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AKADÉMIAI KIADÓ, BUDAPEST

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THE KINETICS OF MULLITE FORMATION
IN THE SYSTEM ALUMINIUM FLUORIDE—SILICA, II*
MECHANISM OF MULLITE FORMATION WITH ANHYDROUS ALUMINIUM
FLUORIDE

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Received November 25, 1966

Introduction

It was reported in the first communication of this series [1] that in the course of the reaction between aluminium fluoride and silica, the topaz-like phase of aluminium fluorosilicate formed in the temperature range 580–900 °C is followed by mullite formation at higher temperatures. This reaction takes place in two activation stages, the first between 900 and 1100°. During the reaction, owing to the use of water-containing materials, also the hydrolysis of aluminium fluoride occurs. Thus, in order to obtain quantitative reaction kinetical data, it is necessary to clarify how the mechanism of the reaction between aluminium fluoride and silica is affected by the presence of water.

The mechanism of the reaction is apparently of a complicated nature and it depends on a number of factors. It has been pointed out by earlier investigations that the course of the reaction is actually different in the presence of water-containing materials or in media containing steam. The reaction rate and equilibrium depend also on the temperature gradient applied during the reaction. Quantitative data can only be obtained if all these factors are accurately known and fixed. Both the reaction mechanism and its kinetical conditions are affected by the conditions of the investigation. The quality of the modification of the silica used and the vapour tension of aluminium fluoride are further factors influencing the processes taking place in the system. A quantitative elucidation of the effects of all these parameters requires extensive experimental work. In the present communication mainly the results of researches carried out in order to clarify the role of anhydrous aluminium fluoride are reported.

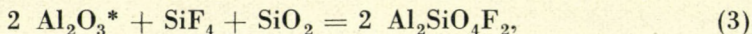
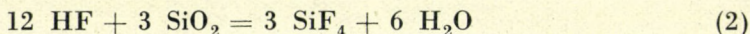
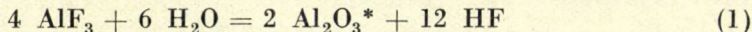
Theoretical

The mechanism of the reaction of topaz formation in the system AlF_3 — SiO_2 has been treated by SCHÖBER and THILO [3] presuming an intermediate

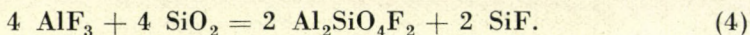
* Part I.: *Acta Chim. Acad. Sci. Hung.* **33**, 197 (1962).

phase of SiF_4 . Accordingly, the process would start with hydrolysis, then the hydrogen fluoride produced would react with silica to give SiF_4 .

The presumed mechanism was as follows:



thus, on summing up reactions (1)–(3):



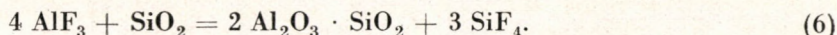
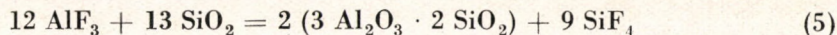
Under such conditions the water would have to play the role of a catalyst. However, this mechanism was not confirmed, since the reaction did not take place according to schemes (1)–(3) or (4), and the reaction product contained only 15.08% of fluorine instead of 20.65%. Topaz formation was observed by SCHÖBER and THILO between 750 and 970°. The difference between the calculated and found contents of fluorine means at the same time that the ignition loss occurring during the reaction cannot correspond to the stoichiometry of reaction (4), because in addition to SiF_4 also HF was formed, due to hydrolysis [4, 5].

The dynamic investigations were carried out in the *Department for Fundamental Researches* of our Institute, with the use of a *Paulik—Paulik—Erdey* instrument [6], for differential thermoanalysis and differential thermogravimetry. The systematic heat treatment of the samples was carried out in air, in nitrogen, further also in vacuum.

The basis of the experiments was the assumption that two extreme cases are to be considered from the aspect of reaction mechanism: aluminium fluoride may react directly with silica in the solid phase, or the end state may also be attained through hydrolysis. In order to elucidate the mechanism of the reaction, it is essential to decide whether aluminium fluoride directly reacts with silica, or the reaction takes place through hydrolysis. In the latter case the formation of silicon tetrafluoride is due only to the reaction of hydrogen fluoride produced as a result of the hydrolysis of aluminium fluoride. Owing to the presence of moisture in the starting materials and in air, there is always a possibility of same hydrolysis of aluminium fluoride during the reaction. The progress of hydrolysis depends again on the thermal gradient applied during the experiment.

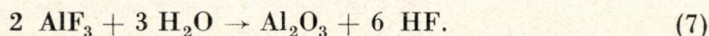
* Al_2O_3 denotes an intermediate phase of active alumina.

It follows from what has been said above that the two extreme cases of the reaction mechanism may be characterized by the hypothetical reaction schemes given below.



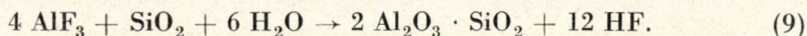
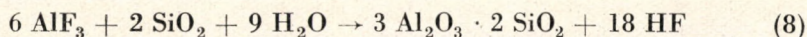
The reaction equations (5) and (6) represent the extreme cases when, during a process taking place in the solid phase, $3 \text{ Al}_2\text{O}_3 \cdot 2 \text{ SiO}_2$ (3/2 mullite) or $2 \text{ Al}_2\text{O}_3 \cdot \text{SiO}_2$ (2/1 mullite) is formed by the direct reaction of aluminium fluoride and silica, without the hydrolysis of aluminium fluoride [7, 8, 9].

The hydrolysis of aluminium fluoride, partial occurrence of which is to be taken into account in the course of the kinetical investigation, follows the scheme:

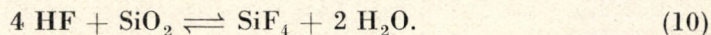


The end state of the reaction depends on the temperature. Hydrolysis begins to occur at $300 \pm 20^\circ$. According to scheme (7) it may take place only above 800° ; solely in that case can alpha-corundum appear as an end product in addition to hydrogen fluoride. At temperatures below 800° a mixture of aluminium oxide fluoride and alpha-corundum is obtained [3], the composition of which depends on the temperature and on the duration of heat treatment.

The state when aluminium fluoride entirely undergoes hydrolysis can be considered as the other extreme case of the reaction mechanism. This is indicated by the two hypothetical reaction schemes:



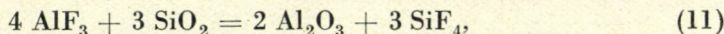
However, hydrogen fluoride formed by hydrolysis reacts with the silica present in the system [1, 3]



The equilibrium of silica and hydrogen fluoride as a function of temperature in a closed system is known. However, this cannot be applied under the prevailing experimental conditions because the investigation is carried out in an open system [5]. The hydrolysis of aluminium fluoride occurs also on the

effect of atmospheric moisture and in the case of fluoride even oxidation may be possible in the opinion of some authors [10].

According to the scheme:



in the absence of the hydrolytic reaction theoretically the formation of corundum and silicon tetrafluoride is expected.

Experimental

Materials

In the course of the present experiments, the following materials were employed (chemical compositions are given in Table I).

1. Quartz sand of *Hohenbocka*, high purity grade as used in the glass industry,
2. Rock crystal,
3. Quartz glass prepared by melting,
4. Christobalite, prepared by ignition of chemically pure silica gel,
5. Anhydrous aluminium fluoride, prepared by the method of RAHLFS and BILTZ [2].

Table I

Composition of materials employed in the experiments

No. of material (see text)	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO MgO	TiO ₂	Na ₂ O K ₂ O	Ignition loss	AlF ₃	H ₂ O %
1	99.73	0.16	0.04	0.03	0.01	0.02	0.04	—	—
2	99.9	0.05	0.02	0.01	0.01	—	—	—	—
3	99.6	0.25	0.05	0.04	0.03	0.03	—	—	—
4	99.3	0.40	0.08	0.03	0.10	—	—	—	—
5	—	—	—	—	—	—	—	99.8	0.2

Method

The experiments were carried out under static and dynamic conditions examining the influence of the temperature.

The static investigations were conducted by two different techniques. In one series always new and other individual samples were treated at different temperatures between 400 and 1200°. In the other series of experiments, the same sample was exposed to gradually increasing temperatures. The weight losses of the treated samples were measured. The reaction products were identified by X-ray investigations and chemical analysis.

The materials listed in Table I were weighed in the stoichiometric ratios shown by equations (5), (6) and (11). The components were mixed and compressed to pills at a pressure of 50 kg/sq. cm. The diameter of pills was 12.4 mm, their thickness varied between 3 and 12 mm, depending on the weight of the sample.

In the evaluation of the experimental results it should also be taken into account that aluminium fluoride undergoes sublimation at higher temperatures. At 900° the tension of aluminium fluoride is 290 torr and at 1290° it attains the value of 1 atm. [10].

The possibility of sublimation means that aluminium fluoride may react with silica also in vapour form. According to SCHÖBER and THILO [3] and REICH [11], between 700 and 900° also silicon tetrafluoride reacts with alumina, leading to the formation of topaz.

Thus, the simultaneous occurrence of the following processes may be assumed:

- (a) reaction of aluminium fluoride and silica in the solid phase,
- (b) hydrolysis of aluminium fluoride,
- (c) reaction of silicon tetrafluoride with alumina,
- (d) reaction of hydrogen fluoride with silica,
- (e) reaction of aluminium fluoride vapour with silica,
- (f) conversion of aluminium fluoride into the oxide.

In the experiments described below we aimed at selecting the actual reaction mechanism from among the possibilities that have been outlined above.

Experimental results

Hydrolysis of aluminium fluoride

During a reaction kinetical investigation of aluminium fluoride the possibility of hydrolysis must always be borne in mind. This process, may start because of the action of atmospheric moisture, and its end state depends on the temperature and the duration of heat treatment. In order to determine the activation energy and the reaction rate of the hydrolysis process, its progress was investigated by a static method. The results are given in Table II. On applying the JANDER correlation [12] to the curve of weight losses (Fig. 1) in the temperature range from 550 to 800°, we obtain:

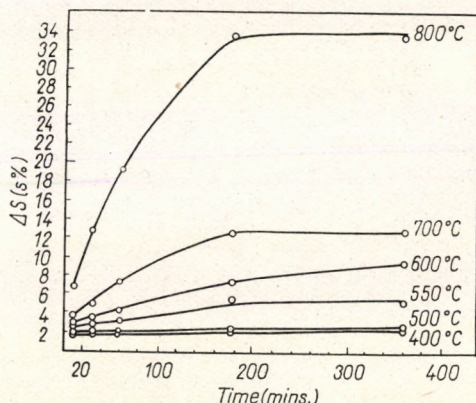


Fig. 1. Hydrolysis of anhydrous aluminium fluoride vs. temperature and time of heat treatment

$$\left(1 - \sqrt[3]{\frac{100 - x}{100}}\right)^2 = Kt \quad (12)$$

where x is the amount of aluminium fluoride converted during time t , a value in Fig. 1 by means of Equ. (7), while K is a constant.

Table II

Progress of the hydrolysis of AlF_3 when acted upon by atmospheric moisture, expressed in per cent by weight, as a function of temperature

Temperature, °C	Time of heat treatment, min.				
	10	30	60	180	360
400	1.69	1.79	1.77	2.13	2.27
500	1.99	2.17	2.17	2.54	2.82
550	2.57	2.92	3.29	5.52	5.35
600	2.98	3.65	4.39	7.52	9.48
700	3.81	5.19	7.45	12.69	12.82
800	6.80	12.69	19.11	33.48	33.64

Relative moisture content of air: 50% at 23°C

The rate constant K has the following values at various temperatures:

$$K_{550^\circ} = 1.3 \cdot 10^{-5}$$

$$K_{600^\circ} = 2.6 \cdot 10^{-5}$$

$$K_{700^\circ} = 8.3 \cdot 10^{-5}$$

$$K_{800^\circ} = 11.0 \cdot 10^{-4}$$

$$\log K = \log A - \frac{E}{2.3 RT} \quad (13)$$

where E is the activation energy, R the gas constant, T the absolute temperatures (°K), and A is a constant.

The energy of activation may be calculated from the values given in Table III. The calculation gives the following result:

$$a = - \frac{E}{2.3R} \quad (14)$$

$$a = - 0.6792 \cdot 10^{-4}$$

$$E = 370 \text{ cal/g} = 31.08 \text{ kcal/mol.}$$

Reaction of silica with anhydrous aluminium fluoride *Dynamic investigations*

The purpose of dynamic investigations was mainly to elucidate the effect of the grain size of silica on the reaction rate and on the progress of reaction. In the range between 0 and 60 microns, fractions of 2–3, 10–15, 25–35

Table III
Data to the calculation of the activation energy of the hydrolysis of AlF_3

n	y_i	x_i	$x_i y_i \cdot 10^4$	$x_i^2 \cdot 10^8$	$(x_i^2)^2 \cdot 10^8$	$T - 273$
	log K	$1/T \cdot 10^4$				
1	- 4.8713	12.15	- 59.2	147.62		550
2	- 4.5884	11.45	- 52.6	131.10		600
3	- 4.0825	10.28	- 42.0	105.68		650
4	- 2.9586	9.32	- 27.6	86.86		800
Total	-16.5008	43.20	-181.4	471.26	1866.24	

$$m = \frac{n \sum xy + \sum x \cdot \sum y}{n \sum x^2 - (\sum x)^2}$$

where K is the rate constant of the hydrolysis at various temperatures (T) and T is the absolute temperature ($^{\circ}K$)

and 40–50 μ grain size were separated by sedimentation from finely ground quartz sand, and mixed with anhydrous aluminium fluoride. The quantity of aluminium fluoride in the mixture was 58.3%.

The experimental results are shown in Figs 2 to 5. In all four cases the curves had the same shape, independently of the grain size of silica. The increase of weight loss was found to be extremely rapid between 600 and 650 $^{\circ}$.

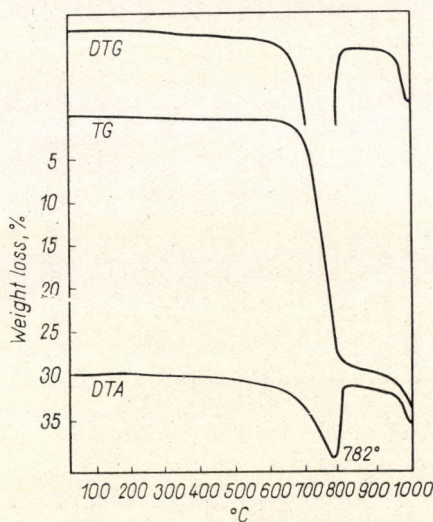


Fig. 2. Derivatogram and DTA curve of a mixture of anhydrous aluminium fluoride and silica of a grain size of 2–5 microns. The stoichiometric ratio in the mixture corresponds to reaction equation (5)

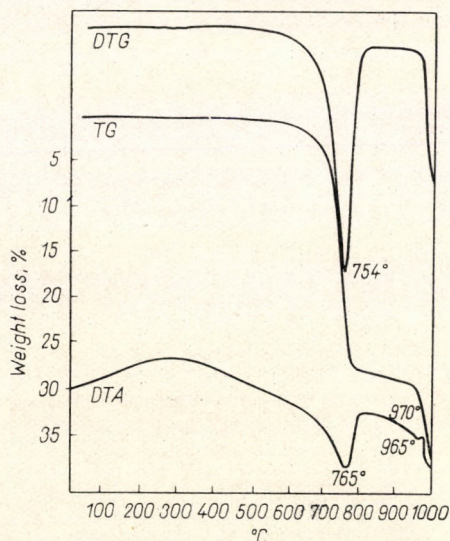


Fig. 3. Derivatogram and DTA curve of a mixture of anhydrous aluminium fluoride and silica of a grain size of 10–15 microns. The stoichiometric ratio in the mixture corresponds to reaction equation (5)

In the range from 750 to 950° the reaction rates appreciably decreased, then another maximum rate appeared above 950°. In the DTA curves, corresponding to the first maximum rate, an effect appeared which directly passed over to a more or less blurred maximum. Subsequently, another endothermic effect was observed in the range 960–980°.

The heating-up rate was 10°/minute. The derivatograph could be operated up to 1000°. It follows from the nature of the recording that the equilibrium corresponding to the end state could not be attained up to 1000°. According to reaction scheme (5) the theoretical ignition loss would be 54.2%. In the case of anhydrous aluminium fluoride the ignition loss averaged 34%.

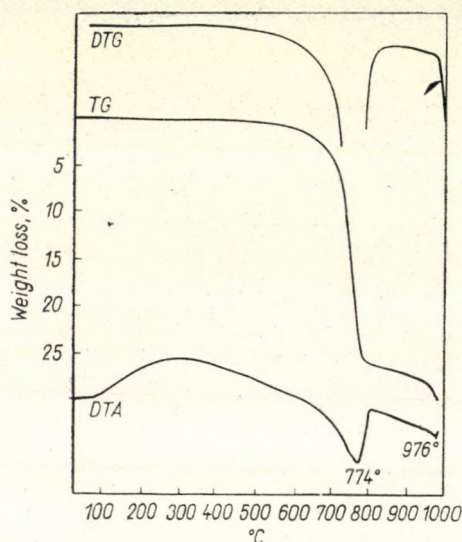


Fig. 4. Derivatogram and DTA curve of a mixture of anhydrous aluminium fluoride and silica of a grain size of 20 to 30 microns. The stoichiometric ratio in the mixture corresponds to reaction equation (5)

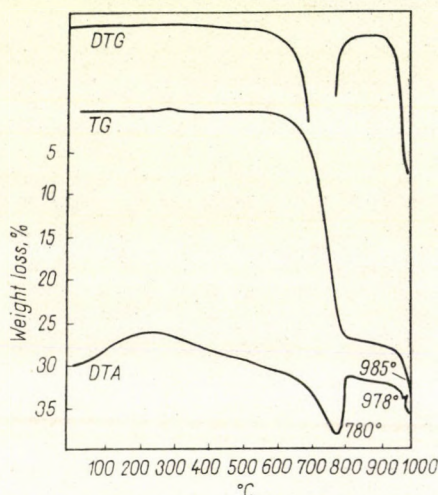


Fig. 5. Derivatogram and DTA curve of a mixture of anhydrous aluminium fluoride and silica of a grain size of 40 to 50 microns. The stoichiometric ratio in the mixture corresponds to reaction equation (5)

It has been investigated by the derivatographic method how the reaction mechanism is affected by the use of various modifications of silica. In experiments with three different modifications, quartz christobalite and quartz glass were applied. The results of the dynamic investigations are presented in Figs 6–10.

The fluorine contents of the three mixtures were 38.2, 39.5 and 44.2%, corresponding to the increasing ratios of AlF_3 used. The difference between the fluorine contents of the first two mixtures is very small though the two reactions theoretically afford two different types of mullite. Under the conditions of the

dynamic investigations, the reaction starts only to a very small extent at a temperature of about 500° . The rate of weight loss (the DTG curves in the diagrams) markedly increases at about 700° and the maximum values are attained in the range between 745 and 770° .

The samples weighed according to the stoichiometry of reaction equations (5) and (6) showed a steady but slight loss above 800° . The only exception was observed with the quartz glass sample weighed according to Eq. (11) where an appreciable weight loss appeared above 800° up to 1000° . In the other

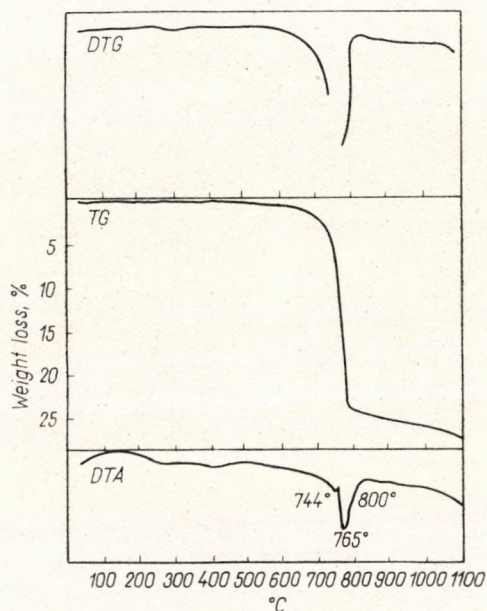


Fig. 6. Derivatogram of a mixture of 56.3% anhydrous aluminium fluoride with quartz glass. Heating-up rate: $10^{\circ}\text{C}/\text{min}$.

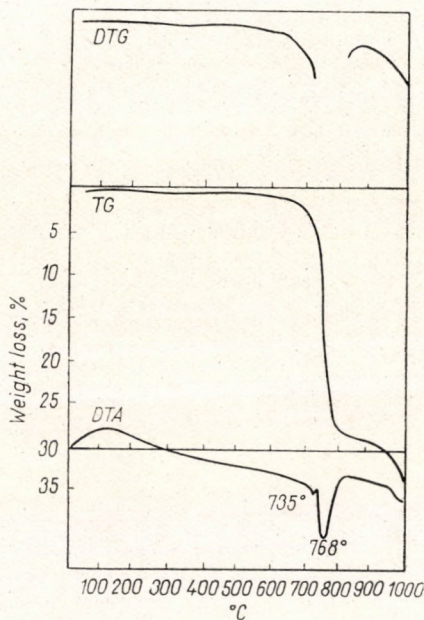


Fig. 7. Derivatogram of a mixture of 65.1% anhydrous aluminium fluoride with quartz glass. Heating-up rate: $10^{\circ}\text{C}/\text{min}$.

samples, the intensive decomposition of topaz did not begin up to 1000° under the applied experimental conditions, at a heating-up rate of $10^{\circ}/\text{min}$. This observation indicates the higher reactivity of quartz glass. The overall ignition losses at 1000° (summarized in Table IV) showed the maximum value in the case of quartz glass, followed by christobalite and quartz; this indicates at the same time the order of reactivities. The actual reaction, *i.e.* conversion into mullite is just begun and it is still far from being completed at this temperature, as proved by two experiments carried out at 1100° when no completion of the reaction could be observed at this temperature either.

Table IV

Ignition losses (per cent by weight) obtained with various modifications of silica up to 1000° at a heating-up rate of 10°/min.

AlF ₃ , % (w/w)	56.3	65.1	58.3
Quartz glass	26.0	34.1	27.7
Christobalite	25.4	27.4	25.2
Quartz	20.6	24.3	23.6

Static investigations

In an investigation under static conditions of the effect of the grain size of silica (quartz sand) on the state of the reaction, results resembling those obtained under dynamic conditions were observed. The data are given in Table V. These experiments were carried out at 625° with quartz sand of grain sizes of 2–3 and 40–50 μ , respectively, applying the heat treatment for 10, 30, 60 and 240 minutes. The experiments were of a continuous nature; after the elapse of certain periods the weight of the sample was determined and the

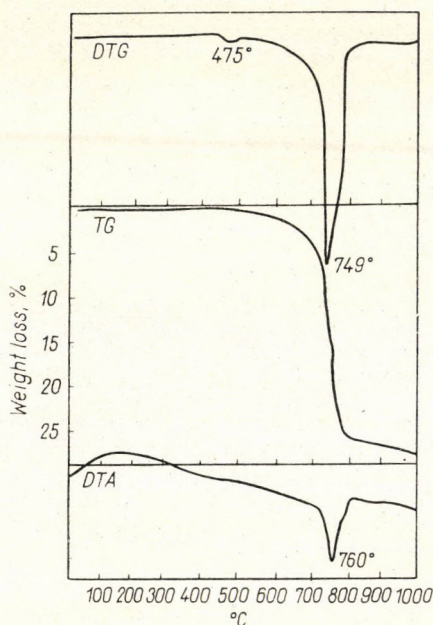


Fig. 8. Derivatogram of a mixture of 58.3% anhydrous aluminium fluoride with quartz glass. Heating-up rate: 10 °C/min.

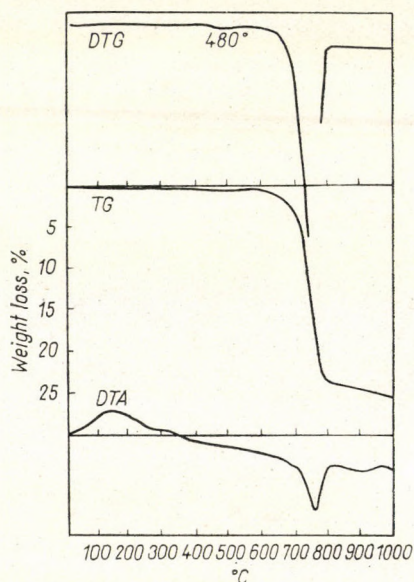


Fig. 9. Derivatogram of a mixture of 56.3% anhydrous aluminium fluoride with christobalite. Heating-up rate: 10 °C/min.

Table V

Effect of the grain size of silica on the reaction rate; static investigation at 625 °C

Sample weight S_0 g	Ignition loss $S_0 - S_i$ g	$\left(1 - \frac{S_i}{S_0}\right) \cdot 100$ %	Duration of heat treatment, min.	Grain size of quartz μ
0.6923	0.0100	1.45	10	2—3
0.6771	0.0200	2.95	30	2—3
0.6980	0.0685	9.90	60	2—3
0.6874	0.1399	20.30	240	2—3
0.6791	0.0064	0.95	10	40—50
0.6896	0.0298	4.31	30	40—50
0.6632	0.0836	12.60	60	40—50
0.6481	0.1333	20.60	240	40—50

test was continued with the same sample. In the case of solid state reaction the experiments showed satisfactorily identical end states with both grain sizes employed. The repeated heat treatment, for another 200 minutes, of samples previously heat-treated for 10, 30 or 60 minutes, gave ignition losses of 20.2—20.9%. This can be explained only by presuming that the reaction proceeds through a vapour phase. On the basis of these results, the investigation of the reaction mechanism was continued with substances of various grain sizes below 60 μ .

The results of continuous isothermal experiments plotted against the temperature are shown in Figs 11 to 15. These experiments were conducted at

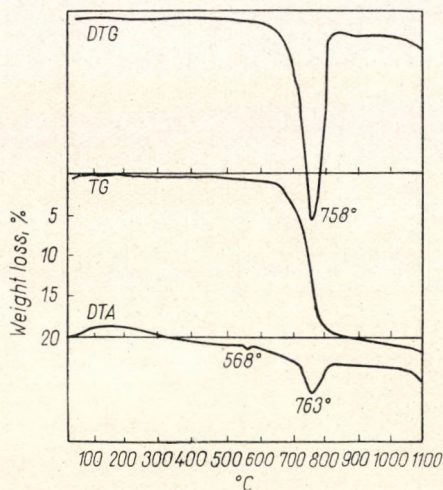


Fig. 10. Derivatogram of a mixture of 56.3% anhydrous aluminium fluoride with quartz. Heating-up rate: 10° C/min.

identical concentrations and the same modifications of silica as those applied in the dynamic investigations. On the basis of the dynamic results, heat treatment was started at 500° and completed at 1200°. Identical samples were subjected to heat treatment in the steps 500—600—650—700—750—800—850—900—1000—1100—1200°. In the cases of aluminium fluoride contents of 56.3 and 58.3%, the weight losses were practically the same, with the exception of quartz glass. This can be interpreted by its amorphous state and higher energy content.

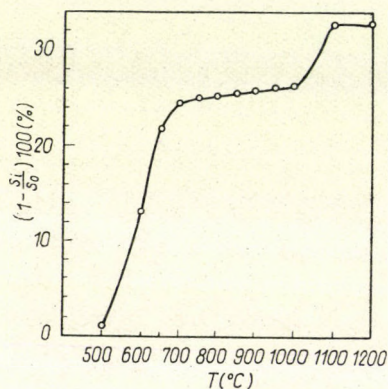


Fig. 11. Weight loss of a mixture of 56.3% anhydrous aluminium fluoride and quartz glass during continuous isothermal heat treatment, as a function of temperature

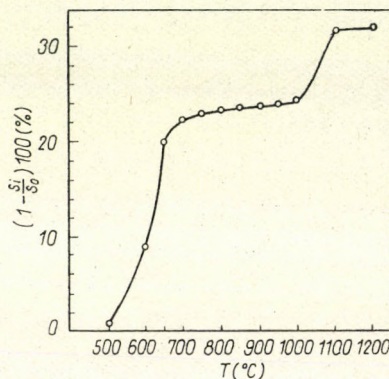


Fig. 12. Weight loss of a mixture of 56.3% anhydrous aluminium fluoride and cristobalite during continuous isothermal heat treatment, as a function of temperature

With the first two ratios of aluminium fluoride the end product of heat treatment was mullite, while in the third variation it consisted of corundum and mullite.

Interaction of AlF_3 and SiO_2 in vacuum

The weight losses observed both in the dynamic and in the static investigations were found to be appreciably lower than the theoretical losses calculated on the basis of reactions (5) and (6). This points to the fact that both the hydrolysis of aluminium fluoride and reaction (11) play an essential role in the reaction mechanism. On the basis of the data obtained so far it also became dubious whether a solid phase reaction of this type is possible directly between aluminium fluoride and silica [1, 3].

In order to study this problem, experiments were conducted in vacuum, at a pressure lower than 10^{-5} torr, in a resistance furnace. The results are listed in Table VI. The values of weight losses accurately follow the theoretical ignition losses calculated on basis of the weight of the samples. The diffracto-

Table VI

Percentage weight loss in vacuum, plotted against the temperature

Temperature °C	300	400	500	600	700	800	900	1000	1300
1	0.7	0.9	1.6	4.9	30.0	37.5	42.3	44.2	53.7
2	0.4	0.8	1.3	5.9	32.0	39.7	44.9	—	—
3	—	—	—	—	—	38.1	—	—	54.2

1: Interrupted heat treatment

2: Continuous heat treatment between 300 and 900 °C

3: Theoretical loss, calculated for the formation of topaz at 800 °C, and for that of mullite and corundum at 1300 °C.

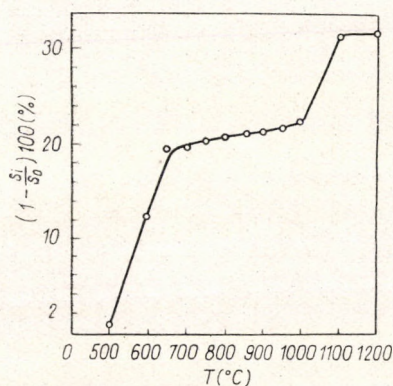


Fig. 13. Weight loss of a mixture of 56.3% anhydrous aluminium fluoride and quartz during continuous isothermal heat treatment, as a function of temperature

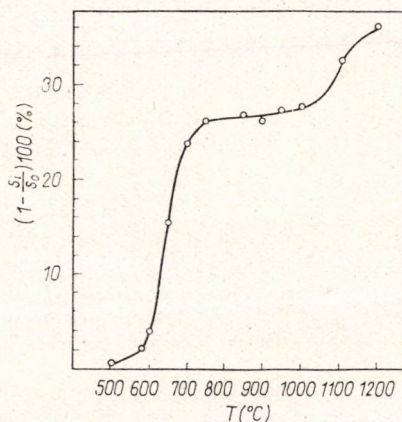


Fig. 14. Weight loss of a mixture of 58.3% anhydrous aluminium fluoride and quartz glass during continuous isothermal heat treatment, as a function of temperature

grams of the substance heat-treated at 800 and 1300° are presented in Table VII.

At 800° topaz of a fluorine content of 20.4% was formed; this value is only slightly lower than the theoretical one. The ignition loss slightly exceeded the theoretical value. Accordingly, the presence of mullite could also be detected in the product to a small extent. In the sample ignited at 1300°, mullite and corundum were simultaneously present. Consequently, up to 1300° no mullite ($2 \text{ Al}_2\text{O}_3 \cdot \text{SiO}_2$) has been formed, only a mixture of $3 \text{ Al}_2\text{O}_3 \cdot \text{SiO}_2$ and corundum.

The derivatogram of the topaz formed at 800° is shown in Fig. 14. Since this derivatogram was prepared in an ordinary furnace (not in vacuum furnace), the hydrolysis of fluoro-topaz started to a small extent also at temperatures below 800° owing to atmospheric moisture, in the sense of reactions (7) and (8).

Table VII

Phases formed in vacuum during the reaction of SiO_2 with AlF_3

Prior to heat treatment			After heat treatment at 800 °C			After heat treatment at 1300 °C		
d kX	I	A	d kX	I	A	d kX	I	A
3.852	17	N	5.338	7	M	5.400	33	M
3.488	98	A	4.392	8	x	3.900	10	N
3.731	37	N	4.110	14	x	3.482	16	C
2.494	4	A	3.858	14	N	3.430	41	M
2.230	4	N	3.705	34	x	3.400	58	M
2.112	18	A	3.400	7	M	2.885	10	M
2.066	4	A	3.208	36	x	2.747	33	N
2.014	3	A	3.038	15	x	2.700	25	M
1.933	4	N	3.000	11	x	2.549	35	M, C
1.756	24	A	2.942	36	x	2.430	8	M
1.728	5	N	2.731	39	N	2.380	8	C
1.581	20	N	2.494	10	x	2.298	10	M
1.557	8	A	2.392	7	x	2.242	3	N
			2.365	18	x	2.210	16	M
			2.309	4	x	2.115	15	M
			2.253	3	x	2.085	18	C
			2.232	3	N	1.938	4	N
			2.205	7	x	1.893	4	M
			2.181	6	x	1.845	5	M
			2.133	3	x	1.736	9	C
			2.104	22	x	1.698	7	M
			2.061	10	x	1.600	20	C
			1.995	3	x	1.581	9	N
			1.933	6	x	1.525	16	M
			1.862	11	x	1.462	4	M
			1.822	5	x	1.442	8	M
			1.799	3	x			
			1.784	3	x			
			1.728	3	N			
			1.675	10	x			
			1.625	5	x			
			1.578	8	N			
			1.532	8	x			

where M denotes mullite, N ammonium chloride, A aluminium fluoride, x topaz, and C corundum

Accordingly, the decomposition of topaz which is complete at 1100° cannot yield the theoretical value of the total ignition loss, since besides silicon tetrafluoride also hydrogen fluoride is split off, corresponding to the equilibrium state which depends on the prevailing temperature of reaction (8).

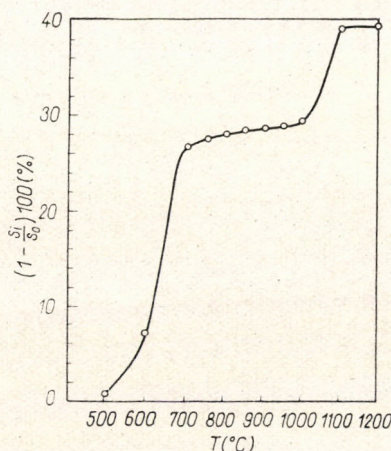


Fig. 15. Weight loss of a mixture of 65.1% anhydrous aluminium fluoride and quartz glass during continuous isothermal heat treatment, as a function of temperature

Investigation by X-ray diffraction of the beginning of the reaction between AlF_3 and SiO_2

It has been proved in the static investigation of the reaction of aluminium fluoride with silica that mullite formation starts also at low temperatures. However, it is still uncertain which phases are formed besides mullite. This investigation was carried out with a thermal diffraction chamber by Dr. T. TAKÁTS in the *Department for Fundamental Researches* of this Institute. The experimental results are shown in Figs 16 to 19. It appears from the series of X-ray diagrams that in the temperature range from 500 to 550° the amount of aluminium fluoride plotted against the time of heat treatment gradually decreases. This can be observed in the diagrams from the decrease of the intensity of the aluminium fluoride line 3.52 kX. After certain decreased level has been attained, mullite formation begins in the material. Parallel with the increase of the mullite content, which is shown by the increase of the intensity of the principal line (3.40 kX), aluminium fluoride completely disappears. In the diffractograms made with the samples after the disappearance of aluminium fluoride, only the mullite line is perceivable. However, also the presence of an amorphous phase can be detected on basis of the convexity of the basic curve of the diagram. The amount of mullite was quantitatively determined using a synthetic mullite preparation ($2 \text{ Al}_2\text{O}_3 \cdot \text{SiO}_2$; 76% Al_2O_3) as internal standard. On the

basis of Fig. 20, a mullite content of 10% can be established by taking into account the ratio of intensities of the line 3.40 kX prior and after the addition of synthetic mullite.

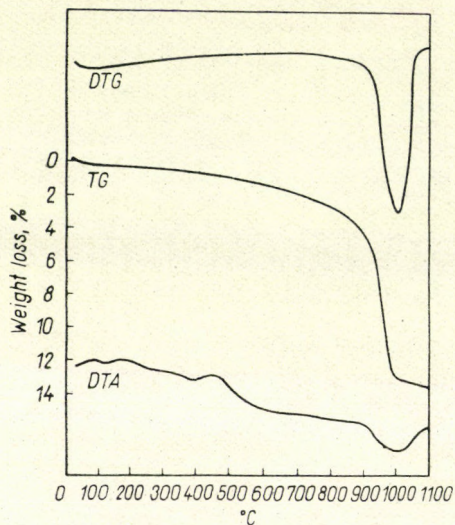


Fig. 16. Derivatogram and DTA curve of topaz synthesized in vacuum at 800 °C. Heating-up rate: 10 °C/min.

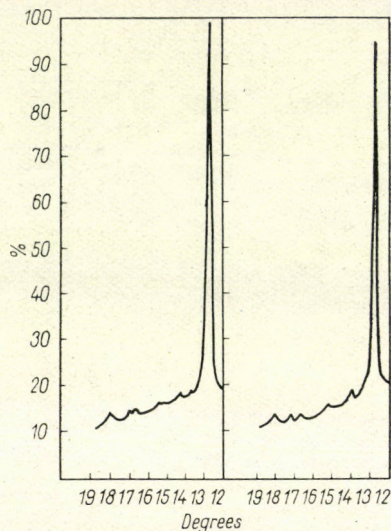


Fig. 17. Thermal diffractogram of a mixture of anhydrous aluminium fluoride and quartz glass. Temperature 500 to 550 °C, exposure 10 and 15 min.

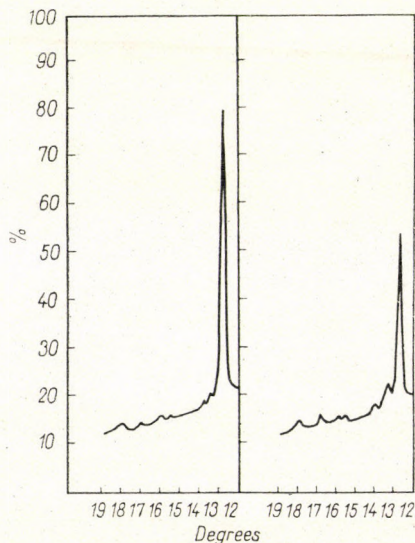


Fig. 18. Thermal diffractogram of a mixture of anhydrous aluminium fluoride and quartz glass. Temperature 500 to 550 °C, exposure 40 and 60 min.

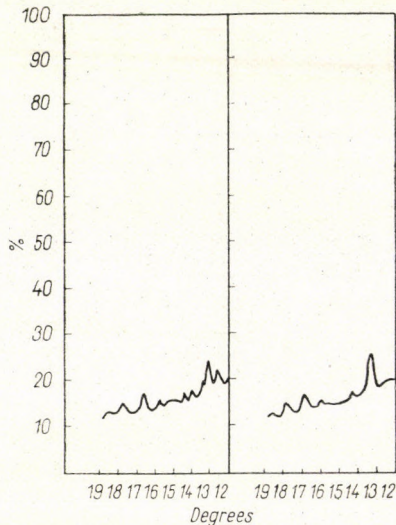


Fig. 19. Thermal diffractogram of a mixture of anhydrous aluminium fluoride and quartz glass. Temperature 500 to 550 °C, exposure 150 to 180 min.

After thermal treatment the fluoride content of the product was 14%. The nature of the diagram, the fluoride content of the product, and the fact that the hydrolysis of aluminium fluoride carried out in the discussed temperature range gave a product with a well-defined X-ray diagram constitute evidence to show that, in addition to 10% of mullite, an amorphous phase of about 90% was formed, which latter contains the mentioned amount of fluoride. The diagram obtained after the hydrolysis of aluminium fluoride at 550° is shown in Fig. 21. It can be seen that the hydrolysis of aluminium fluoride at 550° by

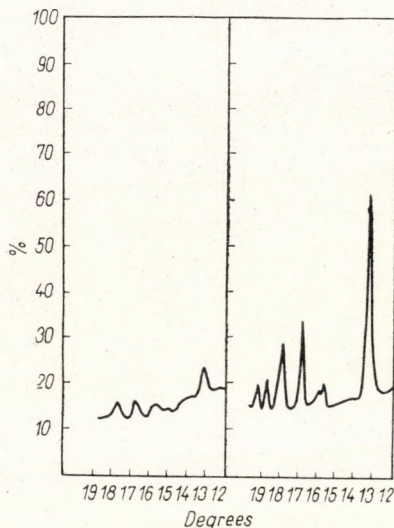


Fig. 20. Thermal diffractogram of a mixture of anhydrous aluminium fluoride and quartz glass. Temperature 500 to 550 °C, exposure 210 min. The diffractogram was obtained in a cold state, after exposure to heat treatment. Diffractogram of the heat-treated substance alone (left), and that of a mixture of the substance with 50% of synthetic mullite (right). On the basis of the intensity ratios of the two diffractograms, the amount of mullite is approximately 10%

the action of atmospheric moisture under conditions identical with those applied in the X-ray investigations is incomplete in 240 minutes. The lines of aluminium fluoride are still perceptible, and also those of the hydrolytic product can be detected in the X-ray diagrams, though attempts to identify them have failed thus far. The product of the hydrolysis of aluminium fluoride is presumed to be aluminium fluoride with undefined contents of fluorine.

Discussion

It has been proved by the static and dynamic investigations with anhydrous aluminium fluoride that the reactions taking place in the system SiO_2 — AlF_3 are characterized by partial hydrolysis of aluminium fluoride occurring

even with atmospheric moisture. The ratio of fluorine split off during the reaction as hydrogen fluoride and silicon tetrafluoride, characterizes also the reaction of aluminium fluoride with silica in the presence of water. It has been confirmed by diffraction studies that in the presence of silica the conversion and decomposition of aluminium fluoride take place more rapidly than the hydrolysis of aluminium fluoride. This points to the possibility of a direct reaction of aluminium fluoride with silica.

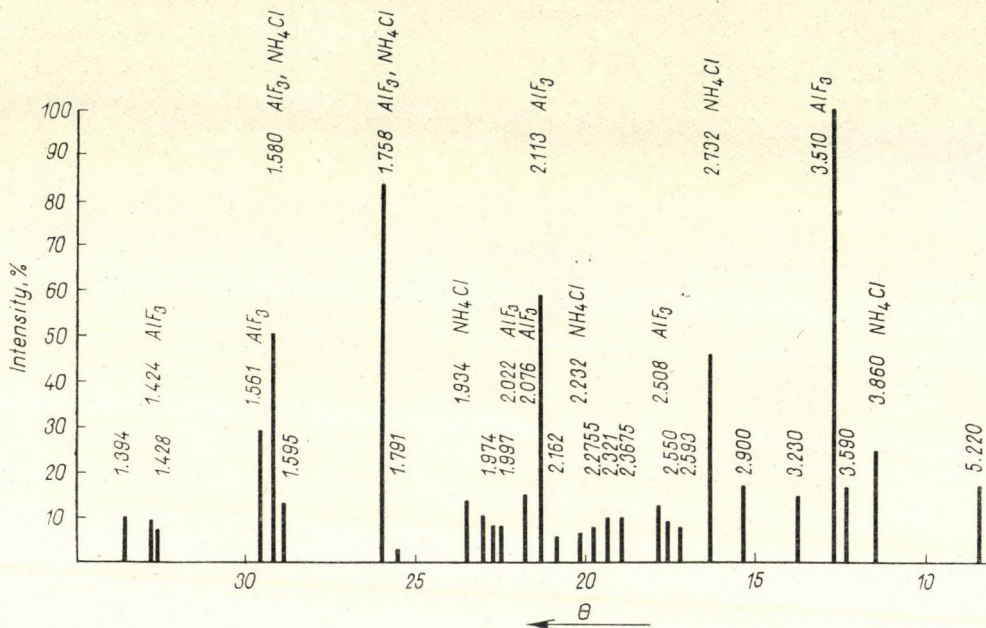


Fig. 21. Diffractogram of anhydrous aluminium fluoride after heat-treatment for 240 min. at 550°C in a medium containing steam

Experiments in a vacuum furnace have shown, indeed, that aluminium fluoride may react directly with silica (cf. Fig. 22) and that the weight loss and the decrease of fluorine content are in accordance with reaction Eq. (6) and indirectly also with reaction (5). Thus, it can be established that under anhydrous conditions the fluorine present leaves the system as silicon tetrafluoride, to an extent determined by the equilibrium state which is defined by the given parameters of temperature and heat treatment. These results support the reality of the reactions (5), (6) and (11) between aluminium fluoride and silica which were considered so far only as hypothetical processes. Investigations conducted in vacuum proved the existence of the fundamental reaction and the formation of fluorotopaz from the aspects of both the weight loss and the fluorine loss. Also the end state corresponds to the theoretical weight loss. In the vacuum furnace at 1300°, besides mullite, also corundum

was formed according to reaction (6), *i.e.* the formation of mullite approaching a composition of 3/2 is possible. The end product contained 75.9% of alumina, 23.9% of silica and 0.4% of fluorine.

Accordingly, the mechanism and progress of the reaction can be characterized with the weight loss and with the decrease of fluoride content by the following relation:

$$\Delta S = \Delta F \frac{R}{100} \cdot A_1 + A_2$$

where ΔS is the weight loss up to temperature T_i , ΔF = decrease of the fluorine content (%), R = the quantity (ratio) of fluorine leaving the system as SiF_4 , while A_1 and A_2 are constants, equal to 4.894 and 0.578.

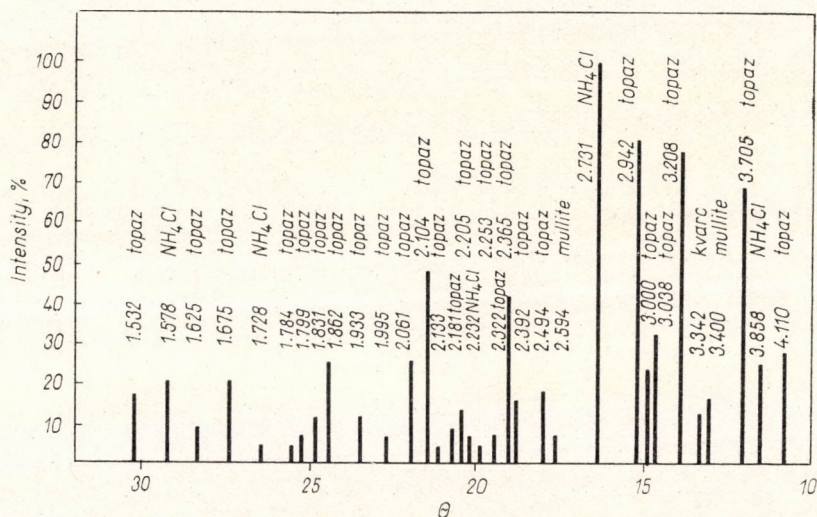


Fig. 22. Diffractogram of fluorotopaz synthesized in vacuum at 800 °C

On the basis of the dynamic and static investigations, the effect of the thermal gradient on the kinetics of the reaction can be qualitatively established. However, it appears advisable to subject this problem to a more thorough quantitative examination.

In the course of the reaction of aluminium fluoride and silica in the presence of water, three processes take actually place:

1. Direct reaction of aluminium fluoride and silica.
2. Hydrolysis of aluminium fluoride.
3. Reaction of silica with hydrogen fluoride formed in the hydrolysis of aluminium fluoride.

The over-all result of this process may be adequately followed by measuring the ratio of fluorine (the so-called "R" value) leaving the system as silicon

tetrafluoride. However, it has not been possible to decide whether silicon tetrafluoride is really formed as a primary or secondary product. Direct reaction is also a possibility, as proved by experiments carried out in vacuum and by thermal X-ray investigations.

During the reaction, amorphous and crystalline aluminium fluorosilicate are formed as the intermediate phases which are then converted into mullite by consecutive thermal decomposition. The fundamental importance of the thermal gradient has been proved by the X-ray diffraction tests which show mullite formation to begin at temperatures below 600° and prove the formation of an amorphous phase. At low temperatures, mullite is formed through an amorphous phase. Namely, the mullite line appears only after the consumption of an appreciable portion of aluminium fluoride. The development of the amorphous phase is of necessity simultaneous with the progress of the hydrolysis and the reaction of aluminium fluoride.

SUMMARY

On the basis of dynamic and static reaction kinetical investigations it has been shown that anhydrous aluminium fluoride can also directly react with silica. This process may quantitatively take place even in a completely anhydrous system. In the presence of water, hydrolysis of aluminium fluoride may begin because of the action of atmospheric moisture, and may markedly affect the reaction mechanism. In the reaction of aluminium fluoride with silica, mullite is formed through an intermediate phase of amorphous and crystalline aluminium fluorosilicate. The formation of mullite starts at temperatures below 600 °C, depending on the thermal gradient of the reaction and on the fluorine content of the system; in this case no crystalline aluminium fluorosilicate phase is developed. Mullite is formed from the amorphous phase at lower temperatures than from topaz, the crystalline form of aluminium fluorosilicate.

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APPLICATION OF ANODIC STRIPPING VOLTAMMETRY IN THE ANALYSIS OF PURE METALS

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Introduction

Our Institute has been working for four years on the subject of determining trace contaminants in various high purity metals and reagents. Besides the methods of spectrography and activation analysis, anodic stripping voltammetry has also been applied with success in this work. The following electrode types have been tested and are in use:

1. Hanging mercury drop electrode at gilded platinum.
2. Mercury drop pool electrode with platinum point contact.
3. Hanging mercury drop electrode with side screw and "Nalgon" tube.
4. Silver electrode covered by plastic material.
5. Graphite electrode.

Some problems in connection with the above electrode types have already been discussed at the *Pure Metals Symposium* in Dresden, in September, 1965 [1] and at the *International Symposium on Microchemical Techniques* in Pennsylvania, in August, 1965 [2]. In the course of a normal routine analysis, copper, lead, cadmium, zinc and gallium can be determined in aluminium of 99.99–99.9999% purity, in a sample of max. 0.2 g, by means of a mercury electrode. Ga is determined in a 0.001 M solution of benzoic acid, and the other components in a hydrochloric acid medium of pH = 3. The copper, lead and cadmium contaminants of high purity gallium are determined in a weak hydrochloric acid medium; the zinc, copper, cadmium and lead contents of high purity manganese in a sodium acetate electrolyte. The time of electrolysis, voltage, rate of mixing and scan rate of stripping which are optimal from the point of view of enrichment are selected in each case depending on the component to be determined, and upon the electrolyte.

The most important condition of this method is the use of reagents of sufficiently high purity for each determination. Our reagents were prepared, in general, in this Laboratory. Ultra-pure hydrochloric acid, nitric acid, acetic acid and ammonia were obtained by the cold distillation process. Sodium acetate, sodium citrate and potassium chloride were freed from undesirable impurities by extraction with dithizone and subsequent recrystallization.

Investigation of the determination of further trace contaminants of aluminium

In the investigation of trace contaminants of high purity aluminium, the problem of silver determination is also encountered. Since very small quantities (1–0.1 ppm) are involved, anodic stripping voltammetry is the only polarographic method which may be used to solve this problem. In this case a stationary mercury electrode is not suitable as the working electrode, since the normal potentials of the systems Ag^+/Ag and $\text{Hg}_2^{2+}/\text{Hg}$ are practically identical [3]. The methods mentioned in the literature for determining silver by anodic stripping voltammetry or by coulometry suggest the use of platinum [4], graphite [5, 6] and carbon paste [7, 8] as the working electrodes.

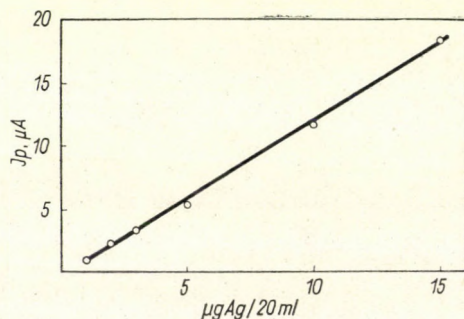


Fig. 1. I_p vs. C_{Ag} in 0.1 M HCl. Enriching electrolysis at -0.7 V vs. S. C. E. for 10 minutes

Graphite which is a good conductor and has an inert character is a very suitable electrode material in anodic voltammetry [9, 10]. Owing to its high oxygen overvoltage, it is especially useful in the determination of anodic oxidation processes and metals of not very negative normal potentials. Graphite has one drawback: the renewal of its surface is a rather complicated procedure. The quality of graphite surface is of decisive importance as far as the residual current is concerned. If the electrode surface is coarse, the residual current is larger [11].

In order to develop a rapid and simple method, 0.1 M HCl was chosen as the supporting electrolyte, since aluminium can be dissolved most readily in this acid. We determined the highest silver concentration which did not give yet a precipitate in 0.1 M HCl under the experimental conditions used. This value was not identical with that calculated from the solubility product, the latter being $1.56 \cdot 10^{-9}$ M. In spite of this, no precipitate was obtained even at silver concentrations of $7.5 \cdot 10^{-6}$ M. This fact is probably due to the formation of a chloro-complex. It is seen in Fig. 1 that the I_p — C_{Ag} function is linear even at higher silver concentrations (the peak current is directly proportional to the concentration), whereas formation of a precipitate should

cause a breaking point in this function (Fig. 1). This means that 0.1 M HCl can be used as the supporting electrolyte, since no silver precipitate is formed in the presence of the small amounts of Ag present in the aluminium of 99.999% purity to be analyzed.

Experimental method

The working electrode had a surface of 3.14 mm² and consisted of spectroscopically pure graphite impregnated with paraffin. The electrode was soaked in a bath of chemically pure hot paraffin for 2 hrs. The electrode surface was prepared by polishing with fine emery cloth

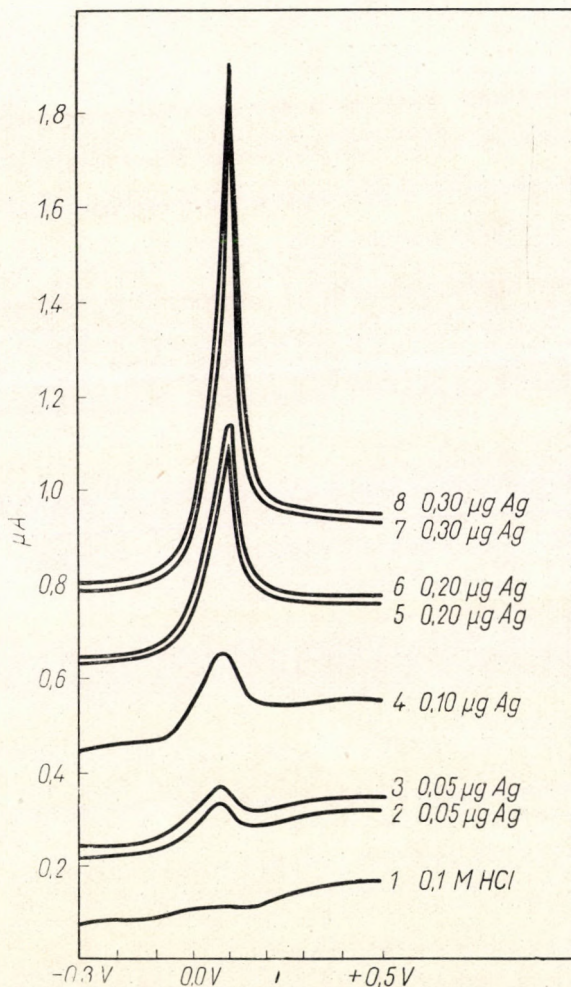


Fig. 2. Current-voltage curves for stripping of silver in 0.1 M HCl. Enriching electrolysis for 10 minutes at -0.7 V vs. S. C. E.

Silver concentration: 1. Supporting electrolyte — 2.—3. $0.05 \mu\text{g Ag}/20 \text{ ml}$ — 4. $0.10 \mu\text{g Ag}/20 \text{ ml}$ — 5—6. $0.20 \mu\text{g Ag}/20 \text{ ml}$ — 7—8. $0.30 \mu\text{g Ag}/20 \text{ ml}$

and with filter paper. The prepared graphite electrode may be polarized in 0.1 M HCl between +1.1 V and -0.7 V *vs.* S. C. E., with the residual current in this range not exceeding 0.2 μ A.

The measuring cell was a quartz beaker covered by a plexiglass cover with three perforations. A saturated calomel electrode which was connected to the cell by a salt bridge was used as the reference electrode. The salt bridge was filled with the supporting electrolyte — in this case with 0.1 M HCl — and the end of the bridge submerged in the calomel electrode was stopped up by a plug made of a twist of filter paper. Generally a solution volume of 20 ml was used. Nitrogen or argon gas was used to remove oxygen from the sample solution. A *Radelkisz Type OH-102 Polarograph* was used for the measurements, and the constancy of material transport was ensured by a magnetic stirrer of constant revolution rate.

Results

In the first part of our work the parameters which influence the determinations were investigated in aluminium-free solutions. The graphs of potential *vs.* peak current, and time of electrolysis *vs.* peak current were obtained during the enriching electrolysis. These curves showed an optimal electrolysis potential of -0.5 to -0.7 V, and an optimal time of electrolysis of 5 to 10 minutes in the concentration range of 10^{-8} M. The scan rate in the stripping process was 1.5 V/min, the peak potential of silver was +0.1 V *vs.* S. C. E. This value varies by some 0.01 V depending on the concentration. Fig. 2 shows some typical silver stripping curves.

The peak currents were reproducible to ± 5 relative % provided the electrode surface had been cleaned before each measurement by electrolyzing for some minutes at +0.8 V. The presence of aluminium slightly modifies the peak potential and the form of the stripping curves. The peak potential takes on the value of 0.0 V relative to the saturated calomel electrode. Fig. 3 shows that the silver stripping curves develop less sharply defined peaks in the presence of aluminium.

The silver concentration *vs.* peak current curve was recorded in the concentration zone of 10^{-8} in the presence of different amounts of aluminium (Fig. 4). These curves show that by increasing the amount of aluminium, the slope of the curves, *i.e.* the sensitivity of the method, decreases.

The determination is disturbed by the presence of metals which have a more positive formal potential than the potential of the enriching electrolysis.

We found that on a graphite electrode Cu and Bi were represented by peaks in the vicinity of the silver peak (Cu $E_{ip} = -0.2$ V, and Bi $E_{ip} = -0.05$ V). Therefore, if these metals are presented in concentrations of a higher order of magnitude, the method is not applicable. Even in amounts of the same order of magnitude their presence interferes with the evaluation and so impairs the accuracy of the method.

The method was tested with aluminium samples of different silver contents. Before dissolving the aluminium of 99.9999% purity, different amounts of silver were weighed and added to it, and the silver content was determined.

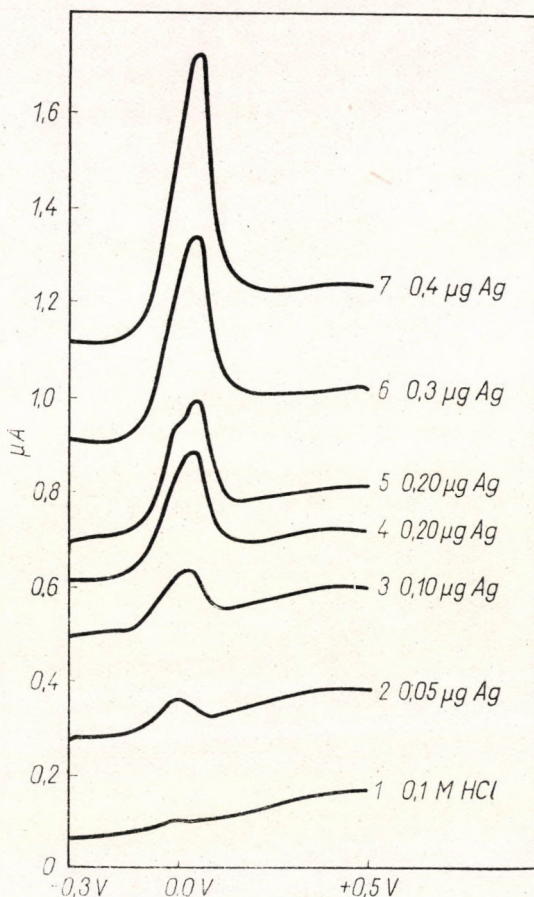


Fig. 3. Current-voltage curves for stripping of silver in 0.5 M HCl in the presence of 0.1 g of Al. Enriching electrolysis at -0.7 vs. S. C. E. for 10 minutes
Silver concentration: 1. Supporting electrolyte — 2. $0.05 \mu\text{g Ag}/20 \text{ ml}$ — 3. $0.10 \mu\text{g Ag}/20 \text{ ml}$ — 4—5. $0.20 \mu\text{g Ag}/20 \text{ ml}$ — 6. $0.30 \mu\text{g Ag}/20 \text{ ml}$ — 7. $0.40 \mu\text{g Ag}/20 \text{ ml}$

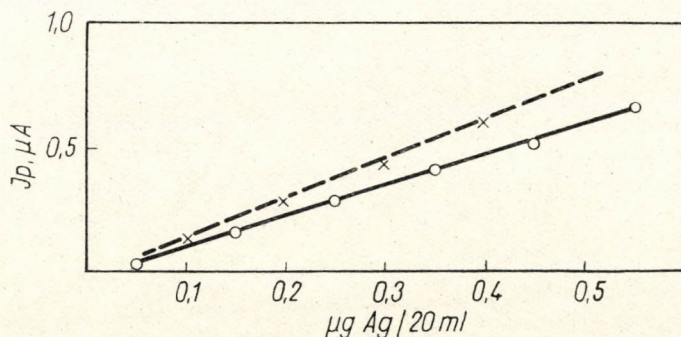


Fig. 4. I_p vs. C_{Ag} in 0.1 M HCl in the presence of 0.1 g and 0.2 g — of Al
Enriching electrolysis at -0.7 V vs. S. C. E. for 10 minutes

It has been found possible to determine 0.5 ppm of silver ($0.05 \mu\text{g}$ of Ag in the presence of 0.1 g of Al in 20 ml of electrolyte); the accuracy of the method is ± 5 (relative) per cent. Parallel determinations were made by activation analysis, and the results were found to be the same as obtained by stripping voltammetry.

Similarly to the analysis of silver, also gold may be determined in aluminium by stripping voltammetry, using a paraffin-impregnated graphite electrode. The development of this procedure is in progress in our Institute.

