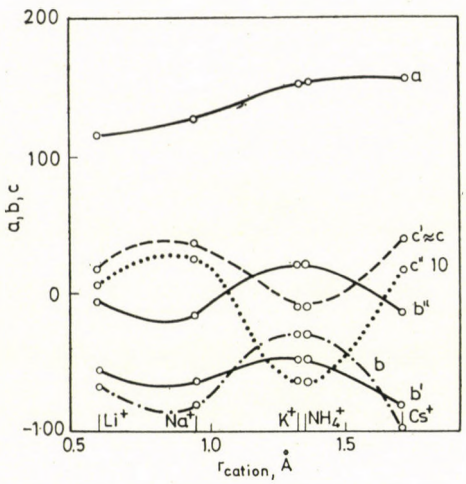

Fig. 1

and b'' and c'', respectively, the curves have an opposite course. Indeed, as $b' + b'' = b$ and $c' + c'' = c$ in the case of $m = 1$, and $c' \gg c''$ according to data in Table I, the curves for the cation radius dependence of the coefficients b and c, which are otherwise concentration dependent on the basis of (2) and (3), show practically a *symmetrically opposite course.*

All these are indicative of the fact that the constants b and b' and b'', and the constants c and c' and c'', respectively, are *characteristic of effects of practically the same magnitude, but acting opposite to each other.* Since the coefficients c become of considerable magnitude at higher concentrations, the coefficient b is according to our opinion characteristic of ion–ion interaction, and this effect is decreased by dielectric effects [7], [3], occurring in the solvent layer bound in the hydrate sphere, by causing relative increase in conduction. In our opinion, the coefficient c is presumed to be characteristic of these dielectric effects. Both coefficients, corresponding to these very similar effects, are composed of two terms, one of them dependent on concentration, the other independent of concentration. Therefore, *viscosity* too, decreasing conduction and dependent also on concentration proper, must

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more negligible as compared to $\frac{\varrho}{c}$, and $m \to \frac{1}{\frac{\varrho_{water}}{c}} = \frac{c}{\varrho_{water}}$. Since $\Lambda = \frac{\varkappa}{c} = \frac{\varkappa \varrho_{water}}{c \varrho_{water}}$, if $c \to 0$, then $\Lambda \to \Lambda_\infty$, and $\Lambda = \frac{\varkappa \varrho_{water}}{c \varrho_{water}} = \frac{\varkappa}{\frac{c}{\varrho_{water}} \varrho_{water}} \to \frac{\varkappa}{m \varrho_{water}} = \frac{\Lambda'_\infty}{\varrho_{water}}$. Thus, $\Lambda'_\infty = \Lambda \varrho_{water}$, and if $c \to 0$, then similarly $\Lambda \to \Lambda_\infty$, form which

$$a = \Lambda'_\infty = \Lambda_\infty \varrho_{water}.$$

indubitably play a role. The member b'' of coefficient b is thought to be characteristic of this effect.

Since $c'' \approx c'$, $c' \approx c$ means that the coefficient c changes only slightly in dilute solutions, and begins to change stronger only in more concentrated solutions. This makes probable the acceptability of our opinion, expounded already in connection with viscosity in the interpretation of the c coefficients of Eq. (2) in paper [3]. According to this, in more concentrated solutions the water molecules get more and more under the action of two-two ions, act as more and more polarized dielectric medium, as more and more strongly oriented permanent dipoles between the two charges, and exert a field of force-decreasing action. We think that coefficient c of Eq. (3) is characteristic of this effect.

Owing to the very complicated conditions, to the *simultaneous presence* of two kinds of fields of force, electrical and mechanical, with considerably more possibility of interaction, further to the influencing effect of viscosity, we think that at present nothing other or more can be said on factors influencing the concentration dependence of electric conduction, and on their dependence on structure.

Nevertheless, the interpretation given above is made rather probable by a comparison with Fig. 6 in paper [3], showing the constants A, B, C and D of the viscosity equation (4) as a function of cation radius. According to this:

1. The course of the cation radius dependence of coefficient A, thought characteristic of ion–ion interaction, is practically the image of the course of coefficient b in Fig. 1 of the present communication, thought similarly characteristic of ion–ion interaction. (This is only natural, as an increase in ion–ion interaction results an *increase* in viscosity and a *decrease* in conduction.)

2. The course of the coefficient C, thought characteristic of the resultant decrease in ion–ion interaction due to the dielectric polarization of hydrated solvent molecules between each of two opposite charges, is with good approximation the same as the course of coefficient c, thought similarly characteristic of this effect. Thus, an increase in cation radius acts similarly, in the *same direction* on conduction and on viscosity. This can be interpreted only by these dielectric effects.

3. A, b and c values relevant to the Na^+ ion present an extremum both on the curves of Fig. 6 of paper [3] and on the curves of Fig. 1 of the present communication. This supports also what was said in the discussion of viscosity [3], according to which the resultant ion–ion interaction will be eventually smaller than expected on the basis of Coulomb and Stoke's law in the case of Li^+ than in the case of Na^+ with larger radius, on account of the larger hydrate sheath of large field force around the positively hydrating

ions of small dimension, and on account of the shielding effect of solvent molecules stronger oriented in this hydrate sheath. Thus, in the case of ions with positive hydration, the values of A and c, *characteristic of the resulting ion–ion interaction*, increase with increasing cation radius, while the value of b decreases accordingly, to attain in the case of Na^+ a maximum and a minimum, respectively.

Calculation of the electric conduction of ternary solution systems from data of their constituent binary systems

In the study of the ternary concentration dependence of electric conduction, the changes in conductivity and molar conductivity have been investigated earlier [5] for cases, in which water concentration has been kept at a constant value. This means actually an investigation of what happens to the electric conduction of the system, when salt is gradually exchanged for HCl, and vice versa, while total concentration is maintained at a constant value.

It could be established that the change in specific conduction in the NaCl–HCl–H_2O system is represented under these conditions by Fig. 2/a, where conductivity is plotted on the ordinate, and the corresponding concentration values on the abscisse axis. The single lines of the figure show the change in conductivity belonging to various $m_{HCl} + m_{NaCl} = m_\Sigma =$ constant values as a function of increasing HCl concentration. The single $A_5, \ldots, A_1$ points give the conductivity of $5, \ldots, 1$ molal aqueous NaCl solutions, while the $B_5, \ldots, B_1$ points that of $5, \ldots, 1$ molal aqueous HCl solution. *In the NaCl–HCl–H_2O system, a linear change of conductivity belongs practically to each constant m_Σ total concentration* (Fig. 2/a), and correspondingly, it will be valid for the single $m_\Sigma =$ constant lines that

$$\varkappa = Am_{HCl} + B \tag{6}$$

where

$$A = \frac{\varkappa^{\Sigma}_{HCl} - \varkappa^{\Sigma}_{NaCl}}{m_{HCl} + m_{NaCl}}$$

and

$$B = \varkappa^{\Sigma}_{NaCl} \tag{8}$$

and $\varkappa^{\Sigma}_{HCl}$ and $\varkappa^{\Sigma}_{NaCl}$ are the conductivities of the aqueous two-component HCl and NaCl solutions of $m_{HCl} + m_{NaCl} = m_\Sigma =$ constant composition, respectively, and m_{HCl} and m_{NaCl} are the actual HCl and NaCl concentrations of the ternary system.

On substituting the values of (7) and (8) into (6), the relationship

$$\varkappa = \varkappa^{\Sigma}_{\mathrm{HCl}} \frac{m_{\mathrm{HCl}}}{m_{\mathrm{HCl}} + m_{\mathrm{NaCl}}} + \varkappa^{\Sigma}_{\mathrm{NaCl}} \frac{m_{\mathrm{NaCl}}}{m_{\mathrm{HCl}} + m_{\mathrm{NaCl}}} \tag{9}$$

is obtained, on the basis of which the conductivity of the ternary NaCl–HCl–H_2O system can be calculated in knowledge and with the aid of the corresponding conductivity values of the binary systems.

Naturally, after division by c_{total}, (9) will be valid also for the computation of the molar conductivity of the ternary solution, when the data of the corresponding composite binary systems are known.

The relatively very high accuracy of the method for the NaCl–HCl–H_2O system is well documented by the practically linear course of diagram 2/a proper, on the basis of which the agreement between the single measured and calculated values is better than 1% (within the 1% limit of error, the measured values are always lower than the calculated values).

Therefore, the conductivities of the NaCl–HCl–H_2O ternary system are composed additively of the corresponding conductivities of the binary aqueous solutions, having a concentration equal to the total concentration.* When these corresponding binary NaCl and HCl solutions of identical ionic strength are mixed, *no excess conductivity* $\Delta\varkappa = \varkappa_{\mathrm{real}} - \varkappa_{\mathrm{ideal}}$ is therefore *manifested, i.e. special* excess effects, different to those met in binary solutions, affecting substantially conduction, *do not or not yet occur in the solution. The system behaves as if it were "ideal" with respect to the two initial binary solutions.*

However, that we do not have here naturally any kind of 'ideality', is very well characterized by diagrams 2/b, c and d. With the exception of very small total concentrations ($m_{\Sigma} < 1$—2), for LiCl [6], CsCl [7] and KCl [8], the mixing of binary salt and HCl solutions of identical concentration, corresponding to that of constant total concentration, *produces* already *in a measure increasing with total concentration a* $\Delta\varkappa$ *excess effect.* In the LiCl–HCl–H_2O system containing Li^+ ions with strong positive hydratation, and as has been seen, within the error limit of 1% also in the NaCl–HCl–H_2O system, a *negative* $\Delta\varkappa$ *excess conductivity* while in the cases of the K^+ and Cs^+ ions with negative hydration *a positive excess conductivity increasing with increasing negative hydration is produced.*

Since the 'quasi-ideal behaviour', where excess conductivity $\Delta\varkappa$ is just zero, falls into the vicinity of that ionic radius value ($\sim$1.3 Å) which is the boundary of positive and negative hydration, it can be followed that the *ensuing excess conductivity* $\Delta\varkappa$ *must be connected with a change in hydration*

* In the concentration range, in which the mixing of the binary solutions corresponding to $m_{\Sigma} = \mathrm{const.}$ can be performed, *i.e.* where $m_{\mathrm{salt}} < m_{\mathrm{salt}}^{\mathrm{saturation}}$.

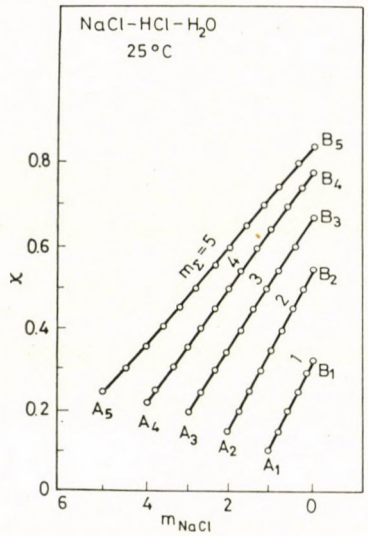

Fig. 2a

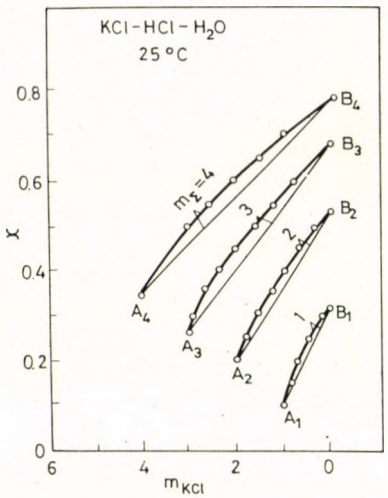

Fig. 2b

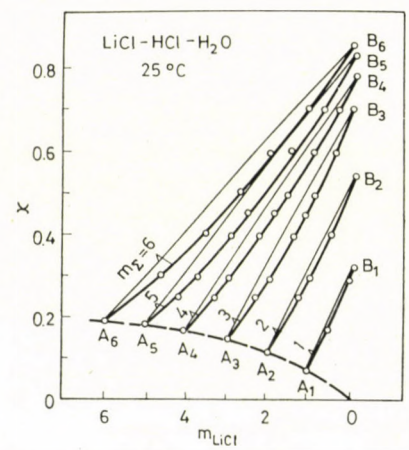

Fig. 2c

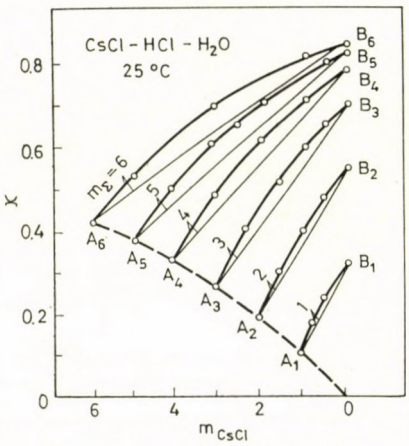

Fig. 2d

conditions, occurring on the mixing of binary solutions, and increasing total concentration.

On the basis of the data of Figs 2/a—2/d, and on the basis of the fact the hydration effects for a given charge are in the case of cations and anions with noble gas configuration practically dependent only on ionic dimension, a correction term can be ordered to the equation written in the general form of type (9)

$$L = f\left(m_{\Sigma}, \frac{m_{\text{salt}}}{m_{\text{acid}}}, r_{\text{cation}}\right) \tag{10}$$

which is characteristic of the change of hydration conditions on mixing, and by the introduction of which the ternary conductivity equation of type (3) will have the general form

$$\varkappa = \varkappa^{\Sigma}_{\mathrm{MeCl}} \frac{m_{\mathrm{MeCl}}}{m_{\Sigma}} + \varkappa^{\Sigma}_{\mathrm{HCl}} \frac{m_{\mathrm{HCl}}}{m_{\Sigma}} + L \,. \tag{11}$$

We start from Figs 2/a—d for the finding of the explicite form of the correction term L. When the points marking $\varkappa$ values corresponding to binary concentrations identical with the m_{Σ} total concentration are connected by a straight line (ideal mixing), the real curve (see *e.g.* for the $MgCl_2$–HCl–H_2O system [9] part a of Fig. 3), and on the other hand the m_{Σ}-dependence of the deviation from the ideal straight line(see *e.g.* for the $MgCl_2$–HCl–H_2O system part b of Fig. 3) can be approximated by each of a parabole.

Therefore, the equation of a parabole, depending on the ratio $\frac{m_{\mathrm{Me}_x\mathrm{Cl}_y}}{m_{\mathrm{HCl}}}$ must be formulated, the maximum of which is a function of $m_{\mathrm{Me}_x\mathrm{Cl}_y}$ (and of m_{HCl}, resp.). This can be achieved by making the maximum independent of m_{Σ} (the expression $\frac{4\, m_{\mathrm{Me}_x\mathrm{Cl}_y} - m_{\mathrm{HCl}}}{m^2}$, where the maximum is always 1, has such properties), and this is then multiplied by the term $\frac{k_1 m_{\Sigma}(k_2 - m_{\Sigma})}{4}$, describing the dependence of the maximum on m_{Σ}.

On the basis of these considerations, the explicit form of L is

$$L = \frac{k_1 m_{\Sigma}(k_2 - m_{\Sigma})\, m_{\mathrm{Me}_x\mathrm{Cl}_y} \cdot m_{\mathrm{HCl}}}{m_{\Sigma}^2} = k_1 (k_2 - m_{\Sigma}) \frac{m_{\mathrm{Me}_x\mathrm{Cl}_y} \cdot m_{\mathrm{HCl}}}{m_{\Sigma}} \tag{12}$$

Thus, the corrected equation (11) will have the following form:

$$\varkappa = \frac{\varkappa^{\Sigma}_{\mathrm{Me}_x\mathrm{Cl}_y} \cdot m_{\mathrm{Me}_x\mathrm{Cl}_y} + \varkappa^{\Sigma}_{\mathrm{HCl}} \cdot m_{\mathrm{HCl}} + k_1 (k_2 - m_{\Sigma})\, m_{\mathrm{Me}_x\mathrm{Cl}_y} \cdot m_{\mathrm{HCl}}}{m_{\Sigma}} \tag{13}$$

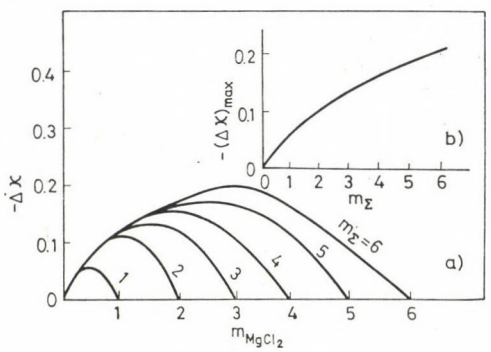

Fig. 3

Table III

	LiCl	NaCl	KCl	CsCl	$MgCl_2$	$CaCl_2$
k_1	−4.1	0.01	4.1	5.5	−46.3	−10.6
k_2	13.9	14.2	14.1	14.3	13.9	14.0

The constants k_1 and k_2 of Eq. (13) must be suitably determined by $\varkappa$-measurement in at least two ternary systems. The k_1 and k_2 values for various metal chlorides are contained in Table III, and their dependence from the ion radius for monovalent cations is shown in Fig. 4.