SUMMARY

The extension of stripping analysis to the determination of trace quantities of silver and gold in aluminium has been investigated. Paraffin-impregnated graphite electrode was used in the experiments. A method has been evolved for the determination of silver in high purity aluminium. The error limit of the method does not exceed ± 5 relative %, the lower limit of sensitivity is 0.5 ppm. Further studies are in progress in our Institute for the determination of gold in aluminium.

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INVESTIGATIONS ON ION-EXCHANGE EQUILIBRIA WITH RADIOACTIVE TRACER METHOD, XI

USE OF LIQUID ION-EXCHANGE FOR INVESTIGATING THE COMPLEX SPECIES
OF INDIUM WITH α -HYDROXYISOBUTYRIC ACID

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Introduction

When investigating the formation and structures of complex species, the possibilities offered by ion-exchange and extraction techniques are the most promising procedures. Though ion-exchange is considered generally useful for systems in which there are only mononuclear complexes, it has some drawbacks as compared with extraction:

(a) When approaching equilibrium, the Donnan penetration is to be taken into account;

(b) Determination of the concentration in the resin phase usually runs into difficulties;

(c) The time required for attaining equilibrium is considerably longer than in case of liquid-liquid partition;

(d) Adaption of the data obtained with the aid of batch equilibrium measurements to column operation necessitates uncertain approximations.

Most of the difficulties and disadvantages of the two methods can be eliminated by using liquid ion-exchangers, and it was actually the primary purpose of the present investigations to prove the applicability and reliability of this technique.

Experimental

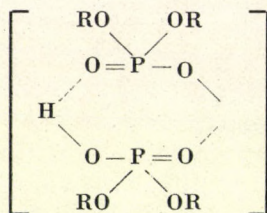
Equilibrium measurements were made using polythene bottles; after shaking for 4 hours at 25° C, the bottles were stored overnight and aliquot portions of both phases were used to determine the concentration and pH if required. The ratio of phases was adjusted to 1 : 1.

Radioactive ^{114}m In was produced by the conventional (n, γ) reaction by irradiating indium metal of spectrographic purity with a thermal neutron flux $2 \times 10^{13} \text{ n.cm}^{-2} \text{ sec}^{-1}$. The irradiated target was dissolved in concentrated nitric acid, and the solution evaporated three times to dryness, in the presence of excess c.p. perchloric acid, to avoid any complexing due to nitrate or chloride ions.

The concentration of indium was maintained at 10^{-4} M . The ionic strength of the aqueous solution was adjusted with HClO_4 to 0.5 M (with the exception of the series where pH was to be changed).

α -Hydroxyisobutyric acid (AHIBA) solutions of the required concentrations were prepared by diluting stock solutions. The free ligand concentration (AHIB^-) was calculated from the dissociation constant values given in the literature [1].

Di-2-ethylhexyl phosphoric acid (DEHPA) dissolved in toluene was chosen as the ion-exchanger representing the organic phase. According to the literature [2], DEHPA is present in dimeric form in a non-polar organic solvent:



(where R denotes the ethylhexyl radical).

The concentration of indium in both phases was determined by a well-type scintillation detector and a *Gamma Scaler type MK-108*, while the pH was measured by *Radiometer PH-4* using a glass-calomel electrode pair.

In measuring the hydrogen ion concentration in the region below pH = 1 troubles due to electrode error were encountered, so in such cases a known volume of a standard sodium hydroxide solution was added to the sample, and the pH of the original solution was determined by calculation.

Results

In order to prove the reliability of the method the first series of experiments was carried out in the absence of any complexing agent. Figs 1 and 2

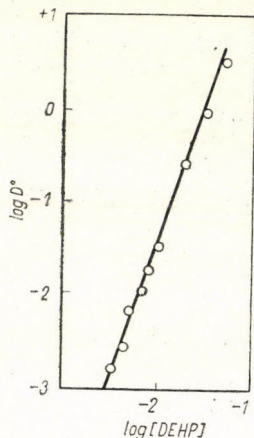


Fig. 1. Distribution ratio as a function of the concentration of di-2-ethylhexyl phosphoric acid $[\text{In}^{3+}] = 10^{-4} \text{ M}$, $[\text{HClO}_4] = 0.5 \text{ M}$

show the dependence of distribution between the organic and aqueous phases as a function of the pH at equilibrium in the aqueous phase, and the initial concentration of DEHPA in the organic phase, respectively. Both sets of data reveal third power dependence (slope = 3) indicating the distribution of the trivalent indium ions.

The results of measurements at various concentrations of α -hydroxy-isobutyric acid are shown in three types of diagrams.

In the first set $1/D$ was plotted against the free ligand concentration at different ionic strengths (Fig. 3). The second set shows the plot $\frac{D^0 - D}{[L]}$ against D (Fig. 4), while in the third, the change of $\log D$ as a function of $\log [\text{DEHPA}]$ is represented (Fig. 5). Each diagram indicates linear correlations.

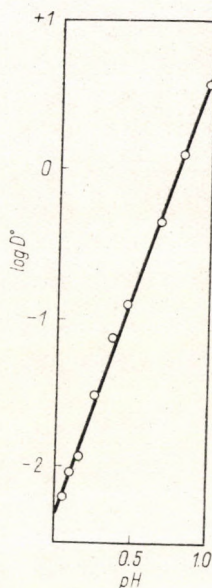


Fig. 2. Distribution ratio as a function of the pH $[\text{In}^{3+}] = 10^{-4} \text{ M}$, $[\text{DEHPA}] = 10^{-2} \text{ F}$

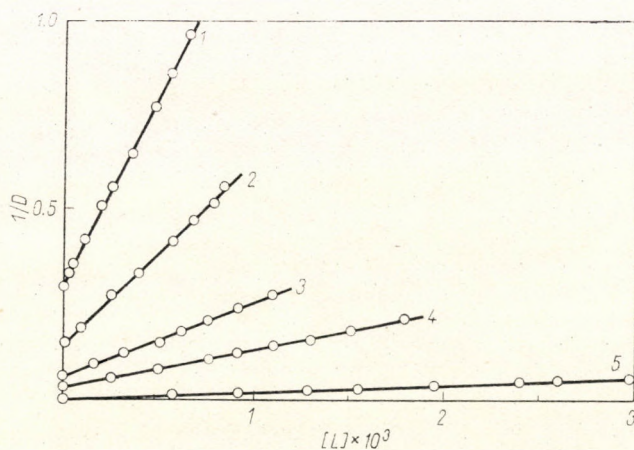


Fig. 3. Inverse of distribution ratio as a function of the free ligand concentration at different ionic strengths $[\text{In}^{3+}] = 10^{-4} \text{ M}$, $[\text{DEHPA}] = 5 \times 10^{-2} \text{ F}$ 1: 0.5 M HClO_4 ; 2: 0.4 M HClO_4 ; 3: 0.3 M HClO_4 ; 4: 0.2 M HClO_4 ; 5: 0.1 M HClO_4

Discussion

In the absence of a complexing agent no complex formation is to be assumed, therefore the exchange between the phases is described by the relation:

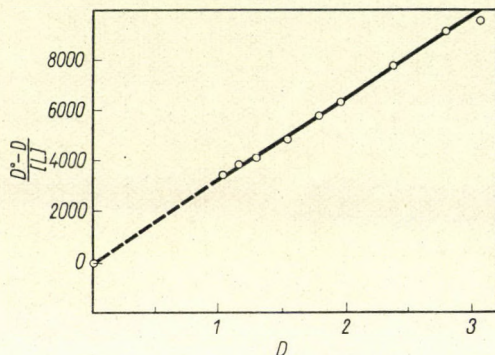
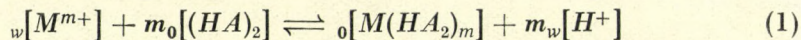


Fig. 4. $\frac{D^0 - D}{[L]}$ vs. D for the system indium- α -hydroxyisobutyrate $[In^{3+}] = 10^{-4}$ M, $[DEHPA] = 5 \times 10^{-2}$ F, $[HClO_4] = 0.5$ M

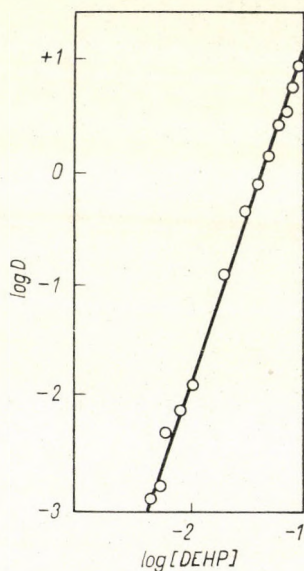


Fig. 5. Distribution ratio as a function of the concentration of di-2-ethylhexyl phosphoric acid in the presence of α -hydroxyisobutyric acid $[In^{3+}] = 10^{-4}$ M, $[HClO_4] = 0.5$ M, p [AHIB] = 3.5 F

for which the law of mass action reads:

$$\frac{{}_0[M(HA_2)_m]}{{}_w[M^{m+}]} = k_0 \frac{{}_0[(HA)_2]^m}{{}_w[H^+]^m} \quad (2)$$

The left side of Eq. (2) might be replaced by the distribution ratio measured in the uncomplexed system, consequently

$$D^0 = k_0 \frac{o[(HA)_2]^m}{w[H^+]^m}, \quad (3)$$

or in terms of logarithms:

$$\log D^0 = m \{ \log_o [(HA)_2] - \log_w [H^+] \} + \log k_0. \quad (4)$$

According to Eqs (3) and (4), when plotting $\log D^0$ against the pH (at constant $[(HA)_2]$), or $\log D^0$ against $\log [(HA)_2]$ (at constant pH), respectively, straight lines with slope = m are obtained.

The value of $\log k_0$, on the other hand, may be determined by extrapolating the straight to the point $\log [(HA)_2] = \log w[H^+]$ where, according to Eq. (4), $\log D^0 = \log k_0$. From Figs 1 and 2 the $\log k_0$ values are — in good agreement with each other — 3.56 and 3.63, respectively.

From the point of view of complex formation Figs 3 and 4 are to be discussed in detail. The first task is to find out whether all the species formally possible, i.e. $[In^{3+}]$, $[InL^{2+}]$, $[InL_2^+]$ and $[InL_3]$ are present, and to determine the stability of the species the formation of which can be proved; the mathematical treatment of the experimental data is considerably simplified if any of the species assumed can be neglected.

In case of a stepwise formation of the complex species of indium with AHIBA in the aqueous phase the distribution ratio (omitting symbols of charge) will be defined as follows:

$$D = \frac{o[M]}{w[M] + w[ML] + w[ML_2] + \dots}. \quad (5)$$

Eq. (5) is valid with the assumption that no charged or uncharged complexes are bound in the organic phase; since this phase contains a cation exchanger, the presence of neutral complexes can be, in fact, neglected. However, the absence (or presence in only negligible amounts) of species $[ML_{i=(m-n)}]$ ($0 < n < m$) was proved only some years ago in the course of similar investigations with liquid ion-exchangers [3–7], partly by using ^{14}C -labelled ligands.

When D^0 is defined with similar simplified notations as

$$D^0 = \frac{o[M]}{w[M]} \quad (6)$$

and introducing the step formation constants

$$k_i = \frac{[ML_i]}{[ML_{i-1}][L]}, \quad (7)$$

Equations (5), (6) and (7) can be combined to give

$$\frac{D^0}{D} = 1 + k_1 [L] + k_1 k_2 [L]^2 + \dots \quad (8)$$

Provided that only the 1 : 1 complex exists, plotting of $1/D$ against $[L]$ gives a linear relation from the slope of which k_1 is obtainable by calculation.

It is striking that values of $1/D$ extrapolated to $[L] = 0$ agree with the values of $1/D^0$ directly determined.

From curve 1 in Fig. 3 the first stability constant was determined in this simple graphical way, and the value $\log k_1 = 3.52$ was obtained.

Analogous values in the range 3.50 to 3.56 were obtained from curves 2–5 of the same Figure, corresponding to different ionic strengths.

The linear relationship indicates that in the aqueous phase species $[M(\text{AHIB})^{2+}]$ predominates.

ROSSOTTI has shown [8] that if both $[M]$ and $[ML]$ partition, so

$$D = \frac{D^0 + D' k_1 [L]}{\sum_0^m k_i [L]^i} \quad (9)$$

If species $[ML]$ is the only complex present in the aqueous phase, k_1 may be calculated according to Eq. (10):

$$k_1 = \frac{D^0 - D}{(D - D')[L]} \quad (10)$$

which, on rearranging, gives

$$\frac{D^0 - D}{[L]} = k_1 D - k_1 D' \quad (11)$$

Plotting the left side of Eq. (11) as a function of D a straight line with slope k_1 is obtained. According to Fig. 4, $\log k_1$ was found to be 3.53, in good agreement with the value got from Fig. 3.

In Fig. 5, where the change of $\log D$ is presented as a function of $\log [\text{DEHPA}]$ at constant $[L]$ ($pL = 3.5$), straight line with slope 3 is obtained which also implies that only the distribution of $[M^{3+}]$ is significant and the concentration of $[ML^{2+}]$ in the organic phase is negligible; this is in good agreement with the data of Fig. 4, from which according to Eq. (11) a D value of about two orders of magnitude less than D might be estimated.

The accuracy of the graphical methods outlined above was checked by a least squares method of numerical calculations. After rearranging, Eq. (8) can be written as follows:

$$X \equiv \frac{D^0}{D} - 1 = \sum_{i=1}^m k_i [L]^i \quad (12)$$

and the task is to find the relation which gives minimum error regarding function X and the argument, *i.e.* to determine the value of k_1 for which the sum of the squares of deviations between the left- and right-hand sides of Eq. (12) is minimum. This value is obtained by making the first derivative equal to zero; the calculations performed yielded a value of $k_1 = 3250$ ($\log k_1 = 3.51$).

The degree of formation of the species present as a function of the free ligand concentration is shown in Fig. 6 from which the conclusion can unambiguously be drawn that in the region investigated species $[M^{3+}]$ and $[ML^{2+}]$ are the dominating ones.

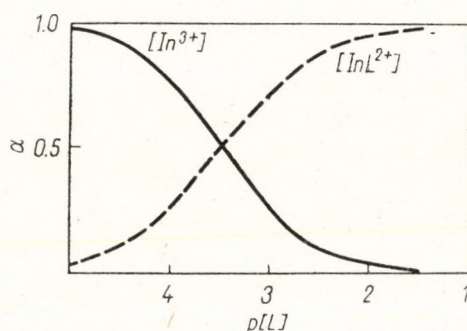


Fig. 6. Degree of formation as a function of the free ligand concentration
 $[In^{3+}] = 10^{-4} M$, $[DEHPA] = 5 \times 10^{-2} F$, $[HClO_4] = 0.5 M$

The authors' thanks are due to Mr. Gy. TóTH for his valuable help in performing the measurements.

SUMMARY

Using di-2-ethylhexyl phosphoric acid as liquid ion-exchanger, the formation of complexes of α -hydroxyisobutyric acid with indium has been studied. It was found that the distribution is characterized by the partition of indium ions between the two phases, and besides the formation of $[In(AHIB)^{2+}]$, other complexes need not be taken into account in the aqueous phase. The first stability constant of indium α -hydroxyisobutyrate has been determined by graphical and numerical methods which gave in good agreement the value of $\log k_1 = 3.51$.

Symbols

AHIBA	α -hydroxyisobutyric acid
AHIB	α -hydroxyisobutyrate ligand
D^0	distribution ratio in the absence of complexing agent
D	distribution ratio in the presence of complexing agent
D'	distribution ratio of a single complex species
DEHPA	liquid ion exchanger: di-2-ethylhexyl phosphoric acid
k_0	stoichiometric equilibrium constant in the absence of complexing agent
k_1	step formation (stability) constant as defined by Eq. (7)
L	ligand
M	metal (indium)
m	stoichiometric coefficient, charge

pL	negative logarithm of free ligand concentration
X	function defined in Eq. (12)
α	degree of formation
	Indices
w	aqueous phase
o	organic phase
m	charge of species

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ULTRASONIC STUDIES WITH POTASSIUM CHLORIDE SOLUTIONS IN THE SYSTEM WATER—TOLUENE—METHANOL

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Introduction

The weight of methanol required just to bring about miscibility of a given mixture of toluene and water is always a constant quantity at a given temperature. A slight change in the ratio of water to toluene will change measurably the quantity of methanol required for miscibility. If potassium chloride is added to the same amount of water, keeping the toluene content unchanged, a different amount of methanol should be required.

The aim of the present investigation is to understand the state of the solute in the solvent mixture from the compressibility data. On the assumption that solvent molecules involved in solvating the ions do not contribute to the compressibility of the solution, PASSYNSKY [1] calculated solvation numbers, H_n , by the formula

$$H_n = \frac{n_1}{n_2} \left[1 - \frac{\beta}{\beta_0} \right] \quad (1)$$

where n_1 is the number of gram-moles of the solvent

n_2 is the number of gram-moles of the solute

β is the adiabatic compressibility of the solution

β_0 is the adiabatic compressibility of the solvent

$\beta = \frac{1}{u^2 \rho}$, where u is the ultrasonic velocity and ρ is the density of the medium.

Apart from the compressibility data, solvation numbers have also been computed and are discussed.

Experimental

The methanol, toluene and potassium chloride used were of BDH Analar grade of purity. Methanol and toluene were further purified before use [2]. The matter used was double distilled. Its specific resistance was $1.11 \cdot 10^5$ ohm-cm (35°C).

The measurements of ultrasonic velocities were made using the DEBYE and SEARS [3] diffraction method. The frequency of the piezoelectric quartz oscillator used in our experiments was 5 Mc/s. The second order diffraction fringes were taken in all cases for measurement. A Hilger's X-Ray Microphotometer L486 was employed with Multiflex galvanometer of sensitivity $8 \cdot 10^{-9}$ A/mm to measure the distance between the fringes. The solution was kept in a specially fabricated water-jacketted stainless steel cubical vessel with chromium-plated

inside, and two optically plane glass windows were cemented on the opposite faces to get perfect transmission of the sodium light used as the source. *Colora* ultrathermostat *Type N* was used, and the cell temperature maintained at $35^{\circ}\text{C} \pm 0.05^{\circ}\text{C}$. For each experiment, the cell required about 105 ml of the solution. Special care was taken to avoid evaporation by closing the cell with two well-fitting slotted covers, such that by introducing the slots in the opposite direction the cell was covered well, except for the piezoelectric crystal holder.

Photographing of the diffraction patterns presented some difficulty, since mixtures of organic liquids gave blurred patterns. This was overcome by giving exposures only for short periods and using fast plates. The accuracy of the velocity measurements was $\pm 0.3\%$.

Measurement of viscosity

A *Cannon-Fenske* type viscometer was used. The viscometer, while making measurements, was kept immersed in a glass-walled thermostat at $35^{\circ}\text{C} \pm 0.05^{\circ}\text{C}$. The flow time of the various solutions varied from 64.3 to 102.4 seconds. The precision reported here is $\pm 0.5\%$.

Density

A 10-ml specific gravity bottle was used, and care was taken that the bottle and contents should attain the thermostat temperature before weighing. A *Sartorius* semi-micro single-pan balance accurate to the fifth place was employed for weighing.

Conductance measurements

A *Philips* conductivity measuring bridge *Type PR 9500/90* was employed. The cell was kept immersed in a thermostat maintained at $35^{\circ}\text{C} \pm 0.05^{\circ}\text{C}$. The instrumental accuracy varied between 1.5% and 3% of the measured resistance. This accuracy was sufficient for our purpose, as we aimed at knowing approximately the equivalent conductance values, in different solutions.

Preparation of solutions

For determining ultrasonic velocities, larger quantities of solutions had to be prepared (of the order of 120 ml). For this, a suitable ratio by weight of toluene and 0.1 *M* potassium chloride in water was placed at 35°C in a conical vessel, and methanol was added till the opalescence produced just disappeared. The weight of methanol added was known. The same ternary mixture without potassium chloride was prepared by taking the same weight percentage ratios of the three solvents as in the previous case. It should be mentioned that in this latter mixture, the content of methanol is slightly more than just required for miscibility. This is necessary to satisfy Passynsky's equation. The density, viscosity, electrical resistance and ultrasonic velocity measurements were done with the above solutions.

Discussion

The last column of Table II gives solvation numbers which are negative in almost all cases except the first. Negative solvation has no physical meaning. Only in one case, SUDGEN [4] reported negative hydration for potassium chlorate and potassium nitrate, and explained it by depolymerization of the water molecules. Based on experiments concerning the coefficient of self-diffusion of water molecules, SAMOILOV [5] predicted the existence of negative hydration for K^+ , Cs^+ , and Cl^- ions. Experiments on the self-diffusion of water molecules by WANG [6] confirmed SAMOILOV's theory. However, the present situation and the technique adopted here for determining solvation numbers are quite different.

At this stage it is appropriate to examine the reliability of PASSYNSKY's equation which has been criticized as being based on dubious assumptions [7]. We feel that PASSYNSKY's equation is based really on logical grounds provided the limiting factors are understood. Around an ion the solvent dipoles orient themselves. The radial distribution of ordering around the ion is purely a function of (a) the ion-dipole interaction and (b) the interaction between the induced dipoles and the other solvent dipoles. In other words, the distance through which induction by the central ion is transmitted is a significant factor. PASSYNSKY's main assumption was that the solvent molecules in the hydration sheath do not contribute to the compressibility, in other words, to the acoustic characteristics of the medium. PASSYNSKY's assumption can be given a rational basis, if the frequency of the acoustic vibrations is also taken into consideration. For example, at very high ultrasonic frequencies, it is reasonable to expect that even the first layer of solvent molecules surrounding an ion will be disturbed, and at still higher frequencies we may expect the ions themselves to undergo some degree of compression. Similarly, at low ultrasonic frequencies only solvent molecules several layers beyond the central ion may be affected. In other words, the so-called solvation number obtainable from PASSYNSKY's method will give an indication about the cluster of solvent molecules around an ion which remains undisturbed for a given frequency of ultrasonic vibrations transmitted through the medium. Therefore, a reasonably reliable estimate of what is known as primary solvation numbers could be obtained only by performing dispersion studies.

Under such conditions, the solvation numbers obtained at a particular ultrasonic frequency such as 5 Mc/s employed in our experiment have no significance in the sense in which solvation numbers are understood in the electrochemical studies of ionic solutions. However, in comparing a series of solutions whose constituents are the same, and which differ merely in concentration, the values of solvation numbers obtained at a specific ultrasonic frequency should qualitatively indicate the type of ordering around an ion.

We shall now analyze the data presented in Tables I and II. Before we understand the state of the solute in the ternary mixture, it will be of interest to know the state of existence of water and methanol molecules in this system. A comparison of viscosity values between Tables I and II shows no fall in viscosity due to the addition of potassium chloride, such as is well known in the case of aqueous potassium chloride solutions at low concentrations, where the effect was explained as due to the breaking of the structure and consequent depolymerization of the water associated molecules. KRISHNAMURTHI [8] explained the behaviour of methanol-water mixtures as due to their mutual destruction of association. Hence, it seems that in the ternary system, water and methanol molecules exist as single depolymerized entities. In fact, the reason for choosing this ternary system to investigate the state of potassium

Table I

Composition by weight in g			Density (g/ml)	Viscosity (centipoise)	Ultrasonic velocity (m/sec)	Adiabatic compress- ibility ($\times 10^{-12} \text{ cm}^2$ dyne^{-1}) (experimental)	Adiabatic compress- ibility ($\times 10^{-12} \text{ cm}^2$ dyne^{-1}) (calculated)	Specific resistance (ohm-cm)
Water	Toluene	Methanol						
6.51	45.48	47.96	0.8277	0.640	1205	83.2	188.9	$1.04 \cdot 10^5$
10.32	31.00	58.60	0.8278	0.683	1220	81.2	224.7	$0.58 \cdot 10^5$
13.50	23.31	63.09	0.8312	0.725	1160	89.4	239.0	$0.95 \cdot 10^5$
16.30	17.94	65.60	0.8344	0.768	1216	81.0	272.7	$0.95 \cdot 10^5$
19.51	13.43	66.86	0.8413	0.814	1268	73.9	326.8	$0.61 \cdot 10^5$
23.16	10.01	66.66	0.8479	0.864	1237	77.1	254.0	$0.78 \cdot 10^5$
27.43	6.79	65.57	0.8579	0.931	1264	73.0	249.3	$0.70 \cdot 10^5$
34.69	3.76	61.29	0.8657	0.974	1292	69.2	250.9	$0.59 \cdot 10^5$

Table II

Composition by weight percentage			Density (g/ml)	Viscosity (centipoise)	Ultra- sonic velocity (m/sec)	Adiabatic compress- ibility ($\times 10^{-12} \text{ cm}^2$ dyne^{-1})	Specific resistance (ohm-cm)	Equi- valent con- duc- tance	Sol- vation number
0.1 M KCl soln.	(Aq.) Toluene	Methanol							
6.56	45.48	47.96	0.8282	0.651	1229	79.9	$0.36 \cdot 10^4$	49.5	144
10.40	31.00	58.60	0.8284	0.689	1213	82.0	$0.19 \cdot 10^4$	58.4	— 26
13.60	23.31	63.09	0.8318	0.728	1152	90.6	$0.14 \cdot 10^4$	61.7	— 18
16.42	17.94	65.60	0.8351	0.773	1201	83.0	$0.11 \cdot 10^4$	66.2	— 48
19.66	13.48	66.86	0.8424	0.820	1231	78.3	$0.09 \cdot 10^4$	67.5	— 101
23.33	10.01	66.66	0.8488	0.871	1216	79.7	$0.07 \cdot 10^4$	68.8	— 51
27.64	6.79	65.57	0.8597	0.931	1256	73.7	—	—	— 13
34.95	3.76	61.29	0.8671	0.980	1271	71.4	—	—	— 38

The precision of the values of solvation numbers reported in this Table varies from $\pm 2.4\%$ to $\pm 5.4\%$.

chloride in it is that previous literature has indicated the existence of free molecules of water and methanol in this system, in contrast to their complicated existence in pure water and pure methanol; the presence of toluene allows a choice of different dielectric constants for the medium. On the other hand, Table IV shows that the adiabatic compressibilities of solutions of potassium chloride in water-methanol systems are lower than in the corresponding water-methanol mixtures. Further, Table V also shows that the adiabatic compressibility of potassium chloride in pure methanol is $109 \cdot 10^{-12} \text{ cm}^2 \text{ dyne}^{-1}$

compared with $126 \cdot 10^{-12} \text{ cm}^2 \text{ dyne}^{-1}$ for the pure solvent. This clearly shows that potassium chloride solutions in methanol are solvated. From Table III, we can see that potassium chloride in water has a compressibility of $40.7 \cdot 10^{-12} \text{ cm}^2 \text{ dyne}^{-1}$ as against $43.6 \cdot 10^{-12} \text{ cm}^2 \text{ dyne}^{-1}$ for pure water, thus giving a Passynsky solvation number 37. As it has been mentioned earlier, even though a solvation number of 37 is not much significant, from known values by other physico-chemical methods it is established that in the case of potassium chloride in water the ions are hydrated.

Table III

Liquid	Density (g/ml)	Viscosity (centipoise)	Adiabatic compressibility ($\times 10^{12} \text{ cm}^2 \text{ dyne}^{-1}$)	Solvation number
Water	0.9941	0.723	43.6	—
Toluene	0.8528	0.547	79.3	—
Methanol	0.7772	0.474	126.0	—
0.1 M KCl soln. (Aq.)	0.9986	0.721	40.7	37

Table IV

Composition by weight percentage			Density (g/ml)	Viscosity (centipoise)	Ultrasonic velocity (m/sec.)	Adiabatic compressibility ($\times 10^{12} \text{ cm}^2 \text{ dyne}^{-1}$)
Water	0.1 M (Aq) KCC soln.	Methanol				
79.7		20.3	0.9598	1.034	1584	41.5
	79.7	20.3	0.9631	1.058	1639	38.7
50.4		49.6	0.9055	1.146	1499	49.4
	50.4	49.6	0.9091	1.161	1504	48.6
19.8		80.2	0.8328	0.795	1260	75.6
	19.8	80.2	0.8336	0.796	1271	74.3

Looking at the last column of Table II, where the solvation numbers are given for the different ternary mixtures containing potassium chloride, one observation is unmistakable. The first system giving a solvation number of 144 stands out distinctly from the rest of the compositions in all of which the solvation number is negative though of different magnitudes. Another interesting point that comes out prominently for consideration is that the compressibility values obtained experimentally as given in Column 7 of Table I, when compared to Column 7 of Table II, show an increase in compressibility of any

one of the ternary compositions when potassium chloride is added. These two observations require explanation. An increase in compressibility should necessarily be explained as due to the creation of more voids in the medium. An observation of significance is that in the first composition where the solvation number is positive, there is a fall in the adiabatic compressibility on adding potassium chloride (from $83.2 \cdot 10^{-12} \text{ cm}^2 \text{ dyne}^{-1}$ to $79.9 \cdot 10^{-12} \text{ cm}^2 \text{ dyne}^{-1}$), whereas in all other cases where the solvation number is negative, the indication is that addition of potassium chloride increases the compressibility. Though no significance at this stage is necessarily attached to the variation in magnitude of the solvation numbers obtained with 5 Mc/s ultrasonic irradiation, the fact that they are negative brings out very important points; firstly, that the ions are not solvated, and secondly, there is an implication that it is the ions that perhaps surround the solvent molecules or clusters of them. One has now to invoke the substitutional and interstitial solutions discussed by GURNEY [9, 10]. From these considerations, it appears that in the ternary system of pure solvent without the electrolyte there are clusters in which methanol and water exist in substitutional state, with toluene in interstitial positions. For the formation of a substitutional solution, the force of attraction between the methanol and water molecules should be strong enough to prevent the constituents from coming together and falling to a state of much lower potential energy, and at the minimum, the force of attraction between a methanol and a water molecule should be of an order that exists between two water molecules or between two methanol molecules. Evidently toluene cannot form a substitutional solution, and if it exists in a homogeneous solution it may only occupy interstitial position with respect to methanol and water.

Three-dimensionally at least 4 molecules will be required to make a cluster around a solvent molecule. Perhaps we may imagine a cluster, around a toluene molecule made up of equal number of methanol and water. The extra molecules of methanol or water, not existing in clusters, must be surmised to be floating among the clusters. When potassium chloride is added to this system, what really happens is solvation of the free water or methanol molecules. In all cases investigated the methanol content was higher than that of water, and by the same Passynsky's method as recorded in Table V, the solvation number of potassium chloride in pure methanol is 223, a positive value at 5 Mc/s

Table V
Data for 0.019 M KCl solution in methanol

Density (g/ml)	Viscosity (centipoise)	Ultrasonic velocity (m/sec)	Adiabatic compressibility ($\times 10^{12} \text{ cm}^2 \text{ dyne}^{-1}$)	Solvation number
0.7782	0.480	1086	109	223

frequency of ultrasonics. Thus the only explanation that can be given for the positive and negative solvation numbers in Table II seems to be that perhaps in all cases there is a solvation of the ions, but in the first case where the magnitude is 144, the binding force between the ions and methanol molecules is strong enough that the 5 Mc/s acoustic oscillation is not able to disrupt it. All other cases where the solvation numbers have a negative sign imply that the force of attraction is too small between the ions and the solvent molecules, thus the 5 Mc/s acoustic vibration is able to disrupt it. The dielectric constants of the ternary systems studied here range from 20 to 43. In the first system, where the solvation number is positive, the dielectric constant is the lowest (20), therefore the electrostatic attraction between the ions and the dipoles must be stronger. With an increase in the dielectric constant, as with other compositions investigated (increasing as we go down in Table II), the ion-solvent attraction becomes less, and it is known that ion-pair formation is more favoured. Hence in the first case of positive solvation number of 144, at a low dielectric constant, addition of potassium chloride orders the arrangement of solvent molecules around the ion in a compact form, and therefore there is a fall in compressibility. In the other cases the increase in compressibility should be ascribed to the effect of increasing the dielectric constant, when the ion-dipole or dipole-dipole interactions get more weakened. Also in the case of clusters this will happen, resulting in a loosening of the cluster shells and thus in an increase of their diameters, which is evidenced by an increase in the compressibility.

Finally, it may be of interest to compare Columns 7 and 8 of Table I. Column 7 gives the experimentally determined adiabatic compressibility values. Column 8 is calculated on the assumption that adiabatic compressibilities are additive, that is

$$\sum_1^i \beta_i x_i = \beta_{1,2\dots i} \quad (2)$$

It is very interesting to note that in all cases the experimental values are far lower than those calculated from Eq. (2). This only means that the formation of the ternary mixture is connected with a heavy reduction in the free space of the medium, which may be perhaps due to depolymerization of the water and methanol molecules as mentioned earlier in the investigations of other workers.

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SUMMARY

Ultrasonic velocities have been measured in solutions of potassium chloride in water-toluene-methanol mixtures. The compressibility values have been examined. The state of existence of the ions with respect to the solvent molecules has been analyzed.

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APPROXIMATE NORMAL COORDINATE ANALYSIS OF 4-HALO-PYRIDINES

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Introduction

Several research workers have dealt with the different spectra of pyridine and 4-halo-pyridines.

The most detailed ultraviolet spectra were published by SPINNER [1]; these were recorded in aqueous solutions. Table I shows only the B-type bands, which are of interest for the present work.

Table I
*Ultraviolet spectra (B-type bands) of pyridine and
the 4-halo-pyridines examined in this paper*

$\lambda_{\max}$ (log ϵ) (nm)		
Pyridine	4-chloropyridine	4-bromopyridine
240 (3.05)**	240 (2.94)**	240 (3.02)**
246 (3.22)**	246 (3.19)**	246 (3.13)**
251 (3.37)	252 (3.25)	252 (3.27)
257 (3.42)	258 (3.34)	258 (3.36)
263 (3.25)	265 (3.22)	265 (3.20)

The corresponding NMR spectra have also been investigated by numerous workers. In Table II the ^1H resonance spectra of the compounds are given on the basis of the measurements of BRÜGEL [2], and WU and DAILEY [3]. Brügel made his measurements in 30% dimethyl-sulphoxide solution and used water as the external reference substance. Wu and Dailey used dioxan solutions and their internal reference was TMS. The chemical shifts δ_i are given in ppm units, while the coupling constants J_{ik} in c/s.

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** Shoulder.

Table II
NMR spectra of pyridine and 4-halo-pyridines studied in this work

	Chemical shift (ppm)		
	δ_α	δ_β	δ_γ
Pyridine ^a	-3.47	-2.26	-2.63
4-chloropyridine ^a	-3.54	-2.38	—
4-bromopyridine ^a	-3.57	-2.62	—
Pyridine ^b	-8.572	-7.235	—
4-chloropyridine ^b	-8.521	-7.372	—
4-bromopyridine ^b	-8.437	-7.515	—

Coupling constant (c/s)

	$J_{23}=J_{56}$	$J_{25}=J_{36}$	$J_{24}=J_{46}$	$J_{34}=J_{45}$	J_{26}	J_{35}
Pyridine ^a	5.5	0.9	1.9	7.6	0.4	1.6
4-chloropyridine ^a	5.4	1.0	—	—	0.4	1.6
4-bromopyridine ^a	5.4	0.8	—	—	0.4	1.8

^a H₂O as external reference (BRÜGEL).

^b TMS internal reference (WÜ and DAILEY).

As it can be seen from the data in Tables I and II, the difference between the spectra of pyridine and 4-halo-pyridines is small.

The above three papers [1, 2, 3] present the spectra of many 4-substituted pyridine derivatives, and on this basis it can be established that the smallest differences between the ultraviolet and NMR spectra of the derivatives and those of pyridine are found for 4-chloro-, 4-bromo-, and 4-methylpyridines.

This small difference is understandable in the case of 4-methylpyridine, but it needs explanation for the first two compounds. It seemed therefore interesting to examine the vibrational force fields of the latter molecules from this point of view.

Vibrational spectra

There have been many papers on the vibrational spectra of pyridine and its derivatives. The first complete vibrational assignments for the bands of pyridine and its deuterated derivatives were given by WILMSHURST and BERNSTEIN [4] using the data of CORRISIN, FAX and LORD [5], and of ANDERSON and co-workers [6]. The normal coordinate analysis of pyridine has been

performed on the basis of different force field models, and to various degrees of precision, by several authors; the most important papers are those by LONG, MURFIN and THOMAS [7], WACHSMANN and SCHMID [8], and last but not least by KOVNER, KOROSTELEV and BEREZIN [9], and BEREZIN [10].

The vibrational spectra of the halo derivatives of pyridine have not been investigated so extensively. There have been groups of research workers dealing with vibrational assignments for some halo-pyridines but no quantitative normal coordinate analyses have been reported so far. The complete vibrational band assignment can be found in the works of GREEN, KYNASTON and PAISLEY [11] and of SPINNER [12].

Calculations

In this work the force field of pyridine, as calculated by Soviet authors [9, 10], has been applied as an approximation for the 4-halo-pyridine molecules and only the halogen-sensitive diagonal force constants have been modified in the course of the calculations. It has become evident from our calculations that only the C—X force constant has to be modified in the A_1 species, but the values of the planar and perpendicular deformation C—C—X force constants need not be changed, since the original values taken from the pyridine calculations provide better approximations for the observed normal frequencies.

In the calculation of the G matrix elements — and in the course of the whole normal coordinate analysis — the effective C_{2v} symmetry of 4-substituted pyridines has been applied.

The distribution of the normal modes among the irreducible representations is the following:

$$\Gamma = 10 A_1 + 9 B_1 + 3 A_2 + 5 B_2.$$

The geometrical data used for the G matrix elements and the "spectroscopical masses" applied for the compensation of the anharmonicity effects were identical to those used by KOVNER, KOROSTELEV and BEREZIN [9, 10]. The length of the C—X bond was regarded as being identical to that of the corresponding halobenzene.

The notation used for the internal coordinates of the planar vibrations are given in Fig. 1.

The internal coordinates of the perpendicular vibrations are the following:

$\psi_2, \psi_3, \psi_5, \psi_6$	(CCCH perpendicular deform.)
ψ_4	(CCCX perpendicular deform.)
$\tau_1, \tau_2, \tau_3, \tau_4, \tau_5, \tau_6$	(CCCC torsion)

Table III
*Geometrical data of the 4-halo-pyridine molecules
 and the spectroscopical masses
 used in the calculations [9, 10]*

	Bond length (Å)	Bond angle
C_2H_2	1.092	$C_6NC_2 \times 114^\circ 46'$
C_3H_3	1.080	$NC_2C_3 \times 125^\circ 04'$
C_4H_4	1.080	$C_2C_3C_4 \times 118^\circ 23'$
NC_2	1.355	$C_3C_4C_5 \times 118^\circ 20'$
C_2C_3	1.378	$NC_2H_2 \times 114^\circ 18'$
C_3C_4	1.397	$C_2C_3H_3 \times 120^\circ 30'$
C_4Cl	1.670	$C_3C_4H_4 \times 120^\circ 50'$
C_4Br	1.86	$C_3C_4X \times 120^\circ 50'$

Spectroscopical mass values

	For planar vibr. $\epsilon = 1.088/\text{Å}$	For perpend. vibr. $\epsilon = 1.008/\text{Å}$
ϵ_H	1.0000	1.0000
ϵ_C	0.0906	0.0839
ϵ_N	0.0777	0.0719
ϵ_{Cl}	0.0307	0.0284
ϵ_{Br}	0.0136	0.0126

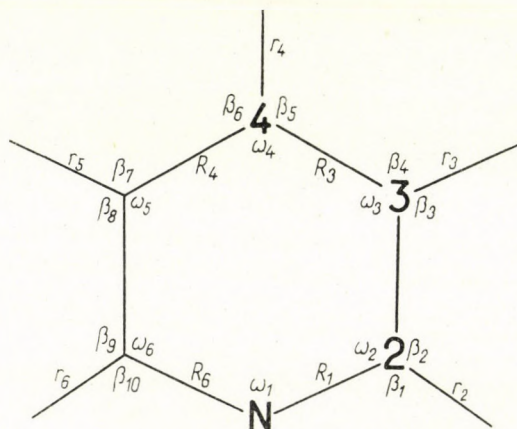


Fig. 1

The symmetry coordinates formed from the linear combinations of the internal coordinates are shown in Table IV.

Table IV
Symmetry coordinates used in the calculations [9, 10]

Species A_1	Species B_1
$Z_1 = 2^{-1/2} (R_1 + R_6)$	$Z_1 = 2^{-1/2} (R_1 - R_6)$
$Z_2 = 2^{-1/2} (R_2 + R_5)$	$Z_2 = 2^{-1/2} (R_3 - R_4)$
$Z_3 = 2^{-1/2} (R_3 + R_4)$	$Z_3 = 2^{-1/2} (r_2 - r_6)$
$Z_4 = 2^{-1/2} (r_2 + r_6)$	$Z_4 = 2^{-1/2} (r_3 - r_5)$
$Z_5 = 2^{-1/2} (r_3 + r_5)$	$Z_5 = 2^{-1/2} (\omega_2 - \omega_6)$
$Z_6 = r_4$	$Z_6 = 2^{-1/2} (\omega_3 - \omega_5)$
$Z_7 = \omega_1$	$Z_7 = 2^{-1/4} (\beta_1 - \beta_{10})$
$Z_8 = \omega_4$	$Z_8 = 2^{-1/2} (\beta_4 - \beta_7)$
$Z_9 = 2^{-1/2} (\beta_2 + \beta_9)$	$Z_9 = 2^{-1/2} (\beta_5 - \beta_6)$
$Z_{10} = 2^{-1/2} (\beta_3 + \beta_8)$	
Species A_2	Species B_2
$Z_1 = 2^{-1/2} (\psi_2 - \psi_6)$	$Z_1 = 2^{-1/2} (\psi_2 + \psi_6)$
$Z_2 = 2^{-1/2} (\psi_3 - \psi_5)$	$Z_2 = 2^{-1/2} (\psi_3 + \psi_5)$
$Z_3 = 2^{-1/2} (\tau_2 + \tau_5)$	$Z_3 = \psi_4$
	$Z_4 = 2^{-1/2} (\tau_3 - \tau_4)$
	$Z_5 = 2^{-1/2} (\tau_1 - \tau_6)$

The G matrices of 4-chloropyridine and 4-bromopyridine have been calculated. These are given in Tables V, Va, VI and VIa.

The approximate force constant matrices used in the calculations are found in Tables VII and VIIa.

The element F_{66} in species A_1 has been modified to 6.0 and 5.0 for chloropyridine and bromopyridine, respectively. These values have been adopted from the works of SVERDLOV and co-workers [13], they are the constants reported for vinyl chloride and vinyl bromide, respectively. In the same papers one can find values for the CCX planar deformation force constants (Cl: 0.32; Br: 0.27); and for the perpendicular deformation modes the values 0.41 and 0.25 are also given. However, the use of the latter values led to poorer results than the use of the original force constants of pyridine.

The eigenvalue calculations for the 5-, 9- and 10-dimensional matrices have been performed on a *National-Elliott 803 B* digital computer. The essence of the method was the following: the maximal eigenvalue was calculated by an iteration method (the so-called power-method), the dimension of the matrix reduced by one using the determined eigenvalue and eigenvector, and this matrix, in turn, was again subjected to the calculation of the maximal eigenvalue, etc. [14, 15].

Table V

The G matrix of 4-chloropyridine (Species A_1 is above the diagonal, species B_1 is below it)
(Calculated on the basis of [15]; the numbers are dimensionless)

Z_1	Z_2	Z_3	Z_4	Z_5	Z_6	Z_7	Z_8	Z_9	Z_{10}
0.1357	-0.0521	0.0000	-0.0373	0.0000	0.0000	-0.0791	0.0000	0.1411	-0.0587
	0.1812	-0.0431	-0.0462	-0.0460	0.0000	0.0844	0.0880	-0.0778	-0.0788
0.2009		0.1382	0.0000	-0.0468	-0.0656	0.0000	-0.0880	-0.0631	0.1413
0.0000	0.2242		1.0906	0.0000	0.0000	-0.0939	0.0000	-0.0617	0.0617
-0.0373	0.0000	1.0906		1.0906	0.0000	0.0000	-0.0856	0.0617	-0.0617
0.0000	-0.0568	0.0000	1.0906		0.1213	0.0000	0.1214	0.0000	0.0000
-0.1155	0.0631	0.1281	-0.0617	0.2675		0.2579	0.0000	0.0045	-0.0468
0.0587	-0.1253	-0.0617	0.1223	-0.1731	0.2506		0.2730	-0.0376	-0.0146
-0.0256	0.0000	-0.0664	0.0000	-0.1145	-0.0033	1.2347		1.2731	-0.1865
0.0000	-0.0161	0.0000	-0.0605	-0.0101	-0.1109	0.0000	1.2684		1.2975
0.0000	-0.1638	0.0000	0.0605	-0.0266	0.1580	0.0000	-0.1684	0.2821	
Z_1	Z_2	Z_3	Z_4	Z_5	Z_6	Z_7	Z_8	Z_9	

Table Va

The G matrix of 4-chloropyridine
(Species B_2 is above the diagonal, species A_2 is below it)
(Calculated on the basis of [15]; the numbers are dimensionless)

Z_1	Z_2	Z_3	Z_4	Z_5
1.7931	-0.3545	0.0751	-0.3890	-0.9396
	1.7082	-0.4255	0.8394	0.3874
1.6777		0.5062	-0.6833	-0.0873
-0.3546	1.6114		1.1487	0.4234
0.5799	-0.5266	0.6173		1.2078
Z_1	Z_2	Z_3		

Table VI
The *G* matrix of 4-bromopyridine
(Species A_1 is above the diagonal, species B_1 is below it)
(Calculated on the basis of [15]; the numbers are dimensionless)

Z_1	Z_2	Z_3	Z_4	Z_5	Z_6	Z_7	Z_8	Z_9	Z_{10}
0.1357	-0.0521	0.0000	-0.0373	0.0000	0.0000	-0.0791	0.0000	0.1411	-0.0587
	0.1812	-0.0431	-0.0462	-0.0460	0.0000	0.0844	0.0880	-0.0778	-0.0788
0.2009		0.1382	0.0000	-0.0468	-0.0656	0.0000	-0.0880	-0.0631	0.1413
0.0000	0.2242		1.0906	0.0000	0.0000	-0.0939	0.0000	-0.0617	0.0617
-0.0373	0.0000	1.0906		1.0906	0.0000	0.0000	-0.0856	0.0617	-0.0617
0.0000	-0.0468	0.0000	1.0906		0.1042	0.0000	0.1214	0.0000	0.0000
-0.1155	0.0631	0.1281	-0.0617	0.2675		0.2579	0.0000	0.0045	-0.0468
0.0587	-0.1253	-0.0617	0.1223	-0.1731	0.2506		0.2730	-0.0376	-0.0146
-0.0256	0.0000	-0.0664	0.0000	-0.1145	-0.0033	1.2347		1.2731	-0.1865
0.0000	-0.0161	0.0000	-0.0605	-0.0101	-0.1109	0.0000	1.2684		1.2975
0.0000	-0.1534	0.0000	0.0605	-0.0266	0.1532	0.0000	-0.1635	0.2407	
Z_1	Z_2	Z_3	Z_4	Z_5	Z_6	Z_7	Z_8	Z_9	

Table VIa
The *G* matrix of 4-bromopyridine
(Species B_2 is above the diagonal, species A_2 is below it)
(Calculated on the basis of [15]; the numbers are dimensionless)

Z_1	Z_2	Z_3	Z_4	Z_5
1.7931	-0.3546	0.0751	-0.3890	-0.9396
	1.7082	-0.4196	0.8394	0.3874
1.6777		0.4744	-0.6698	-0.0873
-0.3546	1.6114		1.1487	0.4234
0.5799	-0.5266	0.6173		1.2078
Z_1	Z_2	Z_3		

Table VII
The F matrix of pyridine
 (Species A_1 is found above the diagonal, the elements of species B_1 are below it)
 (The elements are given in units 10^6 cm^{-2})

Z_1	Z_2	Z_3	Z_4	Z_5	Z_6	Z_7	Z_8	Z_9	Z_{10}
13.568	0.217	— 1.021	0.363	— 0.023	0.255	2.469	— 1.759	— 0.953	0.545
	10.825	0.217	0.340	0.340	0	— 0.830	— 0.830	0.458	0.458
10.195		13.231	— 0.023	0.363	0.226	— 1.759	2.469	0.545	— 0.953
— 1.105	10.095		8.630	0	0	0.353	— 0.071	0	0
0.170	— 0.170	8.530		8.630	0	— 0.071	0.353	0	0
— 0.170	0.170	0	8.630		8.630	— 0.050	— 0.350	0	0
4.005	3.001	— 0.327	0.073	13.187		4.180	— 1.767	— 0.860	0.203
3.001	4.005	0.073	— 0.327	11.014	13.187		4.484	0.203	— 0.860
0.446	0.038	0	0	1.093	0.321	1.405		1.553	— 0.005
0.038	0.496	0	0	0.321	1.093	0.046	1.430		1.535
— 0.088	0.325	0	0	— 0.137	— 0.039	— 0.037	— 0.025	0.726	
Z_1	Z_2	Z_3	Z_4	Z_5	Z_6	Z_7	Z_8	Z_9	

Table VIIa
The F matrix of pyridine
 (Species B_2 is above the diagonal, while species A_2 is below it)
 (The elements are given in units 10^6 cm^{-2})

Z_1	Z_2	Z_3	Z_4	Z_5
0.5717	— 0.0266	— 0.0537	0.0827	0.3055
	0.5487	— 0.0766	— 0.2864	— 0.0830
0.6439		0.6087	0.2690	— 0.0274
— 0.0541	0.6982		0.5108	0.1232
— 0.2907	0.3398	0.5752		0.5896
Z_1	Z_2	Z_3		

The normal frequencies were calculated from the eigenvalues of the GF matrix *via* the formula: $\nu = 10^3 \sqrt{\lambda}$. The normal frequencies obtained are compared with the experimental values in Tables VIII and IX. The first column of the calculated values lists those results which have been obtained by the use of the force field of pyridine, while the second column shows the values derived by the modified force field.

Conclusions

Tables VIII and IX show that the data derived by the use of the pyridine force field [9, 10] reproduce the normal frequencies of 4-halo-pyridines on a relatively small error level (the deviations are smaller than in the case of the modified force field). The results obtained in this work are, therefore, in agreement with the spectra in the ultraviolet region, and they are consistent with the NMR spectra (see Tables I and II).

On this basis it can be inferred that the electron distribution in the rings of the two 4-halo-pyridines well approximates the electron distribution of the pyridine molecule itself. (According to the NMR spectra, the deviations are somewhat greater in the case of 4-bromopyridine, than for 4-chloropyridine.)

The above results may be explained as follows. 4-halo-pyridines can be regarded as such disubstituted benzene derivatives in which one of the substituents is the ring nitrogen atom, that has the effect of a $(-I, -M)$ -substituent, while the other is the halogen atom, which has $(-I, +M)$ -effect. The electron densities on the α -positioned carbon atoms are reduced by the $-I$ and $-M$ effect of the ring nitrogen atom as compared to the benzene molecule, while the halogen atom has only very small influence on such a carbon atom; consequently, the δ_α value of 4-halo-pyridines deviates only slightly from that of pyridine. The cause of the difference is probably found in the change of the shielding effect of the neighbouring ring members. On the carbon atoms in β positions, it is first of all the $-I$ and $+M$ effects of the halogen substituent that prevail. As a result of the two effects, there is hardly any change in the case of chlorine, while with bromine the difference in the δ_β value is greater. This can partly be explained by the change of the shielding effect, and partly by considering that in the case of bromine the inductive effect is relatively greater than the mesomeric effect, as compared to the case of chlorine. (This is so in spite of the fact that in the electronic ground state both effects of bromine are smaller than those of chlorine.)

The greater deviations found between the NMR spectra of 4-halo-pyridines and those of pyridine are substantiated also by the finding that the average of the absolute values of the deviations from the normal frequencies of 4-bromopyridine, as calculated by using the vibrational force field of pyridine, is greater (Table IX) than the similar figure obtained for 4-chloropyridine (Table VIII; 3.61% as compared to 3.15%).

Table VIII

The observed and calculated normal frequencies of 4-chloropyridine and the average of the absolute value of the deviations

Numbering according to Wilson		Frequencies observed, cm ⁻¹ [11]	Calculated frequencies			
			with pyridine force field		with modified force field	
			cm ⁻¹	%	cm ⁻¹	%
A ₁	1	1103	1258	14.0	1189	7.8
	2	3076	3065	— 0.3	3068	—0.2
	6a	712	740	3.9	704	—1.1
	7a	414	417	0.8	393	—5.1
	8a	1575	1603	2.0	1590	0.9
	9a	1219	1216	— 0.3	1217	—0.2
	12	996	1007	1.1	1004	0.8
	18a	1064	1026	— 3.6	1025	—3.6
	19a	1485	1508	1.5	1479	—0.4
	20a	3048	3057	0.3	3051	0.1
Average of the deviations:			2.8		2.0	
B ₁	3	1315	1202	— 9.5	1197	—9.9
	6b	663	668	0.8	660	—0.5
	7b	3048	3037	— 0.3	3037	—0.3
	8b	1564	1548	— 1.0	1544	—1.3
	14	1359	1270	— 6.6	1264	—7.0
	15	300	250	—16.6	530	77.0
	18b	1080	1101	1.9	1096	1.5
	19b	1407	1387	— 1.4	1382	—1.8
	20b	3076	3068	— 0.2	3068	—0.2
Average of the deviations:			4.3		11.1	
A ₂	10a	914	893	— 2.3	893	—2.3
	16a	390	374	— 4.1	374	—4.1
	17a	955	984	3.0	984	3.0
Average of the deviations:			3.1		3.1	
B ₂	4	722	727	0.7	719	—0.4
	5	856	881	2.9	878	2.6
	10b	182	182	0.0	163	—10.5
	11	811	805	— 0.7	798	—1.6
	16b	491	465	— 5.3	389	—20.0
Average of the deviations:			1.9		7.0	

Table IX

The observed and calculated normal frequencies of 4-bromopyridine and the average of the absolute values of the deviations

Numbering according to Wilson		Frequencies observed, cm ⁻¹ [11]	Calculated frequencies			
			with pyridine force field		with modified force field	
			cm ⁻¹	%	cm ⁻¹	%
A ₁	1	1091	1240	13.7	1156	6.0
	2	3072	3065	— 0.2	3068	— 0.1
	6a	680	717	5.5	674	— 0.9
	7a	317	344	7.9	304	— 4.1
	8a	1567	1600	2.1	1583	1.3
	9a	1216	1216	0.0	1216	0.0
	12	992	1006	1.4	1001	0.9
	18a	1062	1026	— 3.4	1026	— 3.4
	19a	1482	1505	1.6	1493	0.7
	20a	3035	3057	0.8	3051	0.5
Average of the deviations:			3.4		1.8	
B ₁	3	1316	1201	— 8.8	1196	— 9.1
	6b	662	662	0.0	660	— 0.3
	7b	3035	3038	0.1	3035	0.0
	8b	1566	1549	— 1.1	1543	— 1.5
	14	1339	1269	— 5.2	1263	— 5.7
	15	256	216	— 15.8	133	— 48.1
	18b	1076	1102	2.4	1097	2.0
	19b	1403	1386	— 1.2	1381	— 1.6
	20b	3072	3068	— 0.2	3067	— 0.2
Average of the deviations:			3.9		7.6	
A ₂	10a	914	893	— 2.4	893	— 2.4
	16a	390	374	— 4.3	374	— 4.3
	17a	961	984	2.4	984	2.4
Average of the deviations:			3.0		3.0	
B ₂	4	722	725	0.4	711	— 1.5
	5	859	882	2.6	877	2.0
	10b	182	164	— 9.9	101	— 39.0
	11	805	803	— 0.2	793	— 1.5
	16b	482	461	— 4.4	323	— 33.0
Average of the deviations:			3.5		15.4	

SUMMARY

The normal frequencies of 4-chloro-, and 4-bromopyridine have been calculated partly on the basis of the force field data of pyridine, and partly by the use of a modified force field. In the former case the results obtained were better. The results — in agreement with the ultraviolet and NMR spectra (^1H nucleus) — show that the π electron distribution of the pyridine ring is the same in the compounds investigated as in pyridine. This result is explained by the inductive and mesomeric effects of the ring nitrogen and of the halogen atoms.

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HAMILTONIAN FORMALISMS IN THE THERMODYNAMIC THEORY OF IRREVERSIBLE PROCESSES IN CONTINUOUS SYSTEMS

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1. Fundamentals

Within the framework of thermodynamics of irreversible processes GYARMATI [1, 2, 3, 4] derived a basic variational principle which is a local formulation of ONSAGER's principle of least dissipation of energy [5, 6] and has the form

$$\delta L = \delta \int_V \mathcal{L} \, dr = 0. \quad (1.1)$$

Here the integration goes over the volume V of the system. The thermodynamic LAGRANGIAN density $\mathcal{L}$ depends on the intensive thermodynamic variables Γ_j and their spatial gradients $\text{grad } \Gamma_j$ (*i.e.*, the thermodynamic forces) and is defined by

$$\mathcal{L}(\Gamma_j, \text{grad } \Gamma_j) = \varrho \dot{s} - \psi, \quad (1.2)$$

or more generally by

$$\mathcal{L}(\Gamma_j, \text{grad } \Gamma_j) = \sigma - \psi,$$

where ϱ is the mass density of the system, $\dot{s}$ is the substantial time derivative of the specific entropy, σ means the entropy production density, and ψ stands for the local dissipation function (dissipation density) given as a homogeneous quadratic function of the thermodynamic forces. The variations necessary in (1.1) are to be seen from the corresponding EULER equations (*cf.* [7])

$$\sum_{\alpha=1}^3 \frac{\partial}{\partial x_\alpha} \frac{\partial \mathcal{L}}{\partial (\partial \Gamma_j / \partial x_\alpha)} - \frac{\partial \mathcal{L}}{\partial \Gamma_j} = 0 \quad (1.3)$$

which are the LAGRANGE equations of irreversible thermodynamics containing, as special cases, the equations of FOURIER, FICK, NAVIER and STOKES, *etc.*

The essential progress in GYARMATI's local formulation of ONSAGER's principle is that it covers very general classes of thermodynamic systems, especially continuous (*i.e.* inhomogeneous) systems. A quite similar variational principle was derived by PRIGOGINE and GLANSDORFF [8] starting from other

considerations, namely from attempts to extend the principle of minimum entropy production to a general evolution criterion of macroscopic physics [9, 10].

Since in (1.1) the time and thus the quantities Γ_j are not varied, it is not possible to correctly construct a HAMILTONIAN formalism by introducing generalized thermodynamic momenta as time derivatives of thermodynamic variables [7], a procedure which would correspond to the methods, *e.g.*, of mechanics or quantum electrodynamics. Within the framework of a multi-dimensional HAMILTONIAN formalism we can, however, define essentially the spatial derivatives of the intensive state variables Γ_j and thus the thermodynamic forces as momenta Π_j which are then canonically conjugate to the Γ_j . The setting-up of a thermodynamical HAMILTONIAN formalism is thus possible as it is to be shown in Chapter 2.

A second and in principle different possibility for constructing a HAMILTONIAN formalism as a very general basis of irreversible thermodynamics (and continuum mechanics, too) is founded on a functional generalization of the original variational principle of ONSAGER [5, 6]. This generalized principle was given earlier by the present author [12]:

$$\delta \int_{t_1}^{t_2} \mathcal{L} \{ \alpha_i, \dot{\alpha}_j \} dt = 0 \quad (1.4)$$

(t = time). Here the thermodynamic LAGRANGE functional, $\mathcal{L}$, depends on the state fields $\alpha_i(r, t)$ which are intensive state variables (*e.g.* densities) derived from extensive state variables, and one has

$$\mathcal{L} \{ \alpha_i(r, t), \dot{\alpha}_j(r', t) \} = \Phi \{ \dot{\alpha}_i, \dot{\alpha}_j \} + \Psi \{ \alpha_i, \alpha_j \} - \dot{S} \{ \alpha_i, \dot{\alpha}_j \} \quad (1.5)$$

where Φ and Ψ are dissipation functionals and $\dot{S}$ is the entropy production functional given by

$$\dot{S} = - \sum_i \sum_k \int_V \int_V s_{ik}(r, r') \alpha_i(r, t) \dot{\alpha}_k(r', t) dr dr' \quad (1.6)$$

with

$$s_{ik}(r, r') = - \left. \frac{\delta^2 S \{ \alpha_j(r'', t) \}}{\delta \alpha_i(r, t) \delta \alpha_k(r', t)} \right|_{\alpha_i(r, t)=0, \alpha_k(r', t)=0} \quad (1.7)$$

The functional derivative of a functional $F \{ \alpha(r, t) \}$ is here defined by

$$\frac{\delta F \{ \alpha(r, t) \}}{\delta \alpha(r', t)} = \lim_{\varepsilon \rightarrow 0} \frac{1}{\varepsilon} (F \{ \alpha(r, t) + \varepsilon \delta(r - r') \} - F \{ \alpha(r, t) \})$$

where $\delta(r - r')$ is the three-dimensional DIRAC delta function (delta distribution).

The functional variational principle (1.4) is equivalent to the corresponding EULER equations

$$\frac{\partial}{\partial t} \frac{\delta \mathcal{L}}{\delta \dot{\alpha}_i} - \frac{\delta \mathcal{L}}{\delta \alpha_i} = 0 \quad (1.8)$$

which are a system of partial functional differential equations for the state fields $\alpha_i(r, t)$ resulting in a system of coupled (linear) integro-differential equations

$$\dot{\alpha}_i(r, t) = \sum_k \int_V L_{ik}(r, r') X_k(r', t) dr' \quad (1.9)$$

(X_k = generalized space- and time-dependent thermodynamic forces). These equations are the most general equations of motions of irreversible thermodynamics, and by specializing the integral kernels L_{ik} — which are, in general, derivatives of delta distributions, or reciprocal GREEN's tensors — we get again FOURIER's law, FICK's law, the NAVIER—STOKES equations, the basic equations of magnetohydrodynamics, etc.

This generalized form of irreversible thermodynamics is valid for arbitrary continuous systems [12], e.g. for anisotropic and nonlocal media (as materials showing natural optical activity or rarified ionized gases at a nonzero temperature). A nonlocal medium is governed by nonlocal constitutive relations, that means, the density of a thermodynamic flux at a given point is not determined solely by the force field at that particular point, but also depends on the forces at all other points of the medium.

A HAMILTONIAN formalism can be introduced into the general functional form of irreversible thermodynamics by means of canonical momenta defined by

$$\pi_i(r, t) = \frac{\delta \mathcal{L} \{ \alpha_j(r', t), \dot{\alpha}_k(r'', t) \}}{\delta \dot{\alpha}_i(r, t)} \quad (1.10)$$

This is a functional generalization of the definition in mechanics, etc. The introduction of a HAMILTON functional, of canonical equations and of a corresponding HAMILTONIAN variational principle is then possible in a straightforward way. This formalism is discussed in Chapter 3.

2. Hamiltonian Formalism in Local Form

The construction of the desired HAMILTONIAN formalism proceeds in four steps. The first step is the definition of canonical momenta. The variational principle (1.1) contains the three space variables X_α , $(X_1, X_2, X_3) = (x, y, z)$ instead of the time variable t of the common HAMILTON principle. Therefore,

spatial derivatives must appear in the definition of the generalized canonical momenta $\Pi_{k\alpha}$. We define

$$\Pi_{k\alpha} = \frac{\partial \mathcal{L}}{\partial (\partial \Gamma_k / \partial x_\alpha)} \equiv \frac{\partial \mathcal{L}}{\partial \Gamma_{k'\alpha}} \quad (2.1)$$

where

$$\Gamma_{k'\alpha} \equiv \frac{\partial \Gamma_k}{\partial x_\alpha} \quad (2.2)$$

Symbolically one may write:

$$\Pi_k = \frac{\partial \mathcal{L}}{\partial (\text{grad } \Gamma_k)}$$

With these momenta a so-called multidimensional HAMILTONIAN formalism is generated: three momenta $\Pi_{k\alpha}$ are conjugate to one variable Γ_k .

For the sake of illustration, we treat one of the simplest possible examples, *viz.* pure heat conduction in a homogeneous isotropic solid without external fields. We use two different formulations [4, 13]: firstly, the so-called FOURIER picture governed by the LAGRANGIAN density $\mathcal{L}_1$ and corresponding to the original theory of FOURIER, and secondly, the formulation with $\mathcal{L}_2$ being strictly consistent with the formal framework of irreversible thermodynamics.

In the FOURIER picture we have $\Gamma(x_\alpha, t) = T(x, y, z, t)$; the thermodynamic force is given by $X = -\text{grad } T$, and [2, 4]

$$\mathcal{L}_1 = \rho c_v T \dot{T} + \frac{\lambda}{2} (\text{grad } T)^2 \quad (2.3)$$

where c_v = specific heat capacity at constant volume, and λ (const.) = heat conductivity coefficient.

The momenta are

$$\Pi_\alpha = \frac{\partial \mathcal{L}}{\partial T_{i\alpha}} = \lambda \frac{\partial T}{\partial x_\alpha} \quad (2.4)$$

or

$$\Pi = \lambda \text{grad } T.$$

In the second picture is $\Gamma(x_\alpha, t) \equiv T^{-1}$, $X = \text{grad } T^{-1}$ and

$$\mathcal{L}_2 = \rho c_v \dot{T} - \frac{L}{2} (\text{grad } \Gamma)^2. \quad (2.5)$$

(For the comparison of the two pictures it is necessary to assume $\lambda = L/T^2 = \text{const.}$, as it is well known.) The momenta are now given by

$$\Pi_\alpha = \frac{\partial \mathcal{L}}{\partial (T^{-1})_{1\alpha}} = -L \frac{\partial T^{-1}}{\partial x_\alpha} \quad (2.6)$$

or

$$\Pi = -L \operatorname{grad} T^{-1}.$$

It is to be seen from (2.4) and (2.6) that here the canonical momentum vectors are identical with the negative heat flux vectors.

The second step is to define the HAMILTONIAN function (or to be more exact, the HAMILTONIAN density) $\mathcal{H}$ by

$$\mathcal{H}(\Gamma_k, \Pi_{k\alpha}) = \sum_\alpha \sum_k \Pi_{k\alpha} \Gamma_{k'\alpha} - \mathcal{L} \quad (2.7)$$

where $\Gamma_{k'\alpha} = \Gamma_{k'\alpha}(\Pi_{mr}, \Gamma_m)$ have to be obtained (if possible!) by solving the set of equations

$$\Pi_{m\beta} = \frac{\partial \mathcal{L}}{\partial \Gamma_{m'\beta}}(\Gamma_e, \Gamma_{e'\alpha})$$

and then substituted into the r.h.s. of (2.5).

In our example:

$$\begin{aligned} \mathcal{H}_1 &= \sum_\alpha \Pi_\alpha \Gamma_{k'\alpha} - \mathcal{L} = \frac{1}{2\lambda} \sum_\alpha \Pi_\alpha^2 - \varrho c_v T \dot{T} = \\ &= \frac{\lambda}{2} \sum_\alpha \left(\frac{\partial T}{\partial x_\alpha} \right)^2 - \varrho c_v T \dot{T} \\ \mathcal{H}_2 &= -\frac{1}{2L} \sum_\alpha \Pi_\alpha^2 - \varrho c_v \dot{T} T = \\ &= -\frac{L}{2} \sum_\alpha \left(\frac{\partial T^{-1}}{\partial x_\alpha} \right)^2 - \varrho c_v \dot{T} \frac{1}{T}. \end{aligned}$$

The third step is to derive the HAMILTON equations. They are, as it can be proved by straightforward calculations:

$$\frac{\partial}{\partial x_\alpha} \Gamma_k = \frac{\partial \mathcal{H}}{\partial \Pi_{k\alpha}} \quad (2.8a)$$

$$\sum_\alpha \frac{\partial}{\partial x_\alpha} \Pi_{k\alpha} = -\frac{\partial \mathcal{H}}{\partial \Gamma_k}. \quad (2.8b)$$

These equations can also be obtained as EULER equations from a variational principle (see the fourth step below).

In our example with $\mathcal{N}_1$ we get:

$$\Pi_\alpha = \lambda \frac{\partial T}{\partial x_\alpha} \quad (2.9a)$$

$$\dot{T} = \frac{\lambda}{\varrho c_v} \Delta T. \quad (2.9b)$$

In the second picture, starting from $\mathcal{N}_2$, we have:

$$\Pi_\alpha = -L \frac{\partial T^{-1}}{\partial x_\alpha} \quad (2.10a)$$

$$\dot{T} = \frac{\lambda}{\varrho c_v} \Delta T. \quad (2.10b)$$

Eqs (2.8a), (2.9a), (2.10a) give once more the definition of the canonical momenta. Eqs (2.8b), (2.9b), (2.10b) are identical with the thermodynamic equations of motion, in the example chosen with the differential equation of heat conduction.

The fourth step is the construction of a variational principle (generalized HAMILTON principle) which gives the canonical equations (2.8a), (2.8b). Starting from (1.1) and using (2.5) we get:

$$\delta L = \delta \int_V \left\{ \sum_\alpha \sum_k \Pi_{k\alpha} \Gamma_{k'\alpha} - \mathcal{H}(\Gamma_j, \Pi_{j\alpha}) \right\} dr = 0. \quad (2.11)$$

From this fundamental variational principle the canonical equations can be obtained by independently varying the variables Γ_k and the canonically conjugate momenta $\Pi_{k\alpha}$:

$$\begin{aligned} \delta L = \int_V \left\{ \sum_\alpha \sum_k \delta \Pi_{k\alpha} \left(\Gamma_{k'\alpha} - \frac{\partial \mathcal{H}}{\partial \Pi_{k\alpha}} \right) + \right. \\ \left. + \sum_\alpha \sum_k \Pi_{k\alpha} \delta \Gamma_{k'\alpha} - \sum_k \frac{\partial \mathcal{H}}{\partial \Gamma_k} \delta \Gamma_k \right\} dr. \end{aligned}$$

The third term in the integrand can be transformed by integration by parts, using $\delta \Gamma_{k'\alpha} = (\delta \Gamma_{k\alpha})$:

$$\int_V \sum_\alpha \sum_k \Pi_{k\alpha} \delta \Gamma_{k'\alpha} dr = - \int_V \sum_\alpha \sum_k \Pi_{k\alpha} \delta \Gamma_k dr,$$

and it follows that

$$\begin{aligned} \delta L = \int_V \sum_{\alpha} \sum_k \left(\Gamma_{k1\alpha} - \frac{\partial \mathcal{H}}{\partial \Pi_{k\alpha}} \right) \delta \Pi_{k\alpha} \, dr - \\ - \int_V \sum_k \left(\sum_{\alpha} \Pi_{k\alpha 1\alpha} + \frac{\partial \mathcal{H}}{\partial \Gamma_k} \right) \delta \Gamma_k \, dr = 0. \end{aligned} \quad (2.12)$$

This results in (2.8a), (2.8b), *q.e.d.* It can be shown in a well-known manner that the variational principle and the HAMILTON equations are completely equivalent. There has thus been found a HAMILTONIAN formalism which is equivalent to GYARMATI's LAGRANGIAN formalism of irreversible thermodynamics and which is as general as that.

3. Hamiltonian Formalism in Functional Form

The construction of the HAMILTONIAN formalism can again be performed in four steps. Starting from the functional variational principle (1.4) with the LAGRANGE functional (1.5) we define at first the generalized canonical momenta according to (1.10) by

$$\pi_i(r, t) = \frac{\delta \mathcal{L}\{\alpha_j, \dot{\alpha}_k\}}{\delta \dot{\alpha}_i} = \frac{\delta \Phi\{\dot{\alpha}_j, \dot{\alpha}_k\}}{\delta \dot{\alpha}_i} - \frac{\delta \dot{S}\{\alpha_j, \dot{\alpha}_k\}}{\delta \dot{\alpha}_i}. \quad (3.1)$$

The entropy production functional has already been given by (1.6) The dissipation functional Φ is a generalization of the dissipation function Φ of ONSAGER and is defined by

$$\Phi\{\dot{\alpha}_j(r, t), \dot{\alpha}_k(r', t)\} = \frac{1}{2} \sum_j \sum_k \int_V \int_V R_{jk}(r, r') \dot{\alpha}_j(r, t) \dot{\alpha}_k(r', t) \, dr \, dr', \quad (3.2)$$

where $R_{jk}(r, r')$ is the inverse of the continuous matrix $L_{jk}(r, r')$. *i.e.* the generalized phenomenological coefficient. In general, $L_{jk} = L_{jk}(\text{grad})$ is a (singular) linear partial differential operator of second order, and R_{jk} is GREEN's tensor belonging to L_{jk} (see below and [12]). Performing the functional differentiation in (3.1) one gets:

$$\begin{aligned} \Pi_i(r, t) = \sum_k \int_V R_{ik}(r, r') \dot{\alpha}_k(r', t) \, dr' + \\ + \sum_k \int_V S_{ik}(r, r') \alpha_k(r', t) \, dr'. \end{aligned} \quad (3.3)$$

The right-hand side of this equation is the transformed equation of motion (1.9). Thus $\pi_i(r, t) \equiv 0$ (all i). This could be expected because the LAGRANGE functional itself is zero. Taking into account fluctuation processes, we have the momentum fields $\Pi_i(r, t) \neq 0$. This fact is connected with the statistical interpretation of the fundamental variational principle (1.4) [12].

An almost trivial example is again pure heat conduction in a (homogeneous) isotropic solid without further external fields [14]. (The distinction between the FOURIER description with force $X = \text{grad } T$ and the consistent thermodynamic description with $X = \text{grad } T^{-1}$ is here not relevant.) We have for the entropy

$$dS(t) = \int_V \varrho(r) ds(r, t) dr = \int_V \varrho(r) \frac{du(r, t)}{T(r, t)} dr$$

where u = specific internal energy. Thus $\alpha = \varrho(u - u_0)$ where u_0 is the equilibrium value of u . From

$$\frac{dS}{dt} = \int_V \frac{1}{T(r, t)} \varrho(r) \frac{\partial u(r, t)}{\partial t} dr = \int_V X(r, t) \dot{\alpha}(r, t) dr \quad (3.4)$$

we find

$$\begin{aligned} X(r, t) &= \frac{1}{T(r, t)} \approx \\ &\approx \frac{1}{T_0} \left(1 - \frac{\delta T(r, t)}{T_0} \right) \left(\text{if } \frac{\delta T}{T_0} \ll 1 \right) \end{aligned}$$

where $\delta T = T - T_0$ and T_0 is the equilibrium temperature. Using (1.9) we obtain

$$\varrho \dot{u}(r, t) = \int_V L'(r, r') \delta T(r', t) dr' \quad (3.5)$$

with $L' = -L/T_0^2$. The ansatz for L'

$$L'(r, r') = \lambda \sum_{\alpha} \frac{\partial^2}{\partial x_{\alpha}^2} \delta(r - r') = \lambda \Delta \delta(r - r') \quad (3.6)$$

leads to

$$\varrho \dot{u}(r, t) = \lambda \Delta \delta T(r, t) = \lambda \Delta T(r, t).$$

With $\dot{u} = c_v \dot{T}$ the differential equation of heat conduction (2.9b) is finally obtained again.

The second step is to define the HAMILTON functional $\mathcal{H}$ by

$$\begin{aligned} \mathcal{H} \{ \alpha_i(r, t), \pi_j(r', t) \} &= \sum_i \int_V \pi_i(r', t), \dot{\alpha}_i \{ \alpha_k(r'', t), \pi_k(r''', t) \} dr' - \\ &- \mathcal{L} \{ \alpha_i(r, t), \dot{\alpha}_j [\alpha_k(r'', t), \pi_k(r''', t)] \}. \end{aligned} \quad (3.7)$$

On the left-hand side of this equation the functionals

$$\dot{\alpha}_r \{ \alpha_s(r'', t), \pi_k(r''', t) \}$$

are to be substituted. They can be obtained by solving Eqs (3.3) for $\dot{\alpha}_r$ by means of relations

$$\int R^{-1}(r'', r) R(r', r) dr' = \delta(r'' - r).$$

Without consideration of the fluctuations, we find $\mathcal{H} = 0$.

The third step is to derive the HAMILTON equations

$$\dot{\alpha}_i(r, t) = \frac{\delta \mathcal{H} \{ \alpha_j(r, t), \pi_k(r', t) \}}{\delta \pi_i(r, t)} \quad (3.8a)$$

$$\dot{\pi}_i(r, t) = - \frac{\delta \mathcal{H} \{ \alpha_j(r'', t), \pi_k(r', t) \}}{\delta \alpha_i(r, t)}. \quad (3.8b)$$

They can be obtained by direct calculations from (3.7) or by starting from the variational principle (3.9). The Hamilton equations are especially interesting if one takes into account fluctuation processes and thus the statistical interpretation of the principle (1.4).

The fourth step is to establish the fundamental variational principle

$$\delta \int_{t_1}^{t_2} \mathcal{L} dt = \delta \int_{t_1}^{t_2} \left(\sum_k \int_V \pi_k(r, t) \dot{\alpha}_k(r, t) dr - \mathcal{H} \{ \alpha_i(r, t), \pi_j(r', t) \} \right) dt = 0. \quad (3.9)$$

This leads to (3.8a), (3.8b) by independently varying the conjugate field variables $\alpha_k(r, t)$ and $\pi_k(r, t)$ in a manner analogous to (2.12) taking all partial derivatives as functional derivatives. The principle (3.9) contains the whole apparatus of generalized irreversible thermodynamics in functional form. The theory has been constructed here for α -type variables (for this notion see [14]), but can be easily generalized for β -type variables. Applications in the field of plasma theory are given elsewhere [15].

It should be mentioned that for thermodynamic systems in magnetic fields principal difficulties appear regarding the whole starting point of the theory, i.e. the definition of entropy and thus entropy production [16]. These problems are especially striking for spin systems [17, 18], which have become so important in physical chemistry (spin resonance spectroscopy). Here only the application of simplified variational principles and HAMILTONian formalisms is possible [19].

The author thanks Dr. GYARMATI and his co-workers for interesting discussion during the Conference on Physical Chemistry in Budapest, April 1966. Exchange of opinions with Dr. GYARMATI was especially stimulating.

Note: While completing the manuscript the author came to know a work by Dr. VERHÁS, a co-worker of Dr. GYARMATI. This paper which will appear in *Ann. Phys.* also treats a multi-dimensional HAMILTONIAN formalism on the basis of the variational principle of GYARMATI. The ideas given there are similar to the content of Chapter 2 of the present work.

SUMMARY

Two methods are given for constructing, within thermodynamics of irreversible processes, HAMILTONIAN formalisms for continuous systems. The first method is based on the fundamental variational principle of GYARMATI which is a local formulation of ONSAGER's principle of least dissipation of energy. A HAMILTONIAN formalism is obtained by introducing generalized canonical momenta as spatial gradients of the intensive state variables. The basic differential equations of irreversible thermodynamics can then be written as HAMILTON equations which themselves result as EULER equations from a HAMILTON principle. The second method starts from a functional generalization of ONSAGER's principle obtained earlier by the author. The LAGRANGE functional containing the entropy production functional gives the HAMILTON functional through a LEGENDRE transformation. The HAMILTON functional is determined by canonical functional differential equations which follow from a functional HAMILTON principle as EULER equations. These equations are identical with the thermodynamic equations of motion being here generally linear integrodifferential equations for the space- and time-dependent state fields. By specializing the integral kernels one obtains the various vectorial or tensorial irreversible processes in any continuous anisotropic and even nonlocal media.

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SYNTHESIS OF PROTEIN MODEL COMPOUNDS BY SIDE GROUP MODIFICATION OF POLYAMINO ACID DERIVATIVES, I.

THE PREPARATION OF BIOLOGICALLY ACTIVE BASIC DERIVATIVES OF POLY-L-
GLUTAMIC ACID*

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Various polyamino acids and their relatively simple derivatives have been often used as model compounds for studying the connections between the chemical structure and the biological activity of proteins. The preparation and biological properties of polyamino acids were summarized by KATCHALSKI and SELA [1, 2], their chemotherapeutic possibilities by STAHMANN [3].

Protein model compounds of another type with variable structural requirements can be synthesized in a relatively simple way from polyamino acids, prepared from trifunctional amino acids, or from their derivatives by the action of properly selected bifunctional reagents. One of the functional groups of these modifying reagents must be a typical protein functional group, the effect of which is supposed to be essential for a given activity and is to be studied, while the other serves only for the junction to the side groups of the starting polyamino acid derivative.

This method was first used for the preparation of biologically active compounds by KOVÁCS and KÓTAI [4]. The demonstrated antiphag [5], antibacterial [6, 7], anticoagulant and antiphlogistic [8–10] activities of the described basic derivatives of polyglutamic acid were similar to the characteristic biological actions of protamines and histones [11–13], the natural basic proteins. Water-soluble polyamino acid derivatives have been synthesized by similar methods for conformational studies by BERGER *et al.* [14, 15] as well as by KULKARNI and BLOUT [16]. Essentially the same reaction has also been applied for the preparation of azo derivatives of some aromatic poly- α -amino acids by SELA and KATCHALSKI [17], further to the attachment of cytotoxic groups to poly-DL-serine by SZEKERKE [18] and by BRUCKNER *et al.* [19].

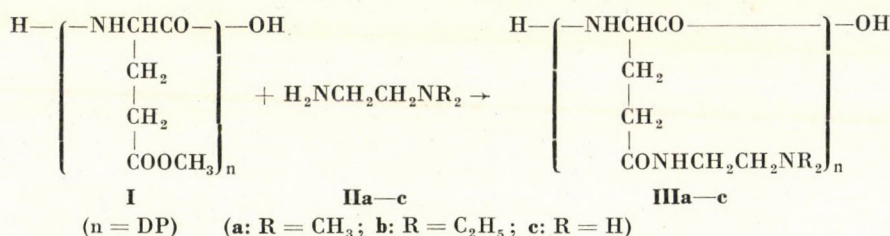
With the side group modification of polyamino acids it is further possible to prepare model compounds structurally more closely related to the proteins, in which diverse, randomly distributed functional groups are connected to the

* A previous report has been published in *Kém. Közl.* **26**, 231 (1966), as part of a lecture, delivered at a session (24.2.1966) of the *Committee of Organic Chemistry of the Hungarian Academy of Sciences*.

peptide backbone. Since the products of these reactions as well as one of their starting materials are polymeric polyfunctional compounds, it follows as a matter of course [20] that the structure of the prepared compounds is greatly influenced not only by the characteristics of the starting materials but also by other reaction conditions. This also means that a series of diverse compounds with different average compositions and molecular weights can be synthesized from the same starting materials depending on the reaction conditions. Thus special substances that have properties fixed in advance can only be made after a detailed study of the experimental conditions of their preparation. Therefore, the purpose of the present investigations has been to elaborate how model compounds of a predetermined structure, suitable thus for the research of proteins, can be synthesized with side group modifications of poly-amino acids.

The present paper, the first of a series, deals with the re-examination and more detailed description of the reaction already reported by Kovács and KÓTAI [4]. It is supposed, however, that most of the conclusions will be applicable, with occasional modifications, to other similar reactions, too.

The reaction of poly- γ -methyl-L-glutamate (I) (in short, PMG) with different diamines (IIa—c) having at least one primary amino group will be discussed. The compounds (IIIa—c) prepared in the illustrated manner are polybasic derivatives of polyglutamic acid — built by a single component



— and have the same average degree of polymerization (DP) as the starting material. This is in practice, however, an ideal borderline case, which is sometimes difficult to achieve. It is far more probable that the indicated reaction will be accompanied by some side-reactions, the results of which are always detectable by careful examination of the products. A frequent side-reaction is alteration of the DP during the course of the reaction. The “regular” monotonous structure of the product will also be changed, if the reaction modifying the side groups is not unambiguous or is not going quantitatively to completion.

When discussing these reactions, it must always be borne in mind that the starting polymers as well as their newly formed derivatives are polymolecular mixtures, simply characterizable only by their average properties. For this reason, in the course of later investigations it will have to be thoroughly

tested whether the biological activity of the materials prepared in this way depends unambiguously on the average properties, or the individual molecular distributions also have to be taken into consideration.

The following factors have been found to have major influence on the average properties of the compounds prepared by side group modification of polyamino acids:

1. The characteristics of the starting polymer
2. The properties of the modifying reagent
3. The temperature and the duration of the reaction
4. Other parameters (*e.g.*, accessory conditions of the reactions, working up of the samples, *etc.*).

The influence of these factors on the products of the reactions modifying the side group can be described as follows:

1. Effects of the characteristics of the starting polymer

One of the most important characteristics of the starting polymer is its DP. The DP of any compound prepared from a definite starting polymer will be limited by or agree with this value, depending on whether or not there has been a DP-change during the reaction. Since many internal (*e.g.* conformational) and external (*e.g.* solubility) properties of the polymers depend on the DP, a similar DP-dependence of the reactivity of the side chain functional groups can also be supposed. The same can be assumed about the extent of the possible DP change during the side group modification of polyamino acids.

To test these effects, different poly- γ -methyl-L-glutamate (**I**) samples were prepared. Their intrinsic viscosities were determined in dichloroacetic acid (DCA) and the weight-average degrees of polymerization (DP_w) were calculated using the molecular-weight—intrinsic viscosity calibration curve prepared by SAKURAI and OKUDA [21].* These starting polymers were reacted with 2-dimethylaminoethylamine under standard conditions. The viscosities of 0.5% solutions in DCA of the resulting different poly-N-(2-dimethylaminoethyl)-L-glutamine (**IIIa**) samples (in short, poly-DMAG) were measured.

The DP-viscosity calibration curve for poly-DMAG is not yet available. In order to obtain information about the possible DP changes the reduced viscosities (η_{sp}/c) of the newly formed modified polymers were divided with that of the starting polymers determined under identical conditions. In first approach these quotients (η_{quot}) — used for comparison — can be regarded as inversely proportional to the DP decrease during the reactions.

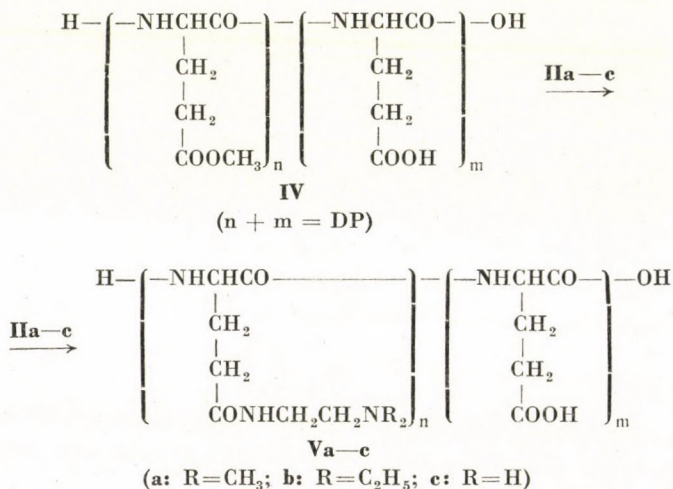
Data indicating the effect of the DP of the starting polymer on the modified polymers are summarized in Table I.

* It is pleasant duty of the author to express his thanks to S. SAKURAI and T. OKUDA for reporting their unpublished results.

Comparing the η_{quot} values of Samples 3, 6 and 15, prepared in other respects under identical conditions, it can be clearly seen that the higher the DP_w of the starting material, the greater is the observed DP decrease. At the same time, a comparison of the percentage conversions of Samples 2, 11a, and 11b indicates that the times needed to complete the reactions of starting polymers with higher DP_w are also longer.

It cannot be concluded at present, however, whether or not the greater DP decrease observed when starting with polymers of higher DP_w indicates a change between the relative rates of the two concurring reactions (aminolysis of ester groups and splitting of peptide bonds). One must namely take into account that the same absolute amount of splitting, undetectable with a polymer of low DP, can cause a very significant drop of viscosity in a polymer of high DP.

Another influencing characteristic of the starting polymer besides its DP is its composition. It has been demonstrated by DORY *et al.* [22] that even the most carefully prepared and stored poly-benzyl-L-glutamate samples contain some acidic groups too, the quantity of which is independent of the DP values. Still more acidic groups can be found in the poly- γ -methyl-L-glutamate (I) samples prepared without special care under technical or normal laboratory routine conditions. On account of the presence of these acidic groups, which are supposed to be glutamyl residues, the starting compound (IV) is a copolymer, and the new modified polymers obtained from it must be copolymers (Va-c) as well.

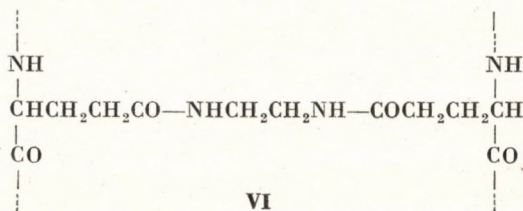


Since the discussed reactions take place mostly in suspensions, the dispersity of the starting polymer may constitute an additional influencing characteristic. It has been attempted to eliminate this factor by using PMG as

thoroughly dispersed as possible. It must be noted, however, that not all samples could be dispersed to the same degree.

2. Effects of the properties of the modifying reagent

The modifying reagents, used for the side group modification of poly-amino acids can be divided into two classes. The reagents of the first class, *e.g.*, 2-dimethylaminoethylamine (IIa), have only one appropriate functional group that is able to react with the starting polymer. The use of such a reagent leads to a chain-polymer, similar to the starting one. Reagents, such as ethylenediamine (IIc), belonging to the second group, contain two (or more) reactive groups. As a result, the formation of branched, cyclic and network structures is possible. To examine the modifying reagents having two reactive groups, PMG was reacted with ethylenediamine (IIc). Two different products could always be isolated. One of them was a gel, insoluble in any solvent but powerfully swelling in water. These properties are characteristic of a network structure, the formation of which can be explained by the presence of double acylated ethylenediamine residues (VI).



The other product (IIIc) was soluble in water, but still contained some of the just mentioned residues, because titration always detected in it less basic groups than would correspond to the quantity of ethylenediamine found in its hydrolysate.

The reagents of both classes can be further characterized by whether they are homogeneous or not. Namely reagents that are a mixture of two or more components can also be used, giving rise to the formation of modified polyamino acid derivatives which have different kinds of side chain functional groups at random distribution. The details of the application of mixed reagents will be discussed in a next publication [23].

3. Effects of temperature and the duration of the reaction

The temperature and the duration of the discussed reactions are the most easily variable influencing factors. Their alterations make possible to prepare either different products from the same starting materials (see Table I), or compounds with the same average properties (within certain limits)

Table I

Data of the prepared poly-DMAG and poly-DEAG samples and the characteristics of their preparation

Characteristics of the prepared materials			Characteristics of the starting PMG				Characteristics of the reaction			
No.	Name ^a indicating composition	$\frac{\eta_{sp}}{c}$ dl./g.	Sign	DP _w	$\frac{\eta_{sp}}{c}$ dl./g.	Glu-cont., mole-%	Temp. ^c °C	Time, hours	Conversion of ester groups, %	η_{quot}^d
1a	poly-DMAG ⁵⁴ MG ⁴² Glu ⁴	0.62	A	210	0.49	4	25	240	56	1.26
1b	poly-DMAG ⁸⁶ MG ¹⁰ Glu ⁴	0.61					25	672	90	1.24
1c	poly-DMAG ⁹³ MG ³ Glu ⁴	0.63					25	2064	97	1.28
1d	poly-DMAG ⁹⁶ Glu ⁴	0.60					25	4200	100	1.22
2	poly-DMAG ⁹⁶ Glu ⁴	0.56					68	100	100	1.14
3	poly-DMAG ⁹⁶ Glu ⁴	0.48					75 ; 95 ^e	3 ; 70 ^e	100	0.98
4	poly-DMAG ⁹⁶ Glu ⁴	0.32					75 ; 140 ^f	1 ; 18 ^f	100	0.65
5	poly-DMAG ⁹³ Glu ⁷	0.75	B	295	0.65	7	70	100	100	1.15
6	poly-DMAG ⁹³ Glu ⁷	0.66					75 ; 95 ^e	3 ; 70 ^e	100	1.01
7	poly-DMAG ⁹³ Glu ⁷	0.47					145	17	100	0.72
8a	poly-DMAG ²⁵ MG ⁷¹ Glu ⁴	1.10	C	480	1.04	4	20	240	26	1.06
8b	poly-DMAG ⁹² MG ⁴ Glu ⁴	—					20	2352	96	—
8c	poly-DMAG ⁹⁶ Glu ⁴	1.13					20	6450	100	1.09
9	poly-DMAG ⁹⁶ Glu ⁴	0.49					70 ; 95 ^g	3 ; 70 ^g	100	0.47
10a	poly-DMAG ²⁴ MG ⁷³ Glu ³	1.43	D	640	1.26	3	20	240	25	1.13
10b	poly-DMAG ⁹² MG ⁵ Glu ³	1.16					20	4250	95	0.92
10c	poly-DMAG ⁹⁷ Glu ³	1.17					20	8700	100	0.93
11a	poly-DMAG ⁵⁶ MG ⁴¹ Glu ³	—					68	100	58	—
11b	poly-DMAG ⁹⁷ Glu ³	0.84					68	200	100	0.67
11c	poly-DMAG ⁹⁷ Glu ³	0.66					68 ; 140 ^h	200 ; 18 ^h	100	0.52
12	poly-DMAG ⁹⁷ Glu ³	0.45					70 ; 140 ⁱ	2 ; 18 ⁱ	100	0.36
13	poly-DMAG ⁹⁷ Glu ³	0.32					70 ; 140 ^j	1 ; 18 ^j	100	0.25
14	poly-DMAG ⁹⁶ Glu ⁴	0.55	E	660	1.29	4	70 ; 95 ^g	3 ; 70 ^g	100	0.43
15	poly-DMAG ⁹⁵ Glu ⁵	0.69	F	700	1.35	5	75 ; 95 ^e	3 ; 70 ^e	100	0.51

16a	poly-DEAG ³⁸ MG ³⁸ Glu ⁴	0.71	}	A	210	0.49	4	{	20	240	40	1.45
16b	poly-DEAG ⁹⁶ Glu ⁴	0.62							20	7880	100	1.29
17a	poly-DEAG ⁹⁰ MG ³ Glu ⁷	0.96	}	B	295	0.65	7	{	20	3150	96	1.47
17b	poly-DEAG ⁹³ Glu ⁷	0.76							20 ; 160 ^k	3150 ; 9 ^k	100	1.17
18	poly-DEAG ⁹⁰ MG ³ Glu ⁷	—							70	67	96	—
19	poly-DEAG ⁴³ MG ³⁸ Glu ⁷	0.64							160	0.5	46	0.98
20	poly-DEAG ⁹⁷ Glu ³	0.36		D	640	1.26	3		70 ; 140 ⁱ	2 ; 18 ⁱ	100	0.29

^a Names are constructed according to Gill III. [30]; DMAG stands for N-(2-dimethylaminoethyl)-L-glutamine, DEAG for N-(2-diethylaminoethyl)-L-glutamine and MG for γ -methyl-L-glutamyl residues

^b c = 0.5%, in dichloroacetic acid

^c The temperature of the heating bath is given in the Table

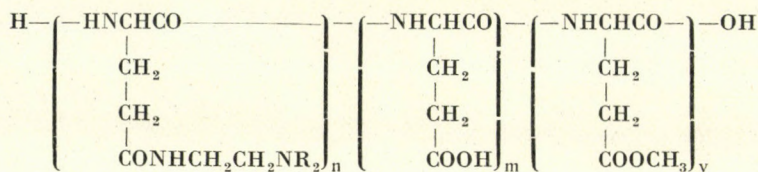
$$d \quad \eta_{\text{quot}} = \frac{\frac{\eta_{\text{sp}}}{c} (\text{product})}{\frac{\eta_{\text{sp}}}{c} (\text{PMG})} \quad (c = 0.5\%, \text{ in dichloroacetic acid})$$

^e Heating at 75 °C for 3 hrs., then at 95 °C for 70 hrs.

f	"	"	75	"	1	"	"	"	140	"	18	"
g	"	"	70	"	3	"	"	"	95	"	70	"
h	"	"	68	"	200	"	"	"	140	"	18	"
i	"	"	70	"	2	"	"	"	140	"	18	"
j	"	"	70	"	1	"	"	"	140	"	18	"
k	"	"	20	"	3150	"	"	"	160	"	9	"

from different starting materials. The importance of the latter possibility is emphasized by the fact that the well reproducible preparation of starting polymers which are identical in all respects is still an unsolved problem.

The side group modification of PMG by 2-dimethylaminoethylamine (IIa) was carried out at different temperatures. The corresponding reaction times that are necessary to reach a certain degree of conversion are shown in Table I. Stopping the conversion before it is complete, then treating the produc-



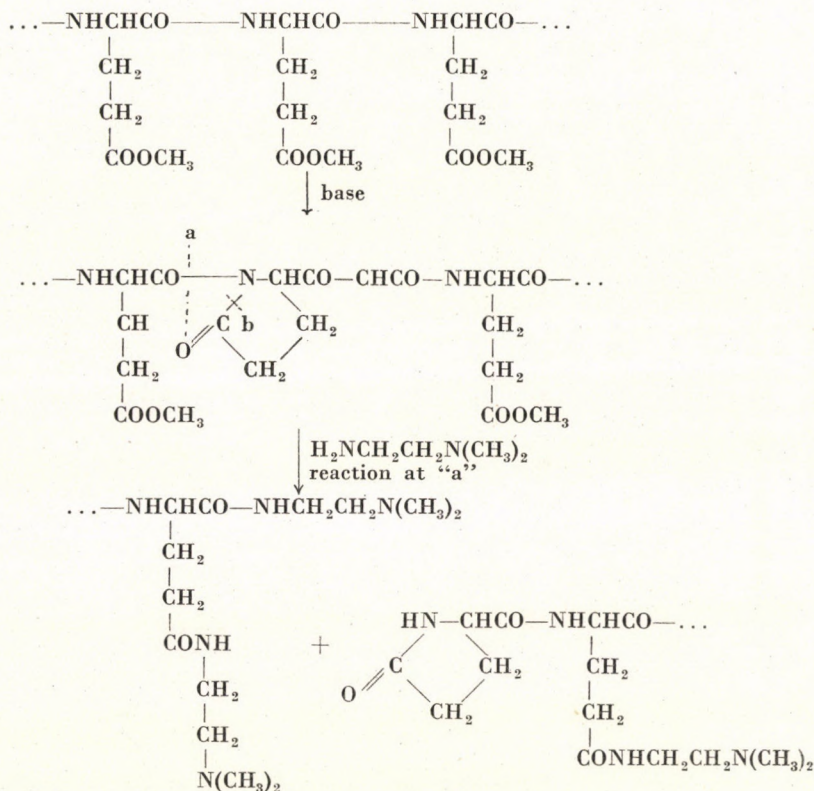
VII

(a: R=CH₃; b: R=C₂H₅) (n + m + q = DP)

ed material (VIIa₁) which contains still unreacted ester groups, with another reagent, make it possible to introduce successively as many different functional groups, as desired. In this way protein-like model compounds can be prepared, which have several functional groups in different relative amounts and at random distribution. From Table I it is also seen how the reaction temperature influences the reduced viscosity of the prepared modified polymers. The effect of temperature was more striking if starting polymers of high DP were used. From the observed data it is obvious that higher temperatures are more favourable to peptide chain splitting than to the aminolysis of ester groups. It may be supposed that at sufficiently low temperatures complete aminolysis of the ester groups can be accomplished without noticeable breaking of the peptide chains.* Since the material, prepared in this way, would have the same DP as the corresponding starting polymers, its η_{quot} value would be the proportionality factor of the viscosities of the two qualitatively different polyamino acid derivatives. With the help of this factor and of the DP-viscosity calibration curve of PMG, the DP of other, partially degraded basic derivatives could also be estimated, assuming that the viscosity-DP relationships of these newly prepared polymers and of the PMG's are parallel or nearly parallel.

* Different criteria — besides the use of independent physical-chemical methods — can be found to prove whether this point has been reached or not: the η_{quot} values of different compounds prepared either from the same starting polymer at different temperatures, or from starting materials of essentially different DP's at identical temperature, have to be compared. It is very probable that the required condition is met at the point where η_{quot} becomes independent of the temperature of the reaction in the first case, or of the DP of the starting polymer in the second. Since several months are needed to complete reactions at about room temperature, sufficient data are not yet available for full evidence. It is supposed, however, that in the preparation of the poly-DMAG sample 1d there occurred no splitting of the peptide chain.

It was not the purpose of the present work to investigate the structure of the terminal residues of the prepared compounds and to discuss the mechanism of the reactions in detail. It should be mentioned, however, that the viscosity of the products was found to depend on the period of preheating, if the reaction mixtures, before subjected to boiling for equal times, were treated at 70° for a shorter or longer period. Since prolonged preheating reduced the amount of available ester groups in the molecule, this observation means that the splitting of the peptide chain occurs mostly (or exclusively) at glutamyl residues bearing ester groups. It seems very probable that chain splitting is in connection with cyclization of γ -alkylated glutamyl residues [24, 25] and takes place as follows:



There is, however, no chain-splitting if the pyrrolidone ring containing structural part, formed intermediately, reacts with the amine at "b".

The available experimental data are yet insufficient to reach any conclusion whether another type of cyclization of glutamic ester residues — leading eventually to isomerization of the glutamyl residues [26–28] — also takes place or not.

As it can be seen from the data of Table I, results similar to the just discussed ones can be obtained when poly-N-(2-diethylaminoethyl)-L-glutamine

(IIIb) samples (in short, poly-DEAG) are prepared from PMG, using 2-diethylamine (IIIb) as the reagent.

4. Effects of other parameters

Besides the most important influencing factors, discussed in detail in the previous parts, some others have also to be considered in order to be able to accomplish the side group modification of polyamino acid derivatives in a reproducible manner. Though their effects may be eliminated if they are constant or nearly constant in a series of experiments, their greater variation may significantly change the properties of the prepared products, therefore they must not be overlooked. Such additional parameters are:

The speed of stirring which has to be controlled, since the reactions always start in a heterogeneous phase, and very often they also end as such.

The bulk of the mixture may influence both the intensity of the stirring and the effect of the temperature. The speed with which the internal temperature can follow the variations of the external heating also depends on this factor.

The working up of the samples is also a very important parameter. The crude products of the reactions that are formed in about 90% yield always contain an excess of the modifying reagents. Some loss (up to about 30%) of the polymeric material cannot be avoided when removing these impurities, and it is possible that some fractionation occurs at this stage of the operations. To test the role of this factor, the viscosities of some compounds were measured before and after purification. No appreciable viscosity change was found in samples of high η_{quot} values, but some increase of the viscosities could be detected after the purification of samples of low η_{quot} values. In the latter cases the loss of purification was also slightly higher than in the others, indicating the removal of a part of the low molecular weight fractions.

Experimental

Poly- γ -methyl-L-glutamate (PMG)

Poly- γ -methyl-L-glutamate (I) samples were made from freshly prepared γ -methyl-L-glutamate-N-carboxy-anhydride in dry ethyl acetate with the use of triethylamine as initiator. γ -methyl-N-carboxy-L-glutamate-anhydride was prepared from L-glutamic acid by a slight modification of the procedure claimed by JAKUS *et al.* [29]; namely the hydrochloride of γ -methyl-L-glutamate was isolated in dry state and suspended again (200 g) in dry dioxan (400 ml) and acetic anhydride (400 ml) before phosgene was bubbled through, and the mixture was worked up as usual.

To a solution of the N-carboxy-anhydride (150 g) in ethyl acetate (1500 ml) triethylamine (1.12 ml; $A/I^* = 100$), diluted with ethyl acetate (10 ml) was added. Polymerization

* A/I = The molar ratio of anhydride to initiator.

proceeded at 20° with the evolution of carbon dioxide to yield a gel. After standing for 72 hr. it was filtered off, washed with ether and dried in vacuum at room temperature over H_2SO_4 and paraffin. The yield was 104–107 g (91–93%). The viscosities of the compounds were measured in dichloroacetic acid (DCA) at five different concentrations. The values were extrapolated to zero. The intrinsic viscosities varied between 0.87 and 1.15 dl/g. This corresponds to DP_v 's ranging from 480 to 700, determined with the use of the calibration curve obtained from SAKURAI and OKUDA [21]. The samples contained 3–5% of glutamyl residues, as calculated from methoxy determinations and titrations with tetraethylammonium hydroxide. For detailed data of the individual compounds, see Table I. It should be noted that in the preparation of sample A more triethylamine initiator (11.2 ml; A/I = 10) was used; sample B was prepared and kindly supplied by CHINOIN Chemical and Pharmaceutical Works Co., Budapest.

Side group modification reactions of poly- γ -methyl-L-glutamate

General procedure: Poly- γ -methyl-L-glutamate (2.0 g) was suspended in the appropriate amine (30 ml) and stirred at temperatures and for periods given in Table I. Then the mixture was cooled to room temperature and worked up as required, and as described below.

Poly-N-(2-dimethylaminoethyl)-L-glutamine (poly-DMAG)

The mixture was diluted with anhydrous ether (120 ml) to obtain an amorphous precipitate. It was centrifuged and washed with ether (3×50 ml) in the centrifuge tube. Then the precipitate was filtered off, washed with ether and dried in vacuum over H_2SO_4 . The crude poly-DMAG (IIIa; 2.3–2.6 g) was treated with anhydrous ethanol (10–15 ml) and after a while with anhydrous ether (100 ml). The precipitate was filtered off and this procedure was repeated (from two to five times) until the material contained less than 0.2% of unreacted 2-dimethylaminoethylamine. The loss of material in a single step of purification was about 5%.

Poly-N-(2-diethylaminoethyl)-L-glutamine (poly-DEAG)

Poly-N-(2-diethylaminoethyl)-L-glutamine (IIIb, resp. Vb) was isolated and purified according to the procedures described formerly for the preparation of poly-DMAG.

The yield was 2.2–2.9 g.

Poly-N-(2-aminoethyl)-L-glutamine

The mixture was diluted with ethanol (30 ml) and centrifuged. The solid was washed in the centrifuge tube with ethanol (4×30 ml) and dried. The product was a swelling gel (0.8–1.0 g), insoluble even in hydrochloric acid. The combined liquids of the former operations were concentrated in vacuum to about 4 ml. The residue was diluted with ethanol (8 ml) and then triturated with ether (8 ml). A gummy precipitate formed that soon solidified. The solid was treated with ethanol (8 ml) and ether (8 ml), then centrifuged. The material was treated with several portions of anhydrous ethanol (8 ml) until it contained less than 0.4% of unchanged ethylenediamine. It was then dried in vacuum over H_2SO_4 and finally over P_2O_5 . The hygroscopic material (0.70–0.79 g) could not be completely freed from the solvents without loss of its solubility. A part of its glutamyl residues (about 22%) was involved in the formation of diacylated ethylenediamine residues (VI).

Analytical procedures

Elemental analysis was of little value for the determination of the exact compositions of the mostly copolymeric compounds. The elemental compositions of the individual structural units did not differ enough to permit accurate calculations and characterization of the products.

Quantitative determination of all basic structural units

The amount of basic structural units was determined by titrating samples (50—100 mg) with solutions of 0.1 *N* perchloric acid in 99.9% acetic acid [31]. The material was dissolved either in 99.9% acetic acid (30 ml) containing two drops of a solution of Crystal Violet (0.2 g in 100 ml of glacial acetic acid), or in the mixture of 99.9% acetic acid (20 ml) and acetonitrile (20 ml). The end-point of the titration was determined in the former case by the appearance of a blue colour and in the latter one potentiometrically (normal glass and calomel electrodes).

*Quantitative determination of the acidic structural units**

The acidic glutamyl residues were determined by titrating samples (20—60 mg) with solutions of 0.01 *N* tetraethylammonium hydroxide in methanol-benzene (1 : 8 v/v), prepared in the same manner as described for tetrabutylammonium hydroxide solutions [32]. The material was dissolved in water (0.5 ml) and diluted with pyridine (10 ml), containing four drops of a solution of Thymol Blue (0.3 g in 100 ml of isopropanol). The determinations were carried out under a nitrogen current, the end-point was determined by the appearance of a bluish green colour.

Quantitative determination of the unneutralized basic structural units

To check the former two determinations, samples (50—100 mg) dissolved in water (40 ml) were titrated with 0.1 *N* HCl. The end-point was determined either potentiometrically (glass and calomel electrodes) or by the appearance of a violet colour in the presence of two drops of a mixed indicator solution (0.2 g of Bromocresol Green and 0.1 g of Methyl Red in 150 ml of 96% ethanol) added before titration. The results of these titrations agreed with the molar differences of the basic and acidic groups.

[Quantitative determination of the ester group containing structural units

The amount of the γ -methyl-glutamyl residues was determined by the use of routine methoxyl determinations.

Calculation of the composition of the prepared compounds from the analytical data

The quantities of each structural unit, expressed in milliequivalents per gram, were summarized and from their sum — supposed to be 100% — their percentages were calculated, giving the composition of the material in mole-percentages.

In order to obtain evidence whether the material in question contained only the supposed and determined structural units or not, its actual analytical data were compared with the calculated ones, expressed from the just determined composition. Agreement — within the experimental error — indicated with great probability the completeness and correctness of the determined composition. This was the case for poly-DMAG and poly-DEAG.

The determined data, however, never fitted the calculated ones if poly-N-(2-aminoethyl)-L-glutamine samples were treated in the formerly described way. These discrepancies could be well explained by assuming the presence of diacylated ethylenediamine residues (VI). Their amount was calculated by subtracting the milliequivalents of the titrated basic structural units from the total ethylenediamine content of the material, determined as follows:

Quantitative determination of the total ethylenediamine content of poly-N-(2-aminoethyl)-L-glutamine samples

Poly-N-(2-aminoethyl)-L-glutamine (80—120 mg) was hydrolyzed in a sealed tube with a solution of 6 *N* HCl (1.0 ml) at 105° for 12 hrs. Ethylenediamine in the hydrolyzate was determined by the method of MAROS *et al.* [33]; the ammonia, liberated through oxidation with periodate, was titrated with a solution of 0.01 *N* HCl. The results were expressed in millimoles per gram.

* For the elaboration of the method and for the measurements I am greatly indebted to Gy. SZÓKÁN.

Other methods of investigation

Paper chromatographic determination of the purity. The material was dissolved in a solution of 0.1 N HCl and two different quantities (5 and 10 γ) were applied on the paper (Whatman 1). The appropriate amine, the removal of which had to be tested from the material, was dissolved in a solution of 0.001 N HCl and applied (0.02 and 0.04 γ) on the same paper. The chromatogram was run (ascending technique) for a period of about 2 hrs. in butanol—acetic acid—water (4 : 1 : 5) system, and afterwards sprayed with an alkaline ninhydrine solution [34]. The intensity of the colour of the developed spots was visually compared.

Viscosity measurements were carried out at 25.0° in an *Ubbelohde* viscometer, in which the flow time of dichloroacetic acid (1.58 ml) along a capillary tube (length: 96 mm) was 166 sec.

Control of the optical purity. A sample (120 mg) of the compound to be tested was heated with a solution of 6 N HCl (2.10 g) at 105° for 16 hrs. in a sealed tube. A mixture of L-glutamic acid and the appropriate amine, corresponding to the quantities formed upon total hydrolysis of the former sample, was treated at the same time under identical conditions. A comparison of the optical activities of the two solutions indicated that — within the limits of experimental error — the glutamic acid obtained by the hydrolysis of the investigated poly-DMAG and poly-DEAG samples, had fully retained its optical activity.

My grateful acknowledgement is due to Prof. V. BRUCKNER, Director of the *Institute of Organic Chemistry*, for his interest and advice.

I wish to express my thanks to our *Microanalytical Laboratory*, supervised by Mrs. H. MEDZIHRADESKY, for the methoxyl analyses and to Mrs. M. ALMÁS for most of the experimental work done always reliably and with high precision.

SUMMARY

The synthesis of various basic polyglutamic acid derivatives prepared from poly- γ -methyl-L-glutamate (PMG) is described. PMG has been transformed with different diamines having at least one primary amino group. It has been demonstrated that a great number of diverse compounds can be prepared from the same starting materials, depending on the conditions of these "side group modifying reactions". The most important influencing factors, that determine both the composition and the average degree of polymerization of the materials prepared, have been investigated. In this respect the characteristics of the starting polymer, the properties of the modifying reagent, the temperature and the duration of the reaction, and some other parameters of minor importance are discussed. It has been shown that the presence of the esterified glutamyl residues is responsible for the partial peptide chain splitting occurring during the reactions.

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NH STRETCHING VIBRATION BANDS AT WAVE NUMBERS LOWER THAN 3000 cm^{-1} , II

DIMERIC STRUCTURES, II PYRIDINE DERIVATIVES

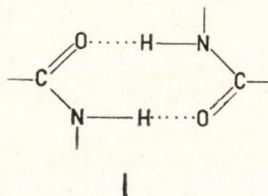
P. SOHÁR and L. FARKAS

(*Pharmaceutical Research Institute, Budapest*)

Received September 19, 1966

Introduction

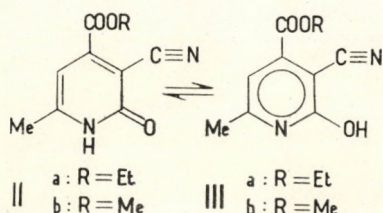
In former investigations we have found that cyclic N-monosubstituted acid amides (lactams) in the solid state (KBr pellets) form cyclic dimer association rings (I) like those noted in the case of carboxylic acids [1–3]. Characteristic for their IR spectra is a broad NH stretching vibration band indented by submaxima and appearing at unusually low frequencies, namely between 3200 and 2500 cm^{-1} , and this band points unmistakably to the associated structure mentioned. For, according to data in the literature, the NH stretching vibration band of amides does never appear at wave numbers below 3000 cm^{-1} .



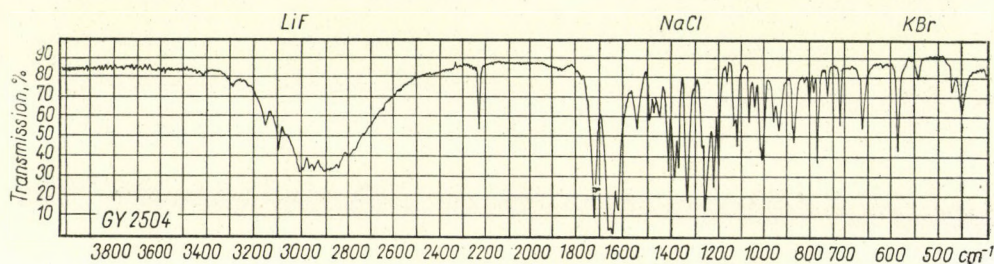
In what follows we report about the investigations of the spectra of some pyridone compounds, among them of some where the NH stretching vibration band characteristic of the associated cyclic dimer appears.

Discussion

The starting material for this family of compounds is 2-methyl-4-carbethoxy-5-cyano-6-pyridone (IIa), and the formation of its iminohydrin (lactim) tautomer of aromatic structure (IIIa) is also conceivable.

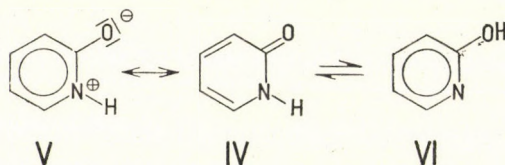


However, the appearance of a rather intensive amide-I band at 1665 cm^{-1} in Spectrum 1 at once excludes this possibility, in accord also with former investigations concerning the structures of pyridone derivatives. These studies have shown that the complete shift of the tautomeric equilibrium between amide $\rightleftharpoons$ imino-hydrin to the amide (lactam) form (IV) is due to the fact



Spectrum 1. 2-methyl-4-carbethoxy-5-cyano-pyridone

that the mesomery energy $\text{IV} \leftrightarrow \text{V}$ of the amide group is greater than the energy liberated by the aromatization involved in the formation of the imino-hydrin tautomer (VI) [4].



Thus the very intensive, diffuse, and indented absorption between 3200 and 2500 cm^{-1} is assignable to NH stretching vibrations. The shape of the band is evidence for a cyclic dimer association structure (VII). Between 3100 and 3000 cm^{-1} the weak stretching vibration bands of the CH group adjacent to the double bond, and in the interval between 3000 and 2800 cm^{-1} the bands of the aliphatic groups (methyl and ethyl) coalesce with the NH stretching vibration band. We suppose that the surplus energy of the very strong association of type VII also contributes to the stabilization of tautomer II, in contra-

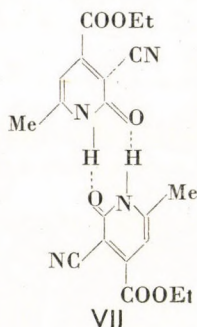


Table I*

	2-methyl-4-carbethoxy- 5-cyano-6-pyridone	Partially deuterated 2-methyl-4-carbethoxy- cyano-6-pyridone	2-methyl-4-carbomethoxy- 5-cyano-pyridone
ν NH, and ν ND bands,** respectively	3200—2400, v.s., with sub-maxima	2400—2000, s., with sub-maxima	3200—2400, v.s., with sub-maxima
ν C $\equiv$ N band	2230, m.	2230, m.	2230, m.
ν C=O (ester) band	1730, s.	1730, s.	1730, s.
Amide-I band	1670—1640, v.s.	1670—1640, v.s.	1680—1650, v.s.
ν C=C bands	1625, m. 1540, m.	1605, m. 1550, m.	1625, m. 1550, m.
Amide-II band	1490, w.	1280, w.	1490, w.
β_s CH ₂ , δ_{as} CH ₃ and δ_s CH ₃ bands	1470, 1450, 1410, 1385, 1370, m.-w.	1470, 1450, 1405, 1390, 1370, m.-w.	1490***, 1440 1415, 1385 m.-w.
ν C—C($\equiv$ N) band	1330, m.	1330, m.	1330, m.
ν C—O—C (conjugated ester) bands	1255, 1220, 1200, 1130, 1120, 1020, 1010, s.	1280, 1255, 1220, 1200, 1120, 1020, 1010, s.	1250, 1220, 1130, 1065, s.
Amide-V (γ NH) band	940, m.	770, m.	960, m.
γ (=CH) band?	760, m.	760, m.	760, m.
Amide-VI (γ C=O) band?	585, m.	585, m.	585, m.

* Values in this Table are given in cm^{-1} . Relative intensities are marked thus, v.s. = very strong, s. = strong, m. = medium, w. = weak. Vibration modes are marked thus, ν_{as} XY, ν_s XY, resp., and δ_{as} XY, δ_s XY, resp. = XY asymmetric, resp. symmetric stretching and vibration and deformation vibration bands; $-\nu$ XY, β XY and γ XY = XY stretching vibration, in plane, deformation vibration and out of plane deformation vibration.

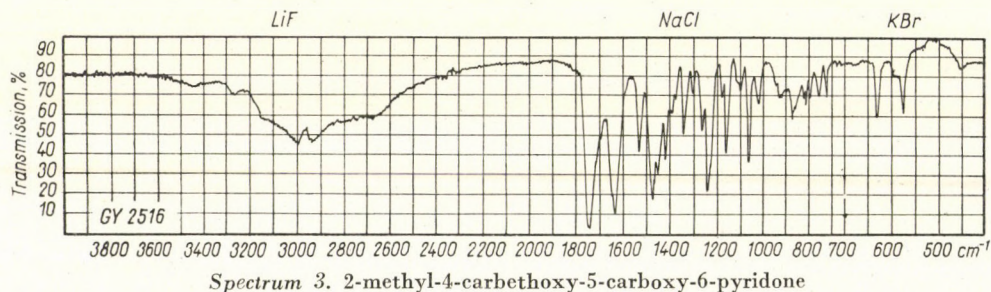
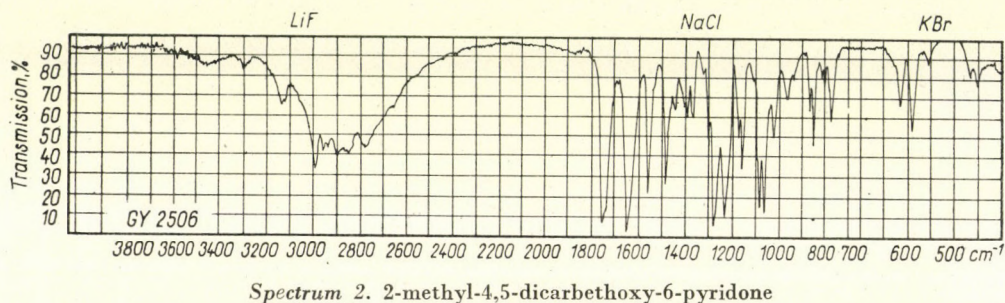
** In cyclic dimer association.

*** Superimposed on the amide-II band.

distinction to simple OH...OH or OH...N-type intermolecular hydrogen bonds possible in structure **III**.

Table I shows the assignments of the main spectrum bands; these assignments are supported by results of partial deuterations. Also the frequencies of the deuterated compound are listed in Table I.

Acid hydrolysis in alcohol [5] of **IIa** yields two substances (cf. Spectra 2 and 3), one of which is 2-methyl-4,5-dicarbethoxy-6-pyridone (**VIIIa**), and the other a half-ester having structure **IXa** or structure **Xa**. The formation of the latter can be visualized as the result of partial hydrolysis of the di-ester



VIIIa. Spectrum 2 of the di-ester (**VIIIa**) is similar in every respect to Spectrum 1 of **IIa**, but, of course, the ester bands are more intensive and splitting (cf. frequency values in Table II), and nitrile bands around 2230 and 1330 cm^{-1} do not emerge. The greater intensity of the amide-I stretching vibration band of the amide group, and that of the C=C double bonds is quite notable and attributable to the increased electron-withdrawing effect, due to the presence of the two ester groups, which decreases the electron density near these groups, and enhances the polarity of the C=O and of the C=C bonds. The unchanged structure of the NH stretching vibration band supports the view that also this compound forms a cyclic dimer association.

Chemically considered, between the alternatives **IXa** and **Xa** the formation of the former may be expected, since a simple hydrolysis of the nitrile group suffices to yield this compound. At the same time, partial hydrolysis

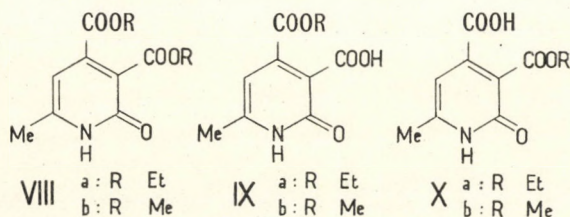
Table II*

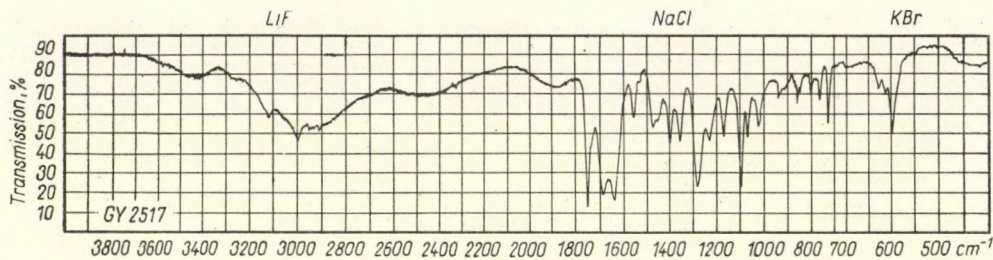
	2-methyl-4,5-dicar- bethoxy-6-pyridone	2-methyl-3-nitro-4,5- dicarbethoxy-6-pyridone
ν NH band**	3200—2400 v.s., with sub-maxima	3200—2600 s., with sub-maxima
ν C=O (ester)band	1750—1730 v.s.	1760 v.s.
Amide-I band	1645 v.s.	1660 s.
ν C=C bands	1560 s. 1485 s.	1620 m. 1570 m.
ν_{as} NO ₂	—	1530 s.
ν_s NO ₂	—	1360 s.
β_s CH ₂ , δ_{as} CH ₃ , δ_s CH ₃ bands	several weak bands in the range between 1460 and 1370	several weak bands in the range between 1460 and 1370
ν C—O—C (conjugated ester) bands	1275, 1230, 1085, 1065 s.	1270, 1225, 1140, 1085 s.
Amide-II band	1490 w.	1490 w.
Amide-III band	1300 m.	1300 m.
Amide-V (ν NH) band?	965 w.	950 w.
ν (=CH) band?	850 m.	850 m.
Amide-VI (ν C=O) band?	590 m.	610 m.

* Cf. footnote * to Table I.

** In cyclic dimer association. The ν CH bands of the saturated and of the unsaturated groups are superimposed.

of the di-ester (VIIIa) is more likely to produce Xa, since the reactivity of substituents at position 4 of pyridine compounds is generally greater [6—9]. To substantiate these suppositions, we synthesized [10] and investigated Spectrum 4 of the products of the partial hydrolysis of VIIIa.