As evidenced by data in Table III, the value of k_2 is practically constant, and depends only very slightly on the ionic radius. On the other hand, as can be seen from Fig. 4, the dependence of k_1 on the cation radius is divided into *two linear sections*, according to cations with positive or negative hydratation, and the two straight lines intersect just near 1.3 Å, similarly as in the case of the cation radius dependence of the constants B and D of the viscosity equations (2) and (4) in paper [3] (see there Fig. 6), or of the constant a of the conduction equation (4) of the present communication (see Fig. 1). It can be followed from all this that *the value of k_1 reflects the measure of change of ion–solvent interaction, while the value of k_2 that of the change of ion–ion interaction in the mixing process of the two constituent binary aqueous solutions, when m_Σ = constant.*

The good applicability of the ternary conduction equation (13) is documented by Table IV.

However, as has been seen, the corrected ternary conduction equation (13) can be used also theoretically only up to the point, at which the total

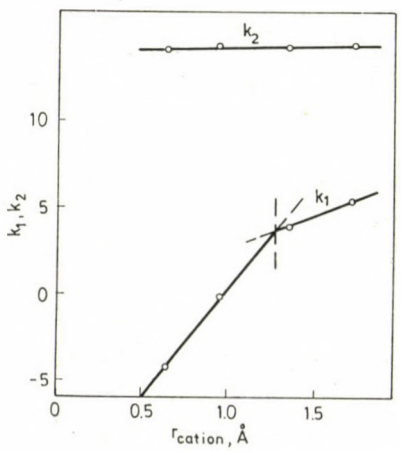

Fig. 4

Table IV

	m_{salt}	m_{acid}	m_{Σ}	$\varkappa_{meas.}$	$\varkappa_{calc.}$	$\Delta\%$
$LiCl–HCl–H_2O$	2	8	10	0.6410	0.6410	−1.09
	5	5	10	0.4350	0.4315	−0.80
	8	2	10	0.2464	0.2578	4.63
	2	6	8	0.6420	0.6287	−2.08
	4	4	8	0.5400	0.4545	1.00
	6	2	8	0.2980	0.3047	2.25
	1	5	6	0.7000	0.7039	0.57
	3	3	6	0.4650	0.4644	−0.13
	5	1	6	0.2640	0.2679	1.48
	1	3	4	0.6000	0.5990	−0.17
	2	2	4	0.4330	0.4363	0.76
	3	1	4	0.3000	0.2940	−2.00
	1	1	2	0.3100	0.3076	−0.77
$MgCl_2–HCl–H_2O$	1	5	6	0.5940	0.6053	1.90
	3	3	6	0.2660	0.2647	−0.49
	5	1	6	0.1160	0.0961	−7.16
	1	3	4	0.5100	0.4993	−1.52
	2	2	4	0.3050	0.2974	−2.48
	3	1	4	0.1800	0.1763	−2.04
	1	1	2	0.2500	0.2559	2.36
$CsCl–HCl–H_2O$	2	8	10	0.7500	0.7601	1.35
	5	5	10	0.6900	0.6869	−0.45
	8	2	10	0.5700	0.5703	0.06
	2	6	8	0.7790	0.7879	1.14
	4	4	8	0.7150	0.7140	−0.14
	6	2	8	0.6070	0.6050	−0.33
	1	5	6	0.8100	0.8086	−0.17
	3	3	6	0.6950	0.6998	0.69
	5	1	6	0.5280	0.5299	0.36
	1	3	4	0.7100	0.7130	0.42
	2	2	4	0.6130	0.6157	0.44
	3	1	4	0.4900	0.4899	−0.02
	1	1	2	0.4040	0.4063	0.82

concentration has attained the saturation concentration of the binary salt solution. The conduction values of solutions falling outside the lined area of the diagram in Fig. 5 can in no way be determined either on the basis of Eq. (11) or (13), because for this the value of $\varkappa^{\Sigma}_{salt}$ ought to be known, and this is impossible in the case of $m^{\Sigma}_{salt} > m^{sat.}_{salt}$.

Therefore, it has been investigated *whether it is possible to calculate the electric conduction* of the single ternary solutions *with the aid of the binary conductivity equation* (1), *proceeding on the basis of the principles established in the calculation of viscosity and using the method of calculation developed* [3], since in principle the application of this method would have no ternary concentration limits.

Our investigations showed that *this approach is not feasible in the case of electric conduction*. The reason for this is that the course of the $\varkappa - m$

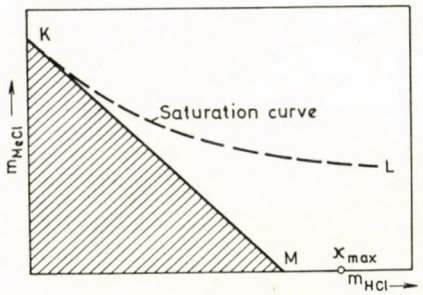

Fig. 5

curves is considerably more complicated than that of the $\eta - m$ curves [3], due to the more complex interactions, caused by the superposed electric field. Thus, an extrapolation on the basis of the binary conductivity equation (1) to concentrations above the saturation concentration cannot be practically realized, since the course of the descending branch of the $\varkappa - m$ curve after the $\varkappa$-maximum cannot be predicted, in contrast to the $\eta - m$ curves. Thus, extrapolation calculations result with increasing salt concentration strongly increasing errors, and in certain cases completely irrealistic results.

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POTENTIODYNAMIC STUDIES WITH PLATINUM CATALYSTS

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Potentiodynamic studies can give valuable information at room temperature on catalytically active metal–hydrogen systems. This method has been used so far for study of smooth and electrolytically deposited metal electrodes. The purpose of the present work was to investigate its extension for 'real' catalyst powders.

Platinum blacks have been prepared by reduction using either hydrogen or sodium borohydride. A method has been developed for potentiodynamic investigation of catalyst powders in an apparatus constructed by the authors, using a potentiostat Type AMEL 551/SU. The potentiodynamic (*i vs. V*) curves obtained have been integrated and the hydrogen content of the catalysts calculated. The applicability of the method and the possible sources of errors have been studied; the effect of the state of the catalyst (preparation, pretreatment, ageing), as well as that of its amount, of the nature of electrolyte and the rate of potential change on the shape of the curves have been determined.

Introduction

With respect to nonstationary polarization methods, the potentiostatic method of electrochemistry has been developed during the last twenty years. It is characterized by generation of a constant potential difference between a working and a reference electrodes using an electronic control unit; the current intensity changes in the period before steady state are measured. A further development is represented by the potentiodynamic method where the electrode potential is varied according to a certain programme (*e.g.* increases or decreases proportionally with time: 'triangular polarization').

This methods was first applied by WILL and KNORR in 1960 [1] for the study of platinum plates and developed further by BÖLD and BREITER [2] as well as by BREITER and GILMAN [3]. Thereafter, BURSHTEIN *et al.* [4] and SKOPIN and SOKOLSKII [5] in the USSR have applied this method for the study of metals.

Data in the literature were initially related to smooth noble metal electrodes, later noble metal layers deposited electrochemically as well as skeletal catalysts have also been investigated. The number of publications concerning powder catalysts is negligibly small. The general opinion of electrochemists is that, due to bad contact and high resistance, it is impossible to

work with powders. Results with respect to disperse electrodes have only been published by ENTINA and PETRII [6, 7].

We attempted to extend the potentiodynamic method well applicable for platinized platinum also for catalyst powders. The importance of doing so is that it could supply information for 'real' catalyst in the range of room temperature; thus the catalyst can be characterized to some extent by determining the amount and nature of sorbed hydrogen having considerable importance in catalytic reactions.

Experimental

1. Catalyst preparation

Platinum catalyst was prepared by reduction with hydrogen and sodium borohydride.

a) *Reduction with hydrogen* [8]

The pH of a solution containing 2 g of platinum as H_2PtCl_6 was adjusted to 8—9 using 20% NaOH solution, then the solution was shaken with hydrogen gas of 1 atm at room temperature. The precipitated catalyst was washed with hot distilled water until a constant potential was reached (potential changes during alkali removal was checked with Pt and calomel electrodes), then dried in a vacuum exsiccator at room temperature, until constant weight was reached.

b) *Reduction with sodium borohydride* [9]

A H_2PtCl_6 solution containing 2 g of platinum has been diluted to 1000 ml. The solution of 4.5 g of $NaBH_4$ in 50 ml of water has been added at 20°C, under mixing. The catalyst was filtered, washed until constant potential with hot water and dried in vacuum exsiccator at room temperature until constant weight was reached.

2. Potentiodynamic measurements

The measurements have been carried out at room temperature, in an apparatus constructed by the authors and shown in Figure 1. A potentiostat Type AMEL 551/SU was used. 11—17 mg of catalyst powder was placed on to the working electrode (A), the apparatus was filled with electrolyte (as a rule, 1 N H_2SO_4) and the hydrogen current to the reference electrode (C) was started. After half an hour the potential of the catalyst was measured (for catalyst stored in dry state this is generally 800—900 mV, *i.e.* in the oxygen range) and the potential was adjusted by cathodic polarization to the value corresponding to the initial value of the potentiodynamic measurement ($E_0 = 50-60$ mV). This was followed by the determination of the potentiodynamic i *vs.* V curve by changing the potential with an appropriate rate (100—1000 mV/min) up to $E_0 + 1000$ mV, then the potential was lowered again to its initial value. This procedure was repeated several times, until the curves became reproducible. The hydrogen peak on these curves (from the start up to about 300 mV; *cf.* Figures 3 and 4) was integrated by weighing the paper. In cases when more than one peak was obtained, corresponding to different types of hydrogen, these were integrated separately. The mean value of three subsequent curves was calculated, then the hydrogen content was determined using Faraday's law (expressed both in C and ml); relating it to the amount of the catalyst, the specific hydrogen content could be determined.

Results and discussion

The most unambiguous characterization of catalysts can be achieved by the measurement of their properties (activity, selectivity, lifetime) in given catalytic reactions. It has long been a justified desire, however, to be

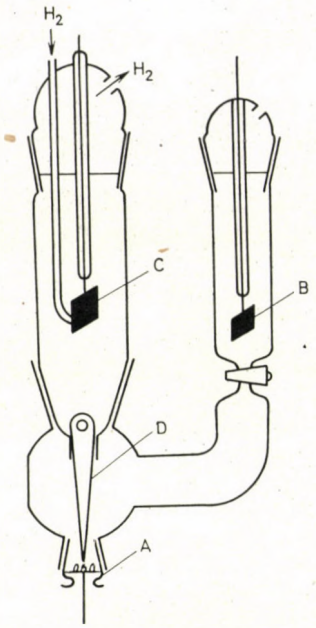

Fig. 1. Cell for potentiodynamic measurements (volume: 80 cm^3). A: Working electrode, Pt plate (appr. 1 cm^2); B: polarizing electrode, Pt plate; C: hydrogen electrode, platinized Pt; D: Luggin capillary

able to characterize catalysts independently of any chemical reaction even if the result is more modest in this case.

It may be of interest how much molecular hydrogen can be activated and bonded by unit surface or unit weight of hydrogenating metal catalysts. The problem what the state of this activated hydrogen is, may be of similar interest. In other words, the amount and the nature (species with different M–H bond strengths) of the total sorbed hydrogen is to be determined.

Correlations have been observed in several cases between the quantitative and 'qualitative' analysis of the metal–hydrogen system and its catalytic activity, especially in reactions of hydrogenation in the liquid phase.

The advantage of potentiodynamic investigations with metal powders is that there is a possibility of direct comparison between them and catalytic properties, whereas this comparison for compact electrodes can be performed only indirectly.

Of relatively simple methods suitable for study of M–H systems, thermodesorption (TPDM) and electrochemical methods can be mentioned. Since noble metal catalysts (except for palladium) contain relatively small amounts of hydrogen (1—3 ml/g), relatively larger samples are required for thermodesorption, where the measurement is carried out throughout a wide temperature range (about 1000°C). The particular importance of electrochemical

methods consists of the possibility to work with 10—20 mg of catalyst, at a given temperature (as a rule, room temperature).

The purpose of the present work was to determine the experimental conditions required for reproducible potentiodynamic measurements with platinum powder catalysts. Having developed the appropriate experimental technique, the amount and 'nature' of hydrogen adsorbed on the catalyst have been determined.

In order to establish the conditions of reproducibility, the effects of the amount, age and pretreatment of the catalyst, as well as of the rate of potential change and the nature of electrolyte on the shape of the curves have been investigated.

1. Ageing of the catalyst

The changes of the potentiodynamic curves of catalysts prepared by hydrogenation and sodium borohydride reduction during storage in 1 N H_2SO_4 have been investigated. The starting potential values (E_0), the rate of potential change as well as C-values corresponding to the first and second peak of the curve have been summarized in Table I. (The third peak corresponding to oxygen adsorption is not discussed here since this was not used for calculations.)

It can be stated that the hydrogen content decreases with the elapse of time: the extent of the decrease was 39% during 4 days of storage for the catalyst prepared with hydrogenation (Figure 2). The decrease is most rapid in the first day: 18 and 23% for the catalysts prepared with sodium borohydride and hydrogenation, respectively.

The ratio between the peaks does not change practically with catalyst ageing (the ratio of the first and the second peak was approximately 2.6 for the hydrogenated platinum and 1.7 for the sample reduced by sodium borohydride), indicating an equilibrium between the two types of hydrogen with different sorption energy.

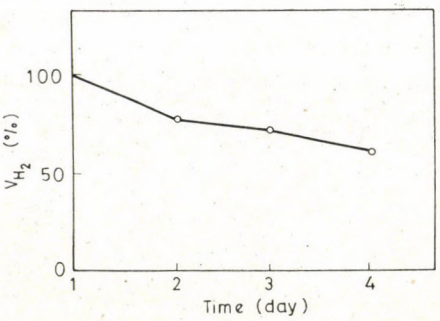

Fig. 2. Hydrogen content of a Pt catalyst prepared by hydrogenation, as a function of time

Table I

Effect of ageing on hydrogen content of Pt catalysts

Method of preparation	Ageing, day	Starting potential, mV	Rate, mV/min	Position of H-peaks, mV		Hydrogen content (*C*)			Ratio of 1st to 2nd peak	Hydrogen content in per cent of initial value
				1st	2nd	1st	2nd	Total		
Reduction by hydrogen	1	20	500	120	—	0.1582	—	0.1582	—	100
	2	35	500	150	275	0.0874	0.0339	0.1213	2.6	77
	3	35	500	140	275	0.0792	0.0330	0.1122	2.4	71
	4	35	500	140	271	0.0716	0.0243	0.0959	2.9	61
Reduction by $NaBH_4$	1	60	100	180	310	0.240	0.137	0.377	1.76	100
	2	60	100	180	300	0.194	0.116	0.310	1.68	82

Table II

Hydrogen content of a Pt-catalyst reduced by $NaBH_4$ in different electrolytes, determined with different starting potentials

Electrolyte	Sample, mg	Starting potential, mV	Rate, mV/min	Hydrogen content						Fraction of different peaks, %		Position of hydrogen peaks, mV	
				C			*C*/g						
				1st	2nd	Total	1st	2nd	Total	1st	2nd	1st	2nd
1 *n* HCl	13.7	50	200	0.158	0.041	0.199	11.55	3.00	14.55	79.5	20.5	139	230
1 *n* H_2SO_4	17.0	50	200	0.125	0.071	0.196	7.37	4.15	11.52	63.7	36.2	135	272
1 *n* HCl	13.7	60	200	0.156	0.046	0.202	11.40	3.36	14.76	77.4	22.6	139	220
1 *n* H_2SO_4	17.0	60	200	0.118	0.077	0.195	6.93	4.53	11.46	60.5	39.5	146	282

The position of the peaks remains also unchanged: for hydrogenated catalyst they appear at 140 and 275 mV and for the other one, at 180 and 300 mV, respectively. Thus — at least during the first four days — ageing does not change the nature (*i.e.* the sorption energy) of the sorbed hydrogen but it does its amount.

2. The influence of the electrolyte

Potentiodynamic curves of platinum reduced by $NaBH_4$ were determined in 1 *N* HCl and 1 *N* H_2SO_4 solutions (Figs 3 and 4). Values calculated from these have been summarized in Table II. (Hereafter, curves having identical starting potentials [50 or 60 mV] are and will be compared.) The specific hydrogen content in HCl has been found to be about 26% higher than that determined in H_2SO_4. The absolute amount of the 'looser' type of hydrogen (first peak) is much higher, that of the more firmly bonded one is lower in HCl than in H_2SO_4.

This difference can probably be attributed to the different sorptivity of Cl^- and SO_4^{2-} ions: different anions replace different amounts of hydrogen on the surface. The ratio between the two peaks, their height and appearance potential also change. Since the fraction of the first hydrogen peak is lower in sulphuric acid (*e.g.* 64% at $E_0 = 50$ mV, as compared with 80% measured in HCl), it can be concluded that the amounts of hydrogen species with various bond strengths depend on the nature of electrolyte. This indicates

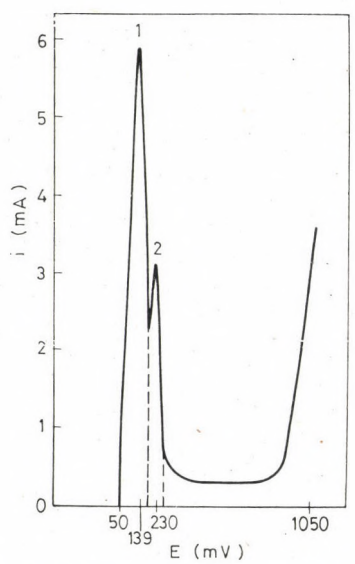

Fig. 3. Potentiodynamic curve of a Pt catalyst prepared by reduction with $NaBH_4$, in 1 *N* HCl. Weight: 13.7 mg; $E_0 = 50$ mV; Rate: 200 mV/min

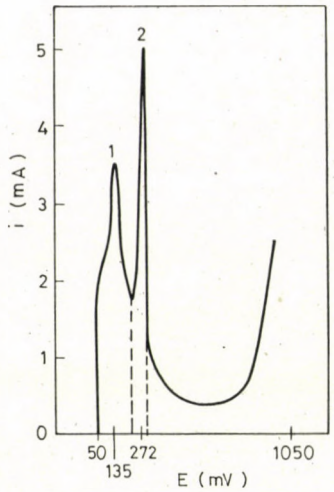

Fig. 4. Potentiodynamic curve of a Pt catalyst prepared by reduction with $NaBH_4$, in 1 *N* H_2SO_4. Weight: 17 mg; $E_0 = 50$ mV; Rate: 200 mV/min

a shift in the equilibrium between the two types of hydrogens, due to the different adsorptivity of different electrolytes. The bond strength of the looser type of hydrogen is not influenced considerably by the nature of the electrolyte; as shown by the nearly identical potential of the first peak: 135 and 146 mV, respectively, in the two types of electrolyte. On the other hand, the adsorption energy of the more strongly bonded hydrogen is higher in sulphuric acid: its potential being 220—230 mV in HCl is shifted into a more positive direction, by about 40—60 mV (*cf.* Table II).

3. Effect of the amount of catalyst and its hydrogen content on the potentiodynamic curves

It has been found that, due to high polarization, the relatively rapid potential changes applied generally for smooth electrodes (1000 mV/min) cannot be used in the case of powders. Evaluable curves were only obtained with lower (< 500 mV/min) rates. The maximum rate is a function of the absolute amount of hydrogen in the sample, thus it is affected by all factors influencing this latter value (the amount of the sample, its relative hydrogen content and the starting potential). In other words, the use of smaller samples or higher starting potential allow to apply higher rates for the same catalyst (Table III). Lower weights are sufficient for catalysts with higher specific hydrogen content, under otherwise identical experimental conditions. The lower limit of the weight of the sample is determined by the amount giving a uniform coverage over the surface of the working electrode. In our case,

Table III

Effect of the rate of potential change on the potentiodynamic curve of Pt prepared by hydrogenation

Sample, mg	Rate, mV/min	Hydrogen content, C			Deviation from average, %		
		1st peak	2nd peak	Total	1st peak	2nd peak	Total
15	100	0.283	0.092	0.375			
	200	0.264	0.084	0.349	3.3	4.5	3.6
11.8	500	0.087	0.034	0.121			
	200	0.098	0.039	0.137	5.9	6.9	6.2

using a platinum plate of about 1 cm^2, the minimum amount necessary was 10 mg of Pt.

It has been found that the rate of potential change influenced the shape of the curves. Table III contains the data of the potentiodynamic curves for the platinum catalyst prepared by hydrogenation, determined with different rates: 100, 200 and 500 mV/min. The difference between hydrogen contents determined by two different rates (mean values) was 3.6 and 6.2%, respectively. This difference can be attributed to the method of evaluation. The relative error is lower for the first peak (loosely bonded hydrogen) and higher for the second one.

For quantitative comparison, it is obviously absolutely necessary to use potentiodynamic curves determined by identical rates of potential change.

Conclusions

The potentiodynamic method used mainly for investigations of compact electrodes so far has been developed further and applied for noble metal powder catalysts.

It was stated that all factors influencing the absolute value of hydrogen content of the sample to be studied (the age, amount, relative hydrogen content of the catalyst) have to be taken into consideration when the experimental conditions for potentiodynamic study are selected. The results have been found to be considerably influenced by the nature of the electrolyte and — using the suggested method of evaluation — the rate of potential change.

It can be concluded that the following factors have to be considered for potentiodynamic investigations of metal powders in practice:

1. The weight of the catalyst sample has to be sufficient to cover the total surface of the working electrode, but most not exceed an upper limit determined by the potentiostat above which, due to the high amount of

hydrogen on the catalyst, it cannot follow the potential supplied by the potential programmer. In our case (surface area of the working electrode: 1 cm^2) the practical sample values were between 10 and 17 mg of Pt powder.

2. The measuring cell has to be prepared in a way that the electrode spaces should be separated but the resistance should not be too high (a liquid film should provide electrical conduction through ground joints).

3. The rate of potential change may be, under given conditions, between 100 and 500 mV/min, depending on the amount and the specific hydrogen content of the sample. Only curves determined by identical rates can be compared.

4. Since the nature of the electrolyte has a considerable effect on the result, its composition and concentration has to be kept constant.

5. In order to eliminate the disturbing effect of dissolved hydrogen, it is advisable to start the potentiodynamic curve from at 50—60 mV.

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INTERACTION OF ACIDS AND SUBSTITUTED ALKANES, II

INVESTIGATION OF HYDROGEN–DEUTERIUM EXCHANGE REACTIONS BETWEEN THE ALKYL CHAIN OF 1-AMINO-5-METHYL-HEXANE AND SULFURIC ACID

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The exchange reactions of 1-amino-5-methyl-hexane and its deuterated derivatives with H_2SO_4 and D_2SO_4 respectively, have been studied. It has been found, in agreement with our earlier results, that only the deuteriums attached to carbon atoms 4 and 6 of the alkyl chain take part in the exchange, with rates of similar magnitude. Performing the exchange in D_2SO_4, all of hydrogen atoms, attached to methyl- and methylene groups adjacent to the tertiary carbon atom, are exchanged to deuteriums.

Our previous papers [1] were concerned with the hydrogen–tritium exchange reactions of iso-alkylamines with concentrated sulfuric acid. We reported kinetic measurements on the T/H exchange between the tritiated derivatives of 1-amino-5-methyl-hexane and concentrated sulfuric acid, under homogeneous reaction conditions. It was found that the tritium atoms attached to carbons 4 and 6 of the alkyl chain exchange at the same rate, in a kinetically first-order process. The tritium attached to the tertiary carbon, *i.e.* to carbon atom 5, is not able to exchange, but splits off as a hydride with the formation of carbonium ion.

This paper reports our measurements on the hydrogen-deuterium exchange of 1-amino-5-methyl-hexane (henceforth: AMH) and its deuterated derivatives, with D_2SO_4 and H_2SO_4, respectively. It has been anticipated that the indication of exchange reactions between hydrogen isotopes by deuterium, unlike the indication by tritium, may also inform on the quantitative features of the exchange, *i.e.* on the number of deuterium atoms introduced into the molecule, and on the statistical distribution of the molecules deuterated to different extents. (It was established in our earlier studies, that there are eight exchangeable hydrogens in 1-amino-5-methylhexane, the hydrogens of the two methyl groups and those of the two methylene groups adjacent to the tertiary carbon atom.)

The studied reactions are summarized in Table I.

Table I

Protium-deuterium exchange reactions of 1-amino-5-methyl-hexane and its deuterated analogues with D_2SO_4 and H_2SO_4, respectively

No.	Reaction
1	AMH-4-d_1 + H_2SO_4 → AMH + $HDSO_4$
2	AMH-6-d_1 + H_2SO_4 → AMH + $HDSO_4$
3	AMH + D_2SO_4 → AMH-d_8 + $DHSO_4$
4	AMH-4-d_1 + D_2SO_4 → AMH-d_8 + $DHSO_4$
5	AMH-6-d_1 + D_2SO_4 → AMH-d_8 + $DHSO_4$
6	AMH-5-d_1 + D_2SO_4 → AMH-d_9 + $DHSO_4$

Abbreviations:

AMH — 1-amino-5-methyl-hexane
AMH-x-d_1 — amino-5-methyl-hexane-x-d_1
AMH-d_8 — 1-amino-5-(methyl-d_3)-hexane-4,4,6,6,6-d_5
AMH-d_9 — 1-amino-5-(methyl-d_3)-hexane-4,4,5,6,6,6-d_6

Notes:

reactions 1 and 2 — see Table II
reactions 3, 4 and 5 — see Table III
reaction 6 — see Table IV

Experimental

General remarks concerning the syntheses of monodeuterated 1-amino-5-methyl-hexane derivatives

The compounds deuterated at carbons 4, 5 and 6 were synthetized through the same intermediates from the precursor 2-methyl-propanol-x-d_1. The percentage of deuteration was calculated from the mass spectra:

$$n_{\%} = \frac{I_{116}}{I_{115} + I_{116}} \; 100$$

where I_{115} and I_{116} are the peak intensities of the molecule ions of undeuterated and monodeuterated compounds, respectively (the effect of ^{13}C of natural occurrence on the intensities has been corrected for).

2-Methyl-propanol-1-d_1. To 7 g (0.167 mol) of lithium aluminium deuteride, suspended in 100 ml of ether, 48 g (0.668 mol) of *i*-butyraldehyde (dissolved in 50 ml of ether) was added dropwise, under intense stirring and cooling. The mixture was boiled for 6 hours, then cooled and decomposed with water. The resulting alcohol was distilled aseotropically, then extracted with ether, dried and distilled. 21 g of product was obtained (yield: 42%); b.p.: 111—118°C.

2-Methyl-propanal-2-d_1. A mixture of deuterium chloride and acetic acid, obtained from 50 ml of D_2O and 10 ml of acetyl chloride was heated on an oil bath at 100—110°C, and 57 g of 1-acetoxy-2-methyl-propene was added dropwise to the mixture under intense stirring. The resulting aldehyde was distilled through a coloumn. 16.5 g of product was obtained (yield: 45.4%); b.p.: 62—66°C.

2-Methyl-propanol-2-d_1 was prepared by reducing 2-methyl-propanal-2-d_1 with $LiAlH_4$, according to the above procedure.

2-Methyl-propanol-3-d_1 was prepared from 3-bromo-2-methyl-propanol according to Ref. 2.

2-Methyl-1-chloropropane-x-d_1. To a mixture of 37.8 g (0.504 mol) of 2-methyl-propanol and 69 g of dimethyl-aniline 72.5 g of thionyl chloride was added dropwise, under intense

stirring and cooling. Thereafter the reaction mixture was heated for 30 minutes at 60—70°C, then 20 ml of hydrochloric acid of 3 : 1 dilution was added, and the stirring was continued while sulfur dioxide was released. When the reaction terminated, the mixture was cooled, diluted with 40 ml of water, the resulting two phases were separated, and the organic phase was dried over $CaCl_2$. 23.6 g of product was obtained (yield: 50.2%); b.p.: 67—71°C.

4-Methyl-pentanol-x-d_1. A metal organic compound was prepared in a usual manner from 13.2 g (0.55 g atom) of magnesium metal and 47.2 g (0.51 mol) of 2-methyl-1-chloropropane-x-d_1 (in 100 ml of ether). Then 44 g of ethylene oxide (dissolved in 100 ml of ether) was added to this mixture. After ten hours the reaction mixture was decomposed with water, and the resulting alcohol was separated by aseotropic distillation. 26 g of product was obtained (yield: 49.6%); b.p.: 75—85°C/60 Hgmm.

1-Chloro-4-methyl-pentane-x-d_1 was prepared from 4-methyl-pentanol-x-d_1 similarly to the preparation of 2-methyl-1-chloropropane. Yield: 72.1%; b.p.: 74—78°C/130 Hgmm.

1-Cyano-4-methyl-pentane-x-d_1. 13.5 g (0.113 mol) of 1-chloro-4-methyl-pentane was reacted for three hours at 80—90°C, under stirring, with 6.6 g of sodium cyanide in 40 ml of dimethylsulfoxide. The reaction mixture was decomposed with 50 ml of water, and the product was extracted with ether. 11.5 g of product was obtained (yield: 91%); b.p.: 80—84°C/30 Hgmm.

1-Amino-5-methyl-hexane-x-d_1. A mixture of 11.5 g (0.102 mol) of 1-cyano-4-methyl-pentane-x-d_1 and 20 ml of abs. ethanol was added dropwise to 13.5 g of finely suspended and vigorously stirred sodium metal (in 170 ml of abs. toluene). The reduction takes place at the boiling point of toluene. The excess of sodium metal was reacted with further amounts of abs. ethanol, and then, after cooling, the reaction mixture was decomposed with water. The resulting amine was distilled aseotropically, neutralized with hydrochloric acid, and the obtained solution of the salt was evaporated to dryness under reduced pressure. 12.3 g of salt was obtained (yield: 79%), which can be recrystallized from 240 ml of benzene. M.p.: 191—192°C (twice recrystallized).

Hydrogen isotope exchange between sulfuric acid and 1-amino-5-methyl-hexane (general method)

Sulfuric acid was used in large excess with respect to the amine, so that the initial amount of the hydrogen isotope in the sulfuric acid practically did not vary during the exchange.

0.38 g (2.5 mmol) of 1-amino-5-methyl-hexane hydrochloride was dissolved in 5 ml of sulfuric acid. The released hydrogen chloride gas was removed by vacuum. The vessel containing the reaction mixture was thermostated at the desired temperature, and the reaction was followed by analysing the withdrawn samples.

Processing of the sample. 0.5 ml samples were taken and poured into ice-water, then 9 ml of a 10% sodium hydroxide solution was added under cooling. The released amine was extracted with ether, dried on solid potassium hydroxide, filtered, and neutralized with 1 ml of 1 *N* hydrochloric acid. The resulting salt solution was evaporated to dryness, 2 ml of water was added, and the evaporation was repeated (in order to remove the deuterium isotopes in the amino group). The dry salt was crystallized from benzene, and its deuterium content was determined by mass spectrometry.

The concentrations of the molecules containing different numbers of deuterium isotopes as a result of exchange reactions can be expressed in percentage form: $c \cdot n\%$ — where c is the amine concentration in the solution, and $n\%$ is the percentage amount of deuterium-containing molecules. In the reaction c is constant, and only $n\%$ varies.

Discussion

The order of hydrogen isotope exchange reactions between the alkyl hydrogens and sulfuric acid

As discussed in our previous papers, in sulfuric acid the exchange of the tritium atoms attached to carbons 4 and 6 of the alkyl chain of AMH is a pseudomonomolecular, *i.e.* kinetically first-order, process (sulfuric acid is

present in large excess). The results of measurements performed at different temperatures indicate that the activation energies for the tritium atoms attached to carbons 4 and 6, respectively, are the same.