Spectrum 4. 2-methyl-4-carboxy-5-carbethoxy-6-pyridone

Spectra 3 and 4 are not identical, and they also differ from Spectra 1 or 2, thus they correspond, indeed, to structures **IXa** and **Xa**. Now it remained to clear whether Spectrum 3 is that of **IXa**, and Spectrum 4 that of **Xa**, as expected.

This task is rather complex. It seemed best to start with Spectrum 4 where in either of the ranges between 2600 and 2200 cm^{-1} , and between 2000 and 1800 cm^{-1} , one very diffuse "immonium" [11] band appears, characteristic of $\geq\text{NH}^+$ -type ionic groups. It is well known that an amide group can only exceptionally form a salt, and that none of the bands of the $>\text{NH}_2^+$ group would appear in the intervals mentioned, but they would have maxima between 2800 and 2400 cm^{-1} , around 2600 cm^{-1} . Therefore, obviously, only a pyridine salt structure (**IIIa**) can be supposed to emerge, at least in part of the molecules, by the formation of zwitterions, with the participation of the free carboxyl group. Accordingly, the asymmetric, the symmetric stretching vibration bands of the carboxylate ion, and those of the $\text{C}=\text{N}^+$ type double bond of the aromatic ring appear at 1685, 1640 and 1400 cm^{-1} , respectively. The $\nu\text{C}=\text{O}$ band of those carboxyl groups that do not participate in zwitterion formation coalesces with the latter.

Spectrum 3 contains no bands characteristic of zwitterions. Compared with Spectrum 1 (*cf.* Table III), the frequency of the amide-I band is lower by about 20 wave numbers. The band at 1745 cm^{-1} of the ester-carbonyl is about twice as intensive as bands of the same origin in Spectra 1 and 4, obviously because it is superimposed on the $\text{C}=\text{O}$ stretching vibration band of the carboxylic-acid groups. The comparatively high frequency of the acid carbonyl band shows that no cyclic dimers are formed with carbonyl groups; conversely, at the same time, the diffusiveness and low wave number of the OH stretching vibration band, to be found superimposed on the NH stretching vibration band between 3200 and 2400 cm^{-1} , further the sharp profile around 930 cm^{-1} of the band due to the out of plane OH deformation vibration, are indicative of the formation of strong intramolecular hydrogen bonds. Taken in conjunction with the mentioned shift towards lower wave numbers of the amide-I band, it is highly probable that the acid hydroxyl group associates intramolecularly with the amide carbonyl to produce a chelate structure.

Table III*

	2-methyl-4-carbethoxy- 5-carboxy-6-pyridone	2-methyl-4-carboxy-5- carbethoxy-6-pyridone
νOH^{**} and νNH^{***} bands superimposed	3200—2400 v.s., diffuse,	—
νOH band****	—	3300—2700 s.
$\nu(\geq\text{NH}^+)$ bands	—	2700—2200 m. 2100—1800 w.
$\nu\text{C}=\text{O}$ (ester) band	1740 v.s., broad*****	1750 s., sharp
$\nu\text{C}=\text{O}$ (acid) and $\nu\text{C}=\text{N}^*$ bands superimposed	—	1685 s.
$\nu_{\text{as}}\text{CO}_2^-$ band	—	1640 s.
$\nu_{\text{s}}\text{CO}_2^-$	—	1400 m.
Amide-I band	1625 s.	—
$\nu\text{C}=\text{C}$ bands	1530 m. 1480***** s.	1560 w. 1480 w.
Amide-III band	1390 w.	—
$\nu\text{C}-\text{O}-\text{C}$ (conjugate ester) bands	1240 s. 1065 s.	1280 v.s., broad 1095 s.
$\nu\text{C}-\text{O}(\text{H})$ (carboxyl) band?	1160 s.	—
νOH^{**} and νNH^{***} bands superimposed	930 m. broad	—
$\beta_{\text{s}}\text{CO}_2^-$ band?	—	600 s.

However, it is only structure IXa that allows such an association. According to expectation, the foregoing seem to support the view that the half-ester produced by acid hydrolysis has structure IXa. Lactam dimers are formed at the same time, thus formula XI that takes account also of associative circumstances corresponds to Spectrum 3. This accounts for the very low wave number of the amide-I band: owing to the chelate structure and the twofold hydrogen bonding, the $\text{C}=\text{O}$ bond order is significantly reduced.

* Cf. footnote * to Table I.

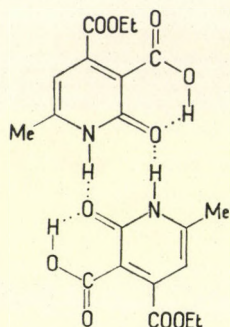
** in intramolecular association.

*** in cyclic dimer association.

**** in very strong intermolecular association.

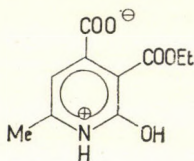
***** $\nu\text{C}=\text{O}$ (carboxyl) band also superimposed.

***** Amide-II band also superimposed.



XI

Thus Spectrum 4 is that of **Xa**; this is supported by the zwitterion structure **XII** whose emergence here is obviously due to significant mesomeric and inductive effects between the carboxylate ion at position 4 and the hetero ring, and this circumstance stabilizes the zwitterion form. Otherwise, also the greater reactivity of position 4 is connected with the possible inductive and mesomeric effects between the ring and the substituent at position 4.

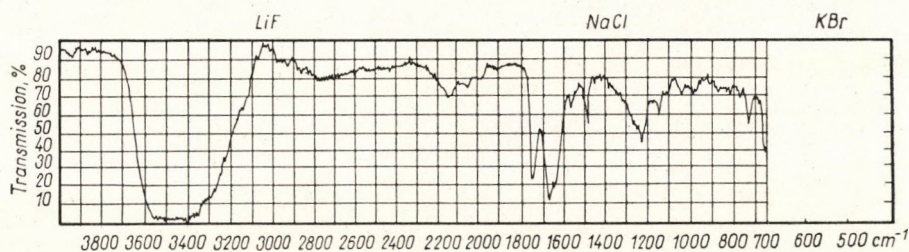


XII

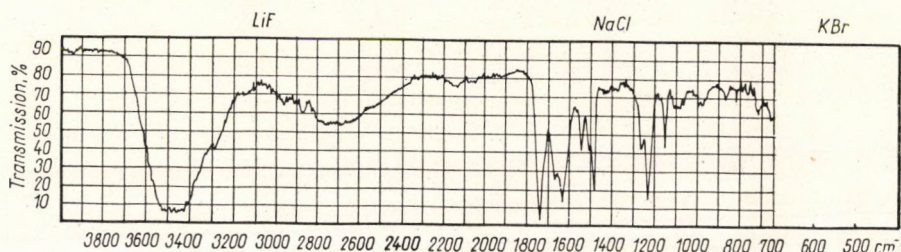
The prerequisite of mesomerism is that the carboxylate ion should be co-planar with the aromatic ring. This requires that the ester group should turn out of the plane of the ring. This explains the higher frequency of the ester bands (the degree of conjugation is lower) compared with the values found in Spectrum 3. For the same reason the phenolic hydroxyl group at position 6 cannot become intramolecularly associated with any of the oxygens of the ester group, therefore it is probable that it forms quite a strong hydrogen bond with the carboxylate ion of an other molecule. Accordingly, in contrast to findings with potassium bromide pellets, in a strongly polar solvent (dimethylsulphoxide) the hydrogen bonds are disrupted and the zwitterion structure is abandoned at the same time, in accordance with the spectroscopic finding that pyridine-carboxylic acids show no zwitterion structure in water [12]. The superimposed stretching vibration bands of the OH and the NH groups solvated by the solvent appear in the 3700 to 3100 cm^{-1} range. At the same time, substance **Xa** with Spectrum 4, investigated in the same solvent, is found to have retained the diffuse band between 3100 and 2200 cm^{-1} , thus here intramolecular

hydrogen bonds are present, in accord with the association structure **X** (cf. Spectra 3a and 4a).

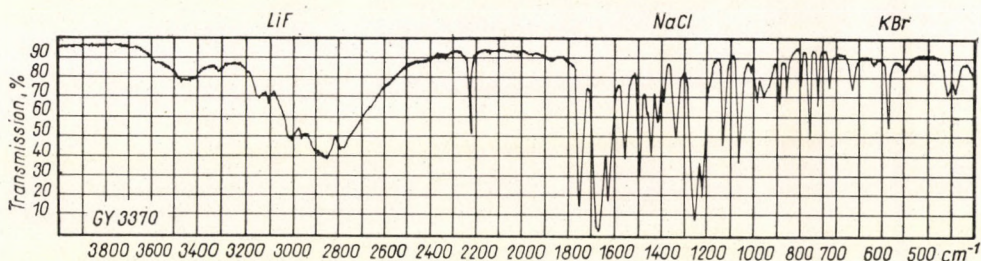
Spectra very similar to those of the carbethoxy derivatives are produced by the carbomethoxy compounds **IIb**, **VIIIb**, **IXb**, and **Xb**, thus for them the



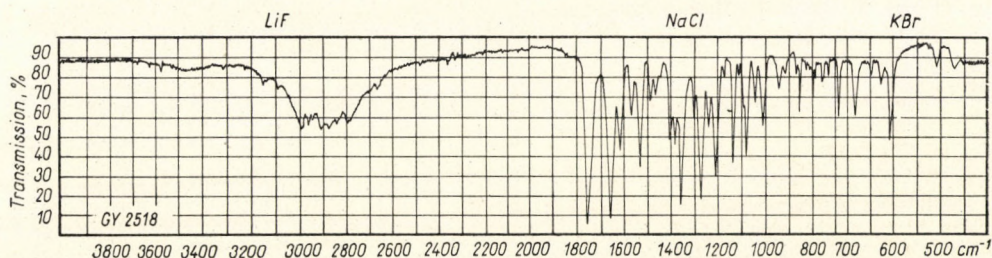
Spectrum 3a. Infrared spectrum of 2-methyl-4-carbethoxy-5-carboxy-6-pyridone in 10^{-3} m/l dimethyl-sulfoxide solution ($4000-700\text{ cm}^{-1}$)



Spectrum 4a. Infrared spectrum of 2-methyl-carboxy-5-carbethoxy-6-pyridone in 10^{-3} m/l dimethyl-sulfoxide solution ($4000-700\text{ cm}^{-1}$)



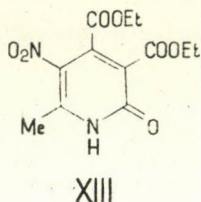
Spectrum 5. 2-methyl-4-carbomethoxy-5-cyano-6-pyridone



Spectrum 6. 2-methyl-3-nitro-4,5-dicarbethoxy-6-pyridone

foregoing statements are valid in every respect. As an example, Spectrum 5, that of 2-methyl-4-carbomethoxy-5-cyano-6-pyridone (**IIIb**) is shown (cf. also Table I).

Di-esters of structure **VIII** and derivatives that carry a nitro group at position 3 give spectra with diffuse NH stretching vibration band of low wave number and indented by sub-maxima, thus also these compounds enter into a cyclic dimer association. As an example, Spectrum 6 of 2-methyl-3-nitro-4,5-dicarbomethoxy-6-pyridone (**XIII**) is shown (cf. also Table II), where loss of intensity of the NH stretching vibration band due to the electron withdrawing



effect of the nitro group is clearly noticeable. This loss of intensity occurs in connection with the lower polarity of the C=O double bond, since, owing to the electron attraction of the nitro group at *para* position, the carbonyl oxygen is less negative, consequently the hydrogen bond formed with it is weaker, thus the polarity of the N—H bond is reduced, and this causes that the NH stretching vibration and the amide-I bands become less intensive [13].

Experimental

Infrared spectra were recorded by an UR-10 double-beam spectrometer of Zeiss, Jena; samples in KBr pellets.

Spectra of solutions were recorded with the sample in a sodium chloride cuvette, path length 10 mm, in concentrations of about 10^{-3} mole substance per litre of dimethyl sulphoxide.

Partial deuteration was carried out in 98% heavy water. 2 g of substance in 10 ml of heavy water was boiled for 1 hr., this was then evaporated in vacuum to dryness. Boiling with another 10 ml of heavy water and evaporation followed, then the substance was dried in vacuum over phosphorus pentoxide at 105° for 24 hrs.

SUMMARY

In the IR spectra of the pyridine derivatives studied, the diffuse, indented NH stretching vibration band extends over the interval of wave numbers lower than 3000 cm^{-1} , between 3200 and 2500 cm^{-1} . Former experiments of ours have shown this to be the consequence of the formation of a cyclic dimer association structure. In the half-esters of pyridine dicarboxylic acids, depending on the position of the free carboxyl group, in the one case this type of hydrogen bond remains intact and also the OH group of the carboxyl becomes associated with the amide carbonyl within the molecule; in the other case, cyclic dimer association is not possible because of the simultaneous emergence of the tautomeric iminohydrin form; this gives rise to zwitterion structures and the bands of the NH^+ and OH groups in intermolecular hydrogen bonds appear in the spectrum. On the basis of the divergent circumstances for association, the relative positions of the free carbonyl and ester groups, *i.e.* the structure of the molecules can be elucidated.

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NH STRETCHING VIBRATION BANDS AT WAVE NUMBERS LOWER THAN 3000 cm^{-1} , III

DIMERIC STRUCTURES, III

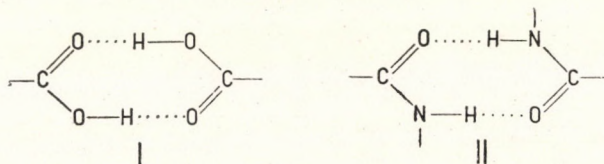
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Introduction

In the course of former studies [1, 2] we have found that contrary to data in the literature [3, 4], cyclic N-monosubstituted amides (lactams) in the solid state (KBr pellets) exhibit spectra in which the NH stretching vibration (νNH) band extends to regions of wave numbers lower than 3000 cm^{-1} ; the band becomes diffuse (appearing in the range between 3200 and 2700 cm^{-1}) and it is indented occasionally by sub-maxima. This shape of a band reminds us of the structure of the νOH bands of dimeric carboxylic acids, and just this fact suggested that these characteristics of the νNH band might be in some connexion with an association structure that is related to the one formed by hydrogen bonds in the case of carboxylic acids. Therefore, compounds were selected for study in which it was reasonable to suppose that an association



structure (II) similar to that of carboxylic acid dimers (I) will occur. Lactams, if they contain no other groups capable of association, are, indeed, liable to form relatively strong hydrogen bonds, since in them the conditions of the emergence of the association structure (II) are given [5, 6], as it will be discussed below.

Discussion

Conditions favourable for the emergence of a cyclic dimeric association structure are the following:

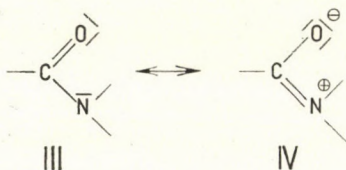
1. *Spatial arrangement of molecules*

A simple, intermolecular association of cyclic compounds is labile, because substantial disruptive forces affect the hydrogen bond; these forces tend

to keep off the molecules from one another. This favours the formation of cyclic dimers, since in the case of a simple intermolecular polymeric association the rings cannot be co-planar; however, they are in the same plane in a cyclic dimer, and thus they present a smaller surface to the attack of disruptive forces. This view is supported by the analogous, generally accepted, and experimentally proved fact that with cyclic compounds or with those of great spatial extension, if at all possible, intramolecular hydrogen bonding is much more probable than some intermolecular linkage between the molecules [7].

2. Spatial structure of the association ring

In N-monosubstituted acid amides the hydrogen atom is nearly co-planar with the NCO group. This follows from the spectroscopic values, notably from the comparatively low frequency values of the amide-I band, and the high frequencies of the amide-II band. These values can be explained by the hybridization of the C=O and N—C stretching vibrations, and by that of the in-plane deformation vibrations of the NH bond. The coupling of these vibra-



tion modes is correlated with the **III** ↔ **IV** mesomerism evidenced in amides; this phenomenon forces the N—H bond into the NCO plane. In the limiting structure of mesomer **IV**, which is the more probable, the hydrogen bonds enhance the deformation of the CONH group into a planar arrangement, therefore the eight-membered association ring can be considered practically planar. The planar arrangement stabilizes the association structure.

3. Twofold linkage

In structure **II** two hydrogen bonds per pair keep the molecules together. Also this twofold linking makes this type of association more probable than any other linkage between the molecules.

4. Symmetry

By the formation of dimers of type **II**, the symmetry of the molecule always increases, and an arrangement is brought about that is centrally symmetric. Since this is favourable energetically, and has, as shown by a number of analogous instances, a stabilizing effect, it can be one of the causes responsible for the formation of structure **II**.

5. Very strong hydrogen bond

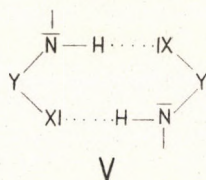
The circumstances listed demonstrate that the cyclic association structure is more favourable than simple intermolecular associations. There is no doubt, however, that the characteristics of the corresponding ν NH band are decisively affected by the fact that in amides especially strong hydrogen bonds are formed, and the diffuse, low wave number band sometimes indented by sub-maxima will emerge in the spectrum only if the hydrogen bonds appropriate to structure **II** are strong enough.

The formation of very strong hydrogen bonds in the case of acid amides is ensured by the following circumstances.

(a) From the outset, the negatively polarized carbonyl oxygen and the NH-hydrogen of acidic character allow the formation of strong hydrogen bonds.

(b) Owing to the **III** $\leftrightarrow$ **IV** mesomerism, the plane-hybrid electron structure of the nitrogen atom is prevailing, thereby a more intensive interaction of the pillar atoms is allowed than by hydrogen bonds in cases when the valencies of the N atom of the NH group are arranged pyramidally [5, 6].

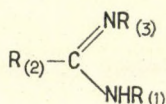
(c) In structure **II**, the two O...H—N atom triads directly involved in the formation of the hydrogen bond, *viz.* the pillar atoms and the proton, are co-linear like in the dimeric carboxylic acids; this again will favour the formation of strong hydrogen bonds. All these together explain the special features of the ν NH band that characterizes the association structure **II** of lactams.



If these ideas are correct, in addition to the case of lactams, a ν NH band of a similar structure may be expected in every other group of compounds which satisfies, at least for the greater part, the conditions listed under Points 1 to 5. If structure **II** is to be wholly generalized it suffices to require that the NH group should remain intact and the other atom X, *i.e.* that in position β , bonded to the nitrogen, should function as an electron reservoir, *i.e.* it should possess at least one lone pair of electrons. Atom Y directly linked to the NH group can be of any kind; thus the general formula for structure **II** may be written as in V. The free valence of the nitrogen atom may form a bond with any group of atoms, or with any atom, thus, *e.g.* ring closure towards Y or X is possible, or it may link up with Y in the form of a Y=N double bond. The hydrogen atom is excepted since with primary acid amides, according to experience, no cyclic dimer association is formed, obviously because the mesomeric

system is shifted towards **III**, and so conditions 2, 5a, and 5b, are not fulfilled. Of course, also the possible further valences of X and Y may serve for any bondings that are actually feasible; the association ring is always imaginable and actually emerging if otherwise allowed by the chemical character and spatial arrangement of the atomic groups involved.

Amidines

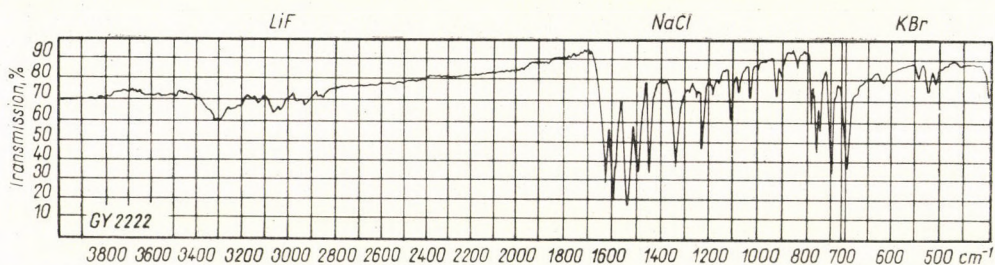


VI

If in the general formula V, Y is a carbon atom and X is a nitrogen atom, further if also the second valence of the nitrogen atom at position X forms a bond with the atom at Y, *i.e.* a double bond $\text{X}=\text{Y}$ or $\text{C}=\text{N}$ is present in the molecule, then an amidine (VI) is formed, of which the cyclic dimer association VII will emerge according to the character of the substituents attached to the carbon and nitrogen atoms. Spectrum 1, that of N,N'-diphenylbenzamidine (VI; $\text{R}_1 = \text{R}_2 = \text{R}_3 = \text{Ph}$) and Spectrum 2, that of N,N'-diphenylacetamidine (VI; $\text{R}_1 = \text{R}_3 = \text{Ph}$; $\text{R}_2 = \text{Me}$) have been studied.

1. Spectrum of N,N'-diphenylbenzamidine

In the spectrum of this compound the rather weak NH stretching vibration band appears between 3400 and 3200 cm^{-1} , with a maximum around 3310 cm^{-1} . This suggests that no cyclic dimer association did emerge, and only



Spectrum 1. N, N' — diphenyl-benzamidine

simple intermolecular conditions of the occurrence of an association structure similar to **II** in mind, it seems highly probable that by the joined electron-withdrawing effect of substituents R_2 and R_3 , the electron donor character

of the nitrogen of the $C=N$ double bond is weakened to a level at which no hydrogen bonds strong enough to cause a lowering of frequency and a diffusiveness as mentioned, can be formed.

The further bands are assigned as follows:

1630 cm^{-1} is a $\nu_{\text{as}}N-C=N$ band of $\nu C=N$ character

1590, 1490 and 1440 cm^{-1} are bands of the vibrations of the aromatic skeleton

1540 cm^{-1} is a βNH band with, possibly, a superimposed band of one vibration mode of the aromatic skeleton

1330 cm^{-1} is a $\nu_s N-C=N$ band of $\nu C-N$ character

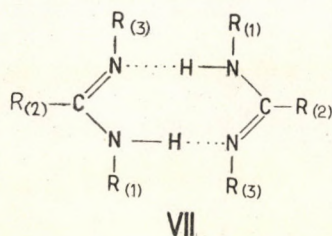
1225 cm^{-1} is a $\nu C(\text{Ph})-N$ band [$\nu C(R_1)-N$, and $\nu C(R_3)-N$ band]

780, 760, 740 and 700 cm^{-1} are aromatic $\gamma(=CH)$ or γCC bands characteristic of monosubstitution

As intermolecular association develops, internal rotation is made possible, so the γNH band gets diffuse. On the band there superpose absorptions also of other origin that appear in the very same region, therefore the γNH band may be suspected only from the deflection between 800 and 400 cm^{-1} of the spectral base line.

2. Spectrum of *N,N'*-diphenylacetamidine

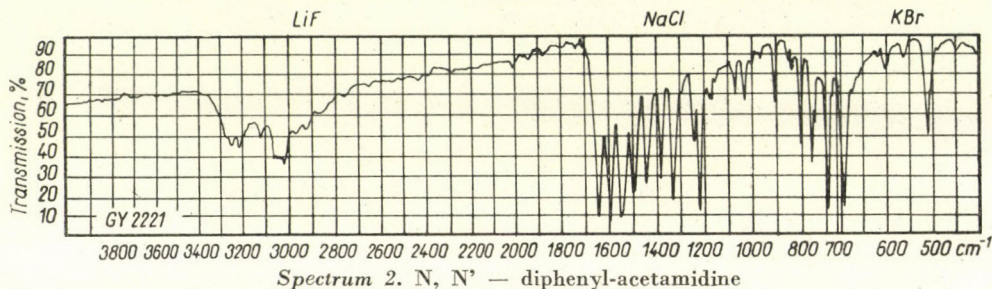
In Spectrum 2, that of this compound, besides a significant rise in intensity, the frequency of the νNH band is lowered by several hundreds of wave numbers. This band extends from 3350 cm^{-1} down to 2500 cm^{-1} and exhibits one less, and one more, pronounced maximum around 3250, and 3050 cm^{-1} , respectively. From this we deduce that with the greater number of the molecules the cyclic dimer (VII; $R_1 = R_3 = \text{Ph}$; $R_2 = \text{Me}$), and with the remainder



a simple intermolecular association is formed. Thus the electron donor effect of the $R_2 = \text{methyl}$ substituent sufficiently increases the electron density at the R atom of the $C=N$ double bond to render the formation of strong hydrogen bonds of type VII possible, at least for a greater part of the molecules. The polarization of the $H-N-C=N$ system is also expressed by the enhanced intensity of the bands of this group. In accordance with the two kinds of association, the bands of the $N-H-C=N$ group are widened or split. The γNH band around 510 cm^{-1} that corresponds to the molecules present in cyclic

dimer association emerges with a sharp outline, since no internal rotation is possible in these molecules, whereas the corresponding band of the molecules with simple intermolecular hydrogen bonds is diffuse also here and causes a shift of the base line towards lower transmission values between 900 and 600 cm^{-1} .

The other bands have the same frequencies as shown by Spectrum 1, and also the bands assignable to the methyl group appear. From among these, the stretching vibration bands coalesce with the νNH absorption.



Spectrum 2. N, N' — diphenyl-acetamide

The further bands are assigned as follows:

- 3400 to 3100 cm^{-1} is a νNH band (in simple intermolecular association)
- 3200 to 2500 cm^{-1} , with a maximum around 3050 cm^{-1} , is a νNH band (in cyclic dimer association) superimposed, at around 2930 and 2860 cm^{-1} , on the $\nu_{\text{as}}\text{CH}_3$ and $\nu_{\text{s}}\text{CH}_3$ bands
- 1645 cm^{-1} is a $\text{N}=\text{C}=\text{N}$ band of $\nu\text{C}=\text{N}$ character; the higher frequency is due to a greater electron density around the bond system than in N,N'-diphenylbenzamidine
- 1590, 1500 and 1450 cm^{-1} are bands of the stretching vibrations of the aromatic skeleton (the maximum around 1450 cm^{-1} is superimposed on the $\delta_{\text{as}}\text{CH}_3$ band)
- 1545 cm^{-1} is a βNH band
- 1380 cm^{-1} is a $\delta_{\text{s}}\text{CH}_3$ band
- 1335 cm^{-1} is a $\nu_{\text{s}}\text{N}=\text{C}=\text{N}$ band
- 1220 cm^{-1} is a $\nu\text{C}(\text{Ph})-\text{N}$ band [$\nu\text{C}(\text{R}_1)-\text{N}$ and $\nu\text{C}(\text{R}_3)-\text{N}$ bands]
- 800 cm^{-1} is a $\delta_{\text{e}}\text{CH}_3$ "sweeping" band?
- 760, 750 and 695 cm^{-1} are aromatic $\gamma(=\text{CH})$ and γCC bands characteristic of monosubstitution
- 510 cm^{-1} is a γNH band (in a cyclic dimer association)
- 900 to 600 cm^{-1} is a diffuse γNH band (in a simple intermolecular association).

Experimental

Spectra were recorded with a double-beam UR-10 infrared spectrometer of Zeiss, Jena; samples in KBr pellets.

Our thanks are due to Dr. K. KÖRMENDY (Dept. of Organic Chemistry, L. Eötvös University, Budapest) for the gift of the substances used in these studies.

SUMMARY

In the spectra of cyclic secondary acid amides (lactams), the NH stretching vibration band extends to wave numbers lower than 3000 cm^{-1} , it is rather diffuse as it appears between 3200 and 2500 cm^{-1} , of and is indented occasionally by sub-maxima. These effects are explained by supposing that a cyclic dimer association structure (II) is formed. The conditions of this are the following: spatial arrangement of the molecule (a planar ring structure or great spatial extension is favourable); planar arrangement of the association ring; a twofold linking of each group of molecules; an increase of symmetry brought about by the association; and the emergence of very strong hydrogen bonds due to the great associative tendency of the amide group enhanced also by mesomerism and co-linearity of the three atoms directly involved in hydrogen bonding. Structure II may be generalized, *e.g.*, if the hydrogen bonds are sufficiently strong, also in the case of amidines the formation of cyclic dimers, and there with the appearance of a νNH band as characterized before, is to be expected. Such a band has been actually identified in the spectrum of *e.g.*, N,N'-diphenylacetamidine.

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DIE ANWENDUNG DER AUTORADIOGRAPHIE ZUM STUDIUM DIFFUSIONSABHÄNGIGER REAKTIONEN BEIM VISKOSESPINNPROZESS*

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Problemstellung

Noch immer stellen die Fasern auf Cellulosebasis den größten Anteil der Chemiefaserproduktion der Welt. Die erheblichen Verbesserungen der textilphysikalischen Eigenschaften der Cellulosefasern in den letzten 10 Jahren zeigen, daß diese Entwicklung noch nicht beendet ist [1].

Das Prinzip des Viskosespinnprozesses ist in Bild 1 dargestellt. Die Viskose, eine alkalische Lösung von Na-Cellulosexanthogenat, wird durch die Spinn Düse in das Spinnbad gefördert; der entstehende Cellulose regeneratfaden wird von einem Aufwickelorgan aufgenommen, säurefrei gewaschen, getrocknet und einer Nachbehandlung unterworfen [2].

Die Zusammensetzung von Viskose und Spinnbad enthält Tabelle I. Die Konzentrationsangaben beziehen sich auf den Superkordspinnprozeß, der

Tabelle I

Aufstellung der Viskose- und Spinnbadbestandteile

<i>Viskose</i>	<i>Spinnbad</i>
6–8 % Cellulose	50–60 g H ₂ SO ₄ /l
5–6 % NaOH	50–70 g ZnSO ₄ /l
42–47% CS ₂	140–160 g Na ₂ SO ₄ /l
Cell—O C=S S [—]	SO ₄ [—]
	Zn ⁺⁺
	H ⁺
CS ₃ [—]	Na ⁺
S [—]	H ₂ O
OH [—]	Modifikator
Na ⁺	
H ₂ O	

* Nach einem Vortrag auf der Konferenz »Über einige Gebiete der physikalischen Chemie« vom 25.—28. April 1966 in Budapest.

von uns untersucht wurde. Des weiteren sind die Hauptbestandteile der Viskose und die Bestandteile des Spinnbades in Ionenform angegeben. Die Modifikatoren werden in Konzentrationen von 1–2 g/l der Viskose oder dem Spinnbad zugesetzt. In Verbindung mit der Superkordspinntechnologie verändern sie wesentlich die textilphysikalischen Eigenschaften von Celluloseregeneratfäden [3].

Als Modifikatoren eignen sich die verschiedensten Substanzen, wie z. B. Cyclohexylamin und seine Derivate oder auch Polyäthylenglycol mit einem Molekulargewicht von 1500 [4].

Für den Herstellungsprozeß der Fäden sind Informationen über die Diffusion der Spinnbadbestandteile erforderlich, denn sie bestimmen die Struktur und somit die textilphysikalischen Eigenschaften des fertigen Fadens.

Die Diffusion der Spinnbadbestandteile wurde bisher während des Spinnvorganges durch den Farbumschlag eines Indikators gemessen und dabei das Verhalten der Wasserstoffionen geprüft [5]. Eine Fragestellung für den Superkordspinnprozeß lautet jedoch:

»Wie verhalten sich die Zinkionen des Spinnbades während der Fadenherstellung?«

Es gibt Autoren, die eine Zinkverteilung über den gesamten Fadenquerschnitt annehmen [6], während andere aus experimentellen Werten eine periphere Verteilung schlußfolgern [7]. Mit herkömmlichen analytischen Methoden ist nur der Gesamtzinkgehalt des Fadens zu bestimmen [8]. Auskünfte über eine örtliche Verteilung sind damit nicht zu erhalten.

Für solche Untersuchungen ist es zweckmäßig, die in den Faden eindiffundierenden Spinnbadkomponenten zu markieren und auf ihrem Weg in den Faden zu verfolgen. Dieser Forderung werden die Radionuklide vollaufgerecht. Die einzelnen Ionen des Spinnbades können radioaktiv markiert werden und mit Hilfe des autoradiographischen Nachweisverfahrens ist eine örtliche Bestimmung des in den Faden hineindiffundierten Nuklids möglich [9].

Als markierte Spinnbadbestandteile verwendeten wir radioaktives Zn (^{69}Zn), radioaktives Sulfat (^{35}S) und einen ^{14}C -markierten Modifikator.

Experimentelles

Die Celluloseregeneratfäden wurden in einer Modellspinnapparatur nach dem Prinzip von Abb. 1 ersponnen. Die Zusammensetzung der radioaktiven Spinnbäder ist im folgenden aufgeführt:

1. Im Reaktor aktiviertes, metallisches Zink (100 mCi/4,6 g Zn) wurde in 7,8 g reiner, konzentrierter H_2SO_4 gelöst; H_2SO_4 und Na_2SO_4 wurden zur Erreichung der Badzusammensetzung von 54 g H_2SO_4 /l, 56 g ZnSO_4 /l und 156 g Na_2SO_4 /l zugefügt. (Spezifische Aktivität des Spinnbades: 0,5 mCi/ml.)

2. ^{35}S wurde in Form von trägerfreiem $\text{Na}_2^{35}\text{SO}_4$ mit einer Aktivität von 20,4 mCi dem Spinnbad (70 g H_2SO_4 /l, 90 g ZnSO_4 /l, 140 g Na_2SO_4 /l) zugesetzt. (Spezifische Aktivität des Spinnbades 0,4 mCi/ml.)

3. Als ^{14}C -markierter Modifikator wurden 162 mg eines Gemisches von Cyclohexylamin und N-Methylcyclohexylamin einer Aktivität von 8,43 mCi verwendet und 81 ml Spinnbad zugesetzt (Modifikatorkonzentration: 2 g/l, spezifische Aktivität des Spinnbades 0,103 mCi/ml).

Der Faden durchlief in den Spinnbädern eine bestimmte Strecke, gelangte dann auf das Aufwickelorgan und wurde mit Lösungen gespült, welche eine weitere Diffusion hemmen bzw. abbrechen. Wir benutzten

1 m Natriumacetatlösung für die Versuche mit ^{69}Zn (um eine weitere Zersetzung des Cellulosexanthogenats zu verhindern) und

1 m Bariumacetatlösung für die Experimente mit ^{35}S (dabei wird das Sulfat als BaSO_4 fixiert).

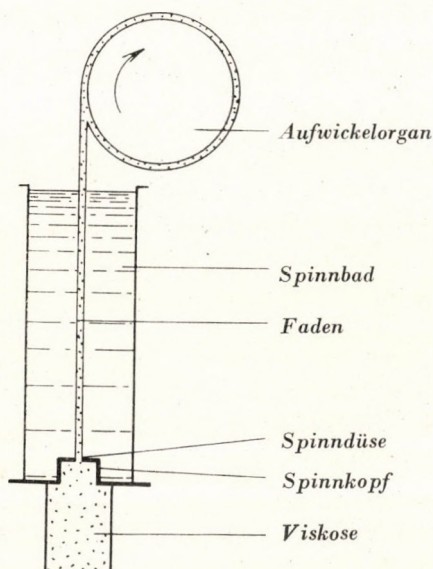


Abb. 1. Schematische Darstellung des Spinnvorganges

Die Diffusion des Modifikators wurde nicht unterbrochen, sondern die Fäden mit dem anhaftenden Spinnbad trocken aufgewickelt. Für die weitere Untersuchung betteten wir die Fäden in einer Mischung von 30% Paraffin, 20% Stearin, 45% Versamid 950® und 5% Dibutylphthalat ein und fertigten mit einem Mikrotom 5 bzw. 10 μm starke Querschnitte an. Diese fixierten wir mit einer Mischung aus Eiweiß-Glycerin auf Objektträgern, lösten das Einbettungsmittel mit Chloroform, überzogen sie mit Polyformaldehyd und brachten auf die 50 geschützten Querschnitte autoradiographische Filmemulsion [10].

Wir verwendeten Strippingfilm *ORWO K 105* mit einem Durchmesser des entwickelten Filmkorns von 0,5 μm [11]. Die Expositionszeiten beliefen sich bei radioaktivem Zink auf 36 h, bei ^{35}S und ^{14}C auf 21 d. Exponiert wurde in Metallkassetten bei $+4^\circ\text{C}$ im Kühlschrank. Nach bestimmten Kontaktzeiten wurden die Filmemulsionen mit *ORWO A 30* 5 min bei 20°C entwickelt und mit saurem Fixiersalz *ORWO A 300* fixiert. Auf dem Film zeigen sich an den Stellen Schwärzungen, die der radioaktiven Strahlung ausgesetzt waren. Aus die Verteilung der Schwärzung über den Fadenquerschnitt kann somit auf die Verteilung des Radionuklids im Faden geschlossen werden.

Ergebnisse

Das Ergebnis unserer Untersuchungen mit ^{69}Zn zeigt Abb. 2. Nur dort, wo sich im Fadenquerschnitt Zink befindet, tritt eine Schwärzung auf. Aus unserer Autoradiographie muß man deshalb schlußfolgern, daß im Faden eine

periphere Zinkverteilung vorliegt. Die Photometerkurve in Abb. 3 bestätigt durch 2 Schwärzungsmaxima am Fadenrand diesen Sachverhalt. Aus dieser Schwärzung läßt sich nicht ableiten, in welcher Form das Zink gebunden ist. Tabelle I zeigt, daß bei der Reaktion der Zinkionen des Spinnbades mit den Viskosebestandteilen $\text{Zn}(\text{OH})_2$, ZnS , ZnCS_3 oder Zn -Cellulosexanthogenat gebildet werden kann. Von diesen Verbindungen ist nur das ZnS exakt nachgewiesen worden [12].

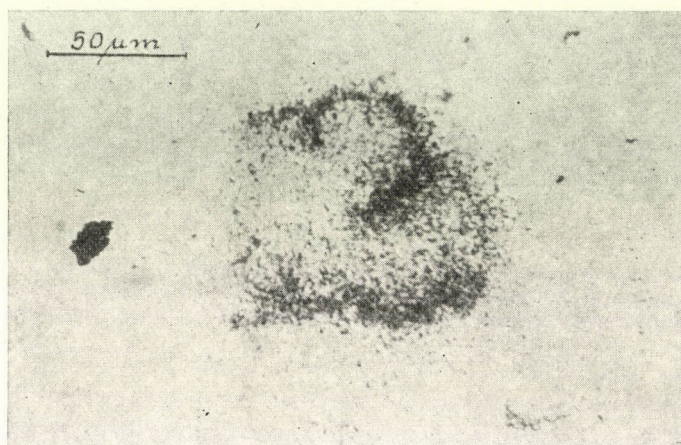


Abb. 2. Autoradiographie eines Fadenquerschnittes (Strippingfilm), Diffusion von markiertem Zink aus einem Spinnbad in Viskosekapillarfäden; Düsenloch $\varnothing$ 100 μm ; Probeentnahme: 25 cm Düsenabstand

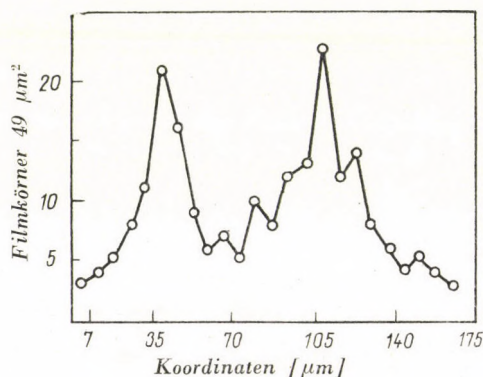


Abb. 3. Radiale Schwärzungsverteilung der Autoradiographie gemäß Abb. 2

Die Diffusion des Sulfatanions bei der Fadenbildung wurde bisher nur an Modellen untersucht, diese Ergebnisse sind nicht ohne Einschränkung auf den technischen Prozeß zu übertragen [13]. Es war zu erwarten, daß die Untersuchungen mit ^{35}S Aufschluß über die Koagulationsvorgänge beim Viskoseprozeß geben.

In Abb. 4 ist die Autoradiographie einer Fadenprobe zu sehen, die 3,5 cm hinter der Spinndüse entnommen wurde. Zu diesem Zeitpunkt ist das markierte Sulfat in die äußeren Bereiche des Fadens eingedrungen.

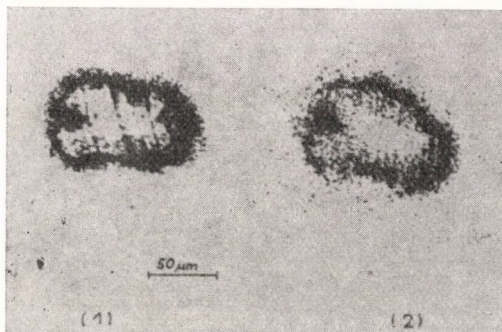


Abb. 4. Autoradiographie eines Fadenquerschnittes; Diffusion von ^{35}S -markiertem Sulfat aus einem Spinnbad in Viskosekapillarfäden; Düsenloch $\varnothing$: 100 μm ; Probeentnahme: 3,5 cm Düsenabstand; links: Fadenquerschnitt, rechts: Autoradiographie

Wie die Autoradiographie in Abb. 5 zeigt, ist nach einer Badstrecke von 13 cm das Sulfat über den gesamten Fadenquerschnitt verteilt. Man muß deshalb diskutieren, daß die Koagulation des Viskosesols sowohl durch die Neutralisation von NaOH durch H_2SO_4 als auch durch in den Faden diffundierendes Na_2SO_4 ausgelöst wird. Wenn man die Eindringtiefe der Sulfationen in den Faden gleich der Halbwertsbreite der autoradiographischen Schwärzung

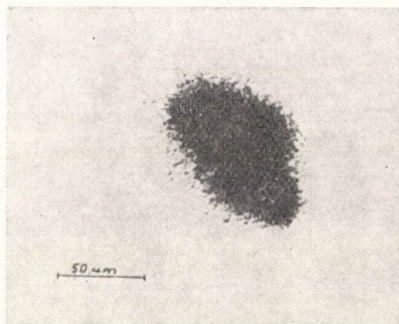


Abb. 5. Autoradiographie eines Fadenquerschnittes; Diffusion von ^{35}S -markiertem Sulfat aus einem Spinnbad in den Viskosekapillarfäden; Düsenloch $\varnothing$: 100 μm ; Probeentnahme: 13 cm Düsenabstand

setzt, läßt sich aus der Zunahme der Halbwertsbreite mit der Zeit der Diffusionskoeffizient des Sulfats abschätzen.

Nach einem von CRANK [14] angegebenen Verfahren errechnet sich ein $D_{\text{SO}_4^-} = (2,4 \pm 1,85) \cdot 10^{-6} \text{ cm}^2/\text{sec}$ in guter Übereinstimmung mit Angaben von MORIMOTO [15] ($D_{\text{SO}_4^-} = (0,200 - 1,78) \cdot 10^{-6} \text{ cm}^2/\text{sec}$).

Für unsere Versuche mit radioaktivem Modifikator setzten wir ein ^{14}C -markiertes N-Methyl-cyclohexylamin dem Spinnbad zu.* Die Autoradiographie eines solchen Versuches zeigt Abb. 6. Der Modifikator ist über den gesamten Faserquerschnitt verteilt. Dieses Ergebnis war überraschend, denn auch hier hätte, ebenso wie bei den Versuchen mit ^{69}Zn , ausschließlich eine periphere Verteilung des Modifikators vorliegen können, denn es ist aus anderen Untersuchungen bekannt, daß dieser Modifikator mit den Zinkionen des

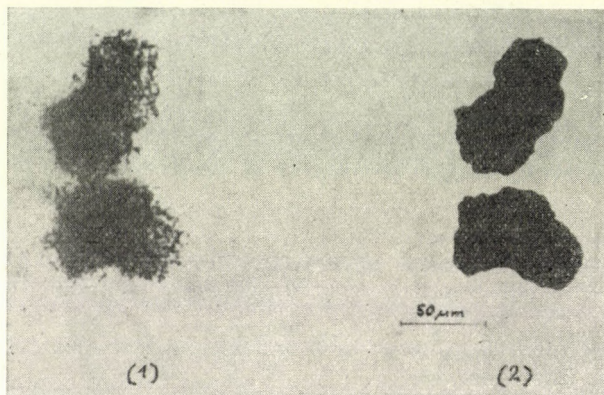


Abb. 6. Autoradiographien von Fadenquerschnitten; Diffusion von ^{14}C -markiertem Modifikator aus einem Spinnbad in Viskosekapillarfäden; Düsenloch $\varnothing$: $100\ \mu\text{m}$; Probeentnahme: 10 cm Düsenabstand; links: Autoradiographie, rechts: Fadenquerschnitt

Spinnbades und den schwefelhaltigen Verbindungen der Viskose schwerlösliches Zinkdithiocarbaminat bilden kann [16]. Unsere Versuche mit ^{69}Zn haben gezeigt, daß die für eine solche Reaktion notwendigen Zinkionen nur am Faserrand anzutreffen sind. Die Autoradiographien demonstrieren, daß der Modifikator nach einer möglichen Reaktion am Faserrand auch das Fadeninnere erreicht und somit kann er an den kolloidchemischen Reaktionen wie Sol-Gelumwandlung auch dann teilnehmen, wenn er dem Spinnbad zugesetzt wird. Damit ist auch die Annahme eines indirekten Einflusses des Modifikators vom Fadenrand aus auf die Strukturbildung im Fadeninneren, wie er von VAN DE VEN diskutiert wird, nicht notwendig [17]. Eine Diffusion des Modifikators aus dem Spinnbad in den Faden erklärt, daß Modifikatoren beim technologischen Prozeß sowohl dem Spinnbad als auch der Viskose zugesetzt werden können [3, 10, 18].

Die autoradiographischen Untersuchungen an Fadenquerschnitten erbringen eindeutige qualitative Aussagen über das Eindringen der markierten Spinnbadkomponenten in den Faden. Die bisherigen Versuche einer quantitativen Auswertung der Mikroautoradiographien zeigten jedoch unbefriedigende Ergebnisse und stellen mehr oder weniger nur Abschätzungen dar.

* Das Präparat war freundlicherweise von Frl. Dr. BUBNER, Zentralinstitut für Kernforschung, Dresden-Rossendorf, hergestellt worden.

ZUSAMMENFASSUNG

In der Arbeit werden die diffusionsabhängigen Reaktionen von radioaktivem Zink, ^{35}S -markiertem Sulfat und eines ^{14}C -markierten Modifikators als Spinnbadkomponenten im Faden untersucht.

Es erfolgt damit erstmalig der Nachweis der Reaktionszonen der Radionuklide im Faden mit der Methode der Mikroautoradiographie.

Mit diesem Verfahren wurde festgestellt, daß Zink nur im Faserrand mit Schwefelverbindungen der Viskose reagiert, während das Sulfat und der Modifikator die Fadenmitte erreichen.

Die Ergebnisse werden im Zusammenhang mit der Fadenbildung beim Viskosespinnprozeß diskutiert.

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ALGEBRAIC TREATMENT OF A CLASS OF CHEMICAL REACTIONS IN STOICHIOMETRY

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1. Introduction

The linear algebraic character of the formal representation of chemical species and their reactions has been more or less recognized by several authors [1–10], among whom especially ARIS [10] has recently presented a mathematically very elegant and fairly complete discussion of the subject. In the present paper we are concerned with so-called simple chemical reactions, already introduced to stoichiometry by the author [11–14]. By the methods of linear algebra several general properties of simple reactions are proved, including that whether or not the ratios of the stoichiometric coefficients in a reaction might be irrational. All these properties are new from a mathematical point of view, too [15]. The search for simple chemical reactions can be applied in chemical reaction kinetics and wherever multicomponent reaction systems occur.

2. Definition of simple chemical reactions and several criteria for their existence

Definition 1. Let us consider the different atomic substances A_i ($i = 1, 2, \dots, m$). Then a chemical species S is characterized by an appropriate linear combination of these A_i :

$$S = \sum_{i=1}^m a_i A_i, \quad (1)$$

where a_i are integers (not all zero). Similarly, for a set of chemical species $\{S_j\}$, the representations

$$S_j = \sum_{i=1}^m a_{ij} A_i, \quad j=1, 2, \dots, n \quad (2)$$

can be written.

Remark 1. According to the above definition a molecule, radical or occasionally even an atom are chemical species. Ions constitute chemical species,

too; they may be derived from corresponding neutral species by addition or subtraction of electrons, which have to be considered as a kind of atom in this context.

Remark 2. On the basis of Eq. (2) a column vector $\mathbf{a}_j = [a_{1j}, \dots, a_{mj}]^*$ can be associated with each chemical species S_j and the matrix $\mathbf{A} = [\mathbf{a}_1, \dots, \mathbf{a}_n] = [a_{ij}]$ can be defined.¹ We wish to mention two properties of $\mathbf{A}$:

a) $\mathbf{A}$ has no column consisting of zero elements² only,

b) we might assume $\mathbf{A}$ to have no row with merely zero elements; provided such a row existed, the corresponding atomic substance A_i could be *a priori* disregarded in the set $\{A_i\}$.

For example, let us consider the atomic substances $A_1 = \text{C}$, $A_2 = \text{H}$, $A_3 = \text{O}$ and the chemical species $S_1 = \text{C}$, $S_2 = \text{C}_2\text{H}_2$, $S_3 = \text{C}_6\text{H}_6$, $S_4 = \text{CH}_2\text{O}$, $S_5 = \text{H}_2$, $S_6 = \text{O}_2$. Then we have

$$\mathbf{A} = [\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3, \mathbf{a}_4, \mathbf{a}_5, \mathbf{a}_6] = \begin{bmatrix} 1 & 2 & 6 & 1 & 0 & 0 \\ 0 & 2 & 6 & 2 & 2 & 0 \\ 0 & 0 & 0 & 1 & 0 & 2 \end{bmatrix}. \quad (3)$$

Definition 2. A reaction among the species $S_j (j = 1, 2, \dots, n)$ is defined as the relation

$$\sum_{j=1}^n s_j S_j = 0,$$

where the numbers s_j , when substituted for x_j , must satisfy the vector equation

$$\sum_{j=1}^n x_j \mathbf{a}_j = 0, \quad (4)$$

or, in matrix representation

$$\mathbf{A}\mathbf{x} = 0, \quad \mathbf{x} = [x_1, \dots, x_n]^*. \quad (5)$$

About the s_j , called stoichiometric coefficients, we stipulate only that they should be real numbers.

Remark 3. Due to the above definition, by any solution $\mathbf{s}$ of Eq. (5) a reaction is determined. Therefore, further on we will use the terms 'reactions' on the one hand, and 'solutions of Eq. (5)' on the other, as synonyms.

Definition 3. In the set of the solutions $\mathbf{s}$ of Eq. (5)

a) the trivial solution should be disregarded, and

b) two solutions $\mathbf{s}$ and $\lambda\mathbf{s}$, $\lambda \neq 0$ being a real number, should be regarded as a single solution.

¹ The transpose of a vector is designated by an asterisk as a superscript.

² Elements or components of a vector are used as synonyms.

So the number of linearly independent different solutions is $n-r$, r being the rank of A .

Remark 4. According to *b*), it is only the ratios of the stoichiometric coefficients that are characteristic of the reaction; in chemistry these ratios are always rational numbers.

For the sake of simplifying the discussion, this circumstance will further on be left out of consideration. We shall come back to it in Part 4 only.

Remark 5. Rewriting Eq. (5) in full, one obtains the following set of homogeneous linear equations:

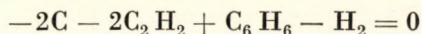
$$\sum_{j=1}^n x_j a_{ij} = 0, \quad i = 1, 2, \dots, m. \quad (6)$$

In chemistry these equations are known as the equations of conservation of mass with respect to the atomic substances A_i . Chemical species with positive stoichiometric coefficients are called products, those with negative ones reactants. If a stoichiometric coefficient vanishes, the corresponding species does not partake in the reaction.

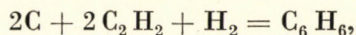
For the previous problem, Eq. (5) becomes the following:

$$\begin{bmatrix} 1 & 2 & 6 & 1 & 0 & 0 \\ 0 & 2 & 6 & 2 & 2 & 0 \\ 0 & 0 & 0 & 1 & 0 & 2 \end{bmatrix} \begin{bmatrix} x_1 \\ x_2 \\ x_3 \\ x_4 \\ x_5 \\ x_6 \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \\ 0 \end{bmatrix}. \quad (7)$$

E.g., one of its solutions, $[-2, -2, 1, 0, -1, 0]^*$, corresponds to the reaction



or



in which the other chemical species: CH_2O and O_2 do not take part.

Definition 4. Let the non-zero elements of the reaction $s = [s_1, \dots, s_n]^*$ be $s_{j_1}, \dots, s_{j_q}$, and $C = \{j_1, \dots, j_q\}$ the corresponding combination of the numbers $1, 2, \dots, n$, taken $q \leq n$ at a time. Then s is called a reaction (solution) over C ; in detail: s is a reaction over the chemical species $S_{j_1}, \dots, S_{j_q}$. (The word "over" and not "among" has been used, cf. Definition 2.)

For example, the former reaction $[-2, -2, 1, 0, -1, 0]^*$ is a reaction over the combination $\{1, 2, 3, 5\}$.

Definition 5. Let us consider the set of equations

$$\sum_{j=1}^n x_j \mathbf{a}_j = 0, \quad x_{j_{q+1}} = x_{j_{q+2}} = \dots = x_{j_n} = 0 \quad (8)$$

where $\bar{C} = \{j_{q+1}, j_{q+2}, \dots, j_n\}$ is a combination of the numbers $1, 2, \dots, n$, taken $n-q$ at a time: $\bar{C}$ denotes, therefore, the complementary set of C in Definition 4. It is clear that a reaction s over C is a solution of Eq. (8). Now, s will be said *simple* if it is the only solution of Eq. (8). In other words: s is called a simple reaction if it is the only reaction among the chemical species $S_{j_1}, \dots, S_{j_q}$.

Remark 6. Considering Definition 3, the reaction s is obviously simple if and only if

$$\text{rank} [\mathbf{a}_{j_1}, \dots, \mathbf{a}_{j_q}] = q - 1. \quad (9)$$

For example the reaction already mentioned $[-2, -2, 1, 0, -1, 0]^*$ ($2C + 2C_2H_2 + H_2 = C_6H_6$) is not simple, whereas the reaction $[0, -3, 1, 0, 0, 0]^*$ ($3C_2H_2 = C_6H_6$) is simple, — as it can be immediately seen from Eq. (9).

Theorem 1. For the number q of the non-zero elements in a simple reaction the inequality holds:

$$2 \leq q \leq r + 1, \quad r = \text{rank } A. \quad (10)$$

Proof. Since the trivial solution of Eq. (5) has been disregarded owing to Definition 3, no reaction with $q = 0$ exists. Nor does a reaction exist with $q = 1$, in accordance with *a)* of Remark 2. Thus, for every solution of Eq. (5), consequently for the simple ones as well, $2 \leq q$ holds. On the other hand, the inequality

$$\text{rank} [\mathbf{a}_{j_1}, \dots, \mathbf{a}_{j_q}] \leq r$$

is always true, hence, owing to Eq. (9):

$$q = \text{rank} [\mathbf{a}_{j_1}, \dots, \mathbf{a}_{j_q}] + 1 \leq r + 1.$$

Q. e. d.

However, the relation (10) does not suffice for s to be a simple reaction.

In our example already mentioned $r = \text{rank } A = 3$, and so $2 \leq q \leq 4$. Note, however, that the reaction $[-2, -2, 1, 0, -1, 0]^*$ is not simple, though for $q (= 4)$ in it the inequality (10) holds.

Definition 6. Let s^1 be a reaction over C^1 and s^2 a reaction over C^2 . The reaction s^1 is said *better* than s^2 if C^1 is a proper subset of C^2 : $C^1 \subset C^2$. In this

case the chemical species partaking in s^1 are contained by those in s^2 (but are not the same).

For example, the reaction $[0, -3, 1, 0, 0, 0]^*$ ($3C_2H_2 = C_6H_6$) is better than $[-2, -2, 1, 0, -1, 0]^*$ ($2C + 2C_2H_2 + H_2 = C_6H_6$).

Definition 7. The reaction s^1 is said *just as good as* s^2 if they are reactions over the same C . In this case the chemical species partaking in the reactions s^1 and s^2 are identical.

For example, the reaction $[-2, -5, 2, 0, -1, 0]^*$ ($2C + 5C_2H_2 + H_2 = 2C_6H_6$) is just as good as that already mentioned $[-2, -2, 1, 0, -1, 0]^*$ ($2C + 2C_2H_2 + H_2 = C_6H_6$).

Theorem 2. A reaction is simple if and only if there does not exist any better one.

Proof. The condition is trivially necessary on the basis of Definition 5. To show that the condition suffices we will prove that, if a reaction is not simple, a better one can always be found. Let s be a not simple reaction over $C = \{j_1, \dots, j_q\}$, then according to Definition 5

$$\text{rank} [a_{j_1}, \dots, a_{j_q}] \leq q - 2.$$

Making, e. g., x_{j_q} in Eq. (8) equal to zero, the new equation

$$\sum_{j=1}^n x_j a_j = 0, \quad x_{j_q} = x_{j_{q+1}} = \dots = 0 \quad (11)$$

becomes such that unchanged

$$\text{rank} [a_{j_1}, \dots, a_{j_{q-1}}] \leq q - 2.$$

Therefore, Eq. (11) will still have a solution s' (in the sense of Definition 3) over some C' , such that $C' \subset C$, so s' is a better solution.

Remark 7. The number of non-zero elements in a simple reaction is at least 2 according to Eq. (10). Thus, a reaction with 2 non-zero elements — if existing — is certainly simple on the grounds of the former theorem.

Theorem 3. A reaction is simple if and only if there does not exist any other just as good reaction.

Proof. The condition is trivially necessary on the basis of Definition 5. The sufficiency will be proved in the form that if a reaction is not simple, another just as good can always be found. Let s be a not simple reaction over $C = \{j_1, \dots, j_q\}$, then Eq. (8) has also another solution, say s' . Let us now form the solution $s + \varepsilon s'$, where $\varepsilon > 0$ is a real number. If ε is small enough, the non-zero elements of s vary only a little, that is, do not become zero. Therefore, $s + \varepsilon s'$ will be a reaction just as good as s .

Remark 8. Dealing with simple reactions the following question may also arise: when does a simple reaction exist over the given chemical species $S_{j_1}, \dots, S_{j_q}$? In this respect, one can immediately realize the following

Theorem 4. Let a combination $C = \{j_1, \dots, j_q\}$ be given. A simple reaction over C exists if and only if

- a) the solution of Eq. (8), say $s = [s_1, \dots, s_n]^*$, is unique, moreover
- b) for this unique solution

$$\prod_{t=1}^q s_{j_t} \neq 0. \quad (12)$$

This theorem is a trivial consequence of Definitions 4 and 5.

Theorem 5. The statement of the previous theorem holds if and only if

$$\text{rank} [\mathbf{a}_{j_1}, \dots, \mathbf{a}_{j_q}] = q - 1, \quad (13)$$

$$\text{rank} [\mathbf{a}_{j_1}, \dots, \mathbf{a}_{j_{t-1}}, \mathbf{a}_{j_{t+1}}, \dots, \mathbf{a}_{j_q}] = q - 1, \quad (14)$$

$$t = 1, 2, \dots, q.$$

In order to formulate this theorem more simply, let us designate a system of linearly dependent vectors as a *simplex* if, by omitting any of them, the remaining vectors become linearly independent. Then the vectors $\mathbf{a}_{j_1}, \dots, \mathbf{a}_{j_q}$ constitute a simplex if and only if Eqs. (13) and (14) hold.

Theorem 5 can now be formulated also in the following way: a simple reaction over $C = \{j_1, \dots, j_q\}$ exists if and only if $\{\mathbf{a}_{j_1}, \dots, \mathbf{a}_{j_q}\}$ forms a simplex.

Proof. At first we show that, if $\{\mathbf{a}_{j_1}, \dots, \mathbf{a}_{j_q}\}$ forms a simplex, the statements a) and b) of Theorem 4 are fulfilled. But, exactly because of Eq. (13), a) obtains. Now we prove that b) holds, too. Should namely any s_{j_t} ($1 \leq t \leq q$) be zero here, Eq. (8) without the term corresponding to $\mathbf{a}_{j_t}$ would have no solution according to Eq. (14), notwithstanding that s was the solution of Eq. (8).

Now we show that, if the statements a) and b) of Theorem 4 hold, the vectors $\mathbf{a}_{j_1}, \dots, \mathbf{a}_{j_q}$ form a simplex. Owing to a) Eq. (13) is true. Now we prove that Eq. (14) is also valid. If namely, in contradistinction to this, after omitting any vector $\mathbf{a}_{j_t}$ ($1 \leq t \leq q$) in the matrix of Eq. (13), the rank of the new matrix were less than $q-1$, then the corresponding s_{j_t} in the unique solution of Eq. (8) would be zero¹ despite the statement b).

For example, no simple reaction exists over the combination already mentioned $\{1, 2, 3, 5\}$, i.e. over the species C, C_2H_2 , C_6H_6 and H_2 .

¹ cf. Appendix.

3. Construction of the simple reactions

In the foregoing it has not yet been mentioned how the simple reactions in a system of chemical species S_j ($j = 1, 2, \dots, n$) can be found. A theorem with respect to this question will now be proved.

Definition 8. In order to solve Eq. (5), let us choose a basis $\{a_{j_1}, \dots, a_{j_r}\}$ among the vectors $a_1, a_2, \dots, a_n$, i.e. let $\text{rank } [a_{j_1}, \dots, a_{j_r}] = r$. After this choice the general solution of Eq. (5) has the following form:

$$s = \sum_{k=r+1}^n x_{j_k} s_{j_k} \quad (15)$$

where the x_{j_k} are the so-called free variables (arbitrary numbers). The vectors s_{j_k} we will designate as base solutions. Consider now all the general solutions of type (15) belonging to the possible bases among $a_1, a_2, \dots, a_n$ and consider the set of the different s_{j_k} in these solutions. Thus we have obtained all the base solutions of Eq. (5).

For example, choosing $\{a_1, a_2, a_4\}$ as a basis in matrix (3), the general solution of Eq. (7) becomes [13]:

$$\begin{bmatrix} x_1 \\ x_2 \\ x_3 \\ x_4 \\ x_5 \\ x_6 \end{bmatrix} = x_3 \begin{bmatrix} 0 \\ -3 \\ 1 \\ 0 \\ 0 \\ 0 \end{bmatrix} + x_5 \begin{bmatrix} 2 \\ -1 \\ 0 \\ 0 \\ 1 \\ 0 \end{bmatrix} + x_6 \begin{bmatrix} -2 \\ 2 \\ 0 \\ -2 \\ 0 \\ 1 \end{bmatrix}.$$

So we have found 3 base solutions. All the base solutions of Eq. (7) will be the column vectors of the following matrix:

$$[s^1, s^2, \dots, s^8] = \begin{bmatrix} 0 & -2 & -6 & -2 & -6 & -2 & 0 & 0 \\ -3 & 1 & 0 & 2 & 0 & 0 & -1 & 0 \\ 1 & 0 & 1 & 0 & 2 & 0 & 0 & -1 \\ 0 & 0 & 0 & -2 & -6 & 2 & 2 & 6 \\ 0 & -1 & -3 & 0 & 0 & -2 & -1 & -3 \\ 0 & 0 & 0 & 1 & 3 & -1 & -1 & -3 \end{bmatrix}. \quad (16)$$

Now, we can formulate the following:

Theorem 6. The simple reactions are identical with the base solutions of Eq. (5).

Proof. At first we show that the base solutions are simple reactions. Consider a base solution according to Definition 8. Without loss of generality

we may assume this base solution to be the solution of the set of equations

$$x_1 \mathbf{a}_1 + \dots + x_r \mathbf{a}_r + x_{r+1} \mathbf{a}_{r+1} = 0, \quad x_{r+2} = \dots = x_n = 0 \quad (17)$$

where $\{\mathbf{a}_1, \dots, \mathbf{a}_r\}$ is a basis. Obviously, this solution is unique and $x_{r+1} \neq 0$. As for the other unknowns, let $x_j, \dots, x_{j_{q-1}}$ ($2 \leq q \leq r+1$) be different from zero, then, owing to Definition 5, the solution of Eq. (17), i.e. the base solution considered, will be a simple reaction over $C = \{j_1, \dots, j_{q-1}, r+1\}$.

We prove now that a simple reaction is a base solution. Let us consider a simple reaction s , without loss of generality assuming it to be of the form $[s_1, \dots, s_q, 0, \dots, 0]^*$, $s_1, \dots, s_q$ being different from zero ($2 \leq q \leq r+1$). s is, due to Definition 5, the unique solution of the equation

$$x_1 \mathbf{a}_1 + \dots + x_q \mathbf{a}_q = 0, \quad x_{q+1} = \dots = x_n = 0. \quad (18)$$

Here, according to Theorem 5, $\{\mathbf{a}_1, \dots, \mathbf{a}_q\}$ is a simplex, so we may complete the vectors $\mathbf{a}_1, \dots, \mathbf{a}_{q-1}$ with $r - (q-1) \geq 0$ new vectors from among $\mathbf{a}_{q+1}, \dots, \mathbf{a}_n$ so as to get a basis. Now we can rearrange Eq. (18) with respect to this basis obtaining an equation of type (17), whose solution is indeed a base solution.

For example we determine all the simple reactions among the chemical species C , C_2H_2 , C_6H_6 , CH_2O , H_2 , O_2 . For this purpose, according to the previous theorem, the base solutions of Eq. (7) have to be determined. These are, as already mentioned, the column vectors of matrix (16), i.e. the following reactions:

- (1) $3C_2H_2 = C_6H_6$,
- (2) $2C + H_2 = C_2H_2$,
- (3) $6C + 3H_2 = C_6H_6$,
- (4) $2C + 2CH_2O = 2C_2H_2 + O_2$,
- (5) $6C + 6CH_2O = 2C_6H_6 + 3O_2$,
- (6) $2C + 2H_2 + O_2 = 2CH_2O$,
- (7) $C_2H_2 + H_2 + O_2 = 2CH_2O$,
- (8) $C_6H_6 + 3H_2 + 3O_2 = 6CH_2O$.

Remark 9. As a consequence of Definition 8, the base solutions belonging to a basis constitute linearly independent solutions of maximum number, i.e. of number $n-r$. It is, therefore, trivial that from the set of all the base solutions one can always choose a maximum number of linearly independent solutions. In other words: from the set of the simple reactions one can always select a maximum number of linearly independent reactions. Hence it follows

that any reaction among the given chemical species may be represented as a linear combination of simple reactions.

In our example we have 8 simple reactions (see Eq. (16)): $s^1, s^2, \dots, s^8$. *E.g.*, take s^1 and any of s^2 and s^3 , take further to these two reactions any of s^4, s^5, s^6, s^7 , and s^8 : the three reactions thereby obtained are linearly independent reactions of maximum number.

4. Rational and irrational reactions

Definition 9. Let $s = [s_1, \dots, s_n]^*$ be a reaction over $C = \{j_1, \dots, j_q\}$. If the ratios of $s_{j_1}, \dots, s_{j_q}$ are rational, the reaction s is said to be rational, otherwise irrational. Naturally only the rational reactions have a sense in chemistry. Mathematically, however, irrational reactions may also exist. Regarding this, interesting is the following

Theorem 7. The simple reactions are rational. If a reaction is not simple but rational, a just as good and irrational reaction can always be found. If a reaction is irrational, a just as good and rational reaction may always be constructed.

Proof. The first part of the theorem is based upon Theorem 6. Since the procedure of solving Eq. (5) contains only rational operations and the elements of the matrix A are rational numbers, it is clear that the base solutions according to Definition 8, that is, by virtue of Theorem 6, the simple reactions, are rational.

The second part of the theorem can be proved as follows. Let s be a not simple, rational reaction. Owing to Theorem 2 there exists a better reaction, say s' , and s' can at once be supposed to have rational stoichiometric coefficients. Consider now the reaction $s + \alpha s'$, where α is some irrational number. Among the non-zero elements of $s + \alpha s'$ there are, because of the construction, both rational and irrational ones, whose ratios will accordingly be irrational as a rule. Therefore, $s + \alpha s'$ is also irrational.

The third part of the theorem can be proved as follows. According to Remark 9 any reaction, therefore any irrational as well, may be represented as a linear combination of simple, *i.e.* rational reactions, in short:

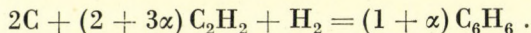
$$s = \sum_e \lambda_e s_e^{\text{rational}}.$$

Here the numbers λ_e must be, in general, irrational. Take such a linear combination, consider the numbers λ_e therein, and take their rational approximations that are *good enough*: λ'_e . Consider now the new reaction

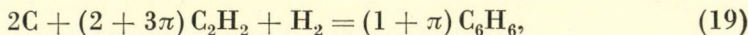
$$s' = \sum_e \lambda'_e s_e^{\text{rational}};$$

it is rational on the one hand, while on the other hand, λ'_e differing only a little from λ_e , it is just as good as s .

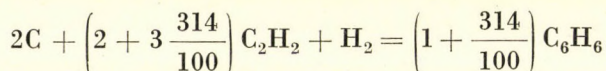
For example the reaction $[-2, -2, 1, 0, -1, 0]^* (2C + 2C_2H_2 + H_2 = C_6H_6)$ is not simple and rational. A better reaction than this is the reaction $[0, -3, 1, 0, 0, 0]^* (3C_2H_2 = C_6H_6)$. Let α be some irrational number, then the irrational reaction $s + \alpha s'$ will be as follows:



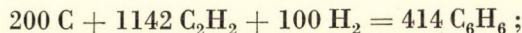
Let us now consider the irrational reaction



where $\pi = 3.1415 \dots$. Take a rational approximation of π , e.g. $314/100$, and the new reaction



or



this reaction is rational and just as good as (19).

Appendix

The system of homogeneous linear equations (4) has a solution in which the unknown x_{j_1} ($j_1 = 1, 2, \dots, n$) is uniquely (identically) zero if and only if the rank of the matrix of Eq. (4) is by one greater than that of the matrix in which the j_1 -th column is dropped [16]:

$$\text{rank} [a_{j_2}, \dots, a_{j_n}] = \text{rank} [a_1, \dots, a_n] - 1 = r - 1.$$

The author takes pleasure in thanking Professor G. SCHAY for reading the manuscript and for his valuable comments on the subject.

Legend

- a_{ij} number of the atomic substance A_i occurring in the chemical species S_j
- $\mathbf{a}_j$ column vector with the typical component a_{ij}
- i index running from 1 to m
- j index running from 1 to n
- m number of the different atomic substances occurring in the chemical species in question
- n number of the chemical species in question
- q number of the non-zero components in a reaction
- r rank of the matrix $\mathbf{A}$
- s_j stoichiometric coefficient of the chemical species S_j
- x_j unknown stoichiometric coefficient of the chemical species S_j
- $\mathbf{x}$ column vector with the typical component x_j
- $\mathbf{A}$ matrix with the typical element a_{ij}
- A_i the i -th atomic substance
- C a combination of the numbers $1, 2, \dots, n$ taken $q \leq n$ at a time
- S_j the j -th chemical species

SUMMARY

Starting from the linear algebraic character of the formal representation of chemical species and their reactions, we are concerned with so-called *simple* chemical reactions, which we have defined as follows: a given reaction will be called simple, if no other reactions may exist stoichiometrically among the chemical species occurring in this given reaction. (Reactions being multiples of each other are to be considered identical.) Several general properties of the simple reactions are proved by the methods of linear algebra and illustrated in an example. The search for simple chemical reactions can be applied wherever multicomponent reaction systems occur.

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MICROANALYSIS OF GERMANIUM IN SOLUTIONS CONTAINING HYDROGEN PEROXIDE AND HYDROGEN FLUORIDE

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For the determination of small quantities of germanium in general spectrophotometric methods have been recommended. The earlier methods are based practically without exception on the spectrophotometric measurement of germano-molybdic acid or of molybdenum blue prepared from the former by reduction with various reducing agents. Nowadays phenylfluorone is the most generally used reagent; the application of this compound to the quantitative determination of germanium was first described by CLULEY [1]. The reagent is insoluble in water and soluble in alcohol only in the presence of strong acids. It forms with germanium, in the molar proportion 1 : 2, a red, scarcely soluble complex which, however, can be kept in solution with the help of some protective colloid and is thus available for photometric determination. CLULEY's method was later modified by several researchers, *e.g.*, some of them suggested instead of the original reagent solution (containing 0.300 g of phenylfluorone and 50 ml of 1 : 6 dilute sulphuric acid in 1 l of ethyl alcohol) other phenylfluorone and acid concentrations, or methyl alcohol as solvent.

Prior to the measurement, the solution under investigation has to be adjusted to a well defined acid concentration, as both the reaction rate and extinction greatly depend on the concentration of the acid, while this latter depends on the preliminary operations necessary for the separation of germanium (distillation or extraction). LUKE and CAMPBELL [2] maintain that at pH 3.1 being the optimum for complex formation, though at this pH other metals are liable to form a precipitate with the reagent. SCHNEIDER and SANDELL [3] recommend the use of hydrochloric acid instead of sulphuric acid, since germanium is normally obtained in a hydrochloric medium from the preliminary operations. In the very considerable number of publications on this subject, there are also differences in the quantity and concentration of the reagent solution in the time while the solution should be allowed to stand in the protective colloid to be used and the quantities that can be determined. Because of these many contradictory data it was necessary to clarify the optimum conditions for photometric measurement.

Compared with the molybdate methods, the procedure using phenylfluorone has the considerable advantage that it is not affected by arsenic and silicon which are often present in materials containing germanium. At the same time the separation of germanium from the interfering ions (Ga, Ti, Sn(II), Sn(IV), Sb, Mo, W, *etc.*) presents no difficulty. Strong oxidizing agents interfere the determination, as they may oxidize the reagent and this fact is highly essential in the present case.

There are reports on attempts to increase the sensitivity of the reaction. KIMURA *et al.* [4] suggest the use of dimethylaminophenylfluorone on the grounds that due to the basic group in the molecule a true solution is obtained in acid media instead of a colloidal system, and germanium can be determined down to concentrations of $0.05 \mu\text{g/ml}$. There are, however, some contradictory reports made by other authors on the applicability of the new reagent. Finally CAMPE and HOSTE [5] settled the problem by very detailed experiments. They found that a solution containing at least 80% alcohol is necessary to achieve the above sensitivity, when the advantage mentioned is lost because of the dilution with alcohol. According to HILLEBRANDT and HOSTE [6] both the phenylfluorone reagent and the complex can be extracted with benzyl alcohol when again a true solution is obtained. We have subjected this method to experimental trial, and measured an about 1.5 times higher extinction coefficient. However, the poor separation of the phase makes extraction cumbersome and the results scatter, so that in our opinion this method is not better than the original.

To separate germanium from the interfering ions we have chosen the extraction method, as in the case of small quantities distillation may involve considerable losses. FISCHER and HARRE [7] were the first to investigate the conditions of extraction. They found that the distribution of germanium between the aqueous and the carbon tetrachloride phase greatly depends on the concentration of the acid. In water and dilute acid the equilibrium is shifted practically entirely in favour of the aqueous phase, while above 6.5 *N* HCl the situation is reversed and the equilibrium is shifted towards the organic phase; above 9 *N* HCl 98–99% of the germanium can be extracted. SCHNEIDER and SANDELL [3] worked out a detailed procedure of the extraction which proved to be very effective in our experiments. Under identical conditions only As(III) was extracted in about 75% together with the germanium, but this did not interfere the phenylfluorone reaction. The method is simpler and more rapid than the distillation, with the added considerable advantage of furnishing a neutral aqueous solution which allows the adjustment of the acid concentration to the optimum value required for spectrophotometric measurement.

To the best of our knowledge, there are no data in the literature on the elimination of the interfering effects of hydrogen fluoride and hydrogen per-

oxide. The purpose of the present work was to develop a microanalytical method for the determination of germanium in $\mu\text{g/ml}$ concentrations in solutions containing HF and H_2O_2 .

Experimental

Determination with phenylfluorone

Because of the contradictory literary data, the optimum conditions of the determination had to be established. As shown by later experiments, a 0.5 *N* acid concentration is the optimum for the formation of a germanium complex. A reagent containing hydrochloric acid as well was prepared whose addition ensured at the same time the final acid concentration. Preliminary experiments have shown that a solution consisting of 0.200 g/l of phenylfluorone and 160 ml/l of concentrated hydrochloric acid in alcohol is the most expedient; this reagent solution was then used throughout the experiments.

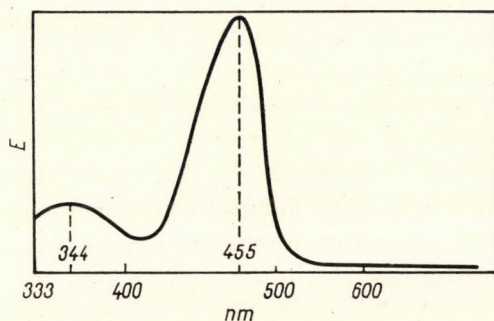


Fig. 1. Absorption spectrum of phenylfluorone

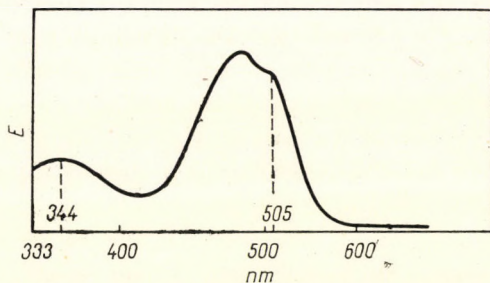


Fig. 2. Absorption spectrum of the germanium complex

First the optical properties of the reagent and of the complex had to be clarified. The spectra of the pure reagent and of the germanium complex were taken with a *Unicam SP-700* spectrophotometer. In the range $50\,000\text{--}30\,000\text{ cm}^{-1}$ no difference was found in the light absorptions of the reagent and the complex. Two flat maxima were observed at $41\,700$ and $38\,500\text{ cm}^{-1}$.

Fig. 1 shows the absorption diagram of the reagent in the range between $30\,000$ and $15\,000\text{ cm}^{-1}$. The curve has a flat maximum at $29\,100$ and a sharp peak at $22\,000\text{ cm}^{-1}$ (455 nm).

In Fig. 2 the absorption maximum of the complex appears in addition at $19\,800\text{ cm}^{-1}$ (505 nm).

Fig. 3 shows the absorption diagram of the complex as compared with that of the pure reagent. The peak at 505 nm appears quite sharply, but unfortunately at this wavelength the absorption of the reagent is not negligible, thus accurate addition must be carefully observed. (Three ml of the above reagent solution diluted to 10 ml shows against distilled water at this wavelength an extinction of $E = 0.306$.)

The next series of experiments was devised to clarify the necessary quantities of the reagent. Samples containing 5 and 10 μg germanium were weighed and mixed with 1 ml of a 0.5% gum arabic solution and various quantities of the reagent in a 10 ml volumetric flask which was then filled up to the mark with distilled water. Solutions prepared in the same way, but without germanium were used as blanks. The results are summed up in Table I.

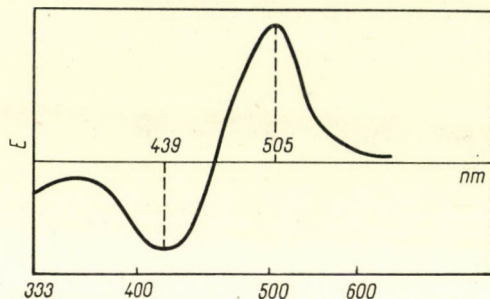


Fig. 3. Absorption diagram of the germanium complex compared to that of the reagent

Table I

Dependence of the extinction on the quantity of the reagent

Reagent ml	5 $\mu\text{g/ml}$ Ge E (505 nm)	10 $\mu\text{g/ml}$ Ge E (505 nm)
0.5	0.243	0.570
1.0	0.540	1.03
1.5	0.567	1.06
2.0	0.600	1.13
2.5	0.600	1.14
3.0	0.600	1.14

In Table I the data show that a considerable excess of the reagent is needed to attain equilibrium, as from the reagent solution of the above concentration about 0.5 ml are required for 10 μg of germanium, considering a molar ratio of 1 : 2.

Optimum hydrochloric acid concentration was checked by adding a further quantity of hydrochloric acid to the solution prepared with the same quantity of reagent and containing 5 $\mu\text{g}/10$ ml of germanium, while in other experiments part of the acid was neutralized. (Three ml of this reagent solution in 10 ml final volume corresponds to about 0.5 N HCl .)

In Table II the data indicate a strong dependence of the extinction on the concentration of the acid, thus the addition of enough acid to the reagent to establish the desired final acid concentration is expedient, since in this way the accurate addition of a single solution achieves the adjustment of the desired concentrations of both the reagent and the acid.

Table III shows the dependence of the extinction on the time of standing before measurement. These data indicate that it is necessary to wait for about 30 to 40 minutes for the full development of the colour. The value of the extinction remains then unchanged for several hours, but decreases about 10% overnight.

Table II

Dependence of the extinction on the concentration of the acid

HCl concentration in the final volume	E (505 nm)
0.1 N	0.528
0.3 N	0.545
0.5 N	0.590
1.0 N	0.562
1.5 N	0.520

Table III

Dependence of the extinction on the time of standing

Time min.	6 $\mu\text{g/ml}$ Ge E (505 nm)	10 $\mu\text{g/ml}$ Ge E (505 nm)
5	0.613	1.10
10	0.626	1.11
15	0.640	1.11
20	0.650	1.11
25	0.660	1.13
30	0.670	1.13
35	0.670	1.13
40	0.668	1.12
45	0.668	1.12
50	0.670	1.12
55	0.670	1.13
60	0.668	1.12
120	0.668	1.11
240	0.668	1.13
17 hrs.	0.610	1.05

Once these data were available, a calibration curve was plotted in the concentration range 0—1—2 $\mu\text{g/ml}$ of Ge by means of a *Spektromom Type 201* photometer (Fig. 4) (the details of this procedure are given below).

A linear correlation should be obtained provided the compound behaved in full agreement with the LAMBERT—BEER law, in spite of the fact that complex formation involves a concentration decrease of the reagent which also absorbs light. Namely, the total extinction at the given wavelength is:

$$(C_r - 2C_k)\varepsilon_r + C_k\varepsilon_k = E$$

where C_r and ε_r are the concentration and extinction coefficient of the reagent, and C_k and ε_k the concentration and extinction coefficient of the complex, respectively. (Two moles of the reagent are used for one mole of the complex.) The $C_r\varepsilon_r$ member is eliminated if the meas-

urements are performed not against water but a blank containing the same quantity of the reagent. Then:

$$C_k \varepsilon_k - 2C_k \varepsilon_r = E_{\text{measured}}$$

or

$$C_k(\varepsilon_k - 2\varepsilon_r) = E_{\text{measured}}$$

resulting in a straight line with a smaller slope. $\varepsilon_k - 2\varepsilon_r = \varepsilon_1$, the apparent molar decade extinction coefficient is $8.6 \cdot 10^4$ for the linear section of the curve, thus the compound fails to observe strictly the LAMBERT—BEER law. For analytical purposes the curve is nevertheless satisfactory. The mean error of the method was calculated from eight measurements, $E = \pm 0.005$, which corresponds to $\pm 0.005 \mu\text{g/ml}$ of germanium.

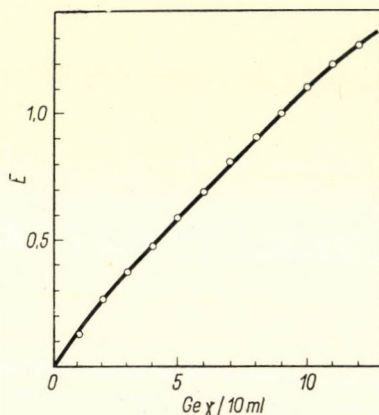


Fig. 4. Calibration curve for germanium obtained on a *Spectromom Type 201* photometer

Determination of germanium in the presence of hydrogen fluoride and hydrogen peroxide

Experiments were made to achieve the separation of germanium from the accompanying impurities, and to eliminate the disturbing effects of hydrogen fluoride and hydrogen peroxide.

As it has been mentioned, separation was carried out by extraction according to SCHNEIDER and SANDELL. Hydrogen fluoride and hydrogen peroxide had to be removed prior to extraction. The solutions used in these experiments contained 4 parts by weight of distilled water, one part by weight of 40% hydrogen fluoride and one part by weight of 30% hydrogen peroxide; the germanium concentration of the solution was $2 \mu\text{g/ml}$. Samples of this solution were measured into polythene flasks with an accuracy of 0.01 g.

Removal of the hydrogen fluoride by neutralization was out of question, since a hydrochloric acid solution was required for the extraction. Binding of the fluoride in complex form gave, however, the desired result. Experiments were carried out with ferric salts and boric acid. This latter compound was more satisfactory, as it could simply be added in the solid state, and the equilibrium conditions were more favourable. The fluoroborate complex no longer attacks the glass, not even in strongly acid solutions. About 0.5 g of boric acid was stoichiometrically required for the largest sample. In the experiments about 1 g of boric acid was used. Boric acid binds not only the free hydrogen fluoride, but also replaces germanium in the fluorogermanate complex and germanium then can be quantitatively extracted as chloride. First, however, hydrogen peroxide must also be removed, or it will later interfere the determination. The removal of hydrogen peroxide was carried out by "titration" with an about 2 N potassium permanganate solution in sulphuric acid medium; the excess of permanganate was reduced with a small amount of hydroxylaminesulphate. Chloride ion must not be present in the solution during these operations, since any evolving gas may carry away some of the volatile germanium chloride. Thus, the hydrochloric acid used for extraction should be added only after the removal of the fluoride and hydrogen peroxide. The results obtained with this method are summed up in Table IV.

Table IV

Values measured after the removal of H_2O_2 and HF and extraction

Weighed Ge μg	Found Ge μg	Difference %
3.02	2.84	-6.3
5.84	5.46	-6.5
7.24	6.84	-5.5
8.81	8.80	0*
8.75	8.44	-3.5*

* Re-extraction with 10 ml of H_2O .

Experience has shown that the negative error of the method can be reduced, if — contrary to literary data — 10 ml of water is used instead of 6 ml for re-extraction and an aliquot part of 5 ml is taken for the measurement.

Method

Reagents

Potassium permanganate solution: about 60 g of crystalline $KMnO_4$ was dissolved in 1 l of water.

Hydrochloric acid (for extraction): 4 parts by volume of conc. HCl were mixed with 1 part by volume of water.

Gum arabic solution: 1 g of solid gum arabic was dissolved in 200 ml of hot water and filtered.

Phenylfluorone reagent solution: exactly 0.200 g of phenylfluorone was dissolved in a mixture of 700 ml of 96% alcohol and 160 ml of conc. HCl. The mixture was made up to 1 l with alcohol, filtered and stored in a tightly closed polythene flask.

Phenylfluorone standard solution (instead of preparing a germanium-free standard for each test it is advisable to make up a larger quantity): 75.0 ml of the phenylfluorone reagent solution was measured into a 250 ml volumetric flask, 25 ml of gum arabic solution was added and the flask was filled up to the mark. The solution was stored in a tightly closed polythene flask.

Germanium stock solution: 0.1441 g of germanium dioxide was weighed into a 1 l volumetric flask and sufficient 0.1 N NaOH was added to dissolve the substance. The solution was slightly acidified with 0.1 N HCl and the flask filled up with distilled water to the mark. The concentration of the solution was then 0.100 mg of germanium per ml. The required dilutions were made from this stock solution immediately before use.

Calibration curve

A solution containing 2.0 $\mu\text{g}/\text{ml}$ of germanium was prepared from the stock solution and 0.50 to 6.00 ml quantities of the dilute solution were measured into a 10 ml volumetric flask. One ml of the gum arabic solution and 3.00 ml of phenylfluorone (from a burette with not greater than 0.05 ml divisions) were added to the samples. The flasks were filled up to the mark with distilled water, the solutions were shaken, and after about 40 minutes standing the extinctions were measured at 505 nm against the phenylfluorone standard solution.

Measurement

A fraction of the solution under investigation containing about 1–10 μg of germanium was measured into a 100-ml polythene beaker. The volume of the solution should not be more than 5 ml; 1 g of solid boric acid and 2 ml of dilute sulphuric acid (1 : 1) were added to the

sample. After the boric acid had dissolved, KMnO_4 solution was slowly added from a burette until the colour persisted. The addition should take place slowly, so that the evolution of the gas should cause no loss. A few crystals of solid hydroxylamine sulphate were added and the solution transferred into a separatory funnel. The volume of the solution was calculated and four times of this volume of conc. HCl was added (some of the acid was used to rinse the beaker). The solution in the funnel was then vigorously shaken for 2 minutes with 10 ml of carbon tetrachloride. After the separation of the organic phase, this was transferred into a second separatory funnel and the procedure repeated by adding 10 ml of carbon tetrachloride to the solution in the first funnel. The combined carbon tetrachloride solutions were shaken with 5 ml of 9 N HCl . After separation the carbon tetrachloride phase was washed in a third separatory funnel with 10 ml of water by shaking for 2 minutes. The organic phase was separated, the aqueous phase filtered through a dry filter into a dry beaker. 5 ml of this solution was measured into a 10 ml volumetric flask, 1 ml of gum arabic solution and 3.00 ml of phenylfluorone reagent solution were added, and after 40 minutes standing the solution was measured photometrically at 505 nm against the standard phenylfluorone solution.

SUMMARY

A method has been developed for the determination of germanium in 10^{-6} g/ml conc. in etching solutions containing hydrogen fluoride and hydrogen peroxide. Interference of hydrogen fluoride is eliminated by forming its boric acid complex. Hydrogen peroxide is removed by "titration" with potassium permanganate. From the resulting solution germanium is extracted with carbon tetrachloride in hydrochloric acid medium, and re-extracted from the organic phase with water. The determination is carried out by means of phenylfluorone reagent in hydrochloric acid measuring the extinction at 505 nm.

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USE OF THE MAXIMUM-LIKELIHOOD METHOD FOR THE EVALUATION OF MAXIMUM SENSITIVITY FOR ACTIVATION ANALYSIS IN THE PRESENCE OF INTERFERING ACTIVITIES

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Interfering reactions

It frequently happens during in-pile irradiation that identical nuclides are produced from different elements by fast and slow neutron activation. Reactions producing the same activity as that to be measured are called interfering reactions. Frequent reactions of this type are, *e.g.*, $^{27}\text{Al}(n, \gamma)^{28}\text{Al}$ and $^{29}\text{Si}(n, p)^{28}\text{Al}$; $^{59}\text{Co}(n, \gamma)^{60}\text{Co}$, $^{60}\text{Ni}(n, p)^{60}\text{Co}$ and $^{63}\text{Cu}(n, \alpha)^{60}\text{Co}$; for other mutually disturbing reactions see the tabulation by OKADA [1].

The problem is usually overcome by exposing the sample to neutron fluxes of different energy distributions, that is by irradiating them once with, then without cadmium filter. The energy dependence of the individual reaction cross-sections being appreciably different, both parent nuclei can be quantitatively determined from the activities produced in the same nucleus when irradiated with fluxes of different energy distributions.

In this case, however, the minimum detectable quantity cannot be determined by the usual practice of activation analysis, requiring simply that the measurable activity should exceed some given level. This is quite obvious if one considers that, *e.g.*, the ^{28}Al activity produced by the $^{27}\text{Al}(n, \gamma)^{28}\text{Al}$ reaction even with minute quantities of aluminium, though well measurable individually, cannot be identified in a sample with considerable silicon contamination because of the statistical error of the much higher ^{28}Al activity produced by ^{29}Si . Or, in the opposite case, since the cadmium ratio as a rule does not exceed two orders of magnitude, when using cadmium filter, the sensitivity to silicon will be considerably reduced by the presence of much aluminium.

It can be said in general that if the radioisotope C is produced from elements A and B, the minimum detectable quantity for either will depend, besides on background activity, also on their relative quantities present.

The maximum-likelihood method

Measurements of a statistical nature can be usually most precisely evaluated by the maximum-likelihood method, though in some cases an appropriately weighted least square fit may yield the same results. The maximum-likelihood method has been described thoroughly by JÁNOSSY [2]. Here we restrict ourselves to consider only the points of present interest.

In practice, quite often the quantities we want to know cannot be directly measured but have to be evaluated from measured data, say, $A_1, A_2, \dots, A_k$ (of course, the method is also applicable when the number of data is greater than that of the parameters). If the statistical distribution of the measured values as a function of the sought parameters, $x_1, x_2, \dots, x_k$, is known, the values of the latter will have minimum standard deviation if calculated by the maximum-likelihood technique. The probability of measuring the values $A_1, A_2, \dots, A_k$ has its maximum when the parameters are calculated by the maximum-likelihood method.

In order to estimate the parameters, we have to write down the distribution probability function $P(A_1, \dots, A_k; x_1, \dots, x_k)$ where the independent variables $x_1, \dots, x_k$ are those to be evaluated from the measurement. This function defines the probability according to which for the parameter values $x_1, \dots, x_k$, the measured values will be $A_1, \dots, A_k$. Obviously, the probability function is at a maximum if the parameters satisfy the condition:

$$\frac{\partial P(A_1, \dots, A_k, \dots, x_k)}{\partial x_i} = 0 \quad (i = 1, 2, \dots, k). \quad (1)$$

The solutions to this set of equations yield the measured values, $\bar{x}_1, \dots, \bar{x}_k$, of the parameters.

The standard deviation of the measured value $\bar{x}_1$ is given by the element M_{ii}^{-1} of the inverse of matrix M , constructed as

$$M_{ik} = \frac{\partial^2 P(A_1, \dots, A_k, x_1, \dots, x_k)}{\partial x_i \partial x_k} \Big|_{x_1 = \bar{x}_1, \dots, x_k = \bar{x}_k}.$$

Use of the method for interfering activities

We shall use the following symbols:

- a, b and a_c, b_c expected total number of counts/ μg of standard, obtained from elements A and B on irradiation without and with cadmium filter, respectively;
- n, n_c total number of counts obtained from sample on irradiation without and with cadmium filter;

y, y_c	total number of background counts during measuring time with and without cadmium;
Y, Y_c	expected total number of background counts, taken separately, for k times the measuring time, with and without cadmium; (The values of y, y_c, Y, Y_c may be substantially different, since the background is given by the activities from both the main component and any other than the contaminants of interest present in the sample; moreover, the different background measuring times need not be identical.)
x_A, x_B	measured values of A and B in sample (in μg);
$\sigma(A), \sigma(B)$	standard deviation (in μg) of the measured values x_A, x_B .

The counts are assumed to obey the Poissonian law of distribution and the statistical error of the standard counts a, a_c and b, b_c, Y, Y_c , as well as the total systematical error are neglected. Using the above symbols, the probability distribution function as given by the folding of the individual Poissonian distributions, takes the following form [3]:

$$P(A_1, \dots, A_k, x_1, \dots, x_k) = \frac{(x_A \cdot a_c + x_B \cdot b_c + y_c)^{n_c} (x_A \cdot a + x_B \cdot b + y)^n (ky_c)^{Y_c} (ky)^Y}{n_c! n! Y_c! Y!} \cdot \exp[-x_A(a + a_c) - x_B(b + b_c) - y_c(1 + k) - y(1 + k)].$$

Hence, we get under condition (1) the set of equations

$$x_A a_c + x_B b_c = n_c - \frac{Y_c}{k}; \quad x_A \cdot a + x_B \cdot b = n - \frac{Y}{k};$$

$$y_c = \frac{Y_c}{k}; \quad y = \frac{Y}{k} \quad (2)$$

which, of course, can also be obtained by simple physical considerations.

The maximum-likelihood method has the advantage to yield, in addition to the expected values of a measurement, also the standard deviation of the measured values. If one constructs the matrix M and considers the diagonal elements of its inverse, Eqs. (2) lead after some calculations to

$$\sigma_A = \frac{[b_c^2(n + Y/k^2) + b^2(n_c + Y_c/k^2)]^{1/2}}{|a_c b - a b_c|} \approx \frac{[b_c^2 n + b^2 n_c]^{1/2}}{|a_c b - a b_c|}$$

$$\sigma_B = \frac{[a_c^2(n + Y/k^2) + a^2(n_c + Y_c/k^2)]^{1/2}}{|a_c b - a b_c|} \approx \frac{[a_c^2 n + a^2 n_c]^{1/2}}{|a_c b - a b_c|} \quad (3)$$

The approximation holds if for adequate sensitivity the background has been measured for a sufficiently long time. In practice, the value of the minimum detectable quantity, $x_{A \min}$, can be reliably established if $x_{A \min} = \alpha \sigma_A$, choosing $\alpha = 6$ for single and $\alpha = 6/\sqrt{N}$ for N times repeated measurements. Introducing this condition into Eq. (3), the minimum detectable quantity of A as a function of that of B is given by the positive solution of the equation:

$$x_A^2(ab_c - a_c b)^2 - x_A \alpha^2(ab_c^2 - a_c b^2) - \alpha^2[x_B b b_c(b + b_c) + b_c^2 y + b^2 y_c] = 0 \quad (4)$$

with a wholly symmetric expression for the sensitivity to B .

The standard data used in the equations can be calculated if the conditions of irradiation and measurement are known, however, one should rather determine them experimentally by irradiating pure elements.

Determination of aluminium and silicon in tungsten

The method described above has been successfully employed for the non-destructive activation analysis of aluminium and silicon in tungsten [5]. Samples of 100 mg were irradiated in a reactor with 5×10^{12} n/cm²·sec thermal flux, first with, then without, cadmium filter. The samples were conveyed to and from irradiation by a pneumatic tube system [6]. A similar pneumatic system was used to take the samples to the measuring assembly, consisting of a 3" × 3" NaI(Tl) scintillation detector and a single-channel differential discriminator. The latter was set to the 1.78 MeV full energy peak of ²⁸Al. For optimum schedule and maximum accuracy [7] the samples were measured for 2×136 sec, that is twice the half-life of ²⁸Al, and after 20 minutes allowed for the decay of ²⁸Al, we evaluated the background activity due in the first place to tungsten. The scheduled two measuring intervals served also as a crude check of activity half-life. The counts from the standards were always normalized to the cooling time of the sample. The aluminium and silicon contents of the sample were evaluated from Equations (2), and the error of the measured values determined from Eq. (3). Since usually a great number of samples had to be analyzed, the calculations were performed on an ICT 1905 computer. Under the given experimental conditions, the values corrected for sample cooling and measuring time were found to be, on the average,

$$\begin{array}{lll} a_c = 200; & b_c = 50; & y_c = 200; \\ a = 1100; & b = 13; & y = 700. \end{array}$$

The curves showing the maximum sensitivity of the method for aluminium and silicon in tungsten, as evaluated from Eq. (4) with $\alpha = 3$ and assuming

high precision background measurement, have been plotted in Fig. 1. It is apparent that for activation with pile neutrons the sensitivity to aluminium decreases only in the presence of large amounts of silicon, while that to silicon is markedly affected even by small quantities of aluminium.

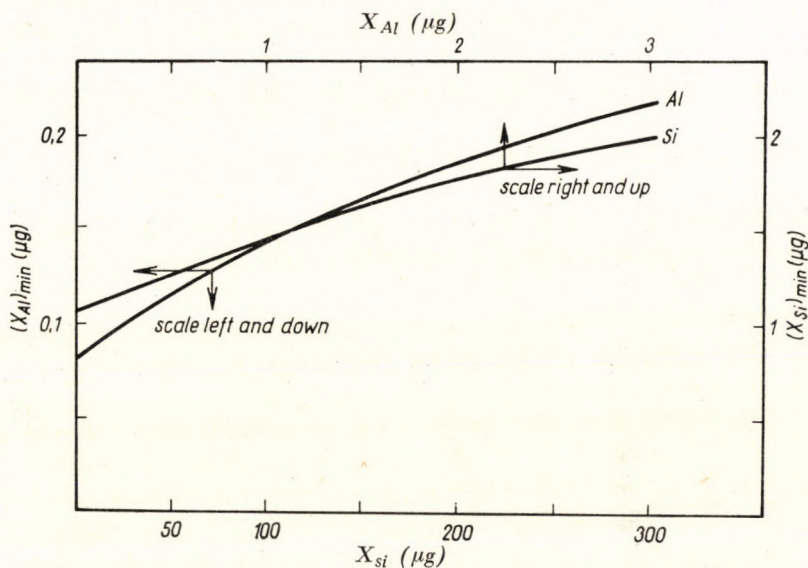


Fig. 1. Minimum detectable quantity of Al in 100-mg Tungsten samples as a function of silicon concentration in sample (lower and left scale), and minimum detectable quantity of silicon as a function of Al concentration (upper and right scale)

Thanks are due to Mr. A. SIMONITS physicist and Mr. A. ELEK chemist for their valuable help in the analysis of tungsten.

SUMMARY

A quite general expression has been obtained with the use of the maximum-likelihood method which permits to evaluate the maximum sensitivity for activation analysis in the presence of interfering activities produced by in-pile irradiation. The application of the formula is illustrated in the determination of aluminium and silicon in tungsten by non-destructive activation analysis.

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UNTERSUCHUNG DER ELEKTRONENANREGUNGS- VORGÄNGE UND DER BINDUNGSVERHÄLTNISSE DER KOMPLEXE VON $3d^n$ ELEMENTEN MIT DER LIGANDENFELD-METHODE, II

OKTAEDRISCHE CHROM(III)- UND KOBALT(III)-KOMPLEXE

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Unsere vorangehende Mitteilung [1] berichtete über die Berechnung der charakteristischen Parameter (Δ , B , C) von normal paramagnetischen $[(t_{2g})^6(e_g)^2]$ oktaedrischen oder pseudo-oktaedrischen Nickel(II)-Komplexen mit $[\text{Ar}]d^8$ -Elektronenkonfiguration. Die Parameter wurden auf Grund der spektralen und magnetischen Daten der Komplexe mit Hilfe der Ligandenfeld-(LF)-Methode berechnet. Unter Verwendung dieser Parameter wurden die Größen β , α^2 und $\delta\%$ erhalten, sowie Schlüsse auf die Natur der in den Molekülen zustandekommenden Bindungen gezogen, und es wurde versucht, Zusammenhänge zwischen der Struktur der Moleküle und den obigen Parametern bzw. Größen zu finden.

Die vorliegende Arbeit behandelt auf Grund der LF-Methode die Absorptionsspektren oktaedrischer Chrom(III)- und Kobalt(III)-Komplexe sowie ihre Struktur- und Bindungsverhältnisse.

Theoretischer Teil

Mit der theoretischen Deutung der Lichtabsorption oktaedrischer Cr^{3+} - und Co^{3+} -Komplexe und solcher von niedrigerer Symmetrie, unter Verwendung der Molekülorbital- und Kristallfeld-Methode haben sich bereits zahlreiche Forscher beschäftigt [2–7]. Unter den Cr^{3+} - und Co^{3+} -Komplexen von äußerst wechselvoller Zusammensetzung und Struktur werden in der vorliegenden Arbeit nur die mit guter Annäherung als oktaedrisch koordiniert (O_h -Symmetrie) zu betrachtenden $\text{Me(III)}X_6$ - und $\text{Me(III)}L_3$ -Moleküle behandelt, wobei die sich aus der eventuellen Verschiedenheit der L-Donoratome ergebende Symmetrieabnahme nicht beachtet wird. Sämtliche Cr^{3+} -Komplexe sind, dem nur-Spin-Wert (3,83 BM) entsprechend, unabhängig von der Natur und Struktur der Liganden, paramagnetisch, während die Co^{3+} -Verbindungen ausnahmslos diamagnetisch sind.

A) Das Cr^{3+} - (d^3) Problem. Die Spektren der Cr^{3+} -Komplexe, ähnlich wie das System d^8 , weisen drei LAPORTE-verbotene Banden mittlerer Intensität auf, die den spinerlaubten Übergängen

$$\nu_1^* = {}^4T_{2g} \leftarrow {}^4A_{2g} \quad (1a)$$

$$\nu_2^* = {}^4T_{1g}^1 \leftarrow {}^4A_{2g} \quad (1b)$$

$$\nu_3^* = {}^4T_{1g}^2 \leftarrow {}^4A_{2g} \quad (1c)$$

zugeordnet sind (Abb. 1). Die Wahrscheinlichkeit des dritten Überganges ist sehr klein, da dieser mit der gleichzeitigen Anregung zweier Elektronen ver-

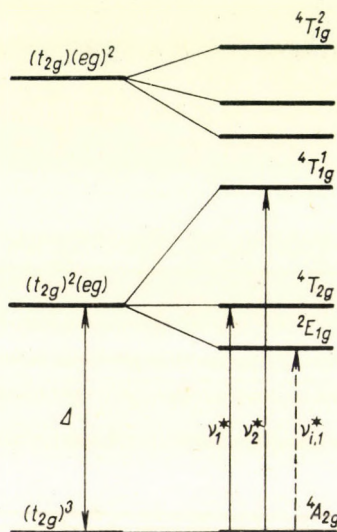


Abb. 1. Energieniveau-Diagramm der Cr^{3+} -Komplexe von oktaedrischer Symmetrie mit den wichtigsten Übergängen

bunden ist und damit kann erklärt werden, daß diese Bande in den Spektren im allgemeinen nicht erscheint. ν_3^* erscheint gut auswertbar z. B. im Lösungsspektrum von $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ und im Kristallspektrum von $\text{K}_2\text{Na}[\text{CrF}_6]$ [8]. An der langwelligen Seite von ν_1^* kann die dem spinverbotenen Übergang

$$\nu_{i,1}^* = {}^2E_g^1 \leftarrow {}^4A_{2g} \quad (1d)$$

zugeordnete Bande bzw. Inflexion beobachtet werden.

Aus den elektrostatischen Matrizen [9] der Quadruplett-Zustände werden nach Elimination von A und unter Berücksichtigung, daß

$$\begin{aligned} (t_{2g})^3 &= -1,2 \Delta, \\ (t_{2g})^2 (e_g) &= -0,2 \Delta \quad \text{und} \\ (t_{2g}) (e_g)^2 &= +0,8 \Delta \quad \text{ist,} \end{aligned}$$

die vier Quadruplett-Zustände, und auf Grund dieser die Energien der Übergänge ν_1^* , ν_2^* und ν_3^* erhalten. Sowohl die den einzelnen Termen wie die den Übergängen entsprechenden Energiewerte stimmen mit den für das System d^8 erhaltenen Werten überein (siehe Formeln 1a bis 1d in Mitteilung I). Wenn nur die diagonalen Elemente berücksichtigt werden, so ergeben sich für die erwähnten Übergänge die folgenden Zusammenhänge:

$$\nu_1^* = A, \quad (2a)$$

$$\nu_2^* = A + 12B, \quad (2b)$$

$$\nu_3^* = 2A + 3B \quad \text{und} \quad (2c)$$

$$\nu_{i,1}^* = 9B + 3C. \quad (2d)$$

Sofern alle drei symmetrieverbotene Banden im Spektrum gut auswertbar erscheinen, kann auch hier der Elektronenwechselwirkungsparameter B aus dem Zusammenhang

$$B = \frac{\nu_2^* + \nu_3^* - 3A}{15} \quad (3)$$

berechnet werden. Da jedoch in der überwiegenden Mehrzahl der bekannten Beispiele nur die Lage von ν_1^* und ν_2^* bekannt ist, kann B im allgemeinen auf Grund der Formel

$$B_1 = \frac{3\nu_2^* \cdot A - (\nu_2^*)^2 - 2A^2}{27A - 15\nu_2^*} \quad (4)$$

berechnet werden, während sich auf Grund der Gleichungen (2a) bis (2d) die Zusammenhänge

$$B_2 = \frac{\nu_2^* - \nu_1^*}{12} \quad (5)$$

und

$$C = \frac{\nu_{i,1}^* - 9B}{3} = \frac{3(\nu_1^* - \nu_2^*) + 4\nu_{i,1}^*}{12} \quad (6)$$

ergeben.

B) *Das Co^{3+} - (d^6) Problem.* Der Elektronenkonfiguration $(t_{2g})^6$ entsprechend ($S = 0$) ist der Grundterm ein Singulett: $^1A_{1g}$. Das Absorptionsspektrum einer jeden oktaedrischen oder mit guter Annäherung als oktaedrisch zu betrachtenden Co^{3+} -Verbindung kann durch zwei voneinander scharf getrennte Banden symmetrischer Form* und mittlerer Intensität charakterisiert werden.

* Nach unseren Berechnungen konnte für ν_1^* eindeutig und für ν_2^* mit guter Annäherung bestätigt werden, daß $\delta_+ \cong \delta_-$ (wobei δ_+ und δ_- die gegen höhere bzw. niedrigere Frequenzen berechneten Halbwertsbreiten der Banden sind).

Diese beiden Banden werden den spinerlaubten, LAPORTE-verbotenen Übergängen

$$\nu_1^* = (t_{2g})^5 (e_g) {}^1T_{1g} \leftarrow (t_{2g})^6 {}^1A_{1g} \quad (7a)$$

$$\nu_2^* = (t_{2g})^5 (e_g) {}^1T_{2g} \leftarrow (t_{2g})^6 {}^1A_{1g} \quad (7b)$$

zugeordnet [9, 10] (Abb. 2). Im Gebiet der größeren Wellenlängen kann auch hier am absteigenden Ast von ν_1^* eine Bande von geringer Intensität bzw.

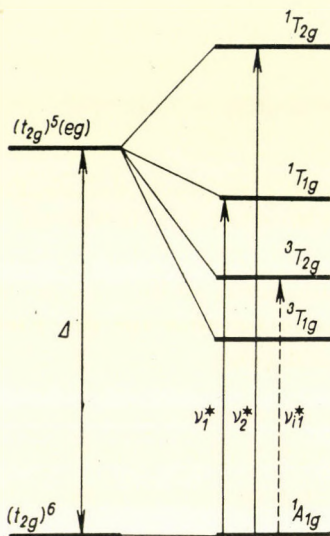


Abb. 2. Energieniveau-Diagramm oktaedrischer Kobalt(III)-Komplexe mit den entsprechenden Übergängen

eine Inflexion beobachtet werden, die einem spinverbotenen Übergang zuzuordnen ist:

$$\nu_{i,1}^* = (t_{2g})^5 (e_g) {}^3T_{2g} \leftarrow (t_{2g})^6 {}^1A_{1g}. \quad (7c)$$

Unter Verwendung der diagonalen Elemente der Matrizen, die der TANABE—SUGANOSCHEN Näherung entsprechen [11], erhält man für die Energien der einzelnen Niveaus die folgenden Werte:

$$E({}^1A_{1g}) = -2,4 \Delta,$$

$$E({}^1T_{1g}) = -1,4 \Delta - C,$$

$$E({}^1T_{2g}) = -1,4 \Delta + 16 B - C,$$

$$E({}^3T_{1g}) = -1,4 \Delta - 3 C \quad \text{und}$$

$$E({}^3T_{2g}) = -1,4 \Delta + 8 B - 3 C,$$

aus denen sich für die entsprechenden Übergänge

$$(t_{2g})^5 (e_g) {}^1T_{1g} \leftarrow (t_{2g})^6 {}^1A_{1g}$$

$$\nu_1^* = E({}^1T_{1g}) - E({}^1A_{1g}) = \Delta - C, \quad (8a)$$

$$(t_{2g})^5 (e_g) {}^1T_{2g} \leftarrow (t_{2g})^6 {}^1A_{1g}$$

$$\nu_2^* = E({}^1T_{2g}) - E({}^1A_{1g}) = \Delta + 16 B - C, \quad (8b)$$

$$(t_{2g})^5 (e_g) {}^3T_{1g} \leftarrow (t_{2g})^6 {}^1A_{1g}$$

$$\nu_{i,1}^* = E({}^3T_{1g}) - E({}^1A_{1g}) = \Delta - 3 C \quad \text{und} \quad (8c)$$

$$(t_{2g})^5 (e_g) {}^3T_{2g} \leftarrow (t_{2g})^6 {}^1A_{1g}$$

$$\nu_{i,2}^* = E({}^3T_{2g}) - E({}^1A_{1g}) = \Delta + 8 B - 3 C \quad (8d)$$

ergibt. Aus den Ausdrücken ist ersichtlich, daß die Kenntnis des experimentell bestimmten Wertes einer spinverbotenen Bande zur eindeutigen Bestimmung der Parameter unbedingt erforderlich ist. Im allgemeinen ist zu diesem Zweck die durch Gl. (8c) charakterisierte Größe, $\nu_{i,1}^*$, geeignet. In Kenntnis dieses Wertes erhält man daher für LF und für die Elektronenwechselwirkungsparameter die folgenden Ausdrücke:

$$\Delta = \nu_1^* + C, \quad (9)$$

$$B = \frac{\nu_2^* - \Delta + C}{16} = \frac{\nu_2^* - \nu_1^*}{16}, \quad (10)$$

$$C = \frac{\nu_1^* - \nu_{i,1}^*}{2}. \quad (11)$$

Diskussion der Daten

In den Tabellen I und II sind die Daten der Komplexe von Typ Me(III)X_6 und Me(III)L_3 einiger einzähniger und zweizähniger Liganden zusammengefaßt. Die angeführten Daten beziehen sich auf den gelösten Zustand; im festen Zustand sind die Spektren fast gleich, die Verschiebung von 20 bis 30 ist den Kristallgitter-Kräften zuzuschreiben.

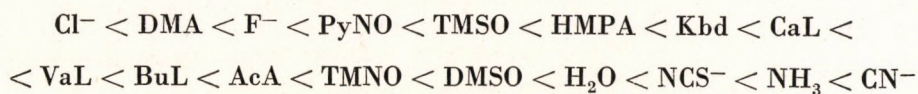
A) Cr^{3+} -Komplexe. Es folgt einerseits aus der Struktur der Liganden und wird andererseits durch Daten der Infrarotspektroskopie bestätigt, daß in den Verbindungen 2 und 4 bis 9 Cr—O Bindungen vorliegen. Aus Tabelle I ist z. B. ersichtlich, daß TMNO ein besserer Komplexbildner als DMSO, PyNO oder HMPA ist. Dies ist leicht verständlich, wenn man bedenkt, daß bei den letzteren infolge der π -Bindung die Elektronendichte am O-Atom, und demzufolge auch die Donor-Eigenschaft des Sauerstoffes verringert wird.

In PyNO ist der Sauerstoff zu einem elektronegativeren N von sp^2 -Konfiguration gebunden, in TMNO hingegen zu einem sp^3 -hybridisierten N, so daß das letztere ein stärkeres Donorvermögen besitzt. Interessant ist es, daß Liganden die S-Donoratome enthalten, ein schwächeres Ligandenfeld besitzen als die O-haltigen, was aus Vergleich der Daten der Oxalat- und Thiooxalat-Komplexe klar hervorgeht. Für ein- und zweizählige Liganden ist die Δ -Serie:

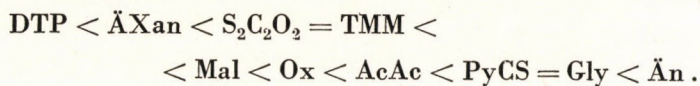
Tabelle I

No.	Komplex*	$\nu_{1,1}^*$	Δ	ν^*	$\nu_{(3),1}^*$	$\nu_{(3),2}^*$
1	$[\text{CrCl}_6]^{3-}$	—	12 500	18 500	28 750	26 500
2	$[\text{Cr}(\text{DTP})_3]$	13 150	14 400	18 900	30 645	29 925
3	$[\text{Cr}(\text{DMA})_6]^{3+}$	—	14 880	21 550	33 545	31 425
4	$[\text{CrF}_6]^{3-}$	15 700	14 900	22 700	35 440	31 750
5	$[\text{Cr}(\text{PyNO})_6]^{3+}$	—	15 385	22 548	35 052	32 561
6	$[\text{Cr}(\text{DMSO})_6]^{3+}$	—	16 773	22 523	35 176	33 232
7	$[\text{Cr}(\text{TMSO})_6]^{3+}$	—	15 748	22 523	35 161	33 188
8	$[\text{Cr}(\text{HMPA})_6]^{3+}$	14 500	15 900	22 300	35 015	33 399
9	$[\text{Cr}(\text{ÄXan})_3]$	—	16 000	20 300	33 610	33 074
10	$[\text{Cr}(\text{Kbd})_6]^{3+}$	14 450	16 100	22 600	35 480	33 823
11	$[\text{Cr}(\text{CaL})_6]^{3+}$	14 250	16 180	22 620	35 565	33 971
12	$[\text{Cr}(\text{VaL})_6]^{3+}$	14 290	16 210	22 620	34 710	34 022
13	$[\text{Cr}(\text{BuL})_6]^{3+}$	14 430	16 230	22 940	35 935	34 137
14	$[\text{Cr}(\text{AcA})_6]^{3+}$	—	16 450	22 940	36 100	34 523
15	$[\text{Cr}(\text{TMNO})_6]^{3+}$	—	16 520	24 700	38 405	35 083
16	$[\text{Cr}(\text{TMM})_3]^{3+}$	—	16 900	23 100	36 660	35 351
17	$[\text{Cr}(\text{S}_2\text{C}_2\text{O}_2)_3]^{3-}$	—	17 000	21 900	35 910	35 224
18	$[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$	15 000	17 360	24 550	37 800	36 517
19	$[\text{Cr}(\text{Mal})_3]^{3-}$	14 450	17 500	23 900	37 945	36 599
20	$[\text{Cr}(\text{Ox})_3]^{3-}$	14 200	17 700	24 100	38 315	36 999
21	$[\text{Cr}(\text{AcAc})_3]$	13 000	17 900	26 300	40 870	37 900
22	$[\text{Cr}(\text{PyCS})_3]$	13 800	18 400	25 000	39 785	38 450
23	$[\text{Cr}(\text{NCS})_6]^{3-}$	—	17 700	23 800	37 940	36 924
24	$[\text{Cr}(\text{Gly})_3]$	14 000	18 400	25 100	39 865	38 474
25	$[\text{Cr}(\text{NH}_3)_6]^{3+}$	15 300	21 500	28 490	45 940	44 746
26	$[\text{Cr}(\text{Än})_3]^{3+}$	15 000	21 800	28 500	46 320	45 274
27	$[\text{Cr}(\text{CN})_6]^{3-}$	—	26 600	32 200	55 100	54 601

* DTP = Diäthylthiophosphat; DMA = N,N-Dimethylacetamid; PyNO = Pyridin-N-oxyd; TMSO = Tetramethylsulfoxyd; DMSO = Dimethylsulfoxyd; HMPA = Hexamethylphosphoramid; ÄXan = Äthylxanthat; Kbd = Karbamid; CaL = ϵ -Caprolactam; VaL = δ -Valerolactam; BuL = γ -Butyrolactam; AcA = Acetamid; TMNO = Trimethyl-N-oxyd; TMM = N,N,N',N'-Tetramethylmalonamid; Mal = Malonat; Ox = Oxalat; AcAc = Acetylaceton; PyCS = Pyridincarbonsäure; Gly = Aminoessigsäure; Än = Äthylendiamin.



bzw.



B_1	β_1	B_2	β_2	C^{**}	$\delta E(^1P - ^1F)$	$\delta\%$
650	0,68	500	0,53	—	9 750	31,3
423	0,44	375	0,39	3258	6 345	55,3
697	0,74	555	0,59	—	10 455	26,4
896	0,95	650	0,69	3283	13 440	5,4
763	0,81	597	0,63	—	11 445	19,4
692	0,73	562	0,59	—	10 380	26,9
696	0,73	564	0,59	—	10 440	26,5
641	0,68	533	0,56	3234	9 615	32,3
394	0,42	358	0,38	—	5 910	58,4
652	0,69	541	0,57	3193	9 780	31,1
643	0,68	537	0,57	3140	9 645	32,1
580	0,61	534	0,56	3161	8 700	38,7
679	0,71	559	0,59	3133	10 185	28,3
646	0,68	541	0,57	—	9 690	31,8
903	0,95	648	0,68	—	13 545	4,6
604	0,64	517	0,54	—	9 060	36,2
454	0,48	408	0,43	—	6 810	52,1
728	0,77	599	0,63	3227	10 920	23,1
623	0,66	533	0,56	3217	9 345	34,2
621	0,66	533	0,56	3134	9 315	34,4
898	0,95	700	0,74	2233	13 470	5,1
639	0,67	550	0,59	2950	9 585	32,5
576	0,61	508	0,54	—	8 640	39,2
651	0,69	558	0,59	2992	9 765	31,2
662	0,70	582	0,61	3354	9 930	30,1
628	0,66	558	0,59	3326	9 420	33,7
500	0,53	467	0,49	—	7 500	47,2

** $C_0 = 3850 \text{ cm}^{-1}$.

Die Werte der Elektronenwechselwirkungsparameter B und C sind für Komplexe im allgemeinen kleiner als die für freie Gasionen berechneten. Diese Verringerung der elektrostatischen Wechselwirkung kann der durch die Gegenwart des Liganden-Atoms hervorgerufenen Orbital-Expansion und der demzufolge zustandekommenden Erhöhung des Kovalenzgrades zugeschrieben werden. Im Falle von Cr^{3+} sind die höheren (e_g)-Niveaus unbesetzt, während z. B. bei Co^{2+} sich bereits im Grundzustand Elektronen an diesen Orbitalen befinden. So stehen die Cr^{3+} -Orbitale den eintretenden Elektronen viel leichter

Tabelle II

No	Komplex ^a	$\nu_{i,1}^*$	ν_i^*	ν_2^*	Δ	B^b	β	C	$\delta\%$
1	$[\text{Co}(\text{AcAc})_3]$	12 200	16 700	23 700	18 950	438	0,41	2250	58,9
2	$[\text{Co}(\text{Aes})_3]$	—	17 550	23 050	—	344	0,32	—	67,7
3	$[\text{Co}(\ddot{\text{A}}\text{Xan})_3]$	8 860	16 200	20 800	19 870	288	0,27	3670	73,0
4	$[\text{Co}(\text{Cys})_3]$	10 650	17 200	22 600	20 475	338	0,32	3275	68,3
5	$[\text{Co}(\text{CO}_3)_3]^{3-}$	8 000	16 300	22 800	20 500	406	0,38	4200	61,9
6	$[\text{Co}(\text{Ox})_3]^{3-}$	8 350	16 500	23 800	20 575	465	0,43	4075	56,3
7	$[\text{Co}(\text{H}_2\text{O})_6]^{3+}$	8 500	16 600	24 900	20 650	519	0,49	4050	51,3
8	$[\text{Co}(\text{Gly})_3]$	11 200	19 230	26 730	23 245	469	0,44	4015	56,0
9	$[\text{Co}(\text{Al})_3]$	11 100	19 300	26 770	23 400	467	0,44	4100	56,2
10	$[\text{Co}(\text{Tn})_3]^{3+}$	12 670	20 570	28 670	24 520	506	0,47	3950	52,5
11	$[\text{Co}(\text{NO}_2)_6]^{3-}$	13 250	20 900	28 800	24 725	494	0,46	3825	53,6
12	$[\text{Co}(\text{NH}_3)_6]^{3+}$	13 200	21 050	29 500	24 975	528	0,49	3925	50,4
13	$[\text{Co}(\text{D}\ddot{\text{A}}\text{n})_2]^{3+}$	13 650	21 400	29 500	25 275	506	0,47	3875	52,5
14	$[\text{Co}(\ddot{\text{A}}\text{n})_3]^{3+}$	13 700	21 450	29 500	25 325	503	0,47	3875	52,8
15	$[\text{Co}(\text{NH}_2\text{OH})_6]^{3+}$	13 350	22 800	30 000	27 525	450	0,42	4725	57,7
16	$[\text{Co}(\text{CN})_6]^{3-}$	25 000	32 400	39 000	36 100	413	0,39	3700	61,2

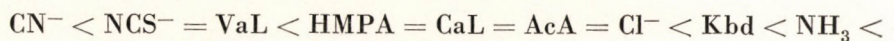
^a Aes = Mercaptoäthylamin; Cys = Cystein; Al = β -Alanin; Tn = Trimethylendiamin; D $\ddot{\text{A}}\text{n}$ = Diäthylentriamin.

^b $B_0 = 1065 \text{ cm}^{-1}$.

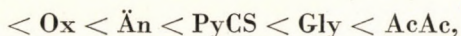
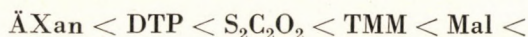
zu Verfügung. Außerdem ändert sich auch die an den (e_g)-Orbitalen zustandekommende Elektron—Elektron-Wechselwirkung viel empfindlicher mit der Natur der Liganden als im Falle von Co^{2+} , wo das Prinzip der partialen Besetzung zu einem gewissen Grad bereits das Zustandekommen der Wechselwirkung begrenzt. So wird der Parameter B bei Cr^{3+} -Komplexen gegenüber der Natur der Liganden wesentlich empfindlicher sein [10]; der Wert von C ändert sich hingegen kaum, da ja auch das Niveau 2E_g aus dem Zustand (t_{2g})³ stammt, und solange die Elektronen in derselben Konfiguration bleiben, wird auch die elektrostatische Wechselwirkung mehr oder weniger konstant sein.