The experiments with AMH-4-d_1 and AMH-6-d_1 confirmed the above results: in sulfuric acid the exchange of deuterium atoms attached to carbons 4 and 6 is also a pseudo-monomolecular process. The results of the investigations are given in detail in Table II. It is to be noted that the rate constants given in the table are similar in magnitude to the k values measured for the T/H exchange processes of tritiated compounds under the same conditions [1]. It is also worth noting that, under similar conditions, no D/H exchange was observed for the AMH-5-d_1 derivative, also in good agreement with the previous results [1].

The deuteration of AMH-4-d_1, AMH-5-d_1 and AMH-6-d_1 in deuterosulfuric acid have also proved to be pseudo-monomolecular reactions (Tables III and IV), despite the fact that eight deuteriums are incorporated simultaneously into the molecule.

Investigating the exchange between iso-butane-1-d_1 and sulfuric acid, OTVOS *et al.* [3] found that this reaction is also a first-order process, preceded by an initial period. In their opinion "the first order rate of exchange of iso-butane-1-d_1 with acid protons indicates that the reaction is proceeding in a steady state. It reaches the steady state after an initial period of increasing specific reaction rate".

Table II

D/H exchange between the deuterated derivatives of 1-amino-5-methyl-hexane (AMH-4-d_1 and AMH-6-d_1) and H_2SO_4 ($c = 98.07\%$) at 25.3°C

No.	Reaction time, min	AMH-4-d_1 n%	AMH-6-d_1 n%
1	0	91	78
2	30	85	74
3	90	76	66
4	180	64	55
5	300	52	42
6	420	39	33

$$n\% = \frac{I_{116}}{I_{115} + I_{116}} 100$$

AMH-4-d_1 — $\tau_{1/2} = 352$ min
$k = 3.27 \cdot 10^{-5}\ s^{-1}$

AMH-6-d_1 — $\tau_{1/2} = 336$ min
$k = 3.45 \cdot 10^{-5}\ s^{-1}$

No exchange was observed under similar conditions between AMH-5-d_1 and sulfuric acid

Table III*

Deuteration of 1-amino-5-methyl-hexane derivatives in D_2SO_4 (D-content 99%, acid content 96%) at 25.3°C

Reaction time, min	AMH $\frac{I_{sd}}{I_{sd}+I_{od}}$	AMH-4-d_1 $\frac{I_{sd}}{I_{sd}+I_{od}+I_{id}}$	AMH-6-d_1 $\frac{I_{sd}}{I_{sd}+I_{od}+I_{id}}$
0	0.00	0.00	0.00
30	—	0.01	0.01
60	—	0.020	0.025
120	0.04	0.04	0.04
210	—	0.07	0.075
240	0.07		
330	—	0.10	0.09
360	0.10		
480	0.13		
510	—	0.14	0.13
600	0.18		

* Under the given conditions all exchangeable hydrogens of the molecules entered the reaction are replaced by deuterium atoms. Thus the only product is the octadeuterated derivative; more precisely, the relative amounts of hexa- and hepta-deuterated molecules correspond to the statistical frequency arising from the less than 100% D-content of sulfuric acid.

Table IV

The joint deuteration of 1-amino-5-methyl-hexane and 1-amino-5-methyl-hexane-5-d_1 in D_2SO_4 (D-content 98.0%, acid content 95%) at 25.0°C

$$n_{\%} = \frac{I_{115} + I_{116}}{I_{115} + I_{116} + I_{122} + I_{123} + I_{124}} 100$$

Reaction time, h	$n_{\%}$	I_{115}/I_{116}
0	100	1.03
4	97.0	1.05
8	93.0	1.04
12	89.5	1.04
23	79.6	1.02
28	75.5	1.06
33	73.2	1.03

$$k = 2.81 \cdot 10^{-6}\ s^{-1}$$

It appears to be probable that the initial period observed by OTVOS *et al.* arises from the time necessary for the saturation of sulfuric acid with iso-butane, and the D/H exchange is not a steady state process, but actually, corresponding to the observations, a pseudo-monomolecular process.

The synchronous exchange of methyl and methylene hydrogen atoms, adjacent to tertiary carbon atom

Investigating the exchange between AMH and D_2SO_4 we found that in the reaction mixture only the deuterated AMH derivative of mass number 123 appeared in addition to the starting compound of mass number 115 (Table III), *i.e.* eight hydrogens of the alkyl chain exchange simultaneously with deuteriums. As indicated in our previous papers, the hydrogens of the methyl and methylene groups adjacent to the tertiary carbon atom take part in the exchange. Accordingly, the exchange can be represented by the equation

$$AMH + n\,D_2SO_4 \rightarrow \begin{matrix} D_3C \\ D_3C \end{matrix}\!\!\diagup CH—CD_2—(CH_2)_3—\overset{+}{N}\!\!\begin{matrix} \diagup \\ \diagdown \end{matrix}$$

The process between D_2SO_4 and isobutane, resulting in the synchronous exchange of all primary hydrogen atoms, was first observed by OTVOS *et al.* and STEVENSON *et al.* [3, 4].

In this field extensive research work was performed by BURWELL and GORDON [5—8], KURSANOV, SETKINA, STERLIGOV, LIBERMAN and MESHCHERYAKOV [9—12], and by HOFFMAN [13]. They have shown that this process is not localized to hydrogens attached to carbons adjacent to tertiary carbon atoms, but may extend to the whole molecule (in our case the hydrogens attached to carbons 1, 2 and 3 are desactivated by the protonated amino group). The hydrogen attached to the tertiary carbon, *i.e.* 'tertiary hydrogen', is the only proton that was inert to exchange in sulfuric acid.

Concerning the mechanism of synchronous hydrogen exchange, it was suggested that the exchange proceeds after a preliminary oxidation of the isoalkane, *via* carbonium ion. Finally the carbonium ion is transformed to isoalkane abstracting a hydride from a tertiary carbon atom.

This suggestion is based on the experimental fact that the tertiary carbon of iso-paraffins may be oxidized to carbonium ion (while sulfuric acid is reduced into sulfurous acid), and on the phenomenon of hydride ion transfer observed by BARTLETT *et al.* [14] between the tertiary carbons of isopentane and tert-butyl chloride in the presence of $AlBr_3$.

In our opinion for the present case this mechanism is very unlikely for the following reasons.

1) The kinetic measurements indicate unanimously a first order reaction with no initial period.

2) The fact that upon one activation step eight deuteriums are incorporated into the AMH molecule is incompatible with a H/D exchange *via* carbonium ions. If the deuterons were introduced in consecutive addition processes, the carbonium ion molecules should be deuterated to different degrees. As all carbonium ions have chances to incorporate hydride ion, the degree of deuteration of the carbonium ion molecules must be reflected in the recombined AMH molecules. The degree of deuteration of the carbonium ion molecules could be the same as that of sulfuric acid only if all elimination and addition reactions took place instantaneously. This is unlikely.

3) Using the isotope dilution method we could follow the consumption of AMH by the hydride abstraction process of tertiary hydrogen atom in sulfuric acid [24]. On the basis of AMH consumption kinetics we observed the isotope effect of tertiary deuterium and tritium atoms: $k_H/k_D = 1.75$ and $k_H/k_T = 2.40$. The fact that isotope effect can be determined on the basis of AMH consumption means that the formation of carbonium ion and its transformation to the nonamine type product are synchronous processes and carbonium ions cannot take part in the hydrogen exchange.

Based on recent investigations of the reactions between alkanes and super-acids (OLÁH *et al.* [15—21] and HOGEVEEN *et al.* [22, 23]) it may be assumed that the hydrogen isotope exchange in sulfuric acid proceeds through non-classical carbonium ions, *i.e.* the activated complex of the reaction contains the protonated C–H σ-bond.

The experimental data given in our previous paper indicate that the tritium atoms attached to carbons 4 and 6 of AMH exchange with the same activation energy. Now, our present experiments have shown that in one molecule the protium atoms attached to carbons 4 and 6 are replaced simultaneously, upon one activation step, by deuterium atoms. Accordingly, it is probable that in the transition complex the proton of acidic origin belongs equally to the methyl and the methylene groups adjacent to the tertiary carbon. This is possible only in the case when it is located in the space surrounded by the methyl and methylene groups. Regarding that the potential energy of the given space arises from the repulsion of the bonding electrons forming the surface of the space, the electric properties of the space are favourable for the proton. The resulting 'non-classical carbonium ion' is stabilized further upon solvation by sulfuric acid molecules. Thus, the protonated methyl or methylene groups act under the given conditions, as a Brönsted acid, and may participate in a fast proton exchange according to an association mechanism.

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INTERACTION OF ACIDS AND SUBSTITUTED ALKANES, III

KINETIC ISOTOPE EFFECT IN THE HYDRIDE ABSTRACTION OF TERTIARY HYDROGEN FROM ISO-ALKANES

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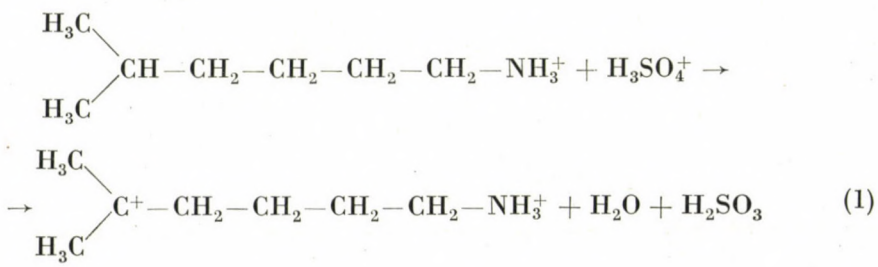
The oxidation of the tertiary carbon atom (C_5) of 1-amino-5-methylhexane into carbonium ion has been studied in 97.5% sulfuric acid solution at 80.6°C. The hydride ion is removed from the tertiary carbon by sulfuric acid, and the latter is reduced into sulfurous acid. Hydride abstraction is a first-order kinetic process since it proceeds in a large excess of sulfuric acid. The corresponding deuterium and tritium derivatives have also been studied to determine the kinetic isotope effects. We have obtained $k_H/k_D = 1.75$, $k_H/k_T = 2.40$, and, from the Swain equation, $\ln(k_H/k_T)/\ln(k_H/k_D) = 1.56$ (theoretical: 1.44). The kinetic equations also support that in the hydride abstraction of the tertiary hydrogen in sulfuric acid there is no exchange with the protons of the acid.

We have reported [1, 2] on the exchange observed between the hydrogen isotopes attached to carbon atoms 4 and 6 of the alkyl chain of 1-amino-5-methylhexane and the protons of concentrated sulfuric acid. However, under similar conditions the hydrogen attached to carbon 5, *i.e.* to the tertiary carbon, is not exchanged, but splits off in hydride form. This process can be represented by the equation



$$\begin{array}{l} H_3C \diagdown \\ \qquad\quad CH-CH_2-CH_2-CH_2-CH_2-NH_3^+ + H_3SO_4^+ \rightarrow \\ H_3C \diagup \end{array}$$

$$\rightarrow \begin{array}{l} H_3C \diagdown \\ \qquad\quad C^+-CH_2-CH_2-CH_2-CH_2-NH_3^+ + H_2O + H_2SO_3 \\ H_3C \diagup \end{array} \qquad (1)$$

As can be seen, the abstraction of hydride ion involves the oxidation of the tertiary carbon and the reduction of sulfuric acid into sulfurous acid.

This work is concerned with the determination of the kinetic isotope effect in the hydride abstraction of the hydrogen isotopes attached to carbon 5.

Experimental

General. The syntheses of 1-amino-5-methylhexane (A_H), 1-amino-5-methylhexane-5-^{2}H (A_D), and 1-amino-5-methylhexane-5-^{3}H (A_T) have been described [3, 4]. Actually, the hydrochlorides of these amines were prepared, which can be crystallized from benzene; mp.: 190—192°C.

The measurements were carried out in 97.5 $\pm$ 0.25% sulfuric acid at 80.6°C. The starting amine concentration of the sulfuric acid solutions was ca. 0.5 mol/l.

Mass spectra were taken on an MI-1305 mass spectrometer, and the activity measurements were performed on a PACKARD TRI-CARB Scintillation Spectrometer Model 574.

The rate constants and the isotope effects were calculated by the method of least squares.

Oxidation of 1-amino-5-methylhexane in sulfuric acid

The consumption of A_H was determined by isotope dilution technique in the following manner. 0.3797 g of A_H hydrochloride was dissolved in 5 ml sulfuric acid. The hydrogen chloride released was removed in vacuum. The reaction mixture was thermostated at 80.6°C. Samples of 0.7 ml volume were periodically removed from the reaction mixture and were added to identical volumes of a solution of 1-amino-5-methylhexane-6-^{3}H with a known concentration (specific activity: 318400 dpm/mg). The amine liberated from this mixture with a 10% sodium hydroxide solution was extracted with ether, dried with potassium hydroxide powder, neutralized with hydrochloric acid, evaporated to dryness, and crystallized from benzene. From the specific activities of the resulting amine hydrochloride samples, the actual concentrations of A_H were calculated, and from the diminution of the concentration with time, the rate constant of the process was determined (the results are given in Fig. 1).

Oxidation of 1-amino-5-methylhexane-5-^{2}H (A_D) and 1-amino-5-methylhexane (A_H) in sulfuric acid

0.2250 g of a mixture of A_D and A_H hydrochlorides was dissolved in 3 ml sulfuric acid. In this solution the concentration of A_H was 0.238 mol/l, and the concentration of A_D was 0.240 mol/l. The reaction mixture was thermostated at 80.6°C, and samples were periodically taken. The unreacted amine was separated from the samples by the manipulations given above, and the ratio I_{115}/I_{116} was determined by mass spectroscopy. From the original concentration of A_H and from the rate constant of its oxidation, the actual concentrations of A_H at the various phases of the reaction were calculated. These concentrations and the ratio I_{115}/I_{116} permits to determine the concentration of A_D, and on the basis of the diminution of this concentration with time the rate constant of the oxidation of A_D was calculated. The results are given in Fig. 1.

Oxidation of 1-amino-5-methylhexane-5-^{3}H (A_T) and 1-amino-5-methylhexane (A_H) in sulfuric acid

0.3940 g of a mixture of A_T and A_H hydrochlorides (specific activity: 19700 dpm/mg) was dissolved in 5 ml sulfuric acid. The reaction mixture was thermostated at 80.6°C. The amine was separated in the form of its hydrochloride from the samples taken, and its specific activity was measured. The actual concentrations of A_H were evaluated from the rate constant of the oxidation of A_H and the total activity was calculated by multiplying the concentration of A_H by the measured specific activity. From the diminution of the total activity with time the rate constant of the oxidation of A_T was calculated. The results are shown in Fig. 1.

Discussion

Kinetic evaluation of the experimental results

Kinetically the oxidation can be regarded as a first-order process with respect to the amine component (Fig. 1). Taking into account that under the given experimental conditions $[H_2SO_4] \gg [A_H]$ and $[H_2SO_4] = \text{const.}$, the

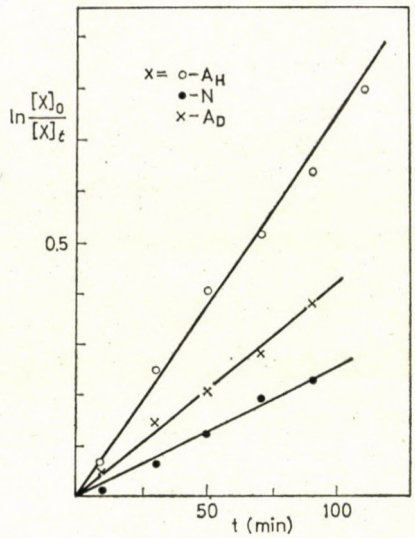


Fig. 1. Plot of $\ln([X]_0/[X]_t)$ *vs.* time for 1-amino-5-methylhexane labelled at carbon 5 with hydrogen isotopes

diminution of the amine concentration with time can be expressed by the equation

$$\ln \frac{[A_H]_0}{[A_H]_t} = k_H [H_2SO_4]\, t = k'_H t \tag{2}$$

Equation (2) can also be used to express the change in the concentration with time of the deuterium-labelled amine (A_D) provided that the left-hand-side contains the corresponding concentrations of A_D.

For the tritium-labelled derivative (A_T) the left-hand-side of Eq. (2) should contain the specific activity related to unit volume, $-N$ (the concentration of A_T is so low that it can be neglected). In a volume of 1 l, $N = [A_H]_t M_s\, 1000n$, in units of dpm/l, where $[A_H]_t$ is the concentration of the amine at time t, M_s is the molecular weight, and n is the specific activity of the amine (dpm/mg).

Performing the appropriate algebraic manipulations, we obtain for the isotope effect the following equations:

$$\ln \frac{[A_H]_0}{[A_H]_t} = \frac{k_H}{k_D} \ln \frac{[A_D]_0}{[A_D]_t} \tag{3}$$

$$\ln \frac{[A_H]_0}{[A_H]_t} = \frac{k_H}{k_T} \ln \frac{N_0}{N_t} \tag{4}$$

The advantage of using Eqs (3) and (4) is that the ratios k_H/k_D and k_H/k_T are independent of the concentration of sulfuric acid, and thereby give immediately the isotope effect.

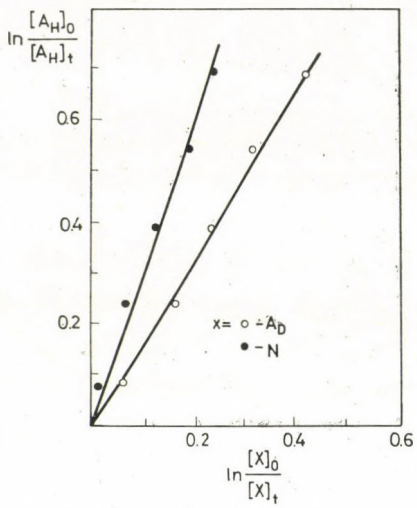


Fig. 2. Plot of $\ln([AH]_0/[AH]_t)$ *vs.* $\ln([X]_0/[X]_t)$ according to Eqs (3) and (4)

The plots according to Eqs (3) and (4) are shown in Fig. 2. The isotope effects calculated from these equations are as follows:

$$\frac{k_H}{k_D} = 1.15$$

$$\frac{k_H}{k_T} = 2.40$$

It is to be noted that $k'_H = 1.18 \times 10^{-4}\ s^{-1}$.

The hydrogen isotope effects were investigated theoretically by SWAIN *et al.* [5]. For the cases when isotope substitution affects only the vibration of the bond, and only the zero-point energies are different (all other effects can be neglected) they derived the equation

$$\ln(k_H/k_T) = 1.44 \ln(k_H/k_D).$$

Our data yield the ratio $\ln(k_H/k_T)/\ln(k_H/k_D) = 1.56$. From a comparison to the values obtained by JONES [6] for reactions of different types it can be concluded that the SWAIN equation is valid to a good approximation also for the reaction type under study.

Correlation of hydride abstraction and hydrogen exchange

STEVENSON *et al.* [7, 8] have found in connection with the hydrogen exchange between iso-alkanes and deuterated sulfuric acid that the maximum number of hydrogen atoms exchanged in any molecule is one less than the total. This non-exchanged hydrogen is the tertiary hydrogen. If the molecule

contains two tertiary carbons, the tertiary hydrogens may also be exchanged. Investigating the reactivities of tertiary hydrogens, KURSANOV *et al.* [18] have found that an isomerization of the alkyl chain may also involve the exchange of the tertiary hydrogen.

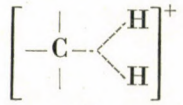
In super-acids (DSO_3F–SbF_5 or DF–SbF_5), in the case of iso-alkanes, the tertiary hydrogen has been found to be the most reactive, both in hydrogen exchange and in hydride abstraction processes [9, 10, 11].

We observed the abstraction of the hydrogen isotope attached to the tertiary carbon, but no exchange with the protons of sulfuric acid. This fact is also supported by the decreasing order of the rate constants of the hydride abstraction processes:

$$k_H > k_D > k_T$$

Mechanism of hydride abstraction

The hydride abstraction of alkane hydrogens in super-acids has been studied extensively by OLÁH *et al.* [9, 10] and HOGEVEEN *et al.* [11, 12, 13]. In their opinion, the carbon–hydrogen bond is protonated under these conditions, and a triangular three-center carbonium ion (A) is formed:



(A)

which can be decomposed into a classical carbonium ion and a hydrogen molecule, or into the starting hydrocarbon and a proton.

From the aspects of the hydride abstraction under study one must attribute relevance to the assumption of LUKAS [14] according to which SbF_5 itself, *i.e.* the Lewis acid, may also act as hydride acceptor. The correctness of this assumption has been proved experimentally by HOGEEVEN, LUKAS and ROOBEEK [13], by the oxidation of methane into methyl cation in SbF_5.

In the hydride abstraction in sulfuric acid the protonation of the tertiary carbon–hydrogen bond must be excluded for the following reasons.

(1) Under the conditions of hydride abstraction no exchange can be observed between the tertiary hydrogen and the protons of sulfuric acid.

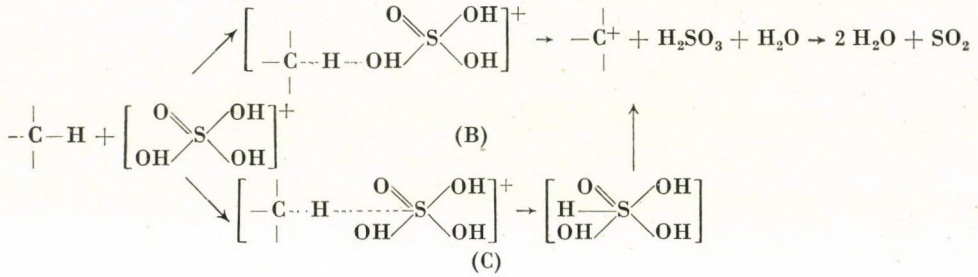
(2) The product formed in the hydride abstraction besides the oxidized derivative is sulfur dioxide instead of hydrogen.

It is known that the sulfuric acid molecule is amphoteric in character, and in concentrated sulfuric acid autoprotolysis takes place [17]:

$$H_2SO_4 + H_2SO_4 \rightleftharpoons H_3SO_4^+ + HSO_4^-$$

The ion product of the autoprotolysis of sulfuric acid is $K = 2 \times 10^{-4}$.

On the basis of the above experimental data it can be assumed that in the given hydride abstraction process the hydride acceptor is the positively charged oxygen or sulfur atom of the protonated sulfuric acid molecule. The linear activated complex (B or C) is a result of a 'face attack', as has already been suggested by COPE *et al.* and DENO *et al.* [15, 16] for other cases:



It also follows unanimously from the above that under the given conditions it is a prerequisite of hydride abstraction that the alkane be unprotonated, unlike in the hydrogen exchange between alkanes and sulfuric acid, in which the activated complex is the protonated form:

$$[C_nH_{2n+3}]^+$$

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MICROBIAL TRANSFORMATION OF STEROIDAL 3-OXO-4-HYDROXY-4-ENES

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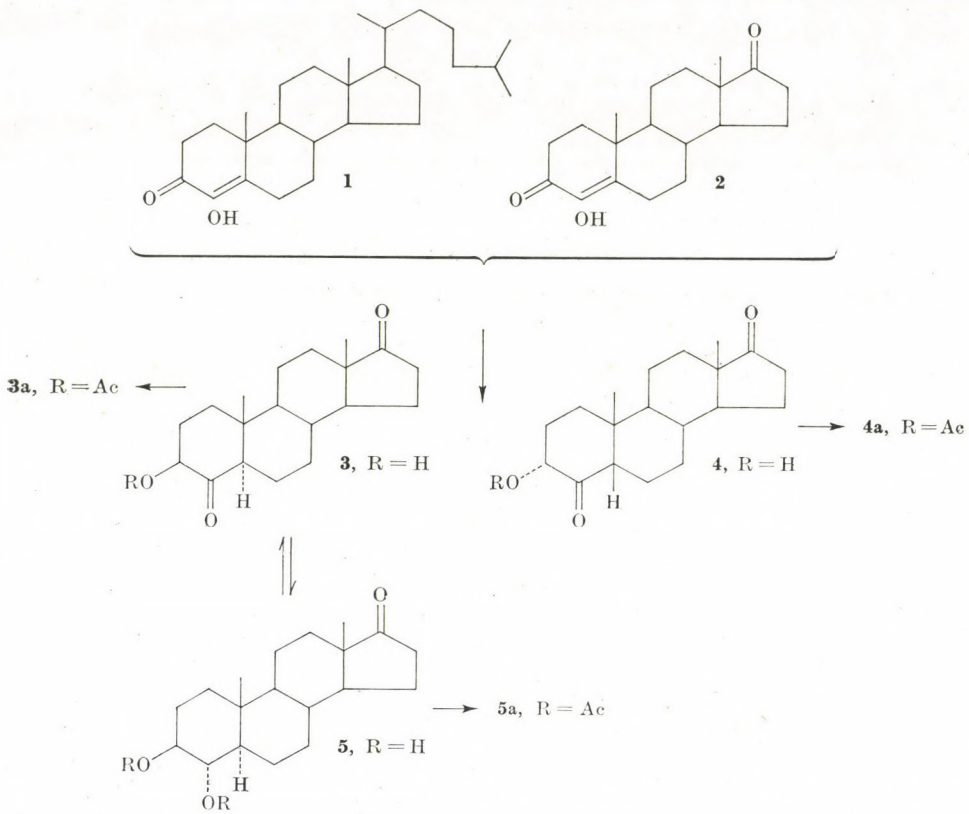
Microbial transformation of 4-hydroxy-4-cholesten-3-one (**1**) and 4-hydroxy-4-androstene-3,17-dione (**2**) with a culture of *Mycobacterium phlei* under aerobic conditions afforded 3β-hydroxy-5α-androstane-4,17-dione (**3**), 3α-hydroxy-5β-androstane-4,17-dione (**4**) and 3β,4α-dihydroxy-5α-androstan-17-one (**5**). The structures of these products were elucidated by IR, NMR and MS, as well as by the investigation of the corresponding 3,4,17-triol derivatives.

A study of the enzyme system converting steroids in *Mycobacterium phlei* (isolated in our Institute [1]) revealed that 3-oxosteroids which have an electronegative substituent at C-4 undergo reductive transformation even under aerobic conditions. Eliminating the electronegative substituent, they are converted into 3-oxo-1,4-diene derivatives [2, 3]. 4-Hydroxy-4-cholesten-3-one (**1**) and 4-hydroxy-4-androstene-3,17-dione (**2**) were transformed under the conditions used previously [2]. At a substrate concentration of 200 μg/ml, both **1** and **2** were converted into the same three products (**3**, **4** and **5** in a ratio of 5 : 5 : 1) in 24 hr, which were extracted with ethyl acetate from the fermentation broth and separated by column chromatography (Scheme 1).

Lack of the UV absorption, characteristic of conjugated ketones, in conjunction with the red colour produced by alkaline 2,3,5-triphenyltetrazolium chloride, suggested the presence of an α-ketol system in compounds **3** and **4**. In the IR spectrum of **3** and **4** strong absorption bands were present, assigned to a hydroxyl and two oxo groups (one in a five-membered and another in a six-membered ring), respectively. Upon acetylation at room temperature in pyridine, ester bands appeared instead of the hydroxyl bands in IR of both acetates (**3a** and **4a**, Scheme 1).

The IR spectrum of **5** was characterized by one keto band (in a five-membered ring) and a hydroxyl band; the latter was transformed into ester band in the IR spectrum of **5a**, obtained by acetylation of **5**. The mass of their molecular ions revealed that **3** and **4** were formed from **2** by the uptake of two, while **5** by the uptake of four hydrogen atoms. Molecular oxygen con-

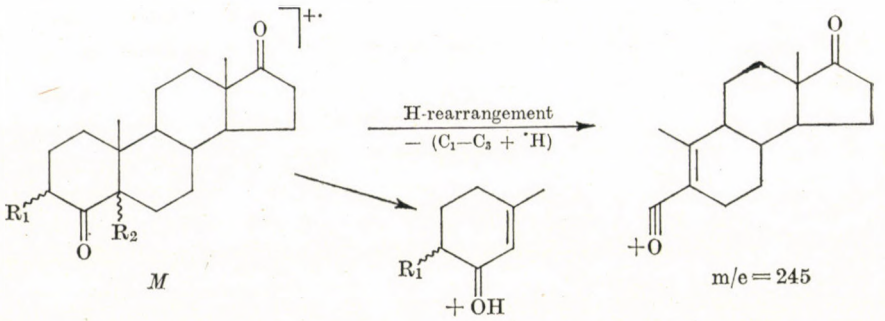


Scheme 1. Microbial transformation of 4-hydroxy-4-cholesten-3-one (**1**) and 4-hydroxy-4-androstene-3,17-dione (**2**)

verted **3** and **4** into 4-hydroxy-4-androstene-3,17-dione (**2**) in alkaline medium. Compounds **3** and **4** gave 5-androstene-4,17-dione in ethanolic sulfuric acid [4].

The 3-hydroxy-4-oxo structure of the α-ketols was confirmed by their mass spectra. The MS fragmentation of epimeric 5α- and 5β-androstan-4-ones was extensively studied [5]. The similarity of the mass spectral behaviour of these two compounds with that of **3**, **3a**, **4** and **4a**, respectively, suggested that **3** and **4** might also be epimeric 4-oxosteroids.

The fragmentation pattern of compounds **3**–**4a** is depicted in Scheme 2. Ion *a* refers to the characteristic ion m/e = 111 of 4-oxosteroids (R_1 = H) [5, 6]. Formation of ion m/e = 245, a well-known fragmentation process of 4-oxosteroids, proves that in each the compounds **3**–**4a** the hydroxyl and acetoxyl groups, respectively, are positioned at C-3. This assignment was confirmed by the mass spectrum of the partially deuterated **4**, as in the case of ion m/e = 245 a considerable part of the label has been lost, whereas ion *a* had the same deuterium content as the molecular ion.



Scheme 2. Fragmentation pattern of compounds **3**, **3a**, **4** and **4a**

The relative abundances of the ions depicted in Scheme 2 are listed in Table I. Based on analogous data of 5α- and 5β-androstan-4-ones, 5β configuration can be assigned to compounds **4** and **4a**, and 5α configuration to **3** and **3a**. On the basis of ZÜRCHER's data [7], the chemical shifts of the C-19 methyl signals in the NMR spectra of **3** and **3a** ($\delta = 0.74$ and 0.80, respectively) are in accordance with a 4-oxo-5α-androstane partial structure. The proton signal in the spectrum of **3a** (part X in an ABX spectrum, $\delta = 5.17$) can represent an *axial* proton, because of the broad 18 Hz band. Based on these data, the structure of 3β-hydoxy-5α-androstane-4,17-dione is proposed for the α-ketol **3**, which is confirmed by its reduced derivatives *(vide infra)*.

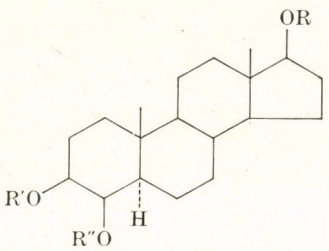
In the NMR spectra of **4** and **4a**, C-19 methyl signals appeared at 1.15 and 1.18, consequently a 4-oxo-5α-androstane partial structure was ruled out. As according to MS data both **4** and **4a** are 4-oxosteroids, they must

Table I

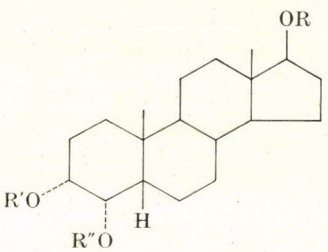
MS data of the ions depicted in Scheme 2

Compound	Substituents		Ions				
			M		m/e = 245	*a*	
	R_1	R_2	m/e	I(%)	I(%)	m/e	I(%)
3	β-OH	α-H	304	100	29	127	1
4	α-OH	β-H	304	100	12	127	5
3a	β-$OCOCH_3$	α-H	346	90	82	169	5
4a	α-$OCOCH_3$	β-H	346	100	3.3	169	22
Compound*					m/e = 231		
5α-androstan-4-one			274	83	39	111	43
5β-androstan-4-one			274	100	6.5	111	77

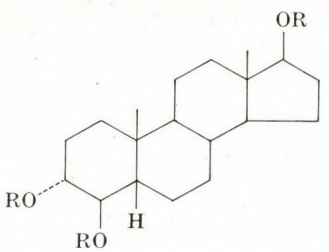
* The relative abundances of these compounds were taken from Figs 3 and 4 in Ref. [5]



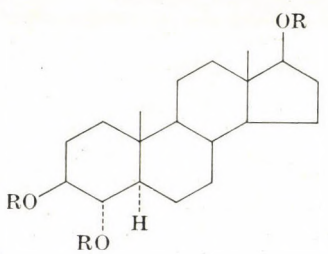
6, R, R', R'' = H
6a, R'' = H; R, R' = Ac
6b, R, R', R'' = Ac
6c, R = H; R' R'' = $C(CH_3)_2$



7, R, R', R'' = H
7a, R'' = H; R, R' = Ac
7b, R, R', R'' = Ac
7c, R = H; R' R'' = $C(CH_3)_2$



8, R = H
8b, R = Ac



9, R = H
9b, R = Ac

Scheme 3. Androstane-3,4,17-triols and their derivatives

have the partial structure of 4-oxo-5β-H. In the NMR spectrum of **4a**, the proton signal representing part X of an analogous ABX spectrum, appeared as a triplet. The 18 Hz wide band indicates an *axial* proton. Accordingly, the structure of 3α-hydroxy-5β-androstane-4,17-dione was assigned to the α-ketol **4**, and this was confirmed by investigation of 3,4,17-trihydroxy-androstanes **6**—**9** (Scheme 3), prepared with sodium borohydride from the α-ketols **3** and **4** and from the dihydroxyketone **5**.