Die Absolutwerte der mit den Formeln 4 und 5 berechneten Parameter B_1 und B_2 sind verschieden, doch ist die Richtung ihrer Änderung die gleiche. Die auf Grund Liganden aufgeschriebenen nephelauxetischen Reihen sind

sowohl für $\text{Cr(III)}X_6$ - als auch für $\text{Cr(III)}L_3$ -Verbindungen von den vorangehend angegebenen spektrochemischen Reihen verschieden:



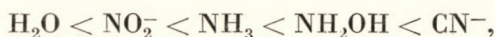
und



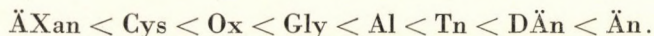
doch entsprechen sie im allgemeinen den in der Literatur (siehe z. B. [10] angegebenen Reihen. Bei Liganden die über O-Donoratome verfügen, ändert sich β in der Reihenfolge $\text{DMSO} \sim \text{TMSO} < \text{H}_2\text{O} < \text{PyNO}$, was durch die stärkere Polarisierbarkeit der S—O Bindung bedingt ist.

Der Wert von C ändert sich in einem sehr engen ($2950-3354 \text{ cm}^{-1}$) Intervall, und demzufolge können die berechneten γ -Werte ($\gamma = C/C_0$) kaum zur Charakterisierung des Bindungstyps herangezogen werden. Hierfür sind die auf Grund der Änderung der Energiedifferenz ${}^4\text{P}-{}^4\text{F}$ berechneten $\delta\%$ Werte viel eher geeignet.

B) Co^{3+} -Komplexe. Die niedrigsten Δ - und gleichzeitig die kleinsten β -Werte ergeben sich für die S-haltigen Verbindungen, ihnen folgen die Komplexe der O, N und C als Bindungsatome enthaltenden Liganden. Δ_{Ox} ist nahezu $\Delta_{\text{H}_2\text{O}}$ gleich, und ähnlich $\Delta_{\ddot{\text{A}}\text{n}} \sim \Delta_{\text{D}\ddot{\text{A}}\text{n}}$. »Tn« bildet einen weniger stabilen Komplex (Sechsering) als »Än« (Fünfering), und dementsprechend besitzt es auch einen niedrigeren Δ -Wert. Entsprechend den Bindungsatomen N und O, kommen »Gly« und »Al« zwischen H_2O und Äthylendiamin zu liegen. Beim Typ $\text{Co(III)}X_6$ gibt Δ die Reihe



während für Bidentate die folgende Reihe gilt:

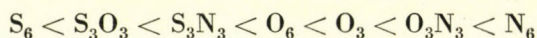


Interessant ist zu bemerken, daß sich bei dieser Verbindungsgruppe Δ innerhalb ziemlich weiten Grenzen ($\sim 19\,000$ bis $\sim 36\,000 \text{ cm}^{-1}$) ändert, so daß die spektrochemische Reihe nach LF leicht festgestellt werden kann. Hingegen weichen die Werte des Wechselwirkungsparameters B bzw. des nephelauxetischen Quotienten β in vielen Fällen kaum voneinander ab. So ist z. B. $\beta_{\text{Gly}} = \beta_{\text{Al}}$, $\beta_{\text{Tn}} = \beta_{\ddot{\text{A}}\text{n}}$, so daß Δ zur Bestimmung des Bindungscharakters bzw. zur Verfügung der Änderung der Bindungsart viel geeigneter erscheint als β , obwohl sich im Falle der $\text{Co(III)}L_3$ Verbindungen auch β auf ähnliche Weise wie Δ ändert.

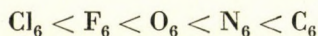
Abgesehen von Δ in Tabelle I, ändert sich der Wert von C kaum oder zumindest nicht in solchem Maße, daß der Quotient γ ($C_0 = 5120 \text{ cm}^{-1}$) Schlüsse zulassen würde. Die Änderung von $\delta\%$ ist gering, dennoch kann aus diesem viel besser auf die Bindungsverhältnisse gefolgert werden, als aus γ .

Allgemeine Bemerkungen

Es kann festgestellt werden, daß die niedrigsten Δ - und gleichzeitig die kleinsten β -Werte von Verbindungen der Liganden mit S bzw. N Donoratomen geliefert werden. So wurde für die diskutierten Cr^{3+} - und Co^{3+} -Komplexe im Falle von zweizähligen Liganden die Δ -Reihe

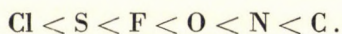


bzw. von einzähligen Komplexen



gefunden.

Diese Reihen entsprechen der Reihe der Liganden-Atome nach abnehmendem Ionenradius [10]:



Bei den Komplexen zweizähliger Liganden mit S_3O_3 , S_3N_3 und O_3N_3 Donoratomen kommt der Wert von Δ , dem »average environment rule« entsprechend, zwischen den Δ -Werten der Komplexe $\text{S}_6\text{—O}_6$, $\text{S}_6\text{—N}_6$ und $\text{O}_6\text{—N}_6$ zu liegen.

Zur Charakterisierung der Glieder dieser beiden Verbindungsgruppen scheinen vor allem die Δ -Werte geeignet zu sein. Bei Cr^{3+} -Komplexen können in bezug auf Bindungsart aus der Änderung von β und $\delta\%$ wertvolle Schlüsse gezogen werden, während sich hierzu bei Co^{3+} -Verbindungen eher die Änderung von $\delta\%$ eignet. Die Änderung von C bzw. γ ist bei weitem nicht von solchem Ausmaß oder so eindeutig, als die der übrigen Parameter bzw. Größen. Die auf Grund von β erhaltenen nephelauxetischen Reihen weichen von den Δ -Reihen ab, doch zeigen sowohl die β , als auch die $\delta\%$ -Werte, daß Bindungen von stärkstem kovalentem Charakter im Falle von S-Verbindungen gebildet werden.

ZUSAMMENFASSUNG

Es wurden für Komplexe vom Typ Me(III)X_6 und Me(III)L_3 ($\text{Me} = \text{Cr}^{3+}, \text{Co}^{3+}$) auf Grund der Ligandenfeld-Theorie charakteristische Parameter (Δ , B , C), sowie mit dem kovalenten Charakter der Bindungen proportionale Größen (β und $\delta\%$) berechnet. Die spektrochemische Reihe der Donoratome ($\text{Cl} < \text{S} < \text{F} < \text{O} < \text{N} < \text{C}$) verläuft mit der Änderung des

Ionenradius parallel. Bei Co^{3+} -Verbindungen ändert sich β kaum, so daß eher $\delta\%$ und besonders Δ zur Charakterisierung der im Molekül zustandekommenden Bindungen geeignet zu sein scheint. Bindungen von stärkstem kovalentem Charakter und mit kleinstem Δ werden in beiden Verbindungsgruppen von den Thio-Verbindungen geliefert.

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INFRARED AND RAMAN SPECTRA OF THE PYRAZINE-DI-N-OXIDE MOLECULE

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In the present work the infrared and Raman spectra of pyrazine-di-N-oxide have been studied, and vibrational assignments as well as the interpretation of some combination bands are given.

Our aim was to clarify bonding relations of the pyrazine-di-N-oxide molecule. A number of possible mesomeric structures may be written for this compound. The most probable ones are shown in Fig. 1. As it is seen from the given representations, the bond order may be one or two for the N—O bond.

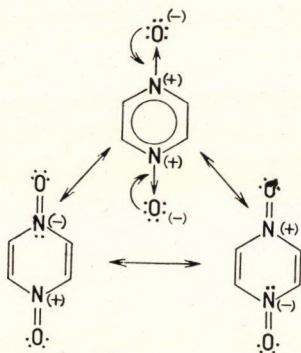


Fig. 1*

In order to solve the bond order problem, it was thought useful to make comparisons between pyrazine-di-N-oxide and *p*-difluorobenzene which are isoelectronic systems. For this purpose pyrazine-di-N-oxide was prepared and the infrared and Raman spectra were measured. The two molecules have been compared on the basis of our assignments of the pyrazine-di-N-oxide frequencies and on the assignments of STOJILKOVIČ and WHIFFEN [1] reported for the frequencies of *p*-difluorobenzene.

The geometrical means of the effective nuclear charges and electronegativities, furthermore the reduced atomic masses are nearly the same for both

* **Errata.** The possible mesomeric structures of pyrazine-di-N-oxide molecule have errors in representation on page 350 of *Acta Chimica* 53 (4). The correct figure of mesomeric structures can be found on the Fig. 1 of this paper.

molecules. The N—O distance was taken to be 1.26 Å [2], that of C—F 1.30 Å [3].

Using the SCHOMAKER—STEVENSON table [4] for the calculation of interatomic distances, the values 1.48 and 1.492 Å are obtained for N—O and C—F, respectively, assuming single bonds. The bond lengths found experimentally are shorter by 0.22 and 0.19 Å, indicating that the bond order must be considerably higher than one. The same authors [4] state that a bond of the order two should correspond to the interatomic distances of about 1.24 and 1.27 Å for CF and NO, respectively. These data are indeed close to the experimentally observed values, therefore, considering also the PAULING principle [5], the bonds in NO and CF must be nearly of order two.

The agreement in terms of masses and electronic structure is emphasized by the extraordinary similarity of the vibrational spectra. Fig. 2 shows the infrared spectrum of crystalline pyrazine-di-oxide recorded with a UR-10 spectrometer in KBr pellet, while Fig. 3 is the spectrum obtained with a

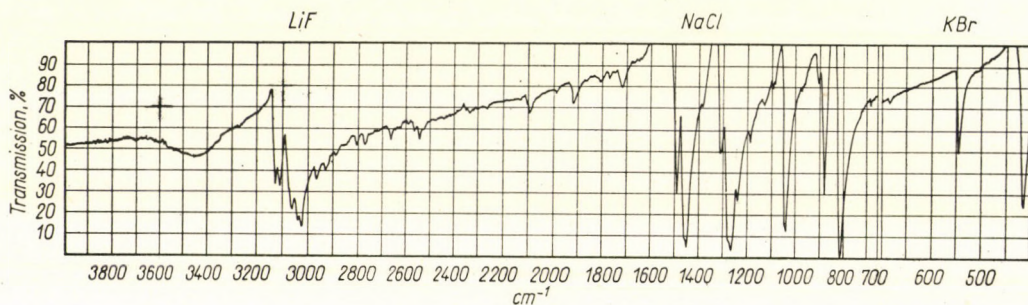


Fig. 2

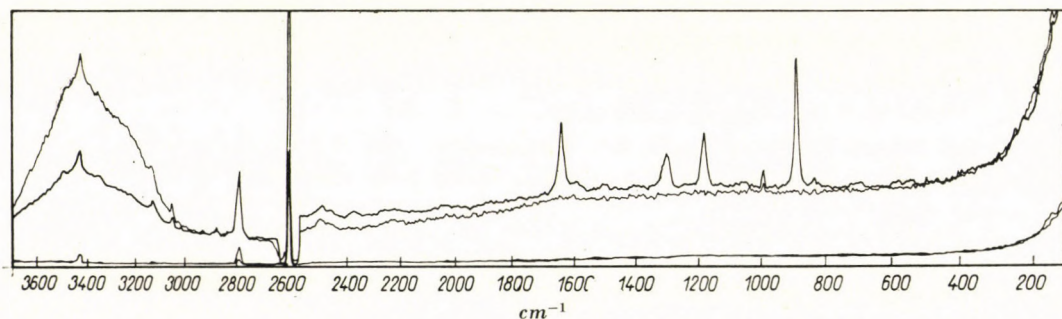


Fig. 3

Hilger Raman spectrograph in saturated aqueous solution. The line in the Raman spectrum at 992 cm⁻¹ is a Ba line, those at 2602, 2290 and 2457 cm⁻¹, are Hg lines.

Preparation of pyrazine-di-N-oxide

The substance was prepared by the method of KOELSCH and GUMPRECHT [6]. A slight modification consisted in crystallizing the compound from water instead of methanol. Contrary to the reported m.p. of 285–295°, the substance does not melt but sublimes at this temperature

Vibrational assignments

The molecules belong to the symmetry point group D_{2h} , having an inversion centre that is very helpful in the assignment, as the mutual exclusion principle can be applied.

The assignments to symmetry species were performed according to [7], a convention accepted generally, thus axis z passes through the NO bonds, and axis x is perpendicular to the plane of molecule. The numbering is analogous to that of benzene, as given by WILSON [8].

Species B_{1u}

The rather intensive skeletal bending frequency band (12) is shifted from 737 cm^{-1} of *p*-difluorobenzene to 880 cm^{-1} in pyrazine-di-oxide. Owing to its high intensity, the band at 1265 cm^{-1} has been assigned to the stretching vibration of the N—O bond; the analogous band in *p*-difluorobenzene is found at 1212 cm^{-1} .

The frequencies of vibrations 18a, 19a, 20a of benzene remained nearly unchanged in comparison to corresponding frequencies in benzene and *p*-difluorobenzene.

Species B_{2u}

The planar bending vibration of the substituents (numbered 15) was observed at 412 cm^{-1} , deviating from the related *p*-difluorobenzene frequency at 350 cm^{-1} . (This vibration was found in pyridine-N-oxide at 462 cm^{-1} [9].) The 18b, 19b and 20b modes are nearly unchanged, so is the C—C vibration (14).

Species A_{1g}

The stretching vibration of the N-oxide molecule at 1300 cm^{-1} is of rather high intensity; this corresponds to the vibration of difluorobenzene at 1245 cm^{-1} . A component arising from splitting of the 606 cm^{-1} (E_{2g}) benzene vibration was assigned at 394 cm^{-1} . This corresponds to the vibrations in pyridine-N-oxide at 545 and in difluorobenzene at 451 cm^{-1} . The breathing vibration observed at 888 cm^{-1} is analogous to the 858 cm^{-1} frequency in difluorobenzene; this is the most intensive band in the Raman spectrum. Vibrations 2, 8a, 9a do not essentially differ from the corresponding frequencies of *p*-difluorobenzene and pyridine-N-oxide.

Species B_{3g}

Vibration 3 differs only moderately from that of *p*-difluorobenzene, and it is in excellent agreement with the 1325 cm⁻¹ frequency of pyridine-N-oxide. No significant deviations were found for the 7b (CH stretching) and 8b (skeletal) vibrations.

It has not been possible to identify mode 6b. We assumed it to be at about 630 cm⁻¹ on the basis of combination tones. Similarly, the 9b in-plane deformation frequency of the substituents could not be found either. This vibration was reported by STOJILKOVIĆ and WHIFFEN to appear at 427 cm⁻¹ in the spectrum of *p*-difluorobenzene; therefore in pyrazine-di-N-oxide it was assumed to be in the region 460–480 cm⁻¹. It is possible that analogously to vibration 15, this frequency shifts towards higher values.

Out-of-plane vibrations*Species B_{2g}*

The frequencies of vibrations 4 and 10b appearing in the Raman spectra are in good agreement with the corresponding frequencies in difluorobenzene. The vibration at 375 cm⁻¹ of difluorobenzene characterizing the substituents is found here at 294 cm⁻¹.

Species B_{1g}

The 830 cm⁻¹ band has been assumed taking into account different combinations. The analogous band was observed in *p*-difluorobenzene at 800 cm⁻¹.

Species B_{3u}

The infrared frequencies of pyrazine-di-N-oxide are very close to modes 11 and 16b of difluorobenzene. Vibration 17b was not observed because it lies in the far infrared at frequencies that could not be observed in our investigations. The value of about 220 cm⁻¹ was obtained on the basis of combinations.

Species A_u

Vibrations 16a and 17a are inactive both in the Raman and in the infrared, however, they can be assigned from combinations. The frequencies of pyrazine-di-N-oxide are given in Table I compared with the corresponding values of difluorobenzene. The interpretation of bands and intensities is given in Table II.

Bonding relations and the properties of spectra

The wave numbers of the corresponding symmetric and antisymmetric stretching modes assigned to C—F and N—O bonds are in close resemblance.

Table I

	Difluorobenzene [1]	Pyrazine-di-N-oxide
A_g	1	858
	2	3084
	6a	451
	7a	1245
	8a	1617
	9a	1142
B_{3g}	3	1285
	6b	635
	7b	3084
	8b	1617
	9b	(427)
B_{1u}	12	737
	13	1212
	18a	1012
	19a	1511
	20a	3050
B_{2u}	14	1285
	15	350
	18b	1085
	19b	1437
B_{1g}	20b	3080
	10a	800
	4	692
B_{2g}	5	375
	10b	928
	16a	—
A_u	17a	943
	11	833
B_{3u}	16b	509
	17b	(186)

Because of the dependence of kinetic energy on the interatomic distances and reduced atomic masses, an agreement between most of the G matrix elements was expected. Following from the structure of the secular determinants when eigenvalues and G elements are similar, the corresponding F matrix elements must also be similar to one another.

Table II

Infrared	Intensity	Raman	Intensity	Interpretation
—		294	w.	B _{2g}
—		394	w.	A _g
412	v. s.	—		B _{2u}
542	s.	545	v. v. w.	B _{3u}
685	v. v. w.	—		400 + 294 B _{2u}
—		694	w.	B _{2g}
810	v. s.	—		B _{3u}
880	s.	—		B _{1u}
—		888	v. s.	A _g
905	w.	—		694 + 220 B _{1u}
1035	v. s.	—		B _{1u}
1040	w.	—		830 + 220 B _{2u}
1090	v. v. w.	—		694 + 400 B _{2u}
1100	v. w.	—		888 + 220 B _{3u}
1130	w.	1125	v. v. w.	B _{2u}
—		1181	s.	A _g
1190	w.	—		810 + 394 B _{3u}
1240	w.	—		830 + 412 B _{3u}
1265	v. s.	—		B _{1u}
—		1300	s.	A _g
1306	m.	—		B _{2u}
1310	w.	1310	w.	B _{3g}
1390	v. v. w.	—		1181 + 220 B _{3u}
1450	v. s.	—		B _{2u}
1491	s.	1492	w.	B _{1u}
1500	v. w.	—		810 + 694 B _{1u}
1510	v. v. w.	—		880 + 630 B _{2u}
1552	v. v. w.	—		1265 + 294 B _{3u}
1570	v. v. w.	—		880 + 694 B _{3u}
—		1620	w.	B _{3g}
—		1644	v. s.	A _g
1710	v. v. w.	—		1300 + 412 B _{2u}
1722	m.	—		1310 + 412 B _{1u}
1760	v. v. w.	—		952 + 810 B _{1u}
1780	w.	—		1491 + 294 B _{3u}
1810	v. v. w.	—		1035 + 400 + 400 B _{1u}
1872	v. v. w.	—		1491 + 394 B _{1u}
1920	m.	—		970 + 952 B _{2u}

Table II continued

Infrared	Intensity	Raman	Intensity	Interpretation
2100	w.	—		1300 + 810 B _{3u}
2135	v. v. w.	—		1265 + 888 B _{1u}
2268	v. v. w.	—		1310 + 970 B _{3u}
2545	v. w.	—		1300 + 1265 B _{1u}
2568	v. v. w.	—		1310 + 1265 B _{2u}
2590	v. v. w.	—		1620 + 970 B _{3u}
2640	v. v. w.	—		1620 + 1035 B _{2u}
2668	w.	—		1644 + 1035 B _{1u}
2668	w.	—		1491 + 1181 B _{1u}
2720	v. v. w.	—		1094 + 1644 B _{2u}
2720	v. v. w.	—		880 + 412 + 1450 B _{1u}
2750	v. v. w.	—		1450 + 1310 B _{1u}
2778	w.	—		1491 + 1300 B _{1u}
2805	w.	—		1491 + 1310 B _{2u}
2855	v. v. w.	—		1491 + 400 + 970 B _{1u}
2893	v. v. w.	—		1644 + 1265 B _{1u}
2932	v. w.	—		1644 + 1306 B _{2u}
2968	w.	—		1265 + 1306 + 412 B _{1u}
2968	w.	—		1782 + 1181 B _{2u}
3000	v. v. w.	—		1712 + 1300 B _{2u}
3000	v. v. w.	—		1491 + 970 + 542 B _{2u}
—		3020	w.	B _{3g}
3025	w.	—		1722 + 1310 B _{2u}
3025	w.	—		1491 + 412 + 1130 B _{1u}
3040	w.	—		1401 + 1644 B _{3u}
3040	w.	—		880 + 1035 + 1130 B _{1u}
3065	m.	—		B _{1u}
3075	v. w.	—		1644 + 1450 B _{2u}
3115	m.	—		B _{2u}
3130	w.	—		1644 + 1491 B _{1u}

The potential energy function of a molecule depends on the atomic arrangement and on the electronic structure; therefore it seemed obvious to extend the analogies found in electronegativity, effective nuclear charge, bond length contraction values and in isoelectronic properties, also in the area of force field calculations.

It was surprising that agreement in the cases of vibrations 6a, 12, 15 and 5 was poorer than expected, which can be explained by the fact that the N—O bond interacts with the ring to a lesser degree than C—F bond does.

All the facts listed above indicate that the bonds containing substituents have indeed nearly double bond character, therefore the mesomeric structure shown in the upper part of Fig. 1 is the more probable representation of the actual molecular structures.

The nearly double bond character at the marked places may result from a partial shift of the fluorine or oxygen electrons into the bond.

This aim of this paper has not been to give a full interpretation and evaluation, or a complete comparison of the spectral data of isoelectronic molecules; our purpose was merely to demonstrate that the transferability of force field elements in isoelectronic molecules is greater than it is usual in the cases of related compounds.

SUMMARY

The frequencies and bond distance contractions found in a study of the infrared and Raman spectra of pyrazine-di-N-oxide indicate that the N—O bond of this compound has double bond character. Great similarities in the normal frequencies of pyrazine-di-N-oxide and *p*-difluorobenzene are the consequence of the fact that the two compounds have isoelectronic structures.

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BINDUNGSSYSTEM DER N-ACYL-SULFILIMINE, V*

IR-SPEKTROSKOPISCHE UNTERSUCHUNG DER N-*p*-NITROPHENYLSULFONYL-SULFILIMINE

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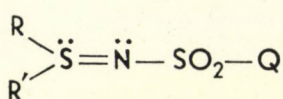
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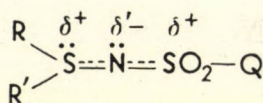
Die erste, eingehendere Information über das Bindungssystem der N-Sulfonyl-sulfilimine ($RR'S^{IV}NS^{VI}O_2Q$) konnte aus IR-spektroskopischen Daten gewonnen werden [1]. In den IR-Spektren dieser Verbindungen war im Bereich von $1020-935\text{ cm}^{-1}$ immer eine intensive Bande aufzufinden, die wir der Valenzschwingung einer $S^{IV}N$ Doppelbindung zuordneten, und zwar aus folgenden Gründen: (a) Die für Sulfilimine der Struktur $(R,R)S^{IV}N(SO_2Q)$ charakteristische intensive Bande kommt in den IR-Spektren der isomeren, substituierten Sulfonamide der Struktur $(R)S^{II}N(SO_2Q, R)$ nicht vor. (b) Die Frequenz dieser Bande wird von den an das S^{IV} -Atom angeknüpften Gruppen R und R' (infolge einer induktiven bzw. konjugativen Wirkung) auf prägnante Art beeinflusst, während eine derartige Wirkung der Gruppe Q kaum zum Ausdruck kommt. (c) Die Gruppe Q übt einen induktiven Effekt auf die ν_{SO_2} -Valenzschwingungen aus. (d) Die Frequenz und integrale Absorption der ν_{SO_2} -Banden wird in Sulfiliminen von der Wechselwirkung der SO_2 - und NS-Gruppe im großen und ganzen ebenso beeinflusst wie in den Sulfonamiden durch die Wechselwirkung der SO_2 - und NH_2 -Gruppe. (e) Die Abweichungen, die in den ν_{SO_2} - bzw. ν_{SN} -Daten zwischen dem Chloramin-T und den N-*p*-Tolylsulfonyl-sulfiliminen bestehen (vgl. Tab. I), d. h. die gleichzeitige Schwächung der SN- und der SO-Bindungen im Chloramin-T im Vergleich zu den analogen Bindungen der N-*p*-Tolylsulfonyl-sulfilimine, ist mit der Annahme unvereinbar, daß in den Sulfiliminen die $d\pi$ -Bindung ausschließlich zwischen den S^{VI} - und N-Atomen lokalisiert wäre. Aus den oben erwähnten Feststellungen haben wir geschlossen, daß in den N-Sulfonyl-sulfiliminen die $S^{IV}N$ -Bindung bedeutend stärker ist als eine einfache Bindung, d. h. die Atome S^{IV} und N sind außer einer σ -Bindung auch noch mit einer $d\pi$ -Bindung verknüpft (I). Gleichwohl konnte die Wechselwirkung dieser Bindung und der SO_2 -Gruppe mit Hilfe der

* IV. Mitteilung: *Acta Chim. Acad. Sci. Hung.* **53**, 97 (1967).

IR-Spektroskopie nicht genau ermessen werden.



I



II

Eine jüngst durchgeführte Röntgenstrahlbeugungs-Untersuchung [2, 3] führte zu dem Ergebnis, daß das S,S-Dimethyl-N-methylsulfonyl-sulfilimin ein sich auf die Atome $\text{S}^{\text{IV}}\text{NS}^{\text{VI}}$ erstreckendes, delokalisiertes $d\pi$ -Bindungssystem enthält (II; $\text{R} = \text{R}' = \text{Q} = \text{CH}_3$); die $\text{S}^{\text{IV}}\text{N}$ und $\text{S}^{\text{VI}}\text{N}$ $d\pi$ -Bindungen sind beide stark. Gleichzeitig weist die für den kristallinen Zustand kennzeichnende (möglicherweise die allergünstigste) Konformation des Sulfilimins darauf hin, daß die Wechselwirkung der $\text{S}^{\text{VI}}\text{O}_2$ Gruppe und des, dasselbe S^{VI} -Atom enthaltenden $\text{S}^{\text{VI}}\text{NS}^{\text{IV}}$ -Bindungssystems minimal ist, daß also der sogenannte II. Fall der Konjugation nach KOCH und MOFFITT [4] verwirklicht ist. Ebendeshalb besteht die Möglichkeit zur Bildung gleich starker SO und SN $d\pi$ -Bindungen, in welchen ein und dasselbe Schwefelatom einbezogen ist. Das anomale Verhalten der S^{IV} -Methylgruppe im IR-Spektralbereich [1], d. h. die gleichzeitige Verringerung der Frequenz und der integralen Absorption der als ν_{SN} bezeichneten Bande von Sulfiliminen, die eine S^{IV} -Methylgruppe enthalten, ist kein alleinstehender Fall. Laut Daten der Röntgenstrahlbeugung ist die $\text{S}^{\text{IV}}\text{C}$ -Bindung in dem untersuchten Sulfilimin auffallend kurz. Dies dürfte einer Art von Hyperkonjugation zugeschrieben werden, die in den Sulfiliminen infolge der günstigen Raumlage der d -Bahnen als Wechselwirkung zwischen dem Elektronensystem der Methylgruppe und dem S^{IV} -Atom auftritt.

Diese neuerdings gewonnenen Kenntnisse über das Bindungssystem der N-Sulfonyl-sulfilimine veranlassen zu einiger Modifizierung der früheren Deutung der IR-Spektren und auch zur Untersuchung neuer Modellverbindungen. Wahrscheinlich ist vor allem, daß die im Bereich von $1020-935\text{ cm}^{-1}$ auftretende Absorptionsbande nicht der Valenzschwingung des mit einer σ - und einer $d\pi$ -Bindung verknüpften $\text{S}^{\text{IV}}\text{N}$ Atompaares zuzuordnen ist, sondern der asymmetrischen Valenzschwingung der Atomgruppe $\text{S}^{\text{IV}}\text{NS}^{\text{VI}}$ mit einem delokalisierten $d\pi$ -Bindungssystem; (eine entsprechende Bezeichnung dieser Bande ist daher: ν_{SNS}).* Eine genauere Erwägung macht die Wirkung der durch das S^{VI} Atom gebundenen Gruppe Q notwendig. Es ist nämlich möglich, daß eine aromatische Q-Gruppe die Bindungssysteme $\text{S}^{\text{VI}}\text{O}_2$ und $\text{S}^{\text{VI}}\text{NS}^{\text{IV}}$, die ein und dasselbe S^{VI} -Atom enthalten, auf verschiedene Weise beeinflußt; man kann z. B. vermuten, daß eine aromatische Q-Gruppe auf das erstere System eine induktive, auf das letztere jedoch eine konjugative Wirkung ausübt;

* Über die Berechnung der normalen Schwingungen wird später berichtet.

dies wäre dann der Fall, wenn der aromatische Ring (ebenso wie das im sp^2 -Hybridzustand befindliche Stickstoffatom) zur SO_2 -Gruppe derart orientiert wäre, wie es dem sogenannten II. Fall der Konjugation entspräche (Abb. 1).

Eine derartige Orientation (die auf die SO_2 -Gruppe eine minimale Wirkung hat) schafft notwendigerweise eine günstige Möglichkeit der Wechselwirkung des aromatischen Systems und des Bindungssystems der $S^{VI}NS^{IV}$ -Gruppe.

Zur Ermittlung der Wirkung der Gruppe Q und eingehenderen Untersuchung des S-Methyleffektes haben wir eine Reihe analoger N-*p*-Tolylsulfonyl-

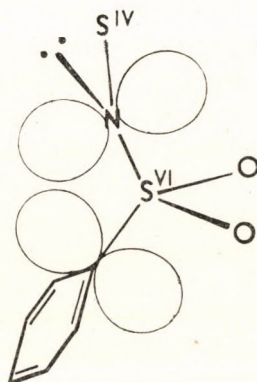


Abb. 1

sulfilimine und N-*p*-Nitrophenylsulfonyl-sulfilimine aufgebaut und ihre IR-Spektren aufgenommen. Die Ergebnisse dieser Untersuchungen sind in den Tab. I—III zusammengefaßt.

Ein Vergleich der spektroskopischen Daten läßt folgende Schlüsse zu.

1. Die Wirkung der Gruppe Q läßt sich besonders gut durch Vergleich der spektroskopischen Daten der Verbindungen vom Typ der S,S-Diäthyl-sulfilimine (Tab. III und Abb. 2—4) feststellen.* Laut den ν_{SNS} - und ν_{SO_2} -Frequenzwerten verstärkt sich die SN-Bindung nach der Reihenfolge $Q = p\text{-Tolyl} < < p\text{-Nitrophenyl} < \text{Benzyl}$, die SO Bindung hingegen im Sinne $Q = \text{Benzyl} < < p\text{-Tolyl} \leq p\text{-Nitrophenyl}$.** Dies weist darauf hin, daß die Gruppe Q die Gruppe SNS auf konjugative, die Gruppe SO_2 hingegen auf induktive Art beeinflußt.

2. Die Wirkung der Gruppen R und R' auf das SNS-Bindungssystem kommt auf gleiche Art zur Geltung in der Reihe der N-*p*-Nitrophenylsulfonyl-

* Zum Vergleich sind S-Äthylderivate deshalb besonders geeignet, weil bei ihnen eine das Spektrum modifizierende Wirkung der S^{IV} -Substituenten nicht zur Geltung kommt.

** Die ν_{SO_2} Werte sind bei analogen Verbindungen der *p*-Tolyl- und der *p*-Nitrophenyl-Reihe fast gleich.

Tabelle I

Frequenz und integrale Absorption der ν_{SO_2} - und ν_{SNS} -Banden der N-p-Tolylsulfonyl-sulfilimine

RR'SNSO ₂ C ₆ H ₄ CH ₃ RR' =	ν_{SO_2} asym. (cm ⁻¹)		ν_{SO_2} sym. (cm ⁻¹)		ν_{SNS} (cm ⁻¹)		$A_{\text{SNS}} \cdot 10^{-4}$
	KBr- Tablette	CHCl ₃ - Lösung	KBr- Tablette	CHCl ₃ - Lösung	KBr- Tablette	CHCl ₃ - Lösung	
S,S-Dimethyl	1274	1300	1138	1146	950	959	1,3
S,S-Diäthyl	1276	1299	1141	1145	978	975	2,2
S,S-Dipropyl	1278	1300	1145	1146	973	981	2,1
S,S-Diisopropyl	1272	1299	1135	1144	972	978	2,2
S,S-Diphenyl	1298	1301	1141	1148	960	970	2,7
S-Methyl-S-phenyl	1281	1301	1145	1146	935	951	1,4
S-Äthyl-S-phenyl	1280	1304	1141	1150	978	973	2,6
S-Propyl-S-phenyl	1284	1301	1143	1148	979	976	2,4
S-Isopropyl-S-phenyl	1284	1301	1149	1147	950	977	2,5
S-tert. Butyl-S-phenyl	1282	*	1145	*	959	*	*
(Chloramin-T)	1258	1258 ^a	1142	1132 ^a	940 ^b	942 ^{a,b}	**

* Die Verbindung ist in Chloroform unlöslich.

** Die Löslichkeit der Verbindung in Chloroform ist zu gering um die Intensität messen zu können.

a) In Acetonitril-Lösung. b) Wert der ν_{SN} -Bande.

Tabelle II

Frequenz und integrale Absorption der ν_{SO_2} - und ν_{SNS} -Banden der N-p-Nitrophenylsulfonyl-sulfilimine

RR'SNSO ₂ C ₆ H ₄ NO ₂ RR' =	ν_{SO_2} asym. (cm ⁻¹)		ν_{SO_2} sym. (cm ⁻¹)		ν_{SNS} (cm ⁻¹)		$A_{\text{SNS}} \cdot 10^{-4}$
	KBr- Tablette	CHCl ₃ - Lösung	KBr- Tablette	CHCl ₃ - Lösung	KBr- Tablette	CHCl ₃ - Lösung	
S,S-Dimethyl	1288	1303	1145	1150	968	977	3,2 ^c
S,S-Diäthyl	1288	1300	1145	1149	975	980	2,4
S,S-Dipropyl	1298	1303	1149	1151	970	985	2,8
S,S-Diisopropyl	1286	1302	1140	1149	980	985	3,0
S,S-Diphenyl	1302	1300	1152	1150	961	962	**
S-Methyl-S-phenyl	1288	1302	1148	1150	940	962	1,7
S-Äthyl-S-phenyl	1299	1303	1149	1151	966	981	3,6
S-Propyl-S-phenyl	1298	1303	1149	1151	982	985	2,9
S-Isopropyl-S-phenyl	1298	1303	1151	1151	972	983	3,9
S-tert. Butyl-S-phenyl	1288	*	1161	*	972	*	*
(Chloramin-N)	1257	1270 ^a	1140	1139 ^a	939, 949 ^b	949 ^{a,b}	1,0

* Die Verbindung ist in Chloroform unlöslich.

** Die Löslichkeit der Verbindung in Chloroform ist zu gering um die Intensität messen zu können.

a) In Acetonitril-Lösung. b) Wert der ν_{SN} -Bande.

c) Der Wert ist wegen der an selber Stelle erscheinenden Deformationsschwingungen der Methylgruppe unsicher.

Tabelle III

Frequenz der ν_{SNS} - und ν_{SO_2} -Banden der S,S-Diäthyl-N-sulfonyl-sulfilimine in Chloroform-Lösung

$(\text{C}_2\text{H}_5)_2\text{SNSO}_2\text{Q}$ Q=	ν_{SNS} (cm^{-1})	ν_{SO_2} asym. (cm^{-1})	ν_{SO_2} sym. (cm^{-1})	$\bar{\nu}_{\text{SO}_2}$ (cm^{-1})
p-Tolyl	975	1299	1145	1222
p-Nitrophenyl	980	1300	1149	1225
Benzyl	993	1298	1115	1207

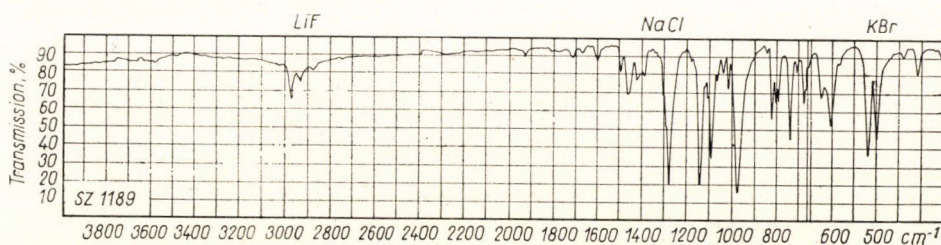


Abb. 2. IR-Spektrum des S,S-Diäthyl-N-p-tolylsulfonyl-sulfilimins

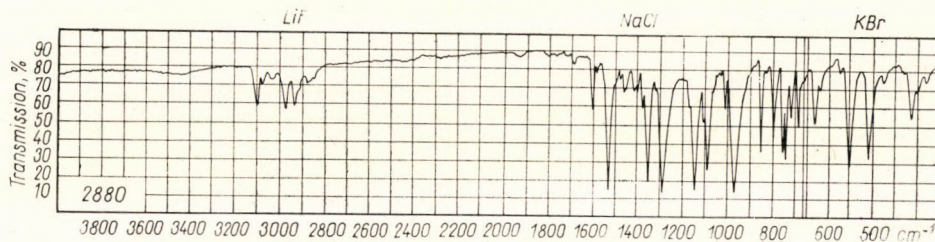


Abb. 3. IR-Spektrum des S,S-Diäthyl-N-p-nitrophenylsulfonyl-sulfilimins

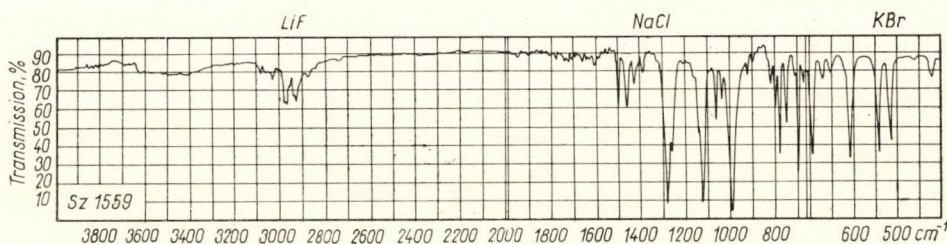


Abb. 4. IR-Spektrum des S,S-Diäthyl-N-benzylsulfonyl-sulfilimins

sulfilimine und der N-p-Tolylsulfonyl-sulfilimine. So äußert sich z. B. der konjugative Effekt der S^{IV} -Phenylgruppe und der hyperkonjugative Effekt der S^{IV} -Methylgruppe auch hier auf recht prägnante Weise in der Verminderung der ν_{SNS} -Frequenz. Besonders bedeutend ist (im Vergleich zum ν_{SNS} -Wert des

S,S-Diäthyl-Derivats) die $\Delta\nu_{\text{SNS}}$ -Frequenzverminderung im Falle des S,S-Diphenyl-⁺ und S-Methyl-S-phenyl-N-*p*-nitrophenylsulfonyl-sulfilimins ($\Delta\nu_{\text{SNS}}$: 18 cm⁻¹), sie ist aber auch beim S,S-Dimethyl-Derivat ($\Delta\nu_{\text{SNS}}$: 3 cm⁻¹; im Vergleich mit anderen S,S-Dialkyl-Derivaten $\Delta\nu_{\text{S-S}}$: 8 cm⁻¹) zu beobachten.

Interessanterweise kommt auch in der Reihe der N-*p*-Nitrophenylsulfonyl-sulfilimine die Regelmäßigkeit zur Geltung, daß die S-Äthyl-S-phenyl-, ferner die S-Propyl-S-phenyl-sulfilimine eher den entsprechenden S,S-Dialkyl-sulfilimin analoge Spektren aufweisen, als den S,S-Diphenyl- bzw. S-Methyl-S-phenyl-sulfilimin.

3. Keine andere S^{IV}-Alkylgruppe zeigt eine derartige Wirkung (»S-Methyleffekt«), wie die S^{IV}-Methylgruppe.

Beschreibung der Versuche

Die auf die Herstellung der untersuchten Sulfilimine bezüglichen Daten sind in Tab. IV. zusammengefaßt.

Tabelle IV

Angaben über die Herstellung der N-Sulfonyl-sulfilimine

RR'SNSO ₂ Q RR' =	Q = C ₆ H ₄ CH ₂ - <i>p</i>	Q = C ₆ H ₄ NO ₂ - <i>p</i>				RR'S Thio- äther
	Herstel- lungsart	Herstel- lungsart	Aus- beute ^a %	Schmp. (°C) (beobachtet)	Schmp. (°C) (Literaturangabe [7])	Herstel- lungsart
S,S-Dimethyl	[5]	**	37	185	187,5—188,5	[8]
S,S-Diäthyl	[5]	**	73	137,5—138,5	137,5—138,5	[9]
S,S-Dipropyl	[5]	**	53	121	121,5—122,5	[10]
S,S-Diisopropyl	[5]	**	65	133	136,0—138,0	[10] ^d
S,S-Diphenyl	[6]	**	26	160—162	160,0—161,0	[11]
S-Methyl-S-phenyl	[6]	**	30	165	164,0—166,0	[12]
S-Äthyl-S-phenyl	[1]	**	46	120—121	117,0—118,0	[13] ^e
S-Propyl-S-phenyl	*	**	30	114—115 ^c	109,0—110,0	[12] ^f
S-Isopropyl-S-phenyl	*	*	28	141—142		[12] ^g
S- <i>tert.</i> Butyl-S-phenyl ...	*	*	20 ^b	105—107		*

* Herstellung s. im Versuchsteil.

** Herstellung nach dem allgemeinen, im Versuchsteil beschriebenen Verfahren.

a) Die Ausbeuten beziehen sich auf (aus Alkohol) umkristallisierte, analysenreine Produkte.

b) Wegen der Hitzeempfindlichkeit der Substanz ist Umkristallisieren aus Methanol angezeigt.

c) Analyse: C₁₅H₁₆N₂O₄S₂ (352,4). Ber. C 51,1, H 4,6%; Gef. C 51,5, H 4,7%.

d) Hergestellt nach dem angegebenen Verfahren, nur wurde Isopropylbromid anstatt Propylbromid verwendet. Ausbeute 34% d. Th.

e) Sdp. 88°/15 mm; n_D^{20} = 1,566. Ausbeute 76% d. Th.

f) Sdp. 98°/13 mm; n_D^{20} = 1,554.

g) Sdp. 95°/15 mm; n_D^{20} = 1,546.

† Dies ist das einzige N-*p*-Nitrophenylsulfonyl-sulfilimin, dessen SN-Bindung schwächer ist, als die des analogen N-*p*-Tolylsulfonyl-sulfilimins.

tert. Butylphenylsulfid. — Es wurde zu 225 ml gerührt und mit Eis gekühlter konz. Schwefelsäure zuerst 65 g Eis, dann 50,4 g (0,6 M) *tert. Butylalkohol* gegeben, nachher ließ man binnen 30 Min. 33 g (0,3 M) Thiophenol zutropfen, darauf achtend, daß die Temperatur des Reaktionsgemisches $+10^\circ$ nicht überschreite. Nach Entfernung des Eisbades wurde das Gemisch bei Raumtemperatur noch 30 Min. weiter gerührt, dann die abgetrennte wäßrige Schicht mit dem gleichen Volumen Wasser verdünnt und zweimal mit insgesamt 60 ml Äther ausgeschüttelt. Die ätherische Lösung wurde mit dem abgetrennten Thioäther vereinigt, dann mit 30 ml 10%iger Natronlauge, hierauf mit Wasser durchgeschüttelt, mit festem Kaliumhydroxyd getrocknet und zum Schluß der Äther abgetrieben. Das rückständige Öl lieferte bei der Vakuumdestillation als Hauptfraktion 22,7 g (55% d.Th.) *tert. Butylphenylsulfid*. Sdp. $85-87/12$ mm, $n_D^{20} = 1,530$, fast übereinstimmend mit der Literaturangabe [14].

S-Propyl-S-phenyl-N-p-tolylsulfonyl-sulfilimin. — Die Verbindung konnte nach der früher beschriebenen allgemeinen Herstellungsart der *N-p-Tolylsulfonyl-sulfilimine* [6] aus Propylphenylsulfid [12] und Chloramin-T in wäßrigem Dioxan in 50%iger Ausbeute gewonnen werden. Schmp. $85,5^\circ$, übereinstimmend mit der Literaturangabe [15].

S-Isopropyl-S-phenyl-N-p-tolylsulfonyl-sulfilimin. — Die Verbindung ließ sich aus Iso-propylphenylsulfid [12] und Chloramin-T in wäßrigem Dioxan nach der allgemeinen Herstellungsart der *N-p-Tolylsulfonyl-sulfilimine* [6] in 53%iger Ausbeute gewinnen. Schmp. $115-116^\circ$, praktisch übereinstimmend mit der Literaturangabe [16].

S-tert. Butyl-S-phenyl-N-p-tolylsulfonyl-sulfilimin. — Eine Lösung von 2,45 g (15 mM) *tert. Butylphenylsulfid* in 50 ml absol. Methanol wurde mit einer Lösung von 4,2 g (15 mM) Chloramin-T in 50 ml absol. Methanol versetzt, wobei Selbsterwärmung zu beobachten war. Das nach 25stündigem Stehen eingedampfte Gemisch ergab einen Rückstand, der nach dem Bearbeiten mit 15 ml absol. Äther 2,8 g rohes (mit Natriumchlorid verunreinigtes), kristallines Sulfilimin lieferte. Das mit 5 ml Wasser verriebene Produkt wurde abfiltriert und noch im nassen Zustand aus 5 ml Methanol umkristallisiert. Auf diese Weise konnte 1,1 g (22% d.Th.) eines analysenreinen Produktes gewonnen werden, das — mit der Literaturangabe [16] übereinstimmend — bei $98-100^\circ$ u. Zers. schmolz. Gegenüber Hitze oder Lauge ist die Substanz besonders empfindlich.

Allgemeine Herstellungsart der N-p-Nitrophenylsulfonyl-sulfilimine. — Die früher angegebene [6] allgemeine Herstellungsart der *N-p-Tolylsulfonyl-sulfilimine* ist auch zur Herstellung von *N-p-Nitrophenylsulfonyl-sulfilimin* geeignet, wenn man Chloramin-N anstatt Chloramin-T verwendet. Die Zusammensetzung des Lösungsmittelgemisches (Dioxan—Wasser) wird fallweise (durch Zugabe von mehr Dioxan) so modifiziert, daß eine homogene Lösung entsteht. — Die Herstellung von Chloramin-N erfolgte auf bereits beschriebene [17, 7] Art. Die umkristallisierte Verbindung erwies sich laut jodometrischer Bestimmung als 99—100%ig, berechnet auf die Formel $O_2NC_6H_4SO_2NNaCl \cdot 1,5 H_2O$.

S-Isopropyl-S-phenyl-N-p-nitrophenylsulfonyl-sulfilimin. — Die Verbindung wurde nach einer zur Herstellung anderer Sulfilimine ausgearbeiteten Methode nach PETRÁNEK, VEČEŘA und JUREČEK [7] in einer Ausbeute von 31% gewonnen, nach den oben von uns angegebenen Verfahren in 28%iger Ausbeute. Das aus Alkohol umkristallisierte Produkt schmolz bei $141-142^\circ$.

$C_{15}H_{16}N_2O_4S_2$ (352,4)	Ber.	C 51,1	H 4,6	N 7,9	S 18,2%
	Gef.	C 51,2	H 4,7	N 7,8	S 18,1%

S-tert. Butyl-S-phenyl-N-p-nitrophenylsulfonyl-sulfilimin. — Eine Lösung von 2,45 g (15 mM) *tert. Butylphenylsulfid* in 50 ml absol. Methanol wurde mit einer Lösung von 4,28 g (15 mM) Chloramin-N in 50 ml Methanol versetzt. Es war Selbsterwärmung zu beobachten, später setzte Kristallausscheidung ein. Nach Stehen über Nacht wurde das kristalline Produkt abfiltriert und mit wenig Methanol gewaschen. Das so gewonnene schwach gelbliche Produkt wog 1,6 g (29% d. Th.) und schmolz bei 103° u. Zers. Das aus absol. Methanol einmal umkristallisierte Produkt (Verlust 30%) war analysenrein; Schmp. $105-107^\circ$ u. Zers.

$C_{16}H_{18}N_2O_4S_2$ (366,5)	Ber.	C 52,4	H 5,0	N 7,6	O 17,5	S 17,5%
	Gef.	C 52,7	H 5,0	N 7,5	O 17,5	S 17,7%

Die IR-Spektrenaufnahmen wurden mit einem Doppelstrahlspektrofotometer vom Typ UR—10 der Fa. Carl Zeiss (Jena) unter Anwendung des KBr-, NaCl- und LiF-Prismas in KBr-Tabletten, ferner in Chloroform-Lösung durchgeführt. Die integrale Absorption wurde nach der Methode von RAMSAY [18] berechnet. Die Fehlergrenze der angegebenen Frequenzwerte beträgt $\pm 2 \text{ cm}^{-1}$.

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ZUSAMMENFASSUNG

Die in den IR-Spektren der N-Sulfonyl-sulfilimine im Bereich von $935\text{--}1020\text{ cm}^{-1}$ liegende intensive Bande ist wahrscheinlich der asymmetrischen Valenzschwingung der $\text{S}^{\text{IV}}\text{NS}^{\text{VI}}$ -Gruppe zuzuordnen (ν_{SNS}). In der Reihe der N-*p*-Nitrophenylsulfonyl-sulfilimine ($\text{RR}'\text{SNSO}_2\text{Q}$; $\text{Q} = \text{C}_6\text{H}_4\text{NO}_2\text{-}p$) beeinflusst die Gruppe Q (ebenso wie im Falle $\text{Q} = \text{C}_6\text{H}_4\text{CH}_3\text{-}p$) die SO_2 -Gruppe auf induktive, die SNS-Gruppe hingegen auf konjugative Art. Bei Sulfilimininen, die als R-Substituenten eine Phenyl- bzw. Methylgruppe enthalten, äußert sich der konjugative bzw. hyperkonjugative Effekt in der Verminderung der Frequenz der ν_{SNS} -Bande ($\Delta\nu_{\text{SNS}}$: $3\text{--}23\text{ cm}^{-1}$), und zwar gleicherweise in beiden Fällen $\text{Q} = \text{C}_6\text{H}_4\text{NO}_2$ und $\text{Q} = \text{C}_6\text{H}_4\text{CH}_3$.

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THE INFLUENCE OF THE FIELD EFFECT UPON THE TENDENCY OF SOME QUINOLIZINONE DERIVATIVES TO FORM KETALS

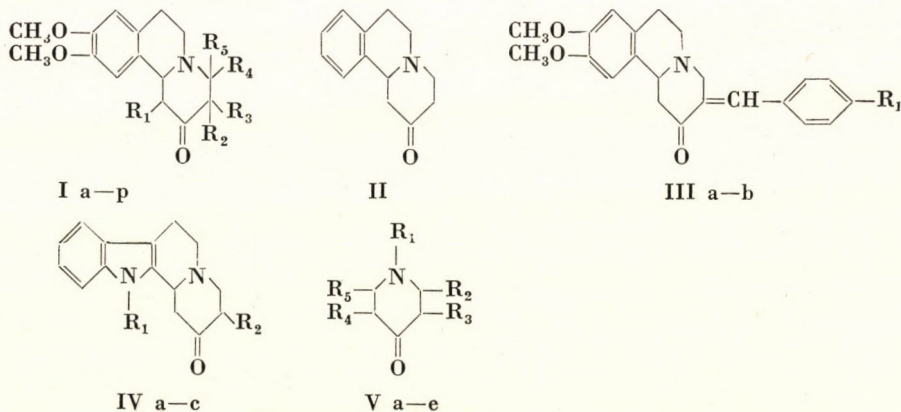
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In the course of our studies [1] on the synthesis and chemical properties of 2-oxo-hexahydro-benzo[a]quinolizines we have noted that the salts of several derivatives readily form stable ketals, and even hydrates. Similar findings have been reported [2] in connexion with some pyridone derivatives. In view of the fact that the hexahydro-benzo[a]quinolizine system is much more rigid than the flexible piperidines, it seemed reasonable to make a more detailed investigation in our case.

When the infrared stretching vibration frequencies of the carbonyl group of the benzo[a]quinolizinone derivatives, **Ia–p**, are compared with the same vibrations of the corresponding salts, it is seen that the carbonyl groups of the salts absorb at wave numbers higher by 5 to 25 cm^{-1} (cf. Table I); only derivatives (**IIIa, b**) that contain the carbonyl group in a position conjugated to a double bond are exceptions. The spectra of the bases in solution (CHCl_3) remain unchanged.



For the sake of comparison, the spectra of some indolo[2,3-a]quinolizinone (**IVa–c**), and piperidone (**Va–e**) derivatives were recorded (cf. Table I).

* This paper is a part of the post-graduate thesis of L. N.

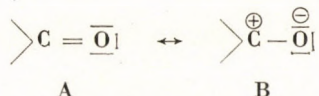
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Table I

Carbonyl stretching vibrations of the bases I—V, and of their hydrochlorides

Compound	R ₁	R ₂	R ₃	R ₄	R ₅	ν C=O (base)	ν C=O (HCl salt)	Δ ν C=O(HCl) — ν C=O (base)	Compound isolated from a soln. of HCl in EtOH
Ia ¹¹	H	H	H	H	H	1718	—	—	ketal HCl
b ¹²	α -furfuryl	H	H	H	H	1715	1740	25	keton HCl
c ¹²	C ₆ H ₅ —CH ₂	H	H	H	H	1715	1735	20	keton HCl
d ¹³	CH ₃	H	H	H	H	1715	1725	10	keton HCl
e ¹¹	H	C ₆ H ₅ CH ₂	H	H	H	1710	1735	25	keton HCl
f ¹¹	H	CH ₃ CH ₂	H	H	H	1710	1725	15	keton HCl
g ¹²	H	CH ₃ CH ₂	CH ₂ CH ₂ CN	H	H	1705	1720	15	keton HCl
h ¹¹	H	CH ₃	H	H	H	1715	1725	10	keton HCl
i ¹⁴	H	C ₆ H ₅	H	H	H	1720	1730	10	ketal HCl
j ¹¹	H	CH ₂ CH(CH ₃) ₂	H	H	H	1715	1720	5	keton HCl
k ¹²	H	H	H	H	α -furyl	1715	1735	20	ketal HCl
l ¹²	H	H	H	H	C ₆ H ₅ NO ₂ (p)	1715	1733	18	ketal HCl
m ¹²	H	H	H	H	C ₆ H ₅	1714	1730	16	ketal HCl
n ¹¹	H	H	H	CH ₃	CH ₃	1715	1730	15	ketal HCl
o ¹²	H	H	H	H	C ₆ H ₅ OCH ₃ (p)	1715	1728	13	ketal HCl
p ¹²	H	H	H	H	C ₆ H ₅ (OCH ₃) ₂ (m,p)	1720	1732	12	ketal HCl
II ¹¹	—	—	—	—	—	1718	1738	20	keton HCl
IIIa ¹¹	H	—	—	—	—	1690	1690	—	keton HCl
b ¹²	OCH ₃	—	—	—	—	1690	1690	—	keton HCl
IVa ¹⁵	H	C ₆ H ₅ CH ₂	—	—	—	1708	1733	25	keton HCl
b ¹⁵	H	CH ₃ CH ₂	—	—	—	1710	1735	25	keton HCl
c ¹⁶	CH ₃	CH ₃ CH ₂	—	—	—	1710	1725	15	keton HCl
Va ¹⁷	C ₆ H ₅ CH ₂	H	H	H	H	1725	1735	10	keton HCl
b ¹⁸	C ₆ H ₅ CH ₂	C ₆ H ₅	CH ₃	H	C ₆ H ₅	1725	1735	10	keton HCl
c ¹⁸	CH ₃	C ₆ H ₅	CH ₃	H	C ₆ H ₅	1730	1735	5	keton HCl
d ¹⁸	CH ₃	C ₆ H ₅	CH ₃	CH ₃	C ₆ H ₅	1713	1730	17	keton HCl
e ¹⁹	H	C ₆ H ₅	CH ₃	H	C ₆ H ₅	1705	1725	20	keton HCl

Obviously, the cause of the shift of the carbonyl frequency is to be sought — as compared to the base — in the positive charge appearing on the nitrogen atom which thus exerts a strong inductive effect. Owing to this effect, the resonance structure B of the carbonyl group will be considerably less important, therefore a greater amount of energy will be needed to generate stretching vibrations.



The shift observed is in agreement with the order of magnitude of the increase of the stretching vibration frequencies of the carbonyl group of cyclohexanones when a halogen atom is introduced to it in α -equatorial position (20 cm^{-1}) [3]. Thus the shift is so great that it cannot be explained by an effect imposed on the σ -electrons; therefore we think that the effect is exerted across space (field effect). KIRKWOOD and WESTHEIMER [4] showed as early as nearly 30 years ago that a quantitative description of the effect of charged substituents is possible even when field effects alone are taken into account, and polarization acting through σ -electrons is neglected. For the decrease of the polarization along σ -electrons, *i.e.* of the classic inductive effect, WATERS [5] gives 0.022 as the factor of transmission for one methylene group; accordingly, after two methylene groups this effect is already negligible. Recently, DEWAR *et al.* [6] concluded that the "inductive effect" of substituents is, in general, an electrostatic interaction effective across space much more than a classic inductive effect.

The validity of this conclusion is supported by our following observations.

The potential energy of the interaction between the charge and the carbonyl group diminishes approximately with the square of the distance [10], and supposing chair conformation for the salts of compounds I—V, the distance between the centre of the positively charged nitrogen and that of the carbon of the carbonyl group is about 4 Å or, owing to the flexible conformation, possibly less; therefore, a strong interaction can be expected.

Besides the frequency shift of the carbonyl group, the tendency to form ketals affords further evidence in this respect. If no substituent disturbs the situation on ring C (Ia), the hydrochloride is obtained as pure hydrate even from water, and like in the case of chloral hydrate, dehydration is not easily achieved.

Substituents on the C—4 atom likewise do not perceptibly reduce the tendency to form ketals. In contrast to this, in the presence of alkyl or aralkyl groups at C—1 or C—3, *i. e.* on the carbon atoms in α -position to the carbonyl group, the tendency to form stabile ketals is absent. This may also be explained primarily with the inductive effect of these substituents operating across space. Since this effect is positive in this instance, it becomes manifest in a field effect that diminishes the influence of the charged nitrogen.

Table II
Analytical data of compounds VIa—d,

Analysis				
Compound	M. P. °C	Empirical formula	Mol. weight	C%
VIa HCl	174	C ₁₉ H ₃₀ NO ₄ Cl	371.89	61.35
VIa	97—98	C ₁₉ H ₂₉ NO ₄	333.43	68.43
VIa CH ₃ I	149—150	C ₂₀ H ₃₂ NO ₄ I	477.38	50.52
VIb HCl	142—144	C ₂₅ H ₃₄ NO ₄ Cl	447.99	67.02
VIb	155—156	C ₂₅ H ₃₃ NO ₄	411.52	72.96
VIc HCl	148—150	C ₂₆ H ₃₆ NO ₅ Cl	478.02	65.32
VIc	121—123	C ₂₆ H ₃₅ NO ₅	441.55	70.71
VI _d HCl	130	C ₂₇ H ₃₈ NO ₆ Cl	508.04	63.83
VI _d	141	C ₂₇ H ₃₇ NO ₆	471.58	68.76

For this phenomenon some other explanation might also be sought. Thus, *e. g.* CASY [2] ascribes the acetal forming tendency in piperidones mainly to the fact that in consequence of ketal formation the trigonal carbon atom is converted into the ideal staggered conformation. However, if a substituent is present in α -axial position, then ketal formation leads to unfavourable steric interactions, which is not the case with a β -equatorial substituent.

The behaviour of the compound of structure Ii contradicts this in our, since with a phenyl group at position 3 it readily forms a ketal, and even a hydrate. Thus, a bulky substituent in α -position that does not exert a positive inductive effect also promotes ketal formation since, as against the argumentation of CASY this reaction leads to a loosening of the "compressed" state of the system owing to an interaction with the carbonyl oxygen; the cause of this interaction is similar to that of the "2-alkyl-ketone effect".

Our studies thus support the view that field effects have a determinant character.

Our thanks are due to the Hungarian Academy of Sciences for support of this work, and to Mrs. L. BALOGH, and Mrs. J. VISZT for the microanalyses.

Experimental

2,2-Dihydroxy-9,10-dimethoxy-1,2,3,4,6,7-hexahydro-11bH-benzo[a]quinolizine hydrochloride (VIe. HCl)

2-Oxo-9,10-dimethoxy-1,2,3,4,6,7-hexahydro-11bH-benzo[a]quinolizine (Ia) (1.0 g; 4 mmoles) was dissolved in warm 2 N HCl (3 ml), and the precipitate that separated on cooling was collected by suction. Recrystallization from water (3 ml) gave the hydrochloride of the ketohydrate (0.57 g; 44.6%), m.p. 137—138° (decomp.).*

* BROSSI et al. [17] give m.p. 161° for the HCl salt of Ia. The analysis and the conditions of crystallization are not mentioned.

and of their hydrochlorides

Analysis						
Calculated			Found			
H%	N%	Cl%	C%	H%	N%	Cl%
8.14	3.76	9.53	61.08	8.23	4.03	9.62
8.76	4.20	—	68.34	8.60	4.18	—
6.75	2.93	26.58 (I%)	50.26	6.83	3.01	26.78 (I%)
7.65	3.12	7.91	66.84	7.74	3.34	7.66
8.08	3.40	—	73.13	8.06	3.68	—
7.59	2.93	7.42	65.30	7.80	3.10	7.71
7.99	3.17	—	70.59	8.02	3.28	—
7.54	2.76	6.97	63.67	7.48	2.96	6.78
7.91	2.97	—	68.69	7.65	3.24	—

$C_{15}H_{22}NO_4Cl \cdot H_2O$ (333.81). Calcd. C 53.59; H 7.25; N 4.19; Cl 10.62; H_2O 5.39. Found C 53.86 H 7.24 N 4.30 Cl 10.67 H_2O 5.72%.

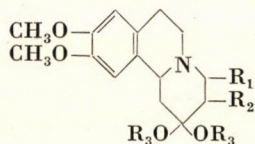
The hydrochloride of the ketohydrate **VI**f was prepared in a similar way starting from salt **I**i. According to the IR spectrum, the crude product contained about 10% ketone hydrochloride. On recrystallization from water the pure hydrochloride **VI**f was obtained, m.p. 173°. ($C_{21}H_{24}NO_3Cl$) · 2 H_2O (396.90). Calcd. C 63.54 H 7.11 N 3.53 Cl 8.93 Found: C 63.27 H 6.92 N 3.54 Cl 8.88%.

2,2-Diethoxy-9,10-dimethoxy-1,2,3,4,6,7-hexahydro-11bH-benzo[a]quinolizine hydrochloride (VIa. HCl)

Into a solution in ethanol (15 ml) of the base **I**a (8.3 g; 32 mmoles) hydrogen chloride gas was introduced for 5 minutes without cooling. The warm solution was allowed to cool to room temperature and the substance that separated was recrystallized from ethanol. The product (**VI**a. HCl) (8.07 g; 68.5%) had m.p. 174°.