The reduction of **3** afforded only the triol **6**. The same triol was the main product in the analogous reduction of compound **2**. The reduction of **4** gave the triols **7** and **8**, in a ratio of 4 : 1, while **5** could be reduced to **9**. The 5α configuration in **6** and the 5β configuration in the triols **7** and **8** were taken evident from the MS and NMR data for **3**, **3a**, **4** and **4a**, respectively. It is well known, that reduction of 17-oxosteroids with sodium borohydride results in 17β-hydroxy compounds. On the other hand, the analogous reduction of 4-oxo-5α-steroids affords mainly *axial* 4β-hydroxy derivatives [8].

Acetylation of the 5α-triol **6** and the 5β-triol **7** in pyridine at room temperature for 24 hr gave the diacetates **6a** and **7a**, whereas the triacetates **6b**

and **7b** were formed at 37°C in 96 hr, indicating the presence of an axial hydroxyl group in both triols. In the NMR spectrum of the diacetate **6a** one *equatorial* proton signal was identified ($\delta = 3.85$, triplet, $J_{ea} = 2.5$ Hz), which appeared as expected in the spectrum of triacetate **6b** at higher δ values ($\delta = 5.23$, triplet, $J_{ea} = 2.5$ Hz). As this *equatorial* proton is coupled only with *axial* ones, it must be assigned to C-4; this means 4β configuration for the hydroxyl group in the 5α series.

The diacetate **7a**, being at our disposal only in minute quantities, was characterized by IR and MS. The NMR spectrum of the triacetate **7b** exhibited a proton signal analogous to that of **6b** ($\delta = 5.36$, triplet, $J_{ea} = 3$ Hz), representing an *equatorial* β-proton at C-4. Since the triols **6** and **7** do form acetonides (**6c** and **7c**), the C-3 and C-4 hydroxyl groups are positioned on the same side of ring A in **6** and **7**. The protons at C-3 and C-17 overlap, giving a broad signal ($\delta = 4.4$–5.0) in the NMR spectra of **6a**, **6b** and **7b**. Thus the structure of 5α-androstane-3β,4β,17β-triol was assigned to the triol **6**, and 5β-androstane-3α,4α,17β-triol to triol **7**. Consequently, the C-3 hydroxyl group in **3** is β and *equatorial*, and in **4** it is α and *equatorial*.

The β or α configuration of the acetoxyl groups in **6b**–**9b** can also be deduced from the δ values of the C-19 methyl singlets, since acetoxyl groups, being *cis* to the angular methyl groups, cause a greater chemical shift, compared to that of the *trans* derivatives. In the case of **6b**, the δ value measured ($\delta = 1.04$) was equal with that calculated on the basis of ZÜRCHER's data [7] for 5α-androstane-3β,4β,17β-triol triacetate, and it was in a good agreement with the value reported by DAVEY *et al.* [9] for the C-19 methyl signal of 5α-cholestane-3β,4β-diol diacetate ($\delta = 1.02$). The analogous signal of the triacetate **7b** occurred at higher field strength ($\delta = 0.95$) than that of 5β-cholestane-3β,4β-diol diacetate ($\delta = 1.04$) [9]. The above comparison is allowed because of the negligible effect of the corresponding C-17 substituents on the chemical shift of the C-19 methyl protons [7].

The other triol (**8**), formed by reduction of **4**, was found to be 5β-androstane-3α,4β,17β-triol. This structure is in accordance with the ease of acetylation, which is complete within 16 hours at room temperature, as well as with the NMR spectra of the triacetate **8b**. The signal of the C-19 methyl protons occurs at lower field strength ($\delta = 0.98$), than in the case of **7b**. Two of the three protons geminal to the acetoxyl groups appear as a broad multiplet ($\delta = 4.3$–4.9) and were assigned to C-3 H and C-17 H. The C-4 proton appears as a triplet at $\delta = 5.32$ with a coupling constant $J_{aa} = 10$ Hz, indicating *axial–axial* interaction and thereby confirming the *axial* conformation of this proton.

The 3,4-dihydroxy-17-one (**5**), also formed in the course of microbial transformations, was converted at room temperature in 16 hours into its diacetate (**5a**). Its NMR spectrum exhibited a broad multiplet between 4.6

to 5.0 assignable to *axial* C-3 and C-4 protons, which implies *equatorial* conformation for both hydroxyl groups. The C-19 methyl signal at 0.98, however gave no sufficient information regarding the conformation of the C-5 proton. The 3β,4α-dihydroxy-5α-androstan-17-one structure of **5** was confirmed by the investigation of the triol (**9**) formed from **5** upon reduction with sodium borohydride. The single product of this reaction differred from the triols **6**, **7** and **8**; it gave no acetonide and afforded a triacetate (**9b**) at room temperature in 16 hours. The NMR spectrum of **9b** showed a broad multiplet (δ = 4.4–4.9) corresponding to three protons. The chemical shift of the C-19 methyl protons (δ = 0.92) was in agreement with the analogous signal of 5α-cholestane-3β,4α-diol diacetate (δ = 0.91) [9].

The three products of microbial transformation (**3**, **4** and **5**) were interconvertable by repeated incubation. After a conversion time of 24 hours, their ratio was 5 : 5 : 1. A follow-up of the incubation indicated that **3** → **5** was the main reaction path (Scheme 1), indicating the identical C-5 configuration of the two molecules. As intact cells have been used, no definite conclusions can be drawn on the enzymic processes, but formation of a 3-oxo-4-hydroxy-4-ene derivative has to be assumed because of the interconvertibility of **3**, **4** and **5**. Such an intermediate, however, could not be detected.

No elimination of the C-4 hydroxyl or oxo group was observed in the present study, not even in the presence of 8-hydroxy-quinoline (an inhibitor of steroid degradation in microorganisms), neither 4-androstene-3,17-dione nor 1,4-androstadiene-3,17-dione were formed. The same microorganism, however, was able to eliminate the 4,5-oxido group and 4-halogen as well from the corresponding 3-oxo- or 3-hydroxy derivatives [2, 3].

Among other observations, this was the basis of our assumption that the 4,5-oxido group was eliminated *via* a 3,5-diol intermediate [2, 10]. Preliminary studies on an analogous conversion of 3-oxo-4,5-dihydroxypregnanes and androstanes, resulting in **3**, **4** and **5**, supported evidence for the elimination of a C-5 hydroxyl group.

These investigations fit into our observation on the steroid-transforming character of *Mycobacterium phlei*, *i.e.* in the absence of a 4,5 double bond [2], or on saturating [3] it, this microorganism does not introduce a 1,2 double bond, which is one of the prerequisites of degradation of the steroid nucleus through 9α-hydroxy-1-enes [1].

Finally, it must be mentioned that 4,17β-dihydroxy-4-androsten-3-one, a substrate similar to **2** has been transformed with a culture of *Nocardia restrictus*, *via* the 9α-hydroxy intermediate, into 3,4-dihydroxy-9,10-seco-1,3,5(10)-androstatriene-9,17-dione [11].

Experimental

IR spectra were recorded on a Perkin—Elmer-457 spectrophotometer, in KBr pellets, the NMR spectra were obtained with a Varian A-60 D spectrometer, at 60 Mc/s, with TMS as internal standard. Chemical shifts are given in δ (ppm). Mass spectra were taken on a Varian-MAT SM-1A instrument, at 70 eV electron energy. Thin-layer chromatograms were obtained on silica gel $PF_{254-366}$(Merck) using the following developing solvents: (a) benzene–ethyl acetate 4 : 1; (b) benzene–ethyl acetate 1 : 1. The spots were visualized by spraying with ethanol–sulfuric acid 1 : 1, followed by heating to 110°C.

4-Hydroxy-4-androstene-3,17-dione (2)

1.0 g of 4β,5β-epoxyandrostane-3,17-dione was kept at room temperature for 16 hr in a mixture of 6 ml of glacial acetic acid and 0.6 ml of conc. sulfuric acid. After dilution with ice-water, the mixture was extracted with benzene. The extracts were washed until neutral and were evaporated to yield, after recrystallization from methanol, 0.6 g of **2**; m.p. 200—204°C; $[\alpha]_D^{20}$ + 171° (c = 1.0, $CHCl_3$); λ_{max}: 277 nm, ε: 12200 (ethanol); R_f(b) 0.81.

$C_{19}H_{26}O_3$ (302.4). Calcd. C 75.47; H 8.66.
Found C 75.27; H 8.51%.

IR: 3415, 3390 (OH), 1743 (C_{17}=O), 1672 (C=O_{conj}), 1636 (C=C).
NMR ($CDCl_3$): 0.91 s (C_{18}—CH_3), 1.19 s (C_{19}—CH_3).

Transformation of 4-hydroxy-4-androstene-3,17-dione (2) with a culture of *Mycobacterium phlei*

The conditions of growing, addition of **2** (3.0 g; 200 μg/ml) and the 24-hr conversion were the same as described previously [1], except that the latter was performed in the absence of 8-hydroxyquinoline. The ethyl acetate extract of the broth (2 times 0.3 volume) was evaporated *in vacuo* and the residue (3.6 g) was separated by chromatography on inactive silica gel with benzene containing increasing amounts of ethyl acetate; 1.7 g of a mixture of **3** and **4**, and 0.18 g of **3β,4α-dihydroxy-5α-androstan-17-one (5)** were isolated; m.p. 226—228°C (from ethanol) $[\alpha]_D^{20}$ + 74° (c = 0.72, ethanol); R_f(b) 0.13.

$C_{19}H_{30}O_3$ (306.4). $M^{+\cdot}$ = 306.
IR: 3400 (OH), 1750 (C_{17}=O).
NMR (CD_3OD): 0.86 s (C_{18}— and C_{19}—CH_3).
MS: $M^{+\cdot}$ = 306 (100%), m/e = 288 (6.5%), m/e = 262 (11%), m/e = 247 (6%).

3β,4α-Dihydroxy-5α-androstan-17-one diacetate (5a). 0.06 g of **5** was acetylated for 16 hr at room temperature in a mixture of 2 ml of pyridine and 0.2 ml of acetic anhydride. In the usual way, 0.06 g of **5a** was isolated. After recrystallization from ether–light petroleum, **5a** had m.p. 219—220°C; R_f(a) 0.47.

$C_{23}H_{34}O_5$ (390.5). Calcd. C 70.75; H 8.77.
Found C 70.79; H 8.59%.

IR: 1732, 1740 (sh.) (C=O_{ac}, C_{17}=O), 1250, 1040 (C—O—C).
NMR ($CDCl_3$): 0.86 s (C_{18}—CH_3), 0.98 s (C_{19}—CH_3), 1.99 s, 2.01 s ($COCH_3$), 4.63—5.00 m (2H C_3 and C_4).

The mixture of **3** and **4** was separated by repeated column chromatography. Recrystallized from ether and acetone–light petroleum **3β-hydroxy-5α-androstane-4,17-dione (3)** was isolated, m.p. (168)—174—178°C; $[\alpha]_D^{20}$: +90° (c = 1.0, acetone); R_f(b) 0.52.

$C_{19}H_{28}O_3$ (304.4). Calcd. C 74.96; H 9.27.
Found C 74.89; H 9.34%.

IR: 3475 (OH), 1735, 1703 (C_{17}=O, C_4=O).
NMR ($CDCl_3$): 0.74 s (C_{19}—CH_3), 0.86 s (C_{18}—CH_3).
MS: $M^{+\cdot}$ = 304 (100%), m/e = 289 (19%), m/e = 260 (9%), m/e = 248 (6%), m/e = = 247 (8.5%), m/e = 245 (29%), m/e = 86 (8.5%).

3β-Hydroxy-5α-androstane-4,17-dione acetate (3a). 0.1 g of **3** was acetylated as described above; 0.11 g of **3a** was isolated from ether. Recrystallized from acetone, m.p. 229—232°C; R_f(a) 0.43.

$C_{21}H_{30}O_4$ (346.4). Calcd. C 72.84; H 8.69.
Found C 72.46; H 8.55%.

IR: 1740, 1735 (C=O_{ac}, C_{17}=O), 1720 (C_4=O), 1230, 1040 (C—O—C).

NMR ($CDCl_3$): 0.80 s ($C_{19}-CH_3$), 0.87 s ($C_{18}-CH_3$), 2.16 s ($COCH_3$), 5.17 q (1H C_3).
MS: $M^{+\cdot}$ = 346 (90%), m/e = 304 (100%), m/e = 286 (55%), m/e = 271 (11%), m/e = 258 (17%), m/e = 245 (82%), m/e = 169 (5%).

3α-Hydroxy-5β-androstane-4,17-dione (4), isolated from the respective fractions, was repeatedly recrystallized from acetone–light petroleum; m.p. 168—170°C; $[\alpha]_D^{20}$ + 112° (c = 0.76, acetone); R_f(b) 0.60.

$C_{19}H_{28}O_3$ (304.4). Calcd. C 74.96; H 9.27.
Found C 74.60; H 9.30%.

IR: 3510 (OH), 1740 (C_{17}=O), 1710 (C_4=O).
NMR ($CDCl_3$): 0.83 s ($C_{18}-CH_3$), 1.15 s ($C_{19}-CH_3$).
MS: $M^{+\cdot}$ = 304 (100%), m/e = 289 (7%), m/e = 286 (8%), m/e = 260 (12%), m/e = = 245 (12%), ml/e = 229 (7%), m/e = 127 (5%).

3α-Hydroxy-5β-androstane-4,17-dione acetate (4a). 0.09 g of **4** was acetylated as described above; 0.1 g of **4a** was isolated. Recrystallized from ether–light petroleum, m.p.148—151°C; R_f(a) 0.55.

$C_{21}H_{30}O_4$ (346.4). Calcd. C 72.84; H 8.69.
Found C 72.65; H 8.75%.

IR: 1740 (C=O_{ac}, C_{17}=O), 1715 (C_4=O), 1250, 1030 (C—O—C).
NMR ($CDCl_3$): 0.86 s ($C_{18}-CH_3$), 1.18 s ($C_{19}-CH_3$), 2.18 s ($COCH_3$), 5.16 t (1H C_3).
MS: $M^{+\cdot}$ = 346 (100%), m/e = 304 (18%), m/e = 286 (24%), m/e = 169 (21.6%).

Transformation of 4-hydroxy-4-cholesten-3-one (1) [12] with a culture of *Mycobacterium phlei*

This compound (**1**) was transformed as described above; the resulting **3**, **4** and **5** were identified by TLC.

Oxidation of 3β-hydroxy-5α-androstane-4,17-dione (3) and 3α-hydroxy-5β-androstane-4,17-dione (4) in alkaline medium

10 mg of **3** was refluxed for 10 min in a mixture of 2 ml of methanol and 0.2 ml of 10% aqueous sodium hydroxide solution. After neutralization, extraction and evaporation, 5 mg of **4-hydroxy-4-androstene-3,17-dione (2)** was isolated, m.p. 180—193°C and mixed m.p. 193—198°C (with an authentic sample); λ_{max} = 277 nm (ethanol).

9 mg of **4** was similarly transformed to obtain 6 mg of **2**, m.p. 193—196°C; mixed m.p. 196—199°C; λ_{max} = 277 nm (ethanol).