A solution of the hydrochloride of **VI**a (5 g) in water (25 ml) was made alkaline with 5% Na_2CO_3 (20 ml). The precipitate was recrystallized from ethanol (5 ml). The ketal (**VI**a) (3.92 g; 87.5%) had m.p. 97–98°.

The ketals **VI**b and their hydrochlorides could be obtained similarly; the physical constants and analyses are listed in Table II.



VI a, $R_1=R_2=H$

b, $R_1=C_6H_5$

c, $R_1=C_6H_5-OCH_3$ (p)

d, $R_1=C_6H_5-(OCH_3)_2$ (m,p)

e, $R_1=R_2=R_3=H$

f, $R_1=R_3=H$

$R_2=H$

$R_2=H$

$R_2=H$

$R_2=C_6H_5$

$R_3=C_2H_5$

$R_3=C_2H_5$

$R_3=C_2H_5$

$R_3=C_2H_5$

The IR spectra were recorded with a Zeiss UR-10 instrument.

SUMMARY

There is relationship between the tendency of some quinolizinone derivatives and their salts to form ketals or hydrates and the shift of their carbonyl stretching vibration frequencies. An explanation for this can be given primarily on the basis of a field effect.

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INDOL UND INDOLDERIVATIVE, I. DEHYDRIERUNG VON INDOLIN UND INDOLINDERIVATEN

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Die Dehydrierung von Indolinderivaten kann einerseits als Modell für die Untersuchung der Dehydrierungsreaktion, andererseits als eine präparative Möglichkeit zur Darstellung von Indolderivaten betrachtet werden. Die Dehydrierung von Indolderivaten ist für präparative Zwecke in denjenigen Fällen von Bedeutung wenn die Einführung eines Substituenten in das Indolin-Gerüst einfacher durchführbar ist als in das Indol. Deshalb haben KONOSHITA und seine Mitarbeiter 6-Nitro- und 5-Nitro-indol durch Dehydrieren von 6-Nitro- bzw. 5-Nitro-indolin mit Palladium-Katalysator dargestellt [1]. Ähnliche Methoden wurden auch von anderen verwendet [2, 3]. JAKONTOW und seine Mitarbeiter haben 6-Methoxy-indolin mit Natrium in flüssigem Ammoniak dehydriert [6]. Auch mit Chloranil konnten mehrere Indolinderivate dehydriert werden [4, 5, 6].

Von den erwähnten Methoden unterschieden sich wesentlich die von LESIAK beschriebenen, in der Dampfphase durchgeführten katalytischen bzw. katalytisch-oxydativen Dehydrierungen [7, 8].

Zur Darstellung von Indolderivaten scheinen die in flüssiger Phase durchführbaren, katalytischen Dehydrierungsmethoden am besten anwendbar zu sein. Es ist jedoch auffallend, daß diese Dehydrierungen, nach den diesbezüglichen Angaben der Fachliteratur, meistens bei verhältnismäßig hohen Temperaturen (mindestens 100°, meist aber 160—210°) durchgeführt wurden, obwohl aus mehreren Gründen darauf zu schließen ist, daß diese Dehydrierungsreaktionen schon bei niedrigeren Temperaturen stattfinden.

Diese Voraussetzung veranlaßte uns zur näheren Untersuchung der Dehydrierung von Indolin und Indolinderivaten. Eines der Resultate unserer hier beschriebenen Versuche ist die Feststellung, daß diese Dehydrierungen, in Lösungsmitteln, mit Raney-Nickel schon bei etwa 70°, mit für kinetische Messungen und auch für präparative Zwecke entsprechenden Geschwindigkeiten durchgeführt werden können.

Der Dehydrierungsapparat und die Methode

Der Apparat besteht aus einem 10 ml fassenden Rundkolben mit Rückflußkühler und Gasbürette mit einem Niveaugefaß (Abb. 1). Im Mantel der Gasbürette und des Rückflußkühlers zirkuliert durch einen Thermostaten Wasser von Zimmertemperatur. Als Sperrflüssigkeit in der Gasbürette dient (gefärbtes) Wasser.

Die Dehydrierung wurde mit Raney-Nickel als Katalysator in einem Lösungsmittel beim Siedepunkt desselben oder bei einer niedrigeren Temperatur

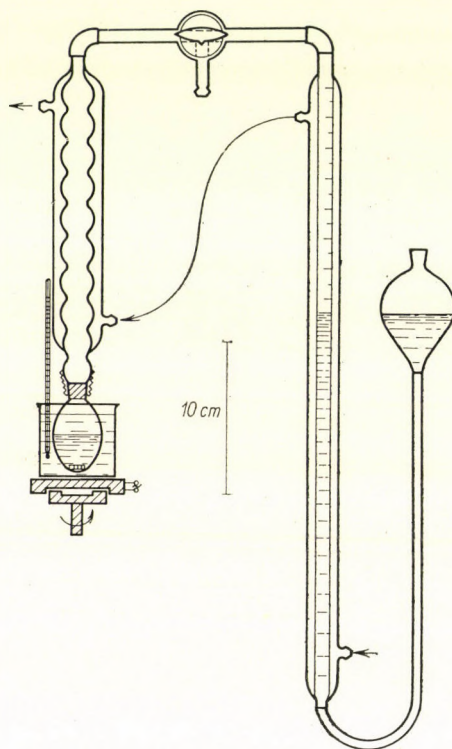


Abb. 1

durchgeführt. Im letzteren Fall wurde die Reaktion unter Rühren mit einem Magnetrührer oder ohne Rühren durchgeführt. Als Lösungsmittel wurden Benzol, Toluol, Xylol, Cyclohexan und Methyleyclohexan verwendet.

Als Katalysator diente in jedem Falle wasserfreies Raney-Nickel. Wo keine diesbezüglichen Bemerkungen zu finden sind, wurde der Katalysator mit der ursprünglichen Korngröße, ohne Fraktionierung entwässert und zum Dehydrieren eingesetzt. Zu einigen Versuchen wurde der Katalysator unter Wasser zerkleinert und durch Sieben in Fraktionen getrennt.

Das Entwässern wurde folgendermaßen durchgeführt: Etwa 10 g wäßriges Raney-Nickel wurde mit 50 ml Cyclohexan versetzt und das Wasser-Cyclohexan-Azeotrop unter ständigem Zutropfen von Cyclohexan abdestilliert. Nach Abdestillieren von 150–200 ml wurde der Siedepunkt des Cyclohexans erreicht, wonach unter Zutropfen von wasserfreiem Cyclohexan noch 150 ml abdestilliert wurden. (Es muß darauf geachtet werden, daß das ganze Raney-Nickel immer mit Cyclohexan bedeckt sein soll.) Auf dieser Weise wird ein stark pyrophores Raney-Nickel erhalten.

Enthält das zu Dehydrierungsreaktionen verwendete Benzol, Toluol oder Xylol Thiophen und Thiophenhomologe, so müssen diese entfernt werden, da sie für das Raney-Nickel als Katalysatorgifte wirken. Die verwendeten Lösungsmittel wurden mit Schwefelsäure bis zur negativen Isatinprobe behandelt, dann mit Wasser gewaschen, getrocknet und destilliert. Cyclohexan und Methylcyclohexan wurden nur destilliert. Die Siedepunkte und Brechungsindexe der gereinigten Lösungsmittel sind in Tabelle I zusammengefaßt.

Tabelle I

	n_D^{20}	Siedepunkt, °C
Benzol	1,5010	80–80,2
Toluol	1,4963	110–110,4
Xylol	1,4960	138–139,5
Cyclohexan	1,4263	81–81,5
Methylcyclohexan .	1,4222	100,2–100,8

Durchführung der Dehydrierung

In dem mit Stickstoff gefüllten Rundkolben wird 0,1 g (± 1 mg) wasserfreies, cyclohexanon-feuchtes Raney-Nickel mit 5 ml Lösungsmittel versetzt und dann etwa 1 mmol ($\pm 0,2$ mg) dehydrierende Substanz zugegeben. Der ganze Luftraum des Apparats wird mit Stickstoff gefüllt. Nach Einstellung des Wasserniveaus auf den Nullpunkt wird das Reaktionsgemisch mit einem Gasbrenner bis zum intensiven Sieden erhitzt, während im Apparat durch Nachstellung des Niveaugefäßes atmosphärischer Druck aufrechterhalten wird. Nach 2–3 Minuten anhaltenden raschen Anwachsens des Gasvolumens ist die Änderung desselben nur mehr auf die Entwicklung von Wasserstoff zurückzuführen. War das Ziel des Versuches die Bestimmung des Gleichgewichtszustandes, so wurde das Reaktionsgemisch so lange im lebhaftem Sieden gehalten, bis 20 Minuten lang keine Gasvolumenänderung zu beobachten war.

Aus den Blindversuchen (nur Lösungsmittel oder Katalysator und Lösungsmittel) ergab sich, daß durch das Erwärmen des Apparats und Anwachsens der Tension des Lösungsmittels eine Volumenvergrößerung von 12–18 ml verursacht wird. (Das nach 2–3 Minuten beobach-

tete maximale Volumen blieb auch nach mehrstündigem Sieden konstant.) Nach Abkühlen stellte sich aber die Sperrflüssigkeit nicht wieder auf den Nullpunkt ein, sondern es war immer eine von der Tension des betreffenden Lösungsmittels abhängige, bestimmte Volumenvergrößerung (V_b) zu beobachten: bei Benzol und Cyclohexan 0,8, bei Methylcyclohexan 0,4, bei Toluol 0,3 und bei Xylol 0,1 ml. Diese Volumenvergrößerung kann nicht irgendeinem Dehydrierungsprozeß zugeschrieben werden, da auch die Blindversuche ohne Raney-Nickel das gleiche Resultat lieferten. Dieses kann also nur als Folge der Erhöhung des Partialdruckes des Lösungsmittels bis zum Gleichgewichtszustand betrachtet werden.

Die durch das Erwärmen des Reaktionsgemisches verursachte Volumenvergrößerung (V_w) war bei den Blindversuchen und Dehydrierungsversuchen genau die gleiche: $V_{d(max)} - V_d = V_{b(max)} - V_b = V_w$. In der Gleichung bedeutet $V_{d(max)}$ das bei der Dehydrierung, $V_{b(max)}$ das beim Blindversuch beobachtete maximale Volumen, und V_d das bei der Dehydrierung nach dem Abkühlen beobachtete Volumen. So konnte im Laufe eines Versuches das Volumen des bis zum Zeitpunkt τ entwickelten Wasserstoffes ($V_{H(\tau)}$) durch das beobachtete Gasvolumen $V_{d(\tau)}$ gut verfolgt werden: $V_{d(\tau)} - V_w = V_b = V_{H(\tau)}$. (Bei der Berechnung der Konversionen wurde zur Volumenreduktion die Tension des Lösungsmittels und der Sperrflüssigkeit selbstverständlich in Betracht gezogen.)

Die Dehydrierung des Indolins

Der zeitliche Ablauf der Dehydrierung in Benzol, Toluol bzw. Xylol, bei Siedetemperatur wurde in Abb. 2 mit den aus dem Gasvolumen berechneten Konversionen (ψ) veranschaulicht.

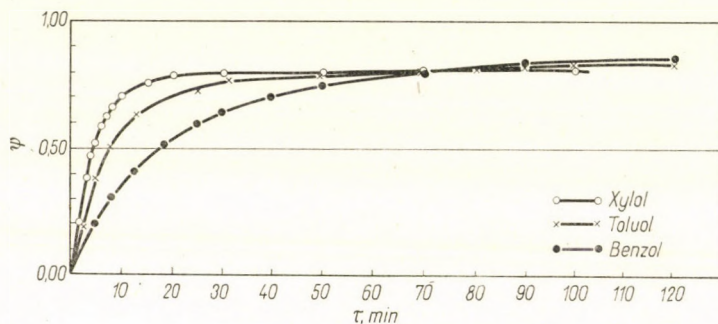


Abb. 2

Auf Grund der Resultaten scheint es, als wäre in der obigen Reihenfolge der Lösungsmittel 15%, 17% bzw. 19% des Indolins nicht dehydriert. Die Annahme, daß diese Prozente des Wasserstoffes zur Hydrierung des Lösungsmittels verbraucht wurden, liegt nahe. Ein experimenteller Beweis für die Richtigkeit dieser Annahme ergab sich aus den in Benzol bei $70^\circ (\pm 1^\circ)$ auf folgendem Grund durchgeführten Versuchen.

Die Desorption des Wasserstoffes im siedenden Reaktionsgemisch wird durch die intensive Dampfbildung derart beschleunigt, daß der an der Oberfläche des Katalysators sich bildende Wasserstoff durch den entweichenden Lösungsmitteldampf ständig abgespült wird. Demgegenüber verläuft die Desorption langsamer, wenn das Reaktionsgemisch nicht bis zum Siedepunkt erhitzt wird, und es ist auch verständlich, daß dann auch das Lösungsmittel

in größerem Maß hydriert wird. Die Resultate dieser Versuche werden durch Abb. 3 illustriert.

Die Linie 2—4—6 zeigt die Konversionen der ersten Periode von drei Versuchen, während welcher das Reaktionsgemisch (Lösungsmittel: Benzol) 2 Stunden, 4 Stunden bzw. 6 Stunden lang bei 70° gehalten wurde. Alle drei Versuche wurden so beendet, daß das Reaktionsgemisch nach der ersten Periode bis zu konstantem Gasvolumen in intensivem Sieden gehalten wurde. So ergab sich eine Konversion von 0,750 beim Versuch 2—2a, von 0,655 beim Versuch 4—4a und von 0,560 beim Versuch 6—6a. Dagegen wurde bei dem Versuch 1,

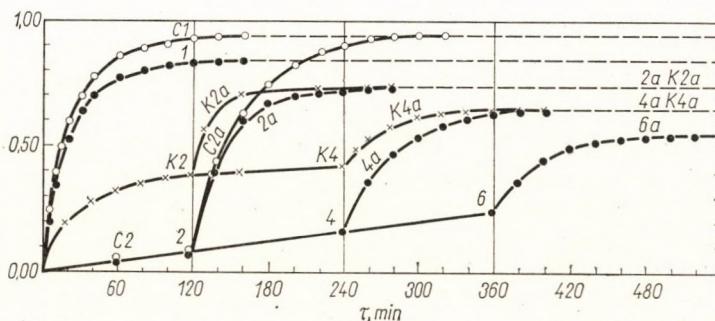


Abb. 3

wo vom Anfang bis zum Ende die Siedetemperatur gehalten wurde, eine Konversion von 0,850 erhalten.

Ähnliche Versuche wurden bei 70° so durchgeführt, daß das Reaktionsgemisch mit einem Magnetrührer in Bewegung gehalten wurde. Die Resultate werden durch die Kurven K2—K4 bzw. K2a und K4a veranschaulicht.

Aus den bei 70° in Benzol durchgeführten Versuchen folgt einerseits, daß durch Verlängerung der ersten Periode der Reaktion immer weniger Wasserstoff freigesetzt, also immer mehr Benzol hydriert wird und andererseits, daß bei 70° in Benzol die Desorption des Wasserstoffs den langsamsten Schritt der Dehydrierungsreaktion darstellt.

Als Folge der obigen Versuche wurde die Dehydrierung selbstverständlich auch in Cyclohexan durchgeführt. Es wurde eine Konversion von 0,94 erreicht, unabhängig davon, ob das Reaktionsgemisch vom Anfang bis zum Ende im Sieden oder in der ersten Periode bei 70° und dann im Sieden gehalten wurde. Die Resultate dieser Versuche zeigen die Kurven C2—C2a und C1.

Die Konversion der Dehydrierung von Indolin hat also nicht einmal in Cyclohexan den Wert von 0,94 überschritten. Um zu beweisen, daß hier schon ein Gleichgewichtszustand eingetreten ist, wurden zwei Versuche beim Siedepunkt des Cyclohexans durchgeführt, wobei zum Reaktionsgemisch auch Indol zugegeben wurde. Die Versuche sind in Tabelle II zusammengefaßt.

Tabelle II

	a	b
Indol, g	0,0769	0,1305
Indolin, g	0,1297	0,1129
Raney-Nickel, g	0,354	0,202
Cyclohexan, ml	5	5
Wasserstoff, ml, uncorr.*	26,7	22,8
Konversion im Gleichgewichtszustand% ..	89,5	87,5

* 20°C, 760,4 Torr, Partialdruck von Wasser und Cyclohexan: 17,5 bzw. 77,5 Torr.

Die Abhängigkeit der Reaktionsgeschwindigkeit von der Menge des Katalysators ist im Reziprokwert der Halbwertszeit ausgedrückt in Abb. 4 dargestellt. Diese Dehydrierungen wurden in 5 ml Cyclohexan, bei dessen Siedepunkt, mit 1 mmol Indolin und mit 0,04 g, 0,10 g, 0,16 g, 0,20 g, 0,25 g

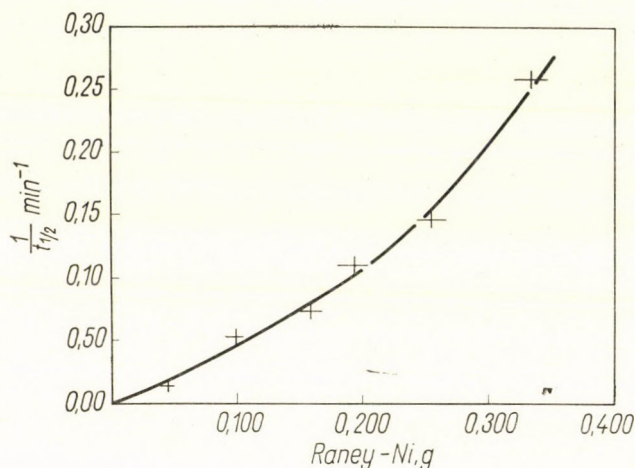


Abb. 4

bzw. 0,33 g Raney-Nickel von der Korngröße $< 0,06$ mm durchgeführt. Die Abweichung vom linearen Zusammenhang weist darauf hin, daß ein Teil des Reaktionsproduktes auf der Oberfläche des Katalysators zurückgehalten wurde.

Präparative Dehydrierung von Indolin

Das aus 2 g Indolin, 50 ml Cyclohexan und 2 g wasserfreiem Raney-Nickel bestehende Reaktionsgemisch wurde unter Rückfluß gekocht, bis in der angeschlossenen Gasbürette keine Volumenvergrößerung mehr zu beobachten war (ca. 2 Stunden). Der kristalline Rückstand der filtrierten Lösung wurde mit 5 ml Petroläther verrührt, filtriert und mit Petroläther gewaschen; 1,62 g Indol (81%).

Vergleich der Dehydrierung von Indolin und Indolinderivativen

Dehydrierung von Indolin, N-Alkyl-indolin, 6-Methoxy-, und 6-Amino-indolin. Die Versuche wurden mit 0,100 g Katalysator, von der Korngröße $< 0,06$ mm, 1 mmol Ausgangsverbindung in 5 ml Cyclohexan beim Siedepunkt desselben durchgeführt. Der zeitliche Ablauf der Reaktionen ist in Abb. 5 gezeigt. Die Konversionen beim Gleichgewichtszustand und die Halbwertszeiten sind in Tabelle III zusammengefaßt.

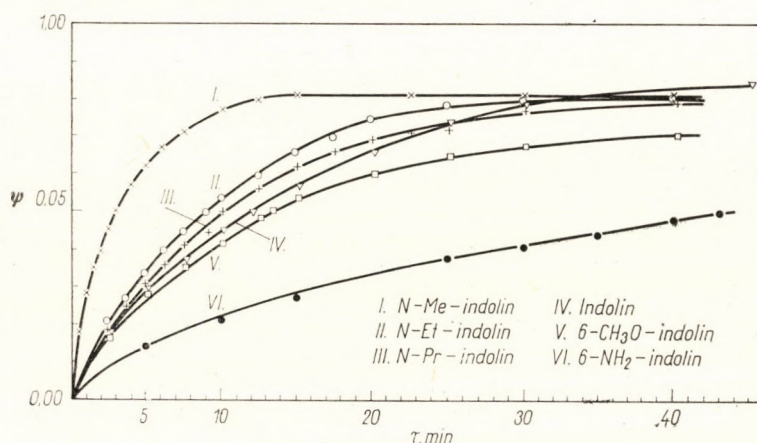


Abb. 5

Tabelle III

	ψ	Halbwertszeit Min.
Indolin	0,955	12
N-Me-indolin	0,819	3
N-Et-indolin	0,825	9
N-Pr-indolin	0,844	10
6-CH ₃ O-indolin	0,870	14

Die Dehydrierung von 6-Amino-indolin konnte wegen der schlechten Löslichkeit in Cyclohexan nur in Benzol durchgeführt werden. So wurde eine Konversion von 0,655 bzw. unter Berücksichtigung der Hydrierung des Benzols während der Dauer der Dehydrierung eine Konversion von 0,80—0,85 und eine Halbwertszeit von etwa 43 Minuten gefunden (Abb. 5, VI.).

Wir danken Frau G. MILKOVITS für die technische Hilfe.

ZUSAMMENFASSUNG

Es wurde die Dehydrierung von Indolin und Indolinderivaten untersucht und festgestellt, daß die Reaktion in Lösungsmitteln mit Raney-Nickel schon bei 70–80° mit einer für kinetische und auch für präparative Zwecke genügenden Geschwindigkeit vor sich geht. Für die zeitliche Verfolgung der Reaktion wurden eine Methode und ein Apparat beschrieben. Als Lösungsmittel diente Cyclohexan, Benzol, Toluol und Xylol. Wurden aromatische Lösungsmittel zur Dehydrierung verwendet, so wurde ein Teil des freigesetzten Wasserstoffs zur Hydrierung des Lösungsmittels verbraucht. Auf die hier beschriebene Weise wurden Indolin, N-Methyl-, N-Äthyl-, N-Propyl-, 6-Methoxy- und 6-Amino-indolin dehydriert.

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INVESTIGATION OF DEHYDROCYCLIZATION ON METAL CATALYSTS, III*

DEHYDROCYCLIZATION OF *n*-HEXANE

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Different mechanisms have been supposed for the dehydrocyclization of saturated aliphatic hydrocarbons in the presence of metal and oxide catalysts, respectively [1]. When oxide catalysts were used, unsaturated hydrocarbons were always detected among the products. These were regarded as intermediates of the aromatization on the basis of a kinetic investigation [2], while adsorption studies indicated that paraffins and olefins were adsorbed on different active centres, and suffered aromatization in parallel, independent reactions [3]. In recent publications assumptions regarding the olefins as intermediates have become predominant. When the different adsorption strengths of paraffins and olefins were taken into account, a kinetic equation in good agreement with the experimental data was obtained [4]. Using metal catalysts, however, no olefins were detected among the reaction products; in fact, it was found that introduction of olefins resulted in the complete deactivation of the catalyst [5]. Therefore, in this case a direct conversion paraffin $\rightarrow$ naphthene was supposed. The detection of 1,1-dimethylcyclohexane in the products of aromatization of 3,3-dimethylhexane served as direct experimental evidence for this assumption: it was supposed that the aromatization of this cycloparaffinic compound, as it must involve demethylation, was of necessity a comparatively slow reaction step, thus accounting for the accumulation of this intermediate [6].

According to both assumptions (directly from paraffins or through olefins), the production of an aromatic hydrocarbon is preceded by the formation of a cyclohexanic precursor; the latter may also come into existence by isomerization of a primary product having other than six-membered ring. The final step is dehydrogenation to benzene which occurs according to dublet mechanism in case of an oxide catalyst and by sextet mechanism in the presence of a metal catalyst [7].

It may be argued, however, that the two mechanisms observed are due to the different experimental conditions used with the two types of catalysts:

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in case of oxide catalysts dehydrocyclization occurred in the 450–550° temperature range, while metal catalysts were employed at about 300°. The reaction sequence paraffin → olefin → naphthene was also supposed in the course of the so-called catalytic reforming process carried out at about 500° under hydrogen pressure in the presence of platinum-alumina catalysts [8]. Thermodynamical and sorption conditions are unfavourable for olefins to appear in the gaseous phase at lower temperatures; at the same time, however, sextet mechanism was supposed as the only possible reaction path of dehydrocyclization in the 300–350° temperature range.

Some recent experimental results and theoretical considerations necessitated to revise critically the above-mentioned assumptions. On the one hand, it has been shown that on oxide catalysts a stepwise dehydrocyclization takes place with subsequent formation of olefinic, diolefinic and triolefinic intermediates finally concluded by cyclization [9]. On the other hand, experiments carried out in our laboratory have revealed that cyclohexene is an intermediate also in the course of cyclohexane dehydrogenation on metal catalysts, and this product can be desorbed from the catalyst under the experimental conditions employed [10]. These experiments have shown that the process of cyclohexane dehydrogenation on a metal catalyst cannot be described by the LANGMUIR—HINSHELWOOD kinetics, because the rates of certain sorption processes are commensurable with the rate of the surface reaction [11]. Using the pulse technique, intermediates with unsaturated rings — cyclohexene and cyclohexadiene — could also directly be detected [12].

It has been reported in previous publications that olefins could be aromatized in the presence of metal catalysts, when dienic intermediates were formed [13, 14]; thus the mechanism of the reaction is identical with that observed over oxide catalysts. These facts have suggested that the possibility of an identical dehydrocyclization mechanism in the presence of metal as well as oxide catalysts cannot be precluded, and different product compositions may be explained with the different experimental conditions, different rates and energy barriers of the individual (reaction and sorption) steps.

Therefore, we thought reasonable to investigate the mechanism of the dehydrocyclization of paraffins on metal catalysts taking the above-mentioned considerations into account.

In the present stage of the experiments we studied mainly the possibility of formation of unsaturated products, *i. e.* the possible conversion of paraffins into olefins.

Experimental

The experiments were carried out using a pulse technique apparatus similar to that described previously [13]. The reactions were studied both in helium and hydrogen carrier gas in the 300–510° temperature range. In addition to pure metallic nickel and platinum [14] and nickel-on-alumina [13], described previously, two types of industrial platinum catalyst

on alumina carrier were employed (Soviet catalyst AP-56: Pt: 0.523%, spec. surface: 165 m²/g; and SINCLAIR-BAKER catalyst RD-150-C: Pt: 0.355%, spec. surface: 312 m²/g). Our method provided a more sensitive detection possibility of the reaction products than the conventional techniques; moreover radioactive tracer studies were also carried out to investigate the reaction path and potential intermediates, so that our apparatus had to be made suitable for measuring radioactivity, too. It was not possible to employ a usual proportional flow counter, because the presence of the helium carrier gas adversely influenced the counting characteristics of the tube. Therefore, absorbing traps were connected into the gas line after the conductivity cell, and the individual components indicated by their chromatographic peaks were trapped in toluene cooled in dry ice-acetone. The radioactivity of the fractions was determined by means of a Packard Tri-Carb Liquid Scintillator. The absolute activities were calculated by using a calibrated channel ratio method [22]. Specific activity was defined as the ratio of the disintegration rate and the chromatographic peak area. The starting hydro-

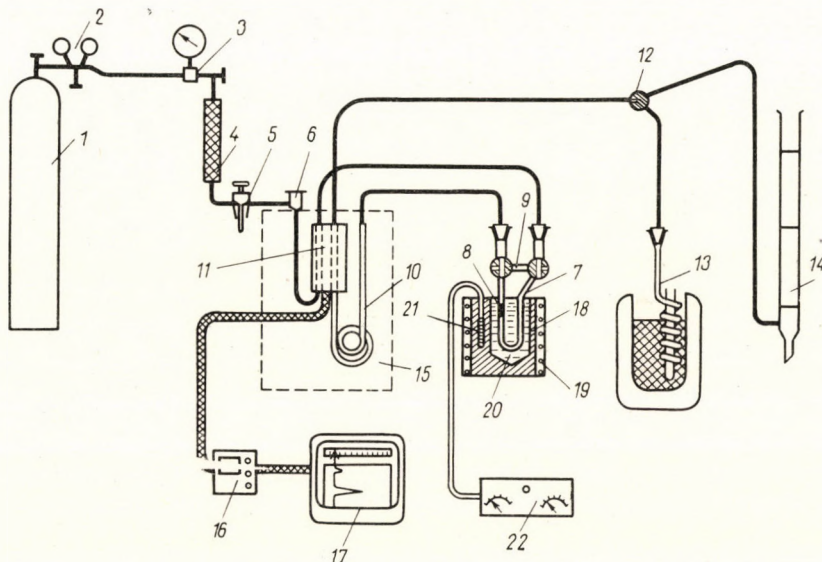


Fig. 1. Diagram of a pulse apparatus for radioactive experiments. 1 — cylinder containing the carrier gas, 2 — pressure reducing valve, type "Precisor", 3 — manometer with throttle valve, 4 — deoxygenator and drier, 5 — stopcock for introducing hydrogen, 6 — sample introduction (heated), 7 — reactor, with stopcocks (packed with quartz), 8 — catalyst bed, 9 — by-pass (for analysis), 10 — separating column, 11 — thermal conductivity cell, 12 — three-way stopcock, 13 — trap to collect fractions in Dewar flask containing dry ice, 14 — soap film flow meter, 15 — ultrathermostat, 16 — bridge of thermal conductivity cell, 17 — recorder (EPP-09; 0-10 mV), 18 — iron furnace block, 19 — electric resistance heating, 20 — molten tin bath, with mercury thermometer (not indicated), 21 — platinum resistance thermometer for temperature regulation, 22 — temperature regulator

carbon mixtures were passed through the system also by-passing the reactor, and the fractions corresponding to those of the final products were collected. So differences in the specific activities before and after the reaction could be evaluated, and errors owing to deviations in the experimental conditions ("tailing" of peaks, radiochemical impurities, imperfect separations, etc.) were possibly minimized.

The diagram of the apparatus suitable for performing radioactive measurements is shown in Fig. 1.

Hexene-1 labelled with ¹⁴C was synthesized from *n*-hexanol-1-¹⁴C* by dehydration over Al₂O₃ catalyst at 370° in nitrogen carrier gas [15]. The crude product was purified by displace-

* Radioactive *n*-hexanol was synthesized by reacting *n*-amylmagnesium bromide with ¹⁴CO₂ and subsequent reduction of the obtained *n*-hexanoic acid-1-¹⁴C by means of LiAlH₄ [16]. The authors are indebted to Mr. B. TANÁCS for kindly accomplishing this.

ment chromatography on silica gel. Pure *n*-hexene-1-(1-¹⁴C) was hydrogenated in a flow reactor at 185° in the presence of nickel metal catalyst prepared by the reduction of nickel hydroxide. Recirculation (two passes) gave a product containing practically no hexene and less than 1% of *n*-pentane and *n*-heptane.

The specific radioactivity of *n*-hexane obtained was 0.56 mC/g; it was diluted with about 4 volumes of inactive *n*-hexane when used.

Investigations concerning the course of the reaction

Saturated hydrocarbons were dehydrocyclized in the presence of our catalysts to an extent commensurable with the reaction of unsaturated hydrocarbons. Using 0.1–1 g of the catalysts, the yields of benzene were between 0.1 and 10%. With the two types of nickel catalysts, the dehydrocyclization reaction could be followed in the 300–400° temperature range, since at higher temperatures cracking reactions consumed the greatest part of the starting material. Using a platinum catalyst, cracking was less expressed and the reactions could be followed up to 510° (the upper temperature limit allowed by the apparatus used).

The product contained unsaturated compounds besides benzene and fragments from cracking. In the presence of the nickel catalysts, the amount of hexenes hardly surpassed the limit of detection (0.1%) while on platinum 0.5–2.5% of hexene and, at temperatures above 450°, trace amounts of conjugated hexadienes were also observed.

Using platinum-alumina catalyst and helium as the carrier gas, the product composition observed was identical with that detected with carrier-free platinum catalyst. The only difference was the greater quantity (several tenths of a per cent) of conjugated dienes. This result is obviously due to differences in the sorption conditions; platinum finely dispersed on the carrier may provide less possibility for dienic compounds to react by irreversible intermolecular surface processes resulting in the formation of coke; furthermore molecules once desorbed from the surface have less probability to reach the surface of a platinum particle possessing dehydrocyclizing activity.

In the presence of platinum metal and hydrogen carrier gas, hexene-1 was hydrogenated at 360° quantitatively to hexane [14]. When hexane was introduced, no reaction could be detected below 375°. Above this value the rate of aromatization both on platinum and platinum-on-carrier catalysts increased with increasing temperature. The product compositions resulting from dehydrocyclization reactions in hydrogen and helium are shown in Table I. It is seen that using hydrogen as the carrier gas, the extent of aromatization above 400° is larger than in the presence of helium, accompanied, however, by a simultaneous but even larger increase of the amount of cracking products. The quantity of hexenes in hydrogen carrier gas is also greater than in helium, and at higher temperature hexadienes could be detected as well.

Table I

Composition of the dehydrocyclization products of hexane in the presence of different carrier gases

Catalyst: 0.16 g Pt; Carrier gas: 55 NTP ml/min. of He or H₂; Charge: 5 μ l doses of hexane

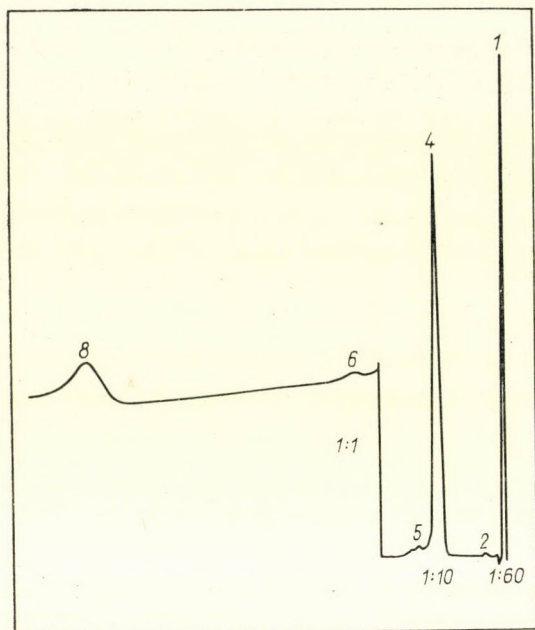
t, °C	Carrier gas	Product composition, % (w/w)					
		Cracking products	Iso-hexanes	n-hexane	hexenes	hexadienes	benzene
300	He	0.5	—	98.4	—	—	1.1
330	He	0.7	—	97.8	—	—	1.5
360	He	1.3	—	96.4	—	—	2.3
	H ₂	0.3	—	99.2	0.5	—	—
390	He	2.0	—	94.9	0.1	—	3.0
	H ₂	2.7	1.5	93.5	1.5	—	0.8
420	He	2.0	—	93.8	0.1	traces	4.1
	H ₂	11.9	3.4	75.1	2.0	0.1	7.5
450	He	2.8	—	92.4	0.1	0.1	4.6
	H ₂	25.4	2.8	52.4	2.5	0.2	16.8
480	He	3.6	—	89.6	0.1	0.1	7.8
	H ₂	21.5	2.2	54.0	4.5	0.5	17.2
510	He	4.3	—	86.8	0.1	0.1	8.7
	H ₂	14.2	1.2	58.2	6.5	2.1	17.8

Note: In the experiments with helium carrier gas the catalyst was regenerated at the temperature of the experiment by introducing about 5 ml of air and 4 ml of H₂. In the measurements with hydrogen carrier gas the catalyst was immersed for regeneration into a bath of 400°, helium was passed through it, and after injecting 5 ml of air it was heated again to the temperature of the experiment in a stream of hydrogen.

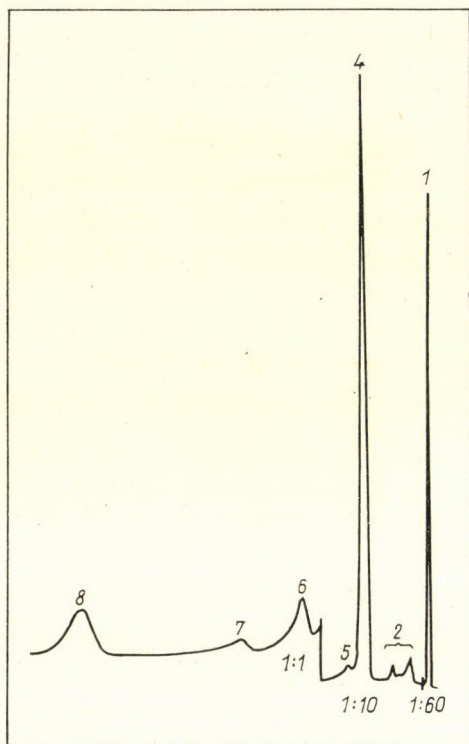
In Fig. 2 the chromatograms obtained under different experimental conditions are compared. It can be seen that variations in the experimental conditions cause no qualitative but only quantitative deviations, the only difference being a slight skeletal isomerization observed in hydrogen.

When nickel catalyst and hydrogen carrier gas were used, aromatization was not observed; the starting materials were converted into lower hydrocarbons in practically quantitative yield.

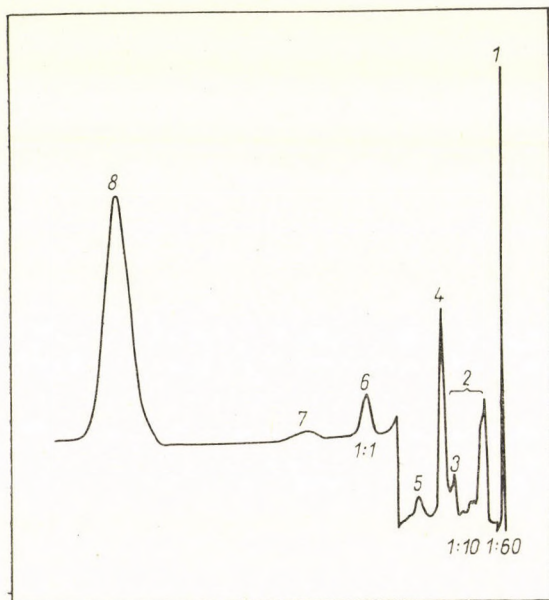
The apparent activation energies of the reactions leading to benzene were determined on the catalysts employed, assuming the rate constants to be proportional to the conversions (Fig. 3). In helium carrier gas, the apparent activation energies in the presence of carrier-free platinum and platinum-on-alumina are practically the same; these values are in good agreement with those obtained for hexene dehydrocyclization in the presence of platinum or nickel catalysts [14].



a)



b)



c)

Fig. 2. Chromatograms of *n*-hexane dehydrocyclization carried out under different conditions. a) $t = 360^\circ\text{C}$; catalyst: 0.76 g Pt; carrier gas: helium; b) $t = 390^\circ\text{C}$; catalyst: 0.44 g RD-150-C; carrier gas: hydrogen; c) $t = 390^\circ\text{C}$ catalyst: 0.44 g RD-150-C; carrier gas: hydrogen. Peaks on chromatograms: 1 — sample injection (appr. 4 μl of *n*-hexane), 2 — cracking products ($\text{C}_1 - \text{C}_5$), 3 — isohexanes, 4 — *n*-hexane, 5 — hexenes, 6 — hexadiene-1,3, 7 — hexadiene-2,4 isomers, 8 — benzene

In case of dehydrocyclization on platinum-on-alumina catalyst in hydrogen atmosphere, the apparent activation energy was about three times higher than that determined in helium. Using pure platinum metal, the activation energy seemed to be still higher between 390 and 450°; above this temperature no straight ARRHENIUS plot was obtained, because no further improvement in the yield with increasing temperature could be observed. This may be due

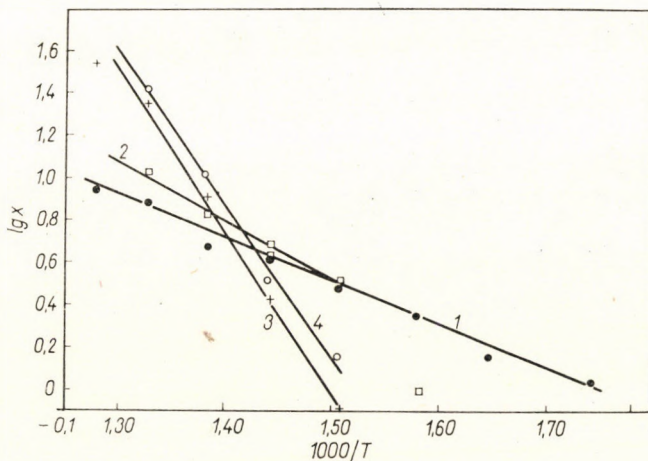


Fig. 3. Apparent activation energies of the dehydrocyclization of *n*-hexane over different metal catalysts

No. of straight lines	Catalyst	Carrier gas	Apparent activation energy, kcal/mole
1	0.16 g platinum	helium	10
2	0.44 g RD-150-C	helium	11.4
3	0.44 g RD-150-C	hydrogen	34
4	0.45 g AP-56	hydrogen	33
5	0.1 g Ni/Al ₂ O ₃	helium	22.4

partly to the fact that the reaction has got in the range of diffusion hindrance, and partly to an increased rate of the rapid hydrocracking reactions effectively concurring with the multistep dehydrocyclization reaction requiring favourable adsorption and being therefore a slower process.

In the experiments with hexane, the deactivation of the catalyst was slower but commensurable to that observed in the case of hexene starting material [14]. To maintain a standard activity level, the platinum catalyst was regenerated with air and hydrogen pulses before injecting the hydrocarbons. As the temperature increased, the activity became considerably more stable; at 480°, the rate of decrease of the activity was approximately by one order

of magnitude smaller than at 360°. The activity of nickel catalysts, both with and without carrier, was more unstable than found in the case of hexene dehydrocyclization; it decreased noticeably in the course of one experiment in spite of regeneration with hydrogen. Large deviations were experienced in the formation of toluene and in the occurrence of demethylation in the aromatization of *n*-heptane over nickel-on-alumina, depending on the previous use of the catalyst; this fact prevented the determination of the apparent activation energy in this case.

Investigations with radioactive tracers

The fact that the reaction paraffin $\rightarrow$ olefin takes actually place is in contrast with the views expressed so far, and regarded as proved, concerning the dehydrocyclization reaction of paraffins in the presence of metal catalysts, [1, 6]; therefore, the occurrence of this reaction had to be supported by additional evidence. For this purpose, investigations with radioactive tracers have been carried out.

The so-called kinetic isotope method has been recommended for the investigation of mechanisms of chemical reactions [23]. In this method, a small amount of the supposed intermediate is admixed to the starting material labelled with a radioactive tracer, and its specific activity is measured in the course of the reaction. In our investigations a mixture of radioactive *n*-hexane-1-¹⁴C and inactive *n*-hexene-1 was subjected to the dehydrocyclization reaction. Quantitative evaluations of the reaction rates could not be accomplished because the space velocity is defined uncertainly in our transient system. Furthermore, if LANGMUIR—HINSHELWOOD kinetics cannot be applied — and we have good reasons to make this assumption [12] — the appearance of radioactivity in the supposed intermediate is determined by the resultant of the rates of the reaction and sorption steps. If in our case, *e. g.*, the desorption of hexenes can be regarded as a relatively slow process as compared with its further aromatization, the specific radioactivity of adsorbed hexene may exactly correspond to the theoretical value resulting from the formation and decomposition rates, but the radioactivity of hexenes in the gaseous phase will be less than this actual value. Of course, the former cannot be directly determined.

The results of our tracer investigations are presented in Tables II and III. In each case an increase in the specific activity of the hexene-fraction was observed, and radioactivity could also be detected in the hexadiene fraction. In case of low overall conversions, the hexene originally added to the starting material diluted the produced radioactive hexenes to a considerable extent, but as the overall conversions increased, a simultaneous rise in the transition of radioactivity into the hexenes could be observed, independently

Table II

Dehydrocyclization of mixtures of n-hexane-(1-¹⁴C) and inactive n-hexene-1 on platinum catalysts

(a) Carrier gas; 55 NTP ml/min. of helium

No.	Weight of Pt g	t, °C	Fraction												Ratio of specific activities (starting hexane and ben- zene fractions)
			hexane			hexene			hexadienes ¹			benzene			
			peak area mm ²	activity tpm	spec. activity tpm/mm ²	peak area mm ²	activity tpm	spec. activity tpm/mm ²	peak area mm ²	activity tpm	spec. activity tpm/mm ²	peak area mm ²	activity tpm	spec. activity tpm/mm ²	
Starting mixture	—	—	2450	270 990	111	1300	6 575	5.1	—	5970	—				
1222	0.76	360	10440	990 320	95	2970	89 110	33.5	200	8000	40 ²	728	24 570	34	3.3
1223	0.76	360	8310	821 900	99	1940	69 100	35.5	140	8500	60 ²	640	23 900	37.5	3.0
Starting mixture	—	—	2680	101 000	38	5880	24 400	4.0	—	—	—				
			2280	88 460	38.5	5200	20 400	3.9	—	—	—				
1854	0.16	360	1530	52 520	34.5	2640	12 200	4.6	—	—	—	115	1 580	14	2.8
1857	0.16	420	1320	47 960	36.5	1780	8 800	4.9	—	—	—	210	1 840	9	4.3
1859	0.16	480	820	28 600	35	960	5 650	6	—	—	—	410	3 510	9	4.3

(b) Carrier gas; 55 NTP ml/min. of hydrogen

Starting mixture	—	—	670	38 260	57	1500	6 710	4.4	—	1200	—				
	—	—	1890	100 000	53	3920	18 800	4.7	25	4500	180 ³				
1860	0.16	480	1950	70 400	36	880	14 840	17	35	1670	21 ²	850	14 300	17	3.1
1861	0.16	480	3520	116 700	33	1500	18 800	12.5	175	2500	14 ²	725	7 550	10.5	5.2
1862	0.16	480	1000	37 460	37.5	360	5 870	16.5	50	700	12 ²	300	3 500	11.5	4.8

¹ Approximate values² Corrected taking into account the radiochemical impurity consisting of *n*-heptane³ *n*-heptane

Table III

Dehydrocyclization of a mixture of n-hexane-(1-¹⁴C) and inactive n-hexene-1 on nickel-alumina catalyst

Catalyst: 0.35 g Ni/Al₂O₃; carrier gas: 55 NTP ml/min. of helium; *t* = 360 °C

No.	Fraction									Ratio of specific activities (starting hexane and benzene fractions)
	hexane			hexene			benzene			
	peak area mm ²	activity tpm	spec. activity tpm/mm ²	peak area mm ²	activity tpm	spec. activity tpm/mm ²	peak area mm ²	activity tpm	spec. activity tpm/mm ²	
Starting material	2 310	95 800	41.5	4 320	12 470	2.9				
	3 200	137 750	43.0	6 000	16 550	2.7				
1356	14 700	481 780	34.0	16 820	44 580	2.6	330	2800	8.5	5.0
1357	5 220	184 840	35.5	4 075	16 420	4.0	217	883	4.1	10
1349	3 800	140 400	37.0	3 020	12 860	4.2	110	900	8.2	5.1
1348	2 720	98 630	36.5	1 890	9 110	4.8	140	650	4.6	9.1
1351	710	23 710	33.4	70	2 600	38	75	1280	17	2.5

of the fact whether the higher conversion was obtained using a larger amount of catalyst, or higher temperature, or hydrogen carrier gas. It should be noted that the experimental error in determining the specific radioactivity of the hexadiene fraction was higher than with the other fractions owing to its smaller absolute quantity causing a larger relative inaccuracy, furthermore, the separation of the radiochemical impurity of about 0.5% heptane from the starting hexane could not always be achieved perfectly. Therefore no quantitative conclusions can be drawn on the basis of the radioactivity of hexadienes; the data in Table II are shown for informative purposes only.

Nickel-on-alumina possessing higher and more stable activity was used as the nickel catalyst in these investigations. A smaller transition of the radioactivity into hexene as well as into benzene was found with this catalyst, as compared with platinum. However, the specific activity in both fractions increased when the overall conversions were higher. The close values of the specific activities of hexene and benzene have indicated that the desorption rates of these two compounds are either of the same order of magnitude, or even the rate of the slower process does not affect the overall rate of the dehydrocyclization.

Discussion

Our results indicate that unsaturated open-chain hydrocarbons are formed during the dehydrocyclization of saturated hydrocarbons also in the presence of metal catalysts. This fact is not influenced by different conditions

of the reaction (such as variation of temperature, the presence or absence of catalyst carrier, the use of helium or hydrogen carrier gas, *etc.*). The concentration of unsaturated compounds in the product is jointly determined by the rates of the sorption processes and surface reactions; the variation of the reaction parameters affects only the relative rates of the part-processes. In previous experiments it has been shown [13, 14] that the unsaturated compounds produced may themselves undergo aromatization under the experimental conditions employed; therefore their formation does not mean a dead-end of the reaction, and they may be regarded as intermediates.

Differences observed in the dehydrocyclization rates of the saturated and various unsaturated products are presented in Table IV.* These differences

Table IV

A comparison of the dehydrocyclization of hydrocarbons of various unsaturation
 $t = 360^\circ\text{C}$; carrier gas: 55 NTP ml/min. of helium

Catalysts: 0.76 g Pt (9.1 m²/g); 0.59 g Ni (3.5 m²/g); 0.35 g Ni/Al₂O₃ (266 m²/g)

Starting hydrocarbon	Relative amount (weight-% of the catalysate)			Absolute amount μg			Specific value $\mu\text{g}/\text{m}^2$ catalyst surface		
	of benzene formation								
	on: Pt	Ni	Ni/Al ₂ O ₃	Pt	Ni	Ni/Al ₂ O ₃	Pt	Ni	Ni/Al ₂ O ₃
<i>n</i> -hexane	5.8	0.07	2.2	150	1.7	60	22	0.85	0.66
hexene-1	7.4	0.8	3.3	190	15	72	28	7.5	0.80
hexene-2	6.4	0.7	2.6	185	17	57	27	8.5	0.63
mixture of hexadienes ¹ . .	9.1	3.1	10	215	43	195	31	21	2.2

¹ Product obtained by deacetylation of 4-acetoxyhexene-1; composition: 0.3% hexane, 1.5% hexene, 20.2% hexadiene-1,4, 50.0% hexadiene-1,3, 24.8% isomeric hexadienes-2,4, 3.1% *iso*-hexadienes.

may be explained by the necessity of dissociative adsorption as a primary step of the dehydrocyclization of saturated hydrocarbons [2, 12], which is a rather slow, more or less hindered step. In case of platinum but a small difference is found between the rates of benzene formation from *n*-hexane and unsaturated hydrocarbons, while with nickel catalyst the dehydrocyclization of hexane is by almost an order of magnitude slower than that of the corresponding olefins. Nickel-on-alumina takes an intermediate position. The same result can be obtained by comparing the specific radioactivities of the benzene

* These data were obtained by comparing benzene yields directly. The values are characteristic of a certain activity level of the catalysts; they are consistent concerning different starting materials on the same catalyst, but the absolute activities of different catalysts can be hardly compared on this basis.

fractions, formed in dehydrocyclizing a mixture of radioactive hexane and inactive hexene, with those of the starting *n*-hexane fractions (Tables II and III); this ratio is in direct proportion to the dehydrocyclization rates of the hexane and hexene, respectively. Unsaturated hydrocarbons were aromatized in the presence of nickel catalyst even if the catalytic activity was insufficient to dehydrocyclize saturated ones. This phenomenon seems to be connected with the repeated heating and cooling of the catalyst causing presumably irreversible modifications of the surface resulting in an increased hindrance of the dissociative adsorption of hexane.

Differences in the dehydrocyclization rates of compounds of various degrees of unsaturation have been found to be considerably less than those observed in case of the dehydrogenation of cyclic hydrocarbons [12, 20, 21]. Thus, on the basis of a mere comparison of the individual reaction rates, no part-process can be precluded from among the rate-determining steps, in contrast to the case of cyclic hydrocarbons.

The presence of hydrogen seems to be necessary on the catalyst surface in order to activate it for the dehydrocyclization to occur. A hydrogen atmosphere did not alter the observed mechanism. Below a certain temperature limit (about 375°), however, a partial hydrogen pressure of about 1 atm. is in equilibrium with such an amount of surface hydrogen which prevents the chemisorption of the hydrocarbons leading to reaction. A similar effect has been reported in connection with the chemisorption of ethane near to room temperature [17]; our results indicate that the analogous phenomenon may occur at elevated temperatures as well. The constancy of the apparent activation energy in helium atmosphere throughout the investigated temperature range suggests that there is no qualitative change either in the adsorption conditions of the hydrogen necessary for catalyst regeneration in helium atmosphere, or in the overall reaction mechanism. Different methods of regeneration (using a constant hydrogen flow replacing helium, or injecting pulses of a few ml of hydrogen) were practically equivalent, indicating that about 1 ml of hydrogen per 1 g of Pt was required to restore catalyst activity. This quantity is of the same order of magnitude as the amount of chemisorbed hydrogen at 250° reported in the literature [18]. Some of the chemisorbed hydrogen is consumed during the reactions; literature data also show an unambiguous parallelism between chemisorptivity and catalytic activity [18, 19].

In hydrogen atmosphere, an abundant amount of hydrogen is supplied by the gaseous phase, which accelerates dehydrocyclization as well as other reactions, such as hydrogenation, hydrocracking, *etc.* The function of a carrier in cases of industrial catalysts is an addition to increasing the dispersity of platinum and serving as an isomerizing catalyst, just to absorb a lot of hydrogen over its large surface, and to ensure thus a high hydrogen concentration in the neighbourhood of the metal particles.

Summarizing the experimental results, it can be stated that in the course of hexene aromatization in the presence of both platinum and nickel catalysts, unsaturated open-chain hydrocarbons — hexenes, and in certain cases hexadienes — are formed. Our previous results have shown [13, 14] that these products can also be dehydrocyclized, so they are certainly intermediates of the reaction. Hydrogen atmosphere has no considerable influence on the reaction mechanism. Our results suggest that the assumption of a stepwise dehydrocyclization *via* unsaturated intermediates can be extended to the case of metal catalysts, too. This assumption does not involve, however, that exclusively this reaction path is in operation. Further investigations are necessary to decide the ratio of aromatics formed through the stepwise dehydrocyclization, and by the reaction path *via* cyclohexane intermediate generally accepted up to now.

*

Authors are indebted to Dr. T. SZARVAS for kindly accomplishing radioactivity measurements.

SUMMARY

The dehydrocyclization reaction of *n*-hexane has been investigated in the presence of platinum and nickel catalysts, used both as carrier-free metals and on alumina carrier. The dehydrocyclization can be followed between 300 and 500° in the case of platinum catalyst, while in the presence of nickel cracking reactions become predominant above 400°. No change in the reaction path has been observed throughout the temperature range studied. Unsaturated compounds — hexenes and hexadienes — have been detected among the reaction products. The present results together with previous ones indicate that these compounds are intermediates of the dehydrocyclization of hexane. The reaction sequence hexane → hexenes → hexadienes → benzene has also been verified by using radioactive tracer technique. The apparent activation energy of hexane dehydrocyclization was determined; only a minor difference from the activation energy of the dehydrocyclization of hexene has been found. An acceleration of the dehydrocyclization reaction in hydrogen atmosphere has also been demonstrated; the character of the intermediates was not influenced by the presence of hydrogen.

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DIE THERMISCHE ANALYSE DER IN DEN HERSTELLUNGSPROZESSEN DER FUNGICIDE CAPTAN UND FALTAN VORKOMMENDEN ORGANISCHEN SYSTEME, I

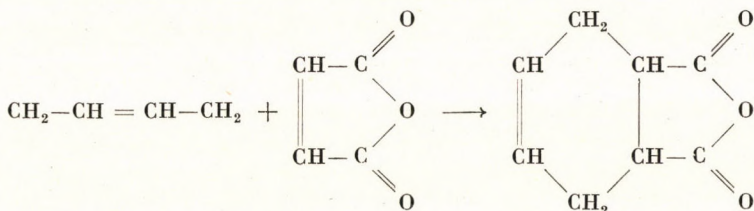
THERMISCHE ANALYSE VON MALEINSÄUREANHYDRID- UND
TETRAHYDROPHTHALSÄUREANHYDRID-GEMISCHEN

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Eines der Nebenprodukte der Äthylenherstellung durch Benzinpyrolyse ist die Butadien, Iso- und Normalbuten sowie Butan enthaltende sog. C₄-Fraktion. Vorbedingung der wirtschaftlichen Äthylenproduktion ist die Verwertung der Nebenprodukte. Zur Verwertung des Butadiens wird dieses mit Maleinsäureanhydrid zu Tetrahydrophthalsäureanhydrid umgesetzt.



Aus diesem wird durch Ammonolyse Tetrahydrophthalimid erhalten. Das Tetrahydrophthalimid wird in natriumhydroxydhaltigem Medium mit Perchlormethylmercaptan gekuppelt, wobei Perchlormethylmercaptotetrahydrophthalimid, d. i. Captan, entsteht.

In der Captan-Herstellung liegen Maleinsäureanhydrid, die Zwischenprodukte (Tetrahydrophthalsäureanhydrid, Tetrahydrophthalimid) sowie das Captan in festem Aggregatzustand vor. Da sich der Derivatograph vor allem zum Studium physikalischer und chemischer Eigenschaften von Feststoffen eignet, lag der Gedanke nahe, die Reinheit sowie die thermischen Verhalten der erwähnten Produkte derivatographisch zu untersuchen.

Die vorliegende Arbeit befaßt sich mit der derivatographischen Analyse des reinen Maleinsäureanhydrids und Tetrahydrophthalsäureanhydrids sowie ihrer Gemische und behandelt das Phasendiagramm dieses binären Systems.

Die thermische Analyse (Differentialthermoanalyse, Thermogravimetrie) wird seit geraumer Zeit sehr ausgedehnt zur Untersuchung anorganischer Ver-

bindungen verwendet. In den letzten 10 Jahren erschienen zahlreiche Publikationen, die sich vor allem mit der thermischen Analyse von Kohlen und Polymeren befassen und einige die die thermische Analyse von anderen organischen Verbindungen zum Gegenstand hatten. So bestimmten VASALLO und HARDEN [1] den Schmelzpunkt und den Siedepunkt von Normalparaffinen und Benzoesäure mit einem DTA-Apparat, wobei verschiedene Aufheizungsgeschwindigkeiten und Thermolemente verschiedener Qualität verwendet wurden. Mit Hilfe der Differentialthermoanalyse untersuchten D. COSTA und G. COSTA [2] die Reinheit von Benzoesäure, Naphthalin und Cellulose, BARRAL und ROGERS [3] das thermische Verhalten von Salicylsäure, CHESTERS und THOMSON [4] die Polysaccharide, MORITA und RICE [5] Benzol, Toluol und verschiedene hochmolekulare Stoffe, WENDLANDT und HOIBERG [6] organische Säuren.

Es erschienen auch mehrere Arbeiten die sich mit der Derivatographie organischer Verbindungen befassen. ERDEY, PAULIK und LIPTAY [7] untersuchten die Zerlegung von Kaliumhydrogen-phthalat, LIPTAY und Mitarbeiter [8] die der Sterole, und SOLYMÁR und Mitarbeiter [9] bestimmten die organischen Bestandteile von Aluminatlaugen auf derivatographischem Wege. Auch in unserem Institut wurde die Derivatographie wiederholt zur Analyse von organischen Stoffen verwendet. So befaßten wir uns mit der Derivatographie von Aldrin und Dieldrin [10] und verschiedenen Metallalkoxydverbindungen [11], ferner mit der derivatographischen Analyse der thermischen Disproportionierung von Kaliumbenzoat [12].

Die lange Reihe der Publikationen, die sich mit den Phasendiagrammen organischer Systeme befassen, kann im Rahmen dieser Arbeit nicht ausführlich besprochen werden. Wir verweisen deshalb auf das Handbuch von LANDOLT-BÖRNSTEIN [13], wo Phasendiagramme verschiedener organischer Systeme und die bezügliche Literatur angegeben sind.

Von den thermischen Daten der in der vorliegenden Arbeit untersuchten Verbindungen sind Schmelzpunkt (52,8 °C) und Siedepunkt (199,9 °C) [14] sowie Schmelzwärme (2,75 kcal Mol) [15] des Maleinsäureanhydrids, ferner der Schmelzpunkt (104 °C) [16] des Tetrahydrophthalsäureanhydrids bekannt. In einer allgemeinen Übersicht der Literatur berichtet BUCKLES [17] über einige thermische Eigenschaften des Tetrahydrophthalsäureanhydrids. Danach entweicht beim Erwärmen Kohlendioxyd aus der Substanz, wobei sich polymere Stoffe bilden.

Experimenteller Teil

Die derivatographischen Untersuchungen wurden mit einem Derivatograph, System PAULIK—PAULIK—ERDEY [18], Modell MOM durchgeführt.

Als erster Schritt unserer Arbeit wurden bei verschiedenen Aufheizungsgeschwindigkeiten (8, 6 und 5 °C/min) Derivatogramme des Maleinsäureanhydrids, Tetrahydrophthalsäureanhydrids und ihrer Gemische verschiedener Zusammensetzungen zur Feststellung der günstigsten Versuchsbedingungen aufgenommen. Auf Grund dieser Messungen wählten wir

für unsere weiteren Versuche eine Aufheizungs-geschwindigkeit von $5^\circ\text{C}/\text{min}$, da sich die einzelnen Vorgänge bei kleineren Aufheizungs-geschwindigkeiten schärfer voneinander abgrenzen. Eine noch langsamere Aufheizung würde jedoch die Dauer der Messungen sehr verlängern. Die Untersuchungen wurden in Gegenwart von Luft durchgeführt, wobei die durch Verdampfung entstandenen gasförmigen Produkte mit einer Wasserstrahlpumpe aus dem Reaktionsraum abgesaugt wurden. Die Einwaage betrug bei allen Versuchen 270 mg, die Empfindlichkeit der Waage 500 mg, die Empfindlichkeit des DTA- und DTG-Galvanometers $1/10$. Bei der Bestimmung der Schmelzwärme der einzelnen Komponenten aus der DTA-Kurve wurde zur Kalibration $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ verwendet [19].

Gleichzeitig mit der derivatographischen Analyse wurden auch die Abkühlungskurven der Maleinsäureanhydrid-Tetrahydrophthalsäureanhydrid-Gemische verschiedener Zusammensetzungen aufgenommen. Die zu untersuchende Substanz wurde in einer Proberöhre geschmolzen, sodann in einen geschlossenen Raum gebracht und die Abkühlung der Probe durch Ablesung der Temperatur in Zeitabständen von 30 sec. verfolgt. Aus der Abkühlungskurve wurde das Phasendiagramm des Systems auf die übliche Weise dargestellt [20].