Reduction of 3β-hydroxy-5α-androstane-4,17-dione (3) with sodium borohydride

40 mg of **3** in 2 ml of 96% ethanol was reduced for 4 hr at room temperature with a solution of 10 mg sodium borohydride in 1 ml of 96% ethanol. The reaction mixture was treated with glacial acetic acid, evaporated to dryness *in vacuo* washed with water and dried. The resulting **5α-androstane-3β,4β,17β-triol (6)** (35 mg) was recrystallized from ethanol, m.p. 263—265°C; R_f(b) 0.24.

IR: 3510, 3350, 3250 (OH).

The m.p. mixed m.p. and IR spectrum of this substance were identical with those of **6** obtained by the analogous reduction of compound **2**, and purified by recrystallization from ethanol; the yield was 0.50 g from 0.85 g of **2**; m.p. 265—269°C.

$C_{19}H_{32}O_3$ (308.5). Calcd. C 73.98; H 10.45.
Found C 73.71; H 10.65%.

NMR ($(CD_3)_2SO$): 0.60 s ($C_{18}-CH_3$), 0.95 s ($C_{19}-CH_3$), 3.81 t (1H C_4, J_{ea} = 3 Hz), 4.01—4.61 m (2H C_3, C_{17}).

5α-Androstane-3β,4β,17β-triol 3,17-diacetate (6a). 0.20 g of **6** was acetylated as described above. The diacetate (**6a**) (0.22 g) was isolated in the usual way and recrystallized from acetone; m.p. 220—225°C; R_f(a) 0.50.

$C_{23}H_{36}O_5$ (392.5). Calcd. C 70.38; H 9.24.
Found C 70.09; H 9.41%.

IR: 3440 (OH), 1730, 1700 (C=O_{ac}), 1280, 1250, 1040 (C—O—C).
NMR ($CDCl_3$): 0.77 s ($C_{18}-CH_3$), 1.10 s ($C_{19}-CH_3$), 2.02 s, 2.06 s ($COCH_3$), 3.85 t (1H C_4, J_{ea} = 2.5 Hz), 4.40—5.00 m (2H C_3, C_{17}).
MS: $M^{+\cdot}$ = 392 (0.3%), m/e = 332 (100%), m/e = 43 (13.5%).

5α-Androstane-3β,4β,17β-triol triacetate (6b). 0.20 g of **6** was acetylated at 37°C in a mixture of 6 ml of pyridine and 6 ml of acetic anhydride for 96 hr. The usual work-up of the reaction mixture gave 0.27 g of **6b**, which was recrystallized from ether–light petroleum, m.p. 144–145°C; R_f(a) 0.72.

$C_{25}H_{38}O_6$ (434.6). Calcd. C 69.08; H 8.83.
Found C 68.95; H 8.83%.

IR: 1740–1730 (C=O_{ac}), 1240, 1030 (C–O–C).

NMR ($CDCl_3$): 0.78 s (C_{18}–CH_3), 1.04 s (C_{19}–CH_3), 1.97 s, 2.03 s, 2.09 s ($COCH_3$), 4.46–5.00 m (2H C_3, C_{17}), 5.23 t (1H C_4, J_{ea} = 2.5 Hz).

MS: $M^{+\cdot}$ = 434 (0.2%), m/e = 374 (15.5%), m/e = 332 (100%), m/e = 314 (15%), m/e = 43 (12%).

5α-Androstane-3β,4β,17β-triol acetonide (6c). 0.10 g of **6** was refluxed for 7 hr in the presence of 25 mg of *p*-toluenesulfonic acid in 50 ml of acetone. The solution was neutralized with solid sodium hydrogen carbonate, and subsequently an ethyl acetate extraction was performed from aqueous solution. 0.06 g of **6c** was isolated from the residue of the organic phase. After recrystallization from a mixture of ether and light petroleum, m.p. 167–170°C; R_f(a) 0.34.

$C_{22}H_{36}O_3$ (348.5). $M^{+\cdot}$ = 348.

IR: 3500–3200 (OH).

NMR ($CDCl_3$): 0.77 s (C_{18}–CH_3), 1.08 s (C_{19}–CH_3), 1.32 s, 1.53 s ((CH_3)$_2$C=), 3.68 t (1H C_{17}, J = 8 Hz), 4.00 m (2H C_3, C_4).

MS: $M^{+\cdot}$ = 348 (0.7%), m/e = 333 (100%), m/e = 273 (44.5%), m/e = 255 (25%), m/e = 107 (15%), m/e = 81 (49%).

Reduction of 3α-hydroxy-5β-androstane-4,17-dione (4) with sodium borohydride

150 mg of **4** was reduced as described above. The mixture of **7** and **8** was separated by TLC (b) to isolate 80 mg of **5β-androstane-3α,4α,17β-triol (7)**, R_f(b) 0.24. Recrystallization from ethanol gave m.p. 238–244°C.

IR: 3410 (OH).

5β-Androstane-3α,4α,17β-triol triacetate (7b). 70 mg of **7** was acetylated as described for **6b**. Recrystallization from light petroleum gave 40 mg of **7b**, m.p. 133–134°C; R_f(a) 0.66.

$C_{25}H_{38}O_6$ (434.6). $M^{+\cdot}$ = 434.

IR: 1740 (C=O_{ac}), 1240, 1040 (C–O–C).

NMR ($CDCl_3$): 0.78 s (C_{18}–CH_3), 0.95 s (C_{19}–CH_3), 1.95 s, 2.03 s, 2.10 s ($COCH_3$), 4.40–4.90 m (2H C_3, C_{17}), 5.36 t (1H C_4, J_{ea} = 3 Hz).

MS: $M^{+\cdot}$ = 434 (2.8%), m/e = 374 (32.5%), m/e = 332 (92.5%), m/e = 314 (100%), m/e = 254 (32.5%).

5β-Androstane-3α,4α,17β-triol acetonide (7c). 20 mg of **7** was transformed as described above to obtain 18 mg of oily material, R_f(a) 0.40.

$C_{22}H_{36}O_3$ (348.5). $M^{+\cdot}$ = 348.

IR: 3400 (OH).

MS: $M^{+\cdot}$ = 348 (1%), m/e = 333 (100%), m/e = 273 (37.5%), m/e = 255 (19%), m/e = 81 (15.5%).

The second product formed in the course of the reduction of **4**, **5β-androstane-3α,4β,17β-triol (8)** (30 mg), slightly contaminated with **7** was acetylated at room temperature, as in the preparation of **5a**. Along with the main product, 36 mg of **8b**, also **7a** was formed. Separation by TLC(a) gave 18 mg of **5β-androstane-3α,4β,17β-triol triacetate (8b)**, m.p. 159–162°C; R_f(a) 0.66.

$C_{25}H_{38}O_6$ (434.6). $M^{+\cdot}$ = 434.

IR: 1745 (C=O_{ac}), 1260, 1050 (C–O–C).

NMR ($CDCl_3$): 0.77 s (C_{18}–CH_3), 0.98 s (C_{19}–CH_3), 1.98 s (1 $COCH_3$), 2.00 s (2 $COCH_3$), 4.30–4.90 m (2H C_3, C_{17}), 5.32 t (1H C_4, J_{aa} = 10 Hz).

MS: $M^{+\cdot}$ = 434 (1.4%), m/e = 374 (16%), m/e = 332 (15%), m/e = 314 (100%), m/e = 259 (18%), m/e = 254 (21%).

The second product of acetylation, **5β-androstane-3α,4α,17β-triol 3,17-diacetate (7a)**, was crystallized from ethanol to obtain 6 mg of the compound, m.p. 174–178°C; R_f(a) 0.56.

$C_{23}H_{36}O_5$ (392.5). $M^{+\cdot}$ = 392.

IR: 3465 (OH), 1745, 1712 (C=O_{ac}), 1260, 1052 (C–O–C).

MS: $M^{+\cdot}$ = 392 (9.4%), m/e = 332 (100%), m/e = 314 (19.2%), m/e = 272 (19%), m/e = 111 (22.5%), m/e = 98 (12.5%), m/e = 43 (38.6%).

Reduction of 3β,4α-dihydroxy-5α-androstan-17-one (5) with sodium borohydride

0.17 g of **5** was reduced as described above. The **5α-androstane-3β,4α,17β-triol (9)** (0.14 g) obtained was recrystallized from ethanol; m.p. 258—259°C; R_f(b) 0.10.

IR: 3530, 3370, 3330 (OH).

5α-Androstane-3β,4α,17β-triol triacetate (9b). 80 mg of **9** was acetylated at room temperature, as described for the acetylation of **5**. After the usual work-up of the reaction mixture, 91 mg of **9b** was isolated. On recrystallization from ether–light petroleum, the product had m.p. 142—147°C; R_f(a) 0.50.

$C_{25}H_{38}O_6$ (434.6). $M^{+\cdot} = 434$.

IR: 1740 (C=O_{ac}), 1260, 1065, 1045 (C—O—C).

NMR ($CDCl_3$): 0.77 s (C_{18}—CH_3), 0.92 s (C_{19}—CH_3), 1.96 s (1 $COCH_3$), 1.99 s (2 $COCH_3$), 4.40—4.90 m (3H C_3, C_4, C_{17}).

MS: $M^{+\cdot} = 434$ (1.6%), m/e = 374 (32%), m/e = 332 (30%), m/e = 314 (100%), m/e = 272 (16.4%), m/e = 254 (18%).

*

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EINE VERBESSERTE SYNTHESE DES O-BENZYL-L-TYROSIN-BENZYLESTERS

(KURZE MITTEILUNG)

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Zur Synthese von Peptiden und Peptidfragmenten, die C-terminales Tyrosin [1, 2, 3] gehalten, kann das O-Benzyl-L-tyrosin-benzylester (**III**) vorteilhaft gebraucht werden. Die Verbindung (**III**) fiel zuerst bei der Darstellung von L-Tyrosin-benzylester (**II**) nach H. K. MILLER und H. WAELSCH [4] als Nebenprodukt an, da die Hauptreaktion teilweise von gleichzeitiger Verätherung der Hydroxylgruppen begleitet war:

$$\underset{\mathbf{I}}{\text{H-Tyr-OH}} \xrightarrow[C_6H_5SO_2OH]{C_6H_5CH_2OH} \underset{\mathbf{II}}{\text{H-Tyr-OBzl}} + \underset{\mathbf{III}}{\text{H-Tyr(Bzl)-OBzl}}$$

Die Ausbeute an Benzyläther-benzylester (**III**) wurde nach E. SCHNABEL [1] durch längeres Erhitzen mit einem kleinen Überschuß von Benzolsulfonsäure so weit gesteigert, daß der Ätheranteil etwa 30% der Reaktionsprodukte betrug. Die Trennung durch fraktionierte Kristallisation der Hydrochloride aus Methanol gelang aber nur mit geringer Ausbeute [1].

Es wird nun über eine wesentlich verbesserte und neue, mit guter Ausbeute verlaufende Synthese des O-Benzyl-L-tyrosin-benzylesters (**III**) berichtet: Zuerst wird O-Benzyl-L-tyrosin (**IV**) nach J. S. MORLEY [5] hergestellt, das dann, nach dem Generalverfahren von H. GIBIAN und E. SCHRÖDER [5], durch Erhitzen mit Benzylalkohol und Benzolsulfonsäure in Benzol und durch azeotrope Destillation des entstandenen Wassers, in guter Ausbeute zu dem entsprechenden Benzylester (**III**) überführt werden kann.

$$\underset{\mathbf{I}}{\text{H—Tyr—OH}} \rightarrow \underset{\mathbf{IV}}{\text{H—Tyr(Bzl)—OH}} \xrightarrow[C_6H_5SO_2OH \text{ in } C_6H_6]{C_6H_5CH_2OH}$$

$$\underset{\text{Bzl}}{\text{H—Tyr—OBzl}}\cdot C_6H_5SO_2OH \xrightarrow{TAA} \underset{\text{Bzl}}{\text{H—Tyr—OBzl}}$$

III. Benzolsulfonat **III**

III. Benzolsulfonat fiel unmittelbar aus dem Reaktionsgemisch als Kristallprodukt aus. Der freie O-Benzyl-L-tyrosin-benzylester (**III**) wurde in Chloroform, nach Zusatz von äquivalentem Triäthylamin, hergestellt und gleichfalls in kristalliner Form erhalten.

Bezüglich dieser Herstellungsart des O-Benzyl-L-tyrosin-benzylesters (**III**) ließ sich feststellen, daß im Vergleich mit der Literaturangabe [2], nicht nur die Ausbeute erhöht werden kann, sondern zugleich ein reineres gut kristallisierendes Produkt von viel höherem Schmelzpunkt und Drehungsvermögen erhältlich ist. Nach den chromatographischen Reinheitsuntersuchungen ist diese Verbindung (**III**) eine einheitliche, reine, ninhydrinpositive, Pauly-negative Substanz. Die Vorteile des beschriebenen Verfahrens sind aus der Tabelle I klar ersichtlich.

Tabelle I

Ausbeute und physikalische Eigenschaften des O-Benzyl-L-tyrosin-benzylesters

Hergestellt	Ausbeute (auf Tyrosin)	Schmp.	$[\alpha]_D^{25}$
Nach dem Literaturverfahren [1, 2]	13.6%	79—81°	−1,5° (c = 1,7; Essigsäure)
Nach der verbesserten Synthese	55,6%	94—96°	+9,6 (c = 2; Essigsäure)

Der aus seinem Benzolsulfonat freigesetzte O-Benzyl-L-tyrosin-benzylester (**III**) konnte unmittelbar mit verschiedenen geschützten Komponenten zu Dipeptid-Derivaten mit guter Ausbeute umgesetzt werden.

Beschreibung der Versuche

O-Benzyl-L-tyrosin-benzylester-benzolsulfonat (IIIb)

10,84 g (0,04 mol) O-Benzyl-L-tyrosin (**IV**) [5] und 7 g (0,044 mol) Benzolsulfonsäure wurden mit 30 ml Benzylalkohol und 20 ml Benzol unter langsamen Abdestillieren von Wasser und Benzol 4—5 Stunden gekocht. Der Benzol-Zusatz wird mit 10 ml erneuert. Das Endprodukt fiel unmittelbar aus dem gekühlten Reaktionsgemisch (oder nach Zusatz von wenig Äther) als kristallin aus. Man filtriert nachher das ausgeschiedene Kristallgut ab und wäscht mit Äther. Das nach dem Trocknen gewonnene Produkt (17,6 g 84,7% d. Th.) lieferte aus Methanol–Äther 14,1 g (67,8% d. Th.) oder aus Äthanol–Äther 13,8 g (66,4% d. Th.) farblose stalle vom Schmp. 198—199°C. $[\alpha]_D^{25} = +1{,}25°$ (c = 4; Dimethylformamid).

$C_{29}H_{29}O_6NS$ (519,6). Ber. C 67,0; H 5,6; N 2,7; S 6,2. Gef. C 66,9; H 5,9; N 2,6; S 6,2%.
Charakteristische Banden des IR-Spektrums (KBr-Tablette): $\nu_{C=O}$(COOBzl): 1735 cm^{-1}, $\nu_{S=O}$(SO_2O^-): 1040, 1220 cm^{-1}, ν_{C-O-C}(Äther): 1255 cm^{-1}.

O-Benzyl-L-tyrosin-benzylester (III)

Man suspendiert 1,56 g (3 mmol) des O-Benzyl-L-tyrosin-benzylester-benzolsulfonats n 6 ml Chloroform. Die mit Eis gekühlte und gerührte Lösung wird tropfenweise mit 0,42 ml. (3 mmol) Triäthylamin versetzt, und weitere 20 Minuten gerührt. Man verdünnt die reine Lösung mit 30 ml Äther, läßt bei Raumtemperatur 1 Stunde stehen, filtriert den ausgeschiedenen Niederschlag (Triäthylamin-benzolsulfonat) dann ab und wäscht mit Äther. Die bei Unterdruck eingedampfte Lösung hinterließ ein weißes, reines Produkt (1,06 g, 98,1% d. Th.), das sich aus Chloroform–Äther umkristallisieren ließ. Schmp. 94—96°C. $R_F = 0{,}95$ (*sec.* Butanol–Ameisensäure–Wasser 75—15—10). $[\alpha]_D^{25} = +9{,}6°$ ($c = 2$; Essigsäure); $[\alpha]_D^{25} = -4{,}8°$ ($c = 2$; Dimethylformamid).
$C_{23}H_{23}O_3N$ (361,4). Ber. C 76,4; H 6,4; N 3,8. Gef. C 76,4; H 6,6; N 3,5%.
Charakteristische Banden des IR-Spektrums (KBr-Tablette): $\nu_{NH}(-NH_2)$: 3380 und 3320 cm^{-1}, $\nu_{C=O}$(COOBzl): 1735 cm^{-1}, ν_{C-O-C}(Äther): 1245 cm^{-1}.

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SYNTHESIS OF D—Phe^2, Phe^3, D—Phe^6—LH—RH, A POTENT INHIBITOR OF LH—RH

(PRELIMINARY COMMUNICATION)

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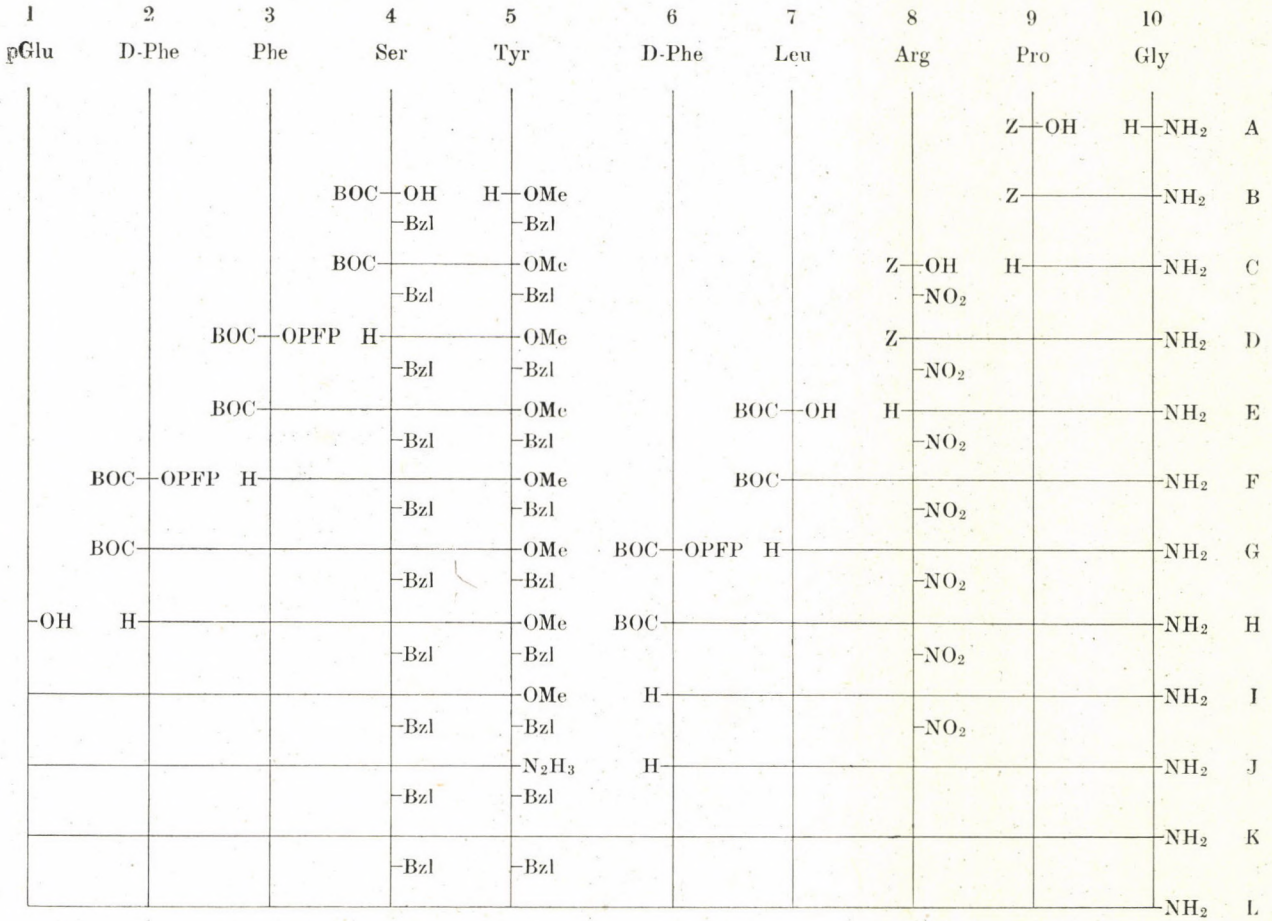
In a continuing search for analogs of LH—RH which competitively inhibit its action on the pituitary receptor cells, we recently found the title compound to be active in rats for up to 6 hours after subcutaneous injection. Making use of this observation, de la Cruz *et al.* [1] were able to block the LH—RH-triggered proestrous gonadotropin surge in rats by a single injection of the peptide. This resulted in an almost complete inhibition of ovulation.

In view of the interesting properties of this compound, we felt it necessary to examine its effects on other animal species, particularly primates, and have therefore developed a synthesis of the peptide by which large amounts of material could be obtained (Fig. 1, see p. 424) with inhibitory activity comparable to the material prepared previously by the solid-phase method [2]. The synthesis is based on the fragment condensation of the two pentapeptides, 1—5 and 6—10, by the azide method. The two pentapeptides were synthesized stepwise, using different methods of coupling.

The dipeptide (C 4—5) was prepared using DCC as the coupling agent. The subsequent two couplings were carried out with pentafluorophenyl esters of the corresponding amino acids [3]. The pentapeptide methyl ester (I 1—5) was prepared using DCC and 1-hydroxybenzotriazole as the coupling reagents, and the pentapeptide hydrazide (F 1—5) was obtained from this by hydrazinolysis. A yield of 61% was attained, based on the starting tyrosine derivative.

The protected dipeptide (B 9—10) was synthesized by DCC coupling using the method of Geiger *et al.* [4] and carbobenzoxy-nitroarginine was coupled to the deprotected dipeptide (C 9—10) by the mixed anhydride procedure, according to the method of Yanaihara *et al.* [5]. The coupling of BOC-leucine to the tripeptide (E 8—10) was effected in the presence of DCC and 1-hydroxybenzotriazole. Finally, the pentapeptide (H 6—10) was prepared by the coupling of BOC-phenylalanine pentafluorphenyl ester with the tetrapeptide (G 7—10), and the nitro group was removed by catalytic hydrogena-


1 pGlu
2 D-Phe
3 Phe
4 Ser
5 Tyr
6 D-Phe
7 Leu
8 Arg
9 Pro
10 Gly
A
B
C
D
E
F
G
H
I
J
K
L
Z—OH
H—NH₂
BOC—OH
H—OMe
Bzl
Z—NH₂
BOC—OMe
Z—OH
H—NH₂
NO₂
BOC—OPFP
H—OMe
Z—NH₂
BOC—OMe
BOC—OH
H—NH₂
BOC—OPFP
H—OMe
BOC—NH₂
BOC—OMe
BOC—OPFP
H—NH₂
OH
H—OMe
BOC—NH₂
OMe
H—NH₂
N₂H₃
H—NH₂
NH₂
NH₂

tion. The deblocking of the BOC groups was carried out in 1*M* HCl/acetic acid, and that of the carbobenzoxy group in 17% HBr/acetic acid solutions.

The two pentapeptides were coupled by the azide method, without isolating the azide. The benzyl-protecting groups were removed by catalytic hydrogenation or by anhydrous hydrogen fluoride.

The crude decapeptide (L 1—10) was purified on a Sephadex G-50 column using 50% acid as eluant, followed by further purification on silica gel. Stepwise elution was used: ethyl acetate–pyridine–acetic acid–water (16 : 4 : 1 : 2) eluted the faster moving contaminants, and ethyl acetate–pyridine–acetic acid–water (12 : 4 : 1 : 2) was applied for the elution of the decapeptide.

Several batches prepared by this method proved to be homogeneous in thin-layer chromatography: R_f (1-butanol : acetic acid : water, 4 : 1 : 5), 0.31; R_f (1-butanol : acetic acid : water : ethyl acetate, 1 : 1 : 1 : 1), 0.73; R_f (ethyl acetate : pyridine : acetic acid : water, 5 : 5 : 1 : 3), 0.78; R_f (2-propanol: 1*M* acetic acid, 2 : 1), 0.66.

Amino acid analysis: Ser 0.91; Glu 1.03; Pro 1.00; Gly 1.00; Leu 0.97; Tyr 0.99; Phe 3.05; NH_3 1.33; Arg 1.01.

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РЕЗЮМЕ

Замещение лиганда и строение комплексов, XI

Комплексы никеля (II) с шиффовыми основаниями аминопиридинов с салициловым альдегидом

Й. ЧАСАР и Я. БАЛОГ

Были исследованы шиффовы основания (SB) между $C_6H_4(OH)CHO$ и 2-NH_2—C_5H_4N, 3-NH_2—C_5H_4N, 2-NH_2-3-CH_3—C_6H_3N, 2-NH_2—4—CH_3—C_5H_3N, 2—NH_2—5—CH_3—C_5H_3N и 2-NH_2-6-CH_3—C_5H_3N, а также их комплексы с никелем(II). Было установлено, что 6-метильное производное дает комплекс состава $[Ni(SB)_2]$, а все остальные производные — $[Ni(SB)_2 \cdot 2H_2O]$. Молекулы сильно искажены. 6-Метильное производное представляет собой трифункциональный лиганд, в то время как другие шиффовы основания ведут себя как бифункциональные лиганды.

Замещение лиганда и строение комплексов, XII

Комплексы шиффовых оснований типа $C_6H_4(OH)CH{=}B{=}CH(OH)C_6H_4$

Й. ЧАСАР и Я. БАЛОГ

Были исследованы шиффовы основания, образующиеся между салициловым альдегидом и гидразином, этилендиамином, 1,3-пропилендиамином и 1,4-бутилендиамином, а также их комплексы с никелем(II). На основе УФ, видимого, ИК и ПМР спектров, а также на основе их магнитных свойств были сделаны заключения относительно строения комплексов.

Спектроскопическое исследование растворов щелочных и фосфониевых цианоферратов с помощью методов Мёссбауэра ИК и ЯМР

Ш. ПАП, П. КВИНТОВИЧ, Ф. НАДЬ, мл. и А. ВЕРТЕШ

Результаты спектроскопических исследований некоторых щелочных и фосфониевых цианоферратов с помощью методов Мёссбауэра, ИК и H^1—ЯМР заключаются в следующем.

Мёссбауэровские параметры замороженных водных растворов щелочных цианоферратов свидетельствуют о том, что при замораживании ионы K^+ ассоциированы с анионами цианоферратов, а ионы Na^+ не ассоциированы. Этот сегрегационный процесс может быть предотвращен, если к раствору добавляют глицерин или четвертичную фосфониевую соль. Эффект первого проявляется за счет увеличения вязкости раствора, а последнего,

вероятно, за счет увеличения взаимодействия между анионом цианоферрата и фосфониевым катионом.

С увеличением донорных свойств растворителя частоты ν_{CN} и ν_{NO} аниона $[Fe(CN)_5NO]^{-2}$ понижаются. Уменьшение валентных колебаний NO более значительно, что указывает на сильное взаимодействие между молекулой донорного растворителя и акцепторной орбитой π^* NO лиганда во время сольватации. Мёссбауэровские параметры, в подобных растворах, не зависят от донорности растворителя. Положение абсорбционных полос трис-трибутилбензилфосфоний-гексацианоферрата(III) в спектрах H^1—ЯМР зависит от концентрации и донорности растворителя.

Исследование электропроводности растворов хлористый металл — H_2O и хлористый металл — HCl — H_2O, I

Э. БЕРЕЦ

Приводятся результаты исследований удельной и молярной удельной электропроводностей тройных систем хлористый металл (в основном хлориды щелочных и щелочноземельных металлов) — HCl — H_2O и их составляющих двойных систем. Исходя из формы кривых электропроводность — концентрация отдельных двойных водных систем, а также из степени и направления изменений электропроводности двойных систем, протекающих вследствие добавления третьего компонента (соль или кислота), а помимо этого, также и из явлений, наблюдаемых в общем для соответствующих систем (инверсионная концентрация HCl, инверсионная концентрация соли, смещение максимумов двойных систем в тройных системах и т. д.) были сделаны заключения относительно структурных условий в двойных и образующихся тройных системах, а также относительно концентрационных зависимостей.

Исследование электропроводности растворов типа хлористый металл — H_2O и хлористый металл — HCl — H_2O, II

Э. БЕРЕЦ

Автором даются уравнения для изотермических условий относительно зависимости от концентрации электропроводности в системах хлористый металл — H_2O и хлористый металл — HCl — H_2O на основе которых можно проводить расчеты. Приводится анализ постоянных уравнений и точности расчета. На основе этого делаются заключения относительно взаимодействий, протекающих в данных системах, и их зависимости от концентрации.

Потенциодинамические исследования на платиновом катализаторе

Й. ПЕТРО и Е. ПОЛЯНСКИ

На основе потенциодинамических исследований могут быть получены ценные сведения относительно каталитически активных систем металл-водород при комнатной температуре. До сих пор этот метод был использован в основном для гладких электродов и электродов с металлической чернью. Целью исследований было изучение возможности распространения потенциодинамических исследований на порошкообразные «истинные» катализаторы.

Порошкообразные платиновые катализаторы были приготовлены восстановлением при помощи водорода или $NaBH_4$. Была разработана методика потенциодинамических исследований порошковых катализаторов в сконструированном для этой цели приборе с потенциостатом марки AMEL 551/Su. Полученные потенциодинамические кривые (I—V) были интегрированы и расчетно было определено содержание водорода. Были изучены возможности применения метода и его погрешности: было определено влияние качества катализатора (способа получения, предварительной обработки и старения), его количества, электролита и скорости изменения потенциала на кривую.

Взаимодействие кислот с замещенными алканами, II

Исследование водородного обмена на дейтерий, протекающего между алкильной цепочкой 1-амино-5-метилгексана и серной кислотой

Я. ЭДЬЕД, Й ТАМАШ, А. НЕСМЕИ и ДЬ. МИНК

Были исследован водородный обен 1-амино-5-метилгексана, а также его дейтерированных производных с H_2SO_4 и D_2SO_4. Было установлено, что в согласии с более ранними заключениями авторов, водороды при 4 и 6 атомах углерода, являются способными к обмену. Этот обмен является псевдомономолекулярным процессом, т. е. кинетически является реакцией первого порядка. Константы скорости при одинаковых условиях являются одинаковыми. Проводя обмен в D_2SO_4 в алкильную цепочку одновременно встраивается восемь атомов дейтерия.

О взаимодействии кислот с замещенными алканами, III

Кинетической изотопный эффект в гидридном отщеплении третичного водорода от изоалканов

Я. ЭДЬЕД, И. КЕНДЕ и Й. ТАМАШ

Было исследовано окисление 5-третичногоу глерода 1-амино-5-метилгексана до карбонийного иона в 97,5%-ой серной кислоте и при 80,6°С. Серная кислота отрывает гидрид от третичного углерода, в результате чего сама восстанавливается до сернистой кислоты. Отрыв гидрида кинетически является процессом первого порядка, т. к. серная кислота присутствует в большом избытке. Было произведено окисление производных, меченных дейтерием и тритием в соответствующем месте, и получен следующий кинетический изотопный эффект: $k_H/k_D = 1{,}75$ и $k_H/k_T = 2{,}40$. Зависимость Свейна дает следующий результат: $\ln (k_H/k_D)/\ln (k_H/k_T) = 1{,}56$ (теоретически 1,44). Кинетические зависимости также подтверждают то наблюдение, что при гидридной абстракции третичного водорода в серной кислоте не наблюдается обмена с протонами последней.

Микробное превращение стероидальных 3-оксо-4-гидрокси-4-енов

Э. ТЁМЁРКЕНЬ, Г. ТОТ, К. ХОРВАТ и К. Г. КЮКИ

Микробное превращение 4-гидрокси-4-холестен-3-она (1) и 4-гидрокси-4-андростен-3,17-диона (2) под влиянием культуры Mycobacterium phlei в аэробных условиях приводит к образованию 30-гидрокси-50-андростан-4,17-диона (4), 30-гидрокси-50-андростан-4,17-диона (3) и 30,40-дигидрокси-50-андростан-17-она (5). Структура этих продуктов была определена на основе ИК, ЯМР и масс-спектров, а также с помощью исследования их соответствующих 3,4,17-триольных производных.

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