Diskussion der Versuchsergebnisse

Abb. 1 zeigt das Derivatogramm des Maleinsäureanhydrids. Die Spitze an der DTA-Kurve bei 50°C zeigt das Schmelzen der Verbindung an. Aus der zu dieser Spitze gehörenden Fläche wurde nach entsprechender Kalibrierung die Schmelzwärme der Verbindung bestimmt, für die sich $2,8 \text{ kcal/Mol}$ ergaben. Nach dem Schmelzen beginnt die Verdampfung der Verbindung, die laut der

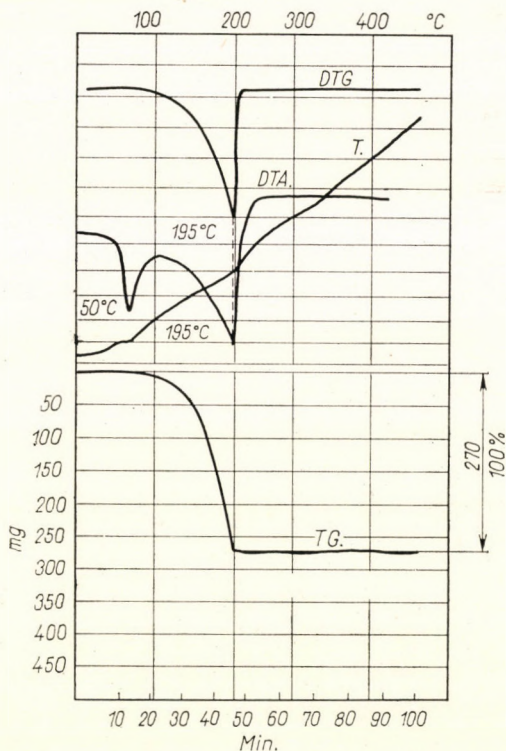


Abb. 1. Derivatogramm von Maleinsäureanhydrid

DTG-Kurve bei 195 °C mit maximaler Geschwindigkeit verläuft. Innerhalb der experimentellen Fehlergrenzen stimmen die vom Derivatogramm ablesbaren Werte für Schmelzpunkt, Siedepunkt und Schmelzwärme mit den bisher bekannten Werten [14, 15] gut überein.

Wie aus dem Derivatogramm des Tetrahydrophthalsäureanhydrids (Abb. 2) zu ersehen ist, schmilzt diese Verbindung bei 100 °C. Aus der Fläche der DTA-Kurve ergaben sich für die Schmelzwärme 5,0 kcal/Mol. Dem Schmelzen folgt eine langsame Verdampfung, die bei 270 °C ihre größte Geschwindigkeit erreicht. Ein stufenweise eintretender, auf die Zersetzung der Verbin-

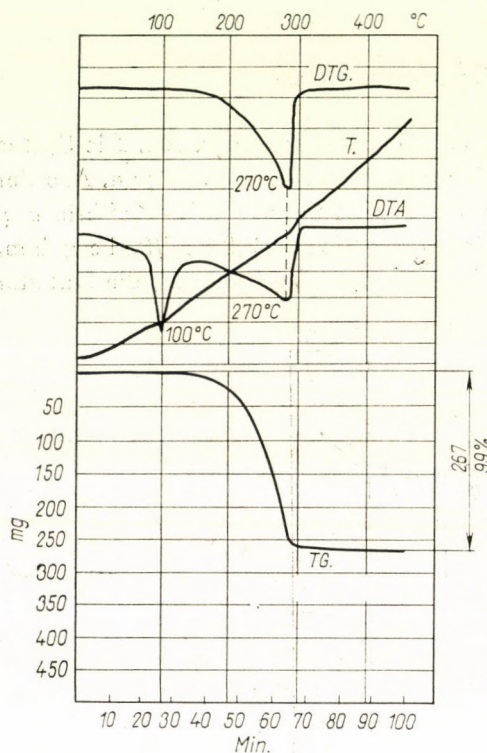


Abb. 2. Derivatogramm von Tetrahydrophthalsäureanhydrid

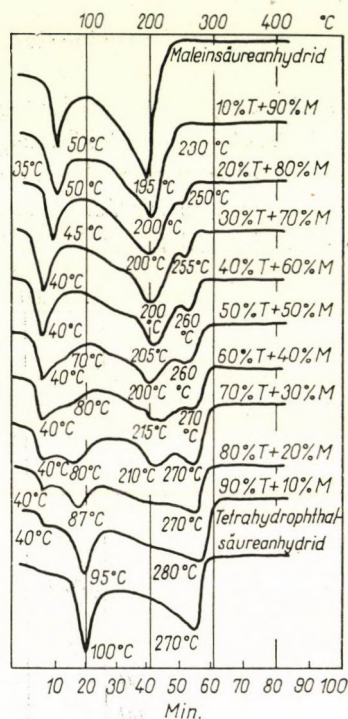


Abb. 3. DTA-Kurven von mechanisch verriebenen Maleinsäureanhydrid-Tetrahydrophthalsäureanhydrid-Gemischen verschiedener Zusammensetzungen

derung deutender Gewichtsverlust ist am Derivatogramm nicht zu beobachten.

Abb. 3 zeigt die DTA-Kurven mechanisch, durch Verreiben hergestellter Maleinsäureanhydrid-Tetrahydrophthalsäureanhydrid-Gemische verschiedener Zusammensetzungen, Abb. 4 die DTA-Kurven ihrer vor der derivatographischen Analyse zusammengeschmolzenen, sodann nach dem Erstarren in einer Reibschale homogenisierten Gemische, Abb. 5 bis 8 die TG- und DTG-Kurven

der verriebenen bzw. zusammengeschmolzenen Gemische. Die Gemische enthielten der Reihe nach 10, 20, 30, 40, 50, 60, 70, 80 bzw. 90 Gew.% Maleinsäureanhydrid. Die zwei verwendeten Arten der Probenzubereitung sollten jene Tatsache klären, ob ein vorangehendes Zusammenschmelzen nicht eventuell Änderungen im Gemisch hervorruft, die dann das thermische Verhalten beeinflussen. Unserer Beobachtung nach können nämlich tatsächlich solche Änderungen auftreten, so daß in diesem Falle die durch Verreiben erhaltenen

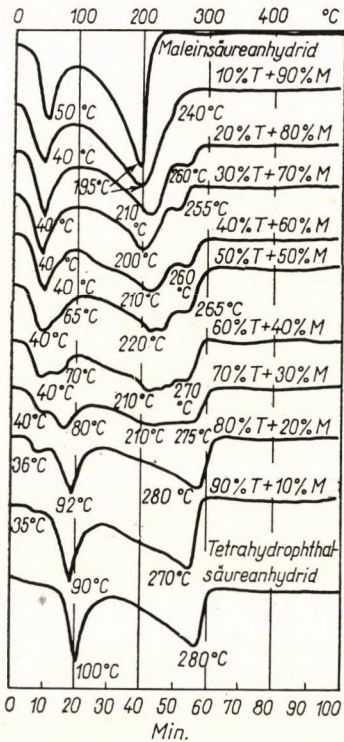


Abb. 4. DTA-Kurven zusammengeschmolzener und nach dem Erstarren in einer Reibschale homogenisierter Maleinsäureanhydrid-Tetrahydrophthalsäureanhydrid-Gemische verschiedener Zusammensetzungen

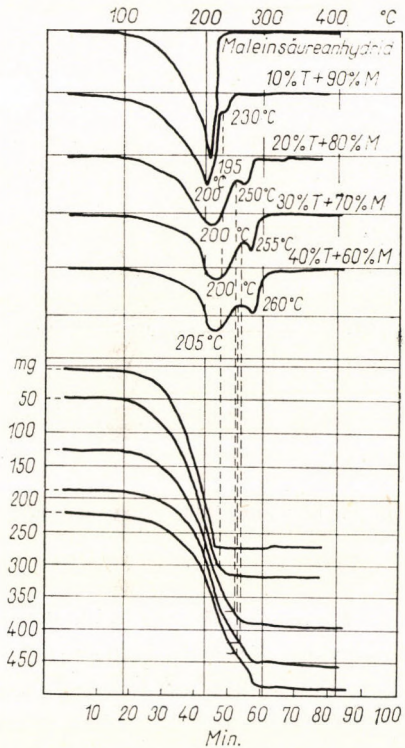


Abb. 5. TG- und DTG-Kurven mechanisch verriebener Gemische mit 0–50% Tetrahydrophthalsäureanhydridgehalt

Gemische zur Aufnahme von Kalibrationskurven für die Analyse der vorangehend zusammengeschmolzenen Proben ungeeignet sind.

Abb. 9 zeigt das Phasendiagramm des Systems Maleinsäureanhydrid-Tetrahydrophthalsäureanhydrid.

Um die Interpretation der derivatographischen Kurven zu vereinfachen, wird zuerst das Phasendiagramm des Systems behandelt. In Abb. 9 ist links am Koordinatensystem der Erstarrungspunkt des reinen Maleinsäureanhydrids, rechts der des reinen Tetrahydrophthalsäureanhydrids aufgetragen. Nach

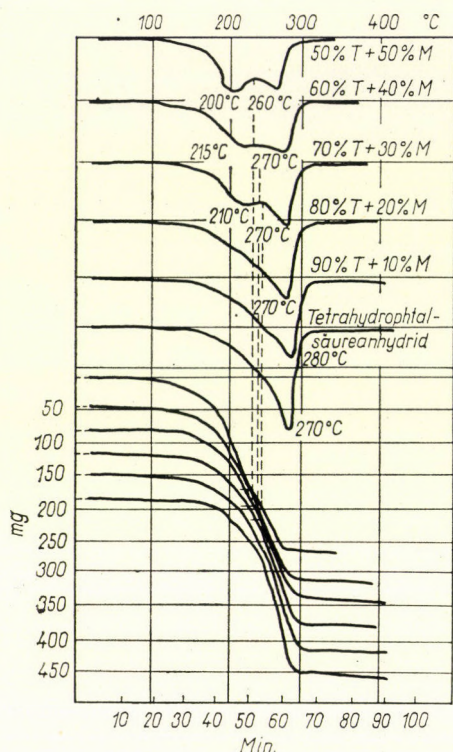


Abb. 6. TG- und DTG-Kurven mechanisch verriebener Gemische mit 50–100% Tetrahydrophthalsäureanhydridgehalt

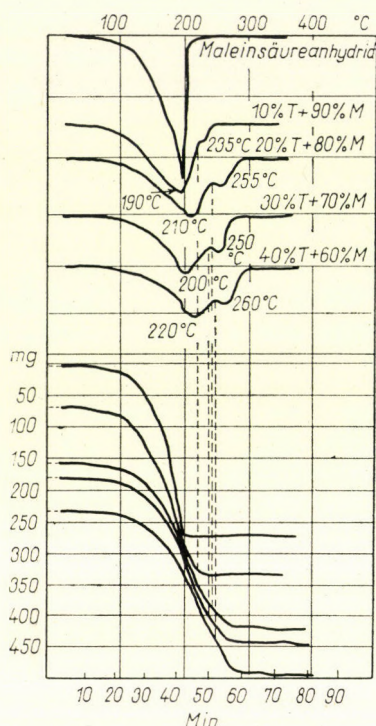


Abb. 7. TG- und DTG-Kurven zusammengeschmolzener Gemische mit 0–50% Tetrahydrophthalsäureanhydridgehalt

dem Diagramm besitzt das System in einem Gemisch mit 31% Tetrahydrophthalsäureanhydrid-Gehalt bei einer Temperatur von 36 °C einen eutektischen Punkt. Es soll bemerkt werden, daß im Konzentrationsbereich von 50 bis 90% Tetrahydrophthalsäureanhydrid die Bildung eines Eutektikums mit Hilfe der Abkühlungskurven (Abb. 9) — vermutlich wegen der abnehmenden Menge der eutektischen Zusammensetzung — nicht beobachtet werden konnte. Auf Grund der Derivatogramme ist aber — wie später gezeigt werden soll — anzunehmen, daß auch in diesem Temperaturbereich ein Eutektikum gebildet wird.

Auf den Derivatogrammen können die in den Gemischen auf Einwirkung von Wärme auftretenden Änderungen verfolgt werden, und zwar im gegebenen Fall, mit Hilfe der DTA-Kurve das Schmelzen der untersuchten Proben und mit Hilfe der DTG- und TG-Kurven das Verdampfen der Gemische.

Abb. 10 zeigt die Änderung der an den DTA-Kurven auftretenden, das Schmelzen der untersuchten Substanzen anzeigenden Spitzentemperaturen, als Funktion der Tetrahydrophthalsäureanhydrid-Konzentration, für mechanisch verriebene bzw. vorangehend zusammengeschmolzene Gemische.

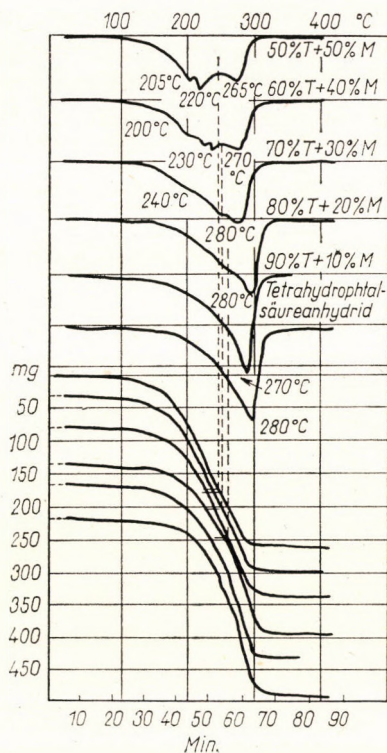


Abb. 8. TG- und DTG-Kurven zusammengesetzter Gemische mit 50–100% Tetrahydrophthal- und Maleinsäureanhydridgehalt

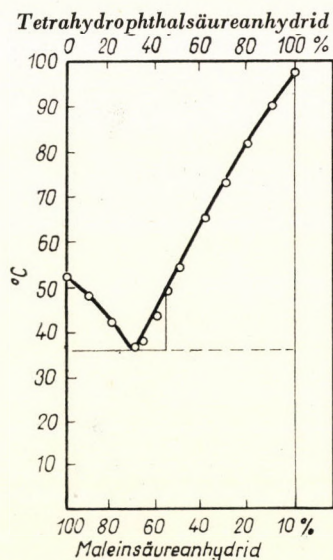


Abb. 9. Phasendiagramm des Systems Maleinsäureanhydrid-Tetrahydrophthal- und Maleinsäureanhydrid

Ein Vergleich der Konzentration-Temperatur-Funktion (Abb. 10) mit dem Phasendiagramm (Abb. 9) zeigt, daß bei Konzentrationswerten, bei denen die Temperaturdifferenz zwischen der Ausscheidungstemperatur der reinen Komponenten und dem Erstarrungspunkt des Eutektikums klein ist (bei 20–40% Tetrahydrophthalsäureanhydridgehalt, Abb. 9), das Schmelzen der Substanz sowohl für mechanisch verriebene als auch für zusammenge-

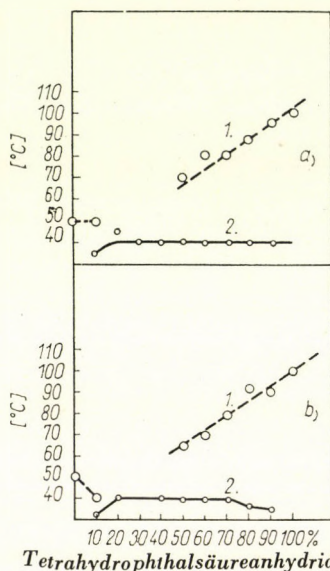
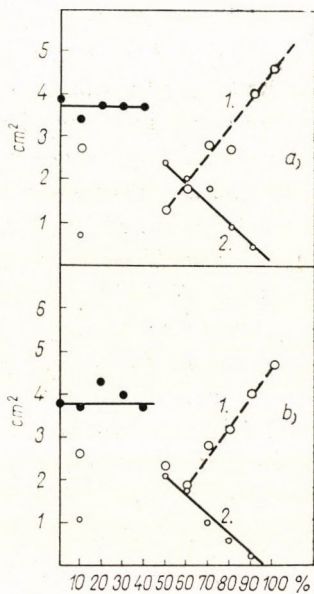


Abb. 10. Die Änderung der das Schmelzen des Tetrahydrophthalsäureanhydrids (1) und des Eutektikums (2) anzeigenden DTA-Spitzentemperaturen in Abhängigkeit von der Tetrahydrophthalsäureanhydrid-Konzentration; a) mechanisch verriebene und b) zusammengeschmolzene Gemische

schmolzene Gemische durch eine einzige Spitze (bei 40 °C) der DTA-Kurve angezeigt wird. Bei Konzentrationswerten, bei denen die erwähnte Temperaturdifferenz größer ist (bei 10%, ferner zwischen 50 und 90% Tetrahydrophthalsäureanhydridgehalt), ist bei 40 °C das Schmelzen des Eutektikums (am Derivatogramm werden die Temperaturwerte nur mit einer Genauigkeit von 5 °C abgelesen, und diese Werte können von den tatsächlichen um ± 10 °C abweichen) und bei höherer Temperatur als der Schmelzpunkt des Eutektikums der herabgesetzte Schmelzpunkt der entsprechenden Komponente abgesondert wahrzunehmen.

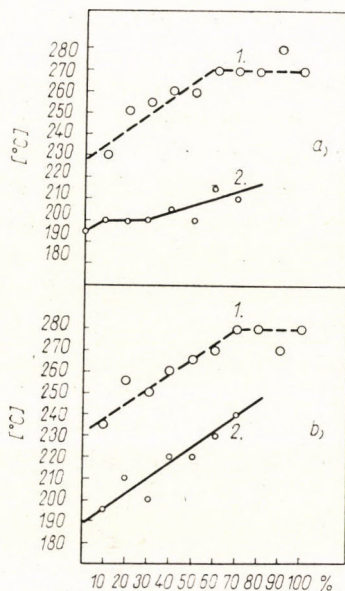
Sind die mechanischen Gemische nicht vollständig homogenisiert, so kann im Konzentrationsbereich von 50 bis 90% Tetrahydrophthalsäureanhydrid neben dem Schmelzpunkt des Eutektikums und dem herabgesetzten Schmelzpunkt des Tetrahydrophthalsäureanhydrids auf der DTA-Kurve auch der Schmelzpunkt des reinen, mit Maleinsäureanhydrid in Berührung stehenden Tetrahydrophthalsäureanhydrids beobachtet werden.

Die Änderung der Größen der zu den einzelnen Schmelzpunktspitzen gehörenden DTA-Flächen als Funktion der Tetrahydrophthalsäureanhydrid-Konzentration ist in Abb. 11 zu sehen. Wie bereits erwähnt wurde, meldet sich im Konzentrationsbereich von 20 bis 50% Tetrahydrophthalsäureanhydrid auf der DTA-Kurve eine einzige Spitze bei 40 °C, daher gehört im ersten Teil der Abb. 11 zu den einzelnen Konzentrationswerten nur jeweils ein Punkt. Über einem Tetrahydrophthalsäureanhydridgehalt von 50% wird mit wachsender Tetrahydrophthalsäurekonzentration die zum Schmelzpunkt des Tetra-



Tetrahydrophthalsäureanhydrid

Abb. 11. Änderung der Größe der zu den das Schmelzen des Tetrahydrophthalsäureanhydrids (1) und des Eutektikums (2) anzeigenden DTA-Spitzen gehörigen Flächen in Abhängigkeit von der Tetrahydrophthalsäureanhydrid-Konzentration; a) mechanisch verriebene Gemische und b) zusammengeschmolzene Gemische



Tetrahydrophthalsäureanhydrid

Abb. 12. Änderung der die Verdampfung des Tetrahydrophthalsäureanhydrids (1) und des Maleinsäureanhydrids (2) anzeigenden DTG-Spitzentemperaturen in Abhängigkeit von der Tetrahydrophthalsäureanhydrid-Konzentration; a) mechanisch verriebene und b) zusammengeschmolzene Gemische

hydrophthalsäureanhydrids gehörende Fläche größer, während die zum Schmelzpunkt des Eutektikums gehörende Fläche kleiner wird.

Untersucht man den Ablauf der DTG- und TG-Kurven bei Gemischen verschiedener Zusammensetzung, so sieht man, daß die das Verdampfen der einzelnen Komponenten anzeigenden Spitzen der DTG-Kurve im Konzentrationsbereich von 0 bis 70% Tetrahydrophthalsäureanhydridgehalt getrennt erschienen. Abb. 12 zeigt die Änderung der DTG-Spitzentemperaturen als Funktion der Tetrahydrophthalsäureanhydrid-Konzentration. In Abb. 12 sind bloß die die Siedepunkte des Maleinsäureanhydrids und des Tetrahydrophthal-

säureanhydrids anzeigenden Spitzentemperaturen eingezeichnet. Vor der für das Maleinsäureanhydrid charakteristischen DTG-Spitze ($195-230^{\circ}\text{C}$) ist ein weiterer Knickpunkt der DTG-Kurve zu beobachten, der vermutlich die Verdampfung der Schmelze eutektischer Zusammensetzung von der Verdampfung des Maleinsäureanhydrids trennt. Der durch diesen Knickpunkt gekennzeichnete Gewichtsverlust wurde in den späteren Darstellungen nicht berücksichtigt, daher wird die TG-Kurve durch die Projektion des zwischen den die Verdampfung der einzelnen Komponenten anzeigenden DTG-Spitzen liegenden Knickpunktes in zwei Teile geteilt. Zur ersten DTG-Spitze ($195-230^{\circ}\text{C}$) gehört stets ein größerer Gewichtsverlust, als dies der eingewogenen Maleinsäureanhydridmenge entsprechen würde. Dementsprechend ist der zur Verdampfungsspitze des Tetrahydrophthalsäureanhydrids gehörende Gewichtsverlust immer kleiner, als der eingewogenen Tetrahydrophthalsäureanhydridmenge entspricht. Mit ansteigender Tetrahydrophthalsäureanhydrid-Konzentration nimmt die Differenz zwischen dem ersten Gewichtsverlustabschnitt und der eingewogenen Maleinsäureanhydridmenge stetig zu. Bei mechanisch hergestellten Gemischen steigt diese Differenz bis zu einem Tetrahydrophthalsäureanhydridgehalt von 30% schneller an, als über 30%. Bei Schmelzen ist der Anstieg gleichmäßig. Wenn man den zu den einzelnen DTG-Spitzen gehörenden Gewichtsverlust als Funktion der eingewogenen Tetrahydrophthalsäureanhydridmenge darstellt (Abb. 13), so erhält man im Falle von mechanisch hergestellten Gemischen Geraden, die bei 31% Tetrahydrophthalsäureanhydridgehalt, also bei der eutektischen Zusammensetzung, einen Knickpunkt aufweisen. Bei Schmelzen konnte dieser Knickpunkt nicht einwandfrei reproduzierbar beobachtet werden. Aus den Kurven der Abb. 13 kann festgestellt werden, daß die Projektion des Knickpunktes, nach der DTG-Spitze bei $195-230^{\circ}\text{C}$, auf die TG-Kurve (Abb. 5–8), im oberen Abschnitt derselben einen Gewichtsverlust anzeigt, der aus der Verdampfung des eingewogenen Maleinsäureanhydrids und eines Teils des mit dem Maleinsäureanhydrid in eutektischer Zusammensetzung befindlichen Tetrahydrophthalsäureanhydrids herrührt, wie dies schon oben angedeutet wurde. Der andere Teil des Tetrahydrophthalsäureanhydridgehaltes destilliert selbst unterhalb eines Tetrahydrophthalsäureanhydridgehaltes von 30%, also bei einem Gehalt, wo das gesamte Tetrahydrophthalsäureanhydrid als Bestandteil des Eutektikums vorliegen müßte, bei höherer Temperatur gesondert ab.

Die beschriebenen thermischen Eigenschaften ermöglichen die qualitative bzw. quantitative Bestimmung von Maleinsäureanhydrid und Tetrahydrophthalsäureanhydrid nebeneinander.

Im Konzentrationsbereich zwischen 0 und 60% Tetrahydrophthalsäureanhydrid wird der Tetrahydrophthalsäureanhydridgehalt — sowohl bei aus der Schmelze als auch bei aus Lösungen erhaltenem Tetrahydrophthalsäureanhydrid — zweckmäßigerweise mit Hilfe der DTG- und TG-Kurven, auf

Grund des Zusammenhanges zwischen dem zur DTG-Verdampfungsspitze des Tetrahydrophthalsäureanhydrids gehörigen Gewichtsverlust und der Zusammensetzung (Abb. 13) bestimmt. Bei Gemischen die 60 bis 100% Tetrahydrophthalsäureanhydrid enthalten, eignet sich die Größe der zum Schmelzen der einzelnen Komponenten gehörigen DTA-Flächen (Abb. 11) zur analytischen Bestimmung des Tetrahydrophthalsäureanhydrids. Da die von den DTA-Kurven von mechanischen Gemischen bzw. Schmelzen aufgenommenen

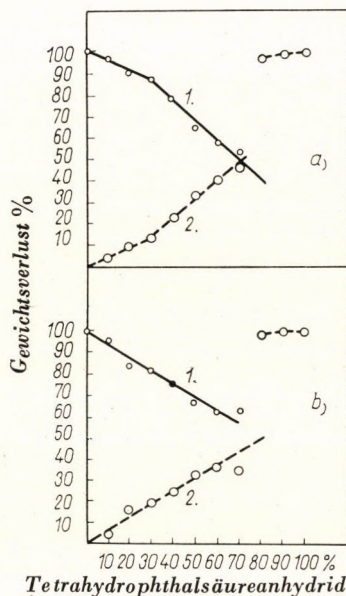


Abb. 13. Die Änderung des zu den die Verdampfung des Maleinsäureanhydrids (1) und des Tetrahydrophthalsäureanhydrids (2) anzeigenden DTG-Spitzen gehörigen Gewichtsverlustes, in Abhängigkeit von der Tetrahydrophthalsäureanhydrid-Konzentration; a) mechanisch verriebene und b) zusammengeschmolzene Gemische

Kalibrationskurven (Abb. 11) nicht wesentlich voneinander abweichen, ist es ratsam, stets die für mechanische Gemische aufgenommene Kalibrationskurve zu verwenden, da bei der vorangehenden Verschmelzung der als Etalon verwendeten Gemische mit einem durch Verdampfung verursachten Verlust der leichter flüchtigen Komponente zu rechnen ist. Dies wird auch durch die für zusammengeschmolzene Gemische aufgenommene Kalibrationskurve in Abb. 11 angezeigt. Diese Kurve stellt die Änderung der Größe der Fläche dar, die zu der das Schmelzen des Eutektikums anzeigenden DTA-Spitze gehört. Wie ersichtlich, schneidet die Kalibrationskurve statt bei 100% bereits bei 96% Tetrahydrophthalsäureanhydridgehalt die Abszisse, da beim Verschmelzen der einzelnen Gemische ein Teil des Maleinsäureanhydrids verdampft ist.

Zur annähernden Bestimmung der Reinheit des Tetrahydrophthalsäureanhydrids kann auch die das Schmelzen des Tetrahydrophthalsäureanhydrids anzeigende Temperatur der DTA-Spitze verwendet werden (Abb. 10).

Das Phasendiagramm kann im ganzen Konzentrationsbereich für die Bestimmung der beiden Komponenten nebeneinander benützt werden. Jener Temperaturwert, bei der an der Abkühlungskurve des Mixtures von unbekannter Zusammensetzung ein Knickpunkt erscheint, wird auf die Liquidus-Kurve projiziert, und der auf diese Weise erhaltene Schnittpunkt auf die Abszisse, an der dann die Zusammensetzung abzulesen ist. Im Konzentrationsbereich von 0 bis 50% Tetrahydrophthalsäureanhydridgehalt kann hier dadurch ein Problem entstehen, daß für einen gegebenen Temperaturwert auf beiden Ästen der Kurve (Abb. 9) Punkte vorliegen. In der Praxis ist jedoch dieser Bereich nicht von Interesse, denn das bei der Herstellung untersuchte Tetrahydrophthalsäureanhydrid enthält im allgemeinen nicht mehr als 20% Verunreinigung. Falls aber bei irgendeinem Mixture die Zusammensetzung in diesem Bereich liegt, wird man so vorgehen, daß man das Mixture mit einer bekannten Menge von Tetrahydrophthalsäureanhydrid versetzt, und wenn dann auf der Abkühlungskurve des erhaltenen Gemisches der Knickpunkt zu niedrigeren Temperaturen hin verschoben wird, erhält man auf der linken Seite des Diagramms die richtige Zusammensetzung, und bei einer Verschiebung gegen höhere Temperaturen hin, auf der rechten Seite.

Das auf der Untersuchung des Phasendiagramms beruhende analytische Verfahren ist sehr schnell, es beansprucht nur etwa 10–15 Minuten und liefert in Anwesenheit von zwei Komponenten sehr genaue Werte. Die derivatographische Bestimmung ist langsamer, sie beansprucht etwa 3 Stunden. Die beiden Methoden ergänzen sich jedoch in dem Fall, wenn das Mixture neben Maleinsäureanhydrid und Tetrahydrophthalsäureanhydrid noch andere Komponenten enthält.

Aus 5 parallelen Messungen berechnet, beträgt der Fehler der Bestimmung sowohl auf Grund der Derivatogramme als auch auf Grund des Phasendiagramms ± 1 rel. %.

ZUSAMMENFASSUNG

Maleinsäureanhydrid, Tetrahydrophthalsäureanhydrid, sowie deren mechanisch verriebene und zusammengeschmolzene Gemische verschiedener Zusammensetzungen wurden derivatographisch untersucht. Das Phasendiagramm dieses binären Systems wurde ebenfalls aufgenommen. Sowohl die Derivatogramme als auch das Phasendiagramm zeigen eindeutig, daß Maleinsäureanhydrid und Tetrahydrophthalsäureanhydrid beim Erwärmen ein Gemisch von eutektischer Zusammensetzung bilden. Wie das Phasendiagramm zeigt, liegt der eutektische Punkt bei 31% Tetrahydrophthalsäureanhydridgehalt bei 36 °C. Auf den Derivatogrammen erscheinen in einem gewissen Konzentrationsbereich die Schmelz- und Siedepunkte des Eutektikums und der reinen Komponenten getrennt. Nach Aufnahme von entsprechenden Kalibrationskurven sind im Konzentrationsbereich von 0 bis 60% Tetrahydrophthalsäureanhydridgehalt die zu den Siedepunkten der einzelnen Komponenten anzeigenden DTG-Spitzen gehörigen Gewichtsverluste zur quantitativen Bestimmung der Komponenten geeignet, während im Konzentrationsbereich von 60 bis 100% Tetrahydrophthalsäureanhydridgehalt

die Größe der zu den den Schmelzpunkt der einzelnen Komponenten anzeigenden DTA-Spitzen gehörigen Flächen für diesen Zweck verwendet werden kann. Aus dem Phasendiagramm können sowohl in mechanisch hergestellten Gemischen als auch in Schmelzen die beiden Komponenten nebeneinander quantitativ bestimmt werden.

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Teréz FLÓRA; Veszprém, Wartha Vince út 3.

Andor ALMÁSY

1,5-DIKETONES, III

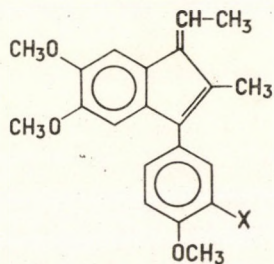
THE STERIC STRUCTURES OF SOME 1-ETHYLIDENE-INDENES

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In Part II [1] of the present series the syntheses of two geometrically isomeric forms of 1-ethylidene-2-methyl-3-anisyl-5,6-dimethoxyindene (I) as well as of the 3-veratryl analogue (II) have been described.



I X=H a: m. p.: 108–109°; b: m. p.: 144–146°

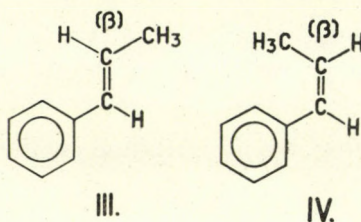
II X=OCH₃ a: m. p.: 146–148°; b: m. p.: 163–165°

Although slight differences could be observed between the IR and UV spectra of the corresponding isomers, their steric structures could not be deduced therefrom. Furthermore, an examination of the STUART models revealed that no significant additional steric strain existed in either of the corresponding isomers in comparison with the other; therefore, their steric structures could not be elucidated on the basis of existing differences in stability, the latter being manifested in the fact that treatment with acid converted the higher melting compounds into their lower melting isomers [1].

As to its type, the geometric isomerism of the 1-ethylidene-indenes investigated may be compared, as a first approximation, with the stereoisomerism of styrenes monosubstituted at the β carbon atom. For the elucidation of steric structures of the latter type the study of the NMR spectra proved to be an excellent tool (cf. e.g. [2]).

An inspection of the structural formulas readily reveals that in *trans*-propenylbenzene (III) the hydrogen in β position approaches the benzene ring

significantly more closely than the corresponding hydrogen of the *cis* isomer (IV). Therefore, as a consequence of the deshielding effect of the benzene ring, the signal of the hydrogen atom in question must be shifted in the *trans* form downfield with respect to the *cis* form. This expectation accords fully with the experimental findings in spite of the non-planarity of the *cis* isomer as contrasted with the planar structure of the *trans* form. However, the disturbing effect



of non-planarity manifests itself in the position of the signal of the terminal methyl group. If, namely, the *cis* form would also be planar, the signal of the methyl group should, again as a consequence of the deshielding effect of the benzene ring, appear at lower fields than the corresponding signal in the NMR spectrum of the *trans* form. In reality, however, this signal is found in the spectrum of the *cis* form at higher fields as a consequence of steric inhibition of the conjugation and hyperconjugation (*cf.* [2]).

The above consideration may be briefly summarized by the statement that, in the NMR spectrum of *trans*-propenylbenzene (III), the signals of both the hydrogen atom and the methyl group are to be found downfield as compared with the corresponding signals of the *cis* form (IV).



Fig. 1

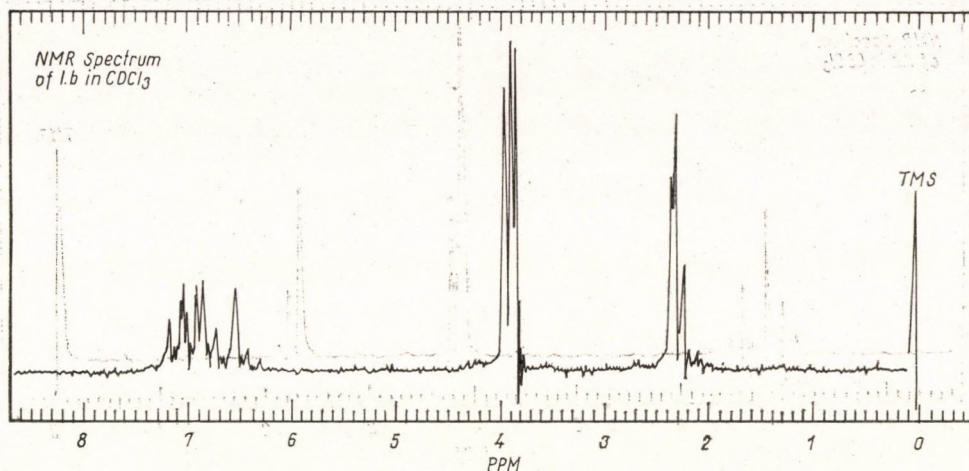


Fig. 2

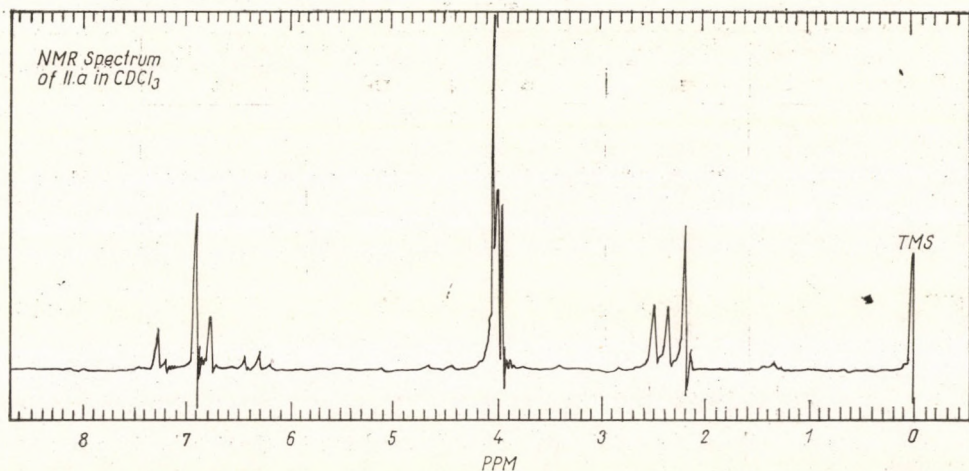


Fig. 3

The NMR spectra of the stereoisomeric forms of 1-ethylidene-2-methyl-3-anisyl-5,6-dimethoxy-indene (**I**) are depicted in Figs 1 and 2. The signals may easily be assigned based on their positions, intensities and multiplicities; see Table I.

In both pairs of isomers the signal of the methine proton of the higher melting form (**Ib**, **IIb**) is found at lower fields, that is the methine hydrogen of the ethylidene group occupies in these compounds the *cis* position with respect to the condensed benzene ring, while the methyl group of the ethylidene chain occupies the *trans* position with respect to the same ring.

It is to be noted that — in contrast to the case of the pair of *cis*- and *trans*-propenylbenzene — the signals of the methine hydrogen and the methyl

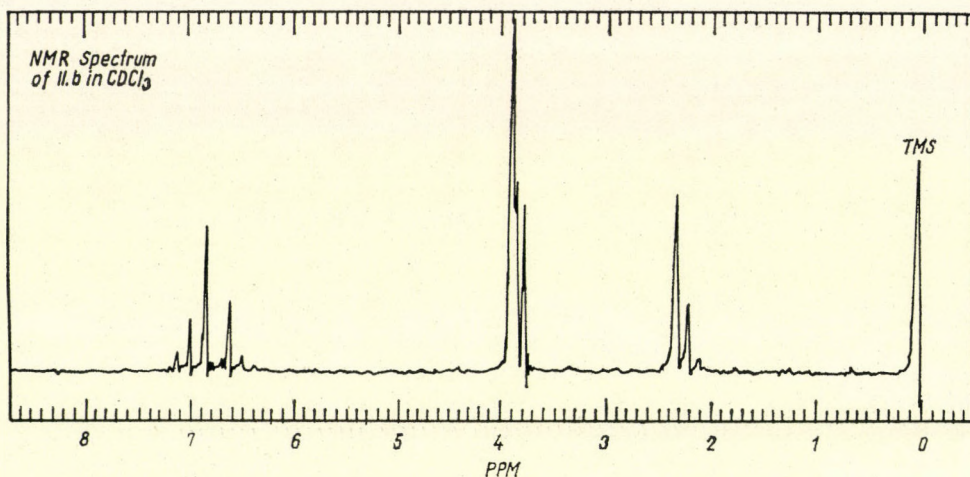


Fig. 4

Table I

Group \ Compound	Chemical shifts (δ , ppm, TMS=0) and coupling constants (J, cps)				Multiplicity
	Ia	Ib	IIa	IIb	
$\text{CH}_3-\text{C}(\text{H})=\text{C}$ $\begin{array}{c} \text{C} \\ \diagup \quad \diagdown \\ \text{C} \end{array}$	2.35 (J=7.2)	2.26* (J=7.2)	2.41 (J=8.4)	2.26* (J=8.4)	doublet
$(\text{CH}_3)-\text{CH}=\text{C}$ $\begin{array}{c} \text{C} \\ \diagup \quad \diagdown \\ \text{C} \end{array}$	6.36 (J=7.2)	6.48* (J=7.2)	6.36 (J=7.2)	6.50** (J=7.2)	quadruplet

* The signal partly overlaps with that of the other methyl group, the maxima, however, are well separated.

** The quadruplet of the methine proton partly overlaps with the signals of the aromatic protons.

group of the ethylidene chain are not shifted in the same, but in opposite directions when turning from one isomer to the other. This difference is undoubtedly a consequence of the fact that ethylidene-indenes, their rigid five-membered ring being built only from sp^2 hybridized carbon atoms, may only negligibly be distorted from planarity, if at all, irrespective of the fact whether the methyl group of the ethylidene chain is *cis* or *trans* to the condensed benzene ring.

Experimental

For the preparation of compounds Ia, Ib, IIa and IIb see [1].

NMR spectra were obtained in approximately 5% CDCl_3 solution at 60 MHz with an instrument of Type JNM-C-60 (Japan Electron Optics Lab.) at room temperature, TMS being used as the internal reference.

The spectra were run by Mr. Gábor TÓTH to whom thanks of the authors are due.

SUMMARY

By NMR spectra, the methine proton in the higher melting isomer of 1-ethylidene-2-methyl-3-anisyl-5,6-dimethoxyindene (**I**) and in the corresponding 3-veratryl derivative (**II**) has been shown to occupy the *cis* position with respect to the condensed benzene ring, while in the lower melting isomers the same hydrogen occupies the *trans* position.

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S-ALKYL vs. S-HETEROCYCLIC BOND CLEAVAGE DURING DESULFURATION UNDER REARRANGEMENT OF S-ALKYL-5,5-DIPHENYL-4-THIOHYDANTOINS BY ALUMINIUM CHLORIDE*

(SHORT COMMUNICATION)

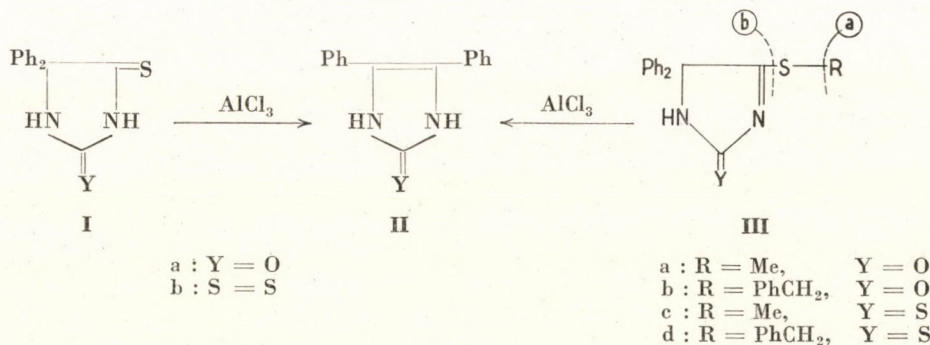
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It has been previously shown that 5,5-diphenyl-4-thiohydantoin (**Ia**) as well as 5,5-diphenyl-dithiohydantoin (**Ib**), when refluxed with an aromatic hydrocarbon as solvent in the presence of aluminium chloride, are desulfurized under simultaneous migration of one of the phenyl groups to yield 4,5-diphenyl-2-imidazolinone (**IIa**) and 4,5-diphenyl-2-imidazolinethione (**IIb**), respectively [1, 2]. The same products were formed starting either with the S-4-methyl (**IIIa**, **c**) or the S-4-benzyl (**IIIb**, **d**) derivatives of **Ia** and **Ib**, respectively [1, 2].

As to the fate of the sulfur atom eliminated during rearrangement it could be shown that, starting from **Ib**, half of the sulfur becomes transformed into hydrogen sulfide while the other half is used to sulfurate the solvent yielding diphenylsulfide and isomeric ditolyl sulfides, if benzene and toluene are used as solvents, respectively [2].



We now wish to report on our results relating to the fate of the methylthio and benzylthio groups which are cleaved from the imidazoline nucleus during rearrangement of **IIIa** and **IIIb**, respectively. *A priori*, there seems to be two possibilities for such a cleavage: the alkylthio group might be

* Hydantoin, Thiohydantoin, Glycocyamidines. Part 26. — Part 25: see [2].

cleaved, firstly, as a whole (cleavage at **b**), or, secondly, it might be cleaved in two successive steps first at **a** and subsequently at **b**, i.e., by cleavage of the alkyl group, **Ia** would firstly form and, subsequently, rearrange normally under elimination of sulfur. Since it has been found previously that S-benzyl derivatives of 5,5-diphenyl-thio- and -dithiohydantoins are readily debenzylated under mild conditions by aluminium chloride to yield the corresponding parent hydantoins (e.g. **IIIb** is debenzylated to **Ia**) [3, 4] the second course was considered as the more probable [2].

When **IIIb** was refluxed with benzene in the presence of aluminium chloride as previously [1, 2] described, evolution of hydrogen sulfide could be observed as in the case of rearrangement of **Ia**, demonstrating that, prior to cleavage at **b**, the benzyl group, in fact, has been cleaved. This finding could be corroborated by GLC of the residue of the reaction mixture after removal of the rearrangement product (**IIa**) and the solvent. By using this technique, the presence of considerable amounts of diphenylmethane and diphenylsulfide, formed by benzylation and sulfuration of the solvent, respectively, could be detected. α -Toluene-thiol and benzyl-phenyl-sulfide which would be the expected products, if the benzylthio group were cleaved as a whole, however, were totally absent. The formation of diphenylmethane clearly shows that not only the sulfur atom, as shown previously [1, 2], but also the benzyl group is eliminated in cationic form.

A substantially different result was obtained when the rearrangement of **IIIa** by aluminium chloride in refluxing benzene was examined by the same technique. In this case, namely, not even traces of hydrogen sulfide, diphenyl sulfide and toluene, the latter two being the expected products of sulfuration and methylation of the solvent, could be detected. Instead of these, large amounts of thioanisole and 1,4-di(methylthio)-benzene were formed. The formation of the latter products clearly demonstrates, firstly, that the methylthio group is cleaved as a whole (cleavage at **b**) and, secondly, that it too is cleaved in cationic form, thereby being enabled to effect electrophilic substitution of the solvent benzene.

It may be, thus, concluded that the mode of cleavage of the alkylthio groups during aluminium chloride induced rearrangement of S-alkyl-5,5-diphenyl-4-thiohydantoins is determined by the kind of the alkyl group. An alkyl group which is sufficiently stable in cationic form, as e.g. the benzyl group, is cleaved separately from the sulfur atom (cleavage at **a**), the latter being eliminated only subsequently (cleavage at **b**). While, if the alkyl group is unstable in cationic form, as e.g. the methyl group, the alkylthio group becomes cleaved as a whole (cleavage at **b**).

GLC experiments were carried out with a *Carlo Erba Fraktovap Model P* gas chromatograph with a thermal conductivity cell detector (column length 1 m, diameter 6 mm, temperature 180°, filling: 5% apiezon L on chromosorb

G; carrier gas: hydrogen; evaporator temperature: 210°; solvent for injection of solid substances: benzene).

All products formed during rearrangement of **IIIa** and **IIIb** were already known and were characterized either by gas chromatography (see above) or by their mp.-s and mixed mp.-s with authentic samples.

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РЕЗЮМЕ

Алгебраическое рассмотрение стехиометрии одного класса химических реакций

А. ПЕТЁ

Исходя из линейного алгебраического характера формального представления химических частиц и их реакций, рассматриваются т. наз. *простые* химические реакции, которые определяются следующим образом: данная реакция называется простой реакцией, если среди химических частиц, принимающих участие в этой данной реакции, стехиометрически не имеют место никакие другие реакции. (Реакции, являющиеся кратными по отношению друг к другу, считаются идентичными.) Некоторые основные свойства простых реакций доказаны методом линейной алгебры и иллюстрированы на примере. Нахождение простых химических реакций может быть произведено и для любых систем многокомпонентных реакций.

Определение микроколичеств германия в растворах, содержащих перекись водорода и фтористый водород

Е. ПУНГОР и А. ХАЛАС

Был разработан метод определения германия, находящегося в концентрации 10^{-6} г/мл в травильных растворах, содержащих перекись водорода и фтористоводородную кислоту. Мешающее влияние фтористоводородной кислоты предотвращалось с помощью образования комплекса последней с борной кислотой. Перекись водорода удалялась титрованием перманганатом калия. Германий экстрагировался из полученного таким образом раствора четыреххлористым углеродом в солянокислотной среде, а затем вновь переносился с водой в водную фазу. Определение германия происходит фотометрически с помощью солянокислого фенилфлуорона, измеряя поглощение при 500 мкм.

Определение максимальной чувствительности активационного анализа реакций, оказывающих мешающее действие друг на друга, с помощью метода максимального подобия

П. КВИТТЕР

Методом максимального подобия определялась максимальная чувствительность активационного анализа в общем случае мешающих реакций, возникающих при облучении в реакторе. Метод применялся для определения без деструкции содержания вольфрама, алюминия и кремния.

Обсуждение процессов электронного возбуждения и структуры связей комплексов ионов металлов с электронной структурой $3d^n$ на основе метода поля лигандов, II. Октаэдрические комплексы хрома(III) и кобальта (III)

М. БАН и Й. ЧАСАР

На основе теории поля лигандов для комплексов типа $Me(III)X_6$ и $Me(III)L_3$ ($Me = Cr^{+3}, Co^{+3}$) были рассчитаны характеристические параметры (Δ , B , C) и величины (β и $\delta\%$), пропорциональные характеру ковалентных связей. Спектрохимический ряд донорных атомов ($Cl < S < F < O < N < C$) соответствует направлению изменения ионного радиуса. Для соединений Co^{+3} β лишь слегка изменяется, поэтому $\delta\%$, а еще лучше Δ кажутся более пригодными для характеристики связей, образующихся в молекуле. В обеих группах соединений наиболее низкие значения Δ и наиболее ковалентные связи получаются в случае тиосоединений.

ИК- и Раман спектры молекулы пиразин-ди-N-оксида

Ш. СЕКЕ, ДЬ. ВАРШАНИ и Э. БАЙТЦ

Из ик- и Раман спектров молекулы пиразин-ди-N-оксида было установлено по данным частот и укорачивания связи, что связь N—O носит характер двойной связи. Значительное подобие нормальных частот молекул пиразин-ди-N-оксида и п-дифторбензола является следствием изоэлектронных свойств.

Система связей N-ацил-сульфилиминов, V. ИК-спектроскопическое изучение N-п-нитрофенилсульфонил-сульфилиминов

А. КУЧМАН, И. КАПОВИЧ и Ф. РУФФ

Интенсивная полоса, появляющаяся в ик-спектре N-сульфонил-сульфилиминов в области $935-1020\text{ см}^{-1}$ вероятно относится к асимметричной полосе валентных колебаний группы $S^{IV}NS^{VI}$ (ν_{SNS}). Группа Q в ряду N—п-нитрофенилсульфонил-сульфилиминов ($RR'SNSO_2Q$; $Q = C_6H_4NO_2-p$), а также как и для $Q = C_6H_4CH_3-p$ влияет на группу SO_2 индуктивным, а на SNS сопряженным путем. В небольшом уменьшении частоты ν_{SNS} ($\Delta\nu_{SNS} = 3-23\text{ см}^{-1}$) в сулфилиминах, содержащих в качестве R - фенильную или метильную группы, можно также наблюдать эффект сопряжения или сверхсопряжения для случая $Q = C_6H_4NO_2$, также как и для $Q = C_6H_4CH_3$.

Влияние стерических эффектов на склонность образования кеталей в случае некоторых хинолизинов-производных

Л. НОВАК, П. ШОХАР и Ч. САНТАИ

Было установлено, что наблюдается взаимосвязь между склонностью образования кеталей или гидратов солей некоторых производных хинолизинона и смещением валентной частоты карбонила. Для объяснения этих явлений следует принимать во внимание, в первую очередь, стерические эффекты.

Индол и производные индола, I

А. ГЕРЕЧ и Т. ТОТ

Было установлено, что реакция дегидрогенизации индолина и его производных в растворе, в присутствии никеля Ренея протекает и при $70-80^\circ\text{C}$ со скоростью, пригодной как для кинетических измерений, так и для препаративных целей. Описывается метод и установка, позволяющие следить за протеканием реакции во времени. В качестве раство-

рителя использовались циклогексан, бензол, толуол и ксилол. В случае ароматических растворителей некоторая часть образующегося водорода расходуется на их гидрирование. Реакции дегидрогенизации подвергались индолин, а также N-метил-, N-этил-, N-пропил-, 6-метокси- и 6-амино-индолины.

Исследование дегидроциклизации на металлических катализаторах

З. ПАД и П. ТЕТЕНИ

Исследовалась реакция дегидроциклизации n-гексана в присутствии платиновых и никелевых катализаторов, применявшихся и в чистом металлическом состоянии, и на носителе окиси алюминия. Дегидроциклизация исследовалась в температурном интервале 300—500° в случае платины, а в присутствии никеля реакции крекинга преобладали выше, чем 400°. Реакции проходили неизменным путём в целом исследованном диапазоне температуры. В катализате обнаруживались ненасыщенные углеводороды — гексены и гексадиены. Настоящие результаты вместе с предыдущими данными говорят о том, что эти соединения являются промежуточными продуктами дегидроциклизации n-гексана. Исследования, с применением соединений, меченных радиокарбоном, также доказали последовательность реакций гексан → гексены → гексадиены → бензол. Определялась кажущаяся энергия активации дегидроциклизации n-гексана, мало чем отличающаяся от энергии активации дегидроциклизации гексенов. Было показано, что атмосфера водорода ускоряла реакции, причём присутствие водорода не оказало влияния на характер промежуточных продуктов.

Термическое изучение органических систем, участвующих в процессах получения фунгицидов Captan и Faltan, I. Термическое изучение смесей ангидридов малеиновой и тетрагидрофталевой кислот

Т. ФЛОРА и А. АЛМАШИ

Изучались механические и сплавленные смеси ангидридов малеиновой и тетрагидрофталевой кислот с различным соотношением компонентов, а также сами компоненты смесей с помощью дериватографии. Снималась фазовая диаграмма этих бинарных систем. Из дериватографических исследований и из фазовых диаграмм было установлено однозначно, что ангидриды малеиновой и тетрагидрофталевой кислот образуют эвтектическую смесь. Согласно фазовой диаграмме точка эвтектики находится при 36 °C и соответствует 31%-ному содержанию ангидрида тетрагидрофталевой кислоты. В определенных областях концентраций отдельно появляются точки плавления и кипения эвтектики и чистых компонентов на дериватограммах. Определение потерь, относящихся к пикам температур кипения отдельных компонентов на кривых ДТГ в области концентраций от 0 до 60% содержания ангидрида тетрагидрофталевой кислоты, и определение величин площадей, относящихся к пикам температур плавления отдельных компонентов на кривых ДТА, в области концентраций от 60 до 100% содержания ангидрида тетрагидрофталевой кислоты, позволяют определить состава компонентов после снятия соответствующих калибровочных кривых. Одновременное определение количества двух компонентов проводится из фазовой диаграммы как в случае механических, так и сплавленных смесей.

1,5-Дикетоны, III. Пространственная структура некоторых 1-этилиден-инденов

М. ЛЕМПЕРТ-ШРЕТЕР и П. ШОХАР

На основе спектров ядерного магнитного резонанса было установлено, что среди двух геометрических изомерных модификаций, как 1-этилиден-2-метил-3-анизил-5,6-диметоксинида (I), так и соответствующего 3 вератрил соединения метиновый протон в более высокоплавящейся модификации находится в цис-положении, а в более низкоплавящейся модификации — в транс-положении по отношению к конденсированному ароматическому кольцу.





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БЕЛА ЛЕНДЕЛ

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EDITOR'S NOTE

This double issue contains papers by authors who obtained their scientific training and degrees in the Soviet Union; other articles published in this number are the results of co-operation of Hungarian and Soviet research institutions.

This material — representing but a selection — has the purpose of demonstrating the valuable help which the Soviet Union has been giving in establishing and in the further education of a Hungarian chemical research staff. It further shows the fruitfulness and mutual benefits of the institutional cooperations of Hungarian and Soviet research workers; this program is extended and intensified steadily.

The editors of Acta Chimica Hungarica wish to commemorate with this publication the 50th Anniversary of the Great October Revolution.

BÉLA LENGYEL

Member of the Hungarian Academy of Sciences,
Editor-in-Chief

INVESTIGATION OF SYNTHETIC INORGANIC ION EXCHANGERS

L. SZIRTES*, L. ZSINKA, K. B. ZABORENKO and B. Z. IOFA

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Received June 16, 1967

A great number of inorganic substances occurring in nature possess ion exchange properties. Their study was rather neglected for a long time; in the last decade, however, problems presented by radiochemical practice have given rise to a sudden increase of interest in these materials. This is mainly due to the fact that, in a favourable contrast to organic resins, inorganic ion exchangers are highly resistant to heat and radioactive relations. The sudden development of this field is indicated by more than fifty papers published so far describing a number of synthetic inorganic ion exchangers. These materials may be classified as follows:

1. Synthetic zeolites;
2. Oxides and oxide-hydrates of multivalent metals;
3. Salts of multivalent metals and multibasic acids (such as zirconium phosphate);
4. Iron(II) cyanate complexes;
5. Salts of heteropolyacids (such as zirconium molybdate).

The majority of the mentioned papers deals with the properties of zirconium phosphate which has the highest exchange capacity among the known compounds. It has been reported that the properties of the substances markedly depend on the conditions of preparation. The investigated substances are, in general, rather stable both from the physical and chemical points of view. They may be prepared as substances having amorphous or microcrystalline structure. The latter form can be best characterized, e.g., in the case of zirconium phosphate, by the formula $\text{Zr}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$, while the structures of the amorphous substances are essentially analogous to the structure of complex zirconium ions present in aqueous medium. It is obviously impossible to describe here the great number of experimental results. The general conclusion may be drawn that in spite of the reliability of many experiments, some experimental results frequently appear dubious; further-

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more, the field is badly in want of systematization, and for the time being the published results and the conclusions based on them are often contradictory.

As it has been mentioned, the substances discussed are very promising from the aspect of radiochemical practice. Thus, further researches concerning their structures and properties are of great interest. The present work is a contribution along these lines.

Experimental

(a) Zirconium, titanium and chromium phosphates were synthesized by the preripitation method. Precipitation was carried out at 60 °C in the case of zirconium and titanium phosphates, while at room temperature for chromium phosphate. The precipitates were dried always at 50 °C. Since the relationships between the properties of the produced substances and the temperature of precipitation and drying had been satisfactorily described in the literature, only the amount of phosphoric acid employed for precipitation was varied during our experiments, as shown in Table I. In case of the preparation of microcrystalline samples, the precipitates obtained in the above-described manner were subjected to a further treatment with 10 M phosphoric acid. However, in the case of chromium phosphate, this method did not afford the desired result under the applied conditions [1].

Table I
List of samples

No. of sample	CP-I	CP-II	CP-III	TP-I	TP-II	TP-III	ZP-I	ZP-II	ZP-III	ZP-IV
Ratio PO_4 : metal	0.60	0.83	1.0	0.8	1.0	1.90	1.0	1.2	1.37	1.94
Percentage of excess H_3PO_4 used in precipitation	0	100	200	0	100	200*	0	100	200	200*

* Samples treated with 10 M H_3PO_4

ZP = zirconium phosphate
TP = titanium phosphate
CP = chromium phosphate

(b) The contents of metal and phosphate were determined in the samples after alkaline fusion, followed by extraction, and consequently by the Winkler method [2]. Metals were obtained thus as oxides, while the PO_4^{3-} content as MgNH_4PO_4 .

(c) Volumetric method and krypton gas used for the determination of the specific surface area of the samples at the temperature of liquid nitrogen [3].

(d) Changes in the weight of the samples in the temperature range from 25 to 1000 °C were established by a derivatograph (type MOM) using a heating-up rate of 5–10°/min. The weights of the samples were chosen so as to maintain a constant metal ion content (Zr, Ti, Cr).

(e) pH values were determined by a pH-meter (type Radiometer), using calomel and glass electrodes. The accuracy of these measurements was ± 0.01 pH.

(f) The dependence of the exchange capacity of the samples on the pH on the ionic radius and on the exposure to radioactive radiation was also studied; the distribution coefficients for some ion pairs (Sc^{3+} — Ca^{2+} , Fe^{3+} — Co^{2+}) — selected in advance as models — were determined.

The measurements were carried out under stationary conditions by the tracer technique, taking into account the times required to attain equilibrium, which had been established previously. In these measurements, ^{42}K or the corresponding radioactive isotopes were employed as traces. When measuring the exchange capacities, the concentration of the solution of the

counter-ion was chosen so as to be 5–6 times as high as the expected capacity. In the knowledge of the load, the amount of adsorbed ion could be concluded from the decrease of the measured radioactivity before and after equilibrium using samples of identical amount. The radioactivity of the samples was measured by means of a NaI/Tl well type crystal or an appropriate crystal for detection of β -particle employing a counter of Type NK-108. It has been shown by calculations [4] that the error of measurements did not exceed $\pm 5\%$. When it

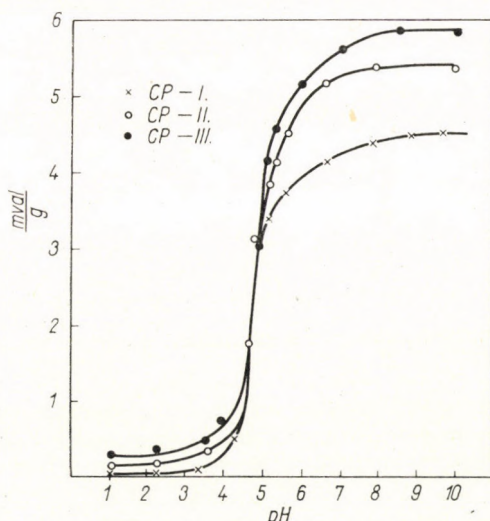


Fig. 1. Exchange capacity of chromium phosphate as a function of the pH, measured by tracer technique

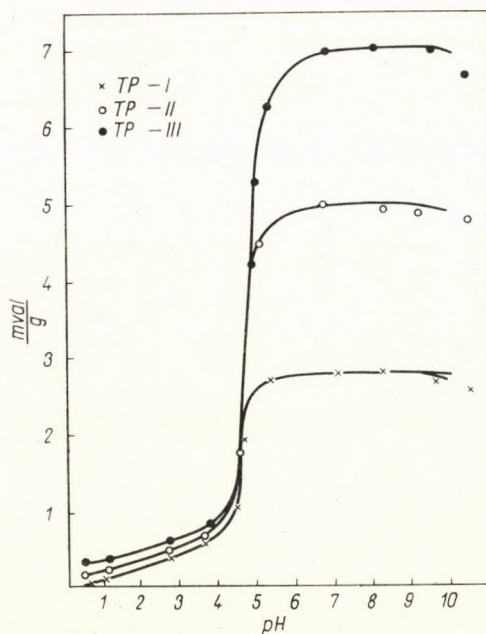


Fig. 2. Exchange capacity of titanium phosphate as a function of the pH, measured by tracer technique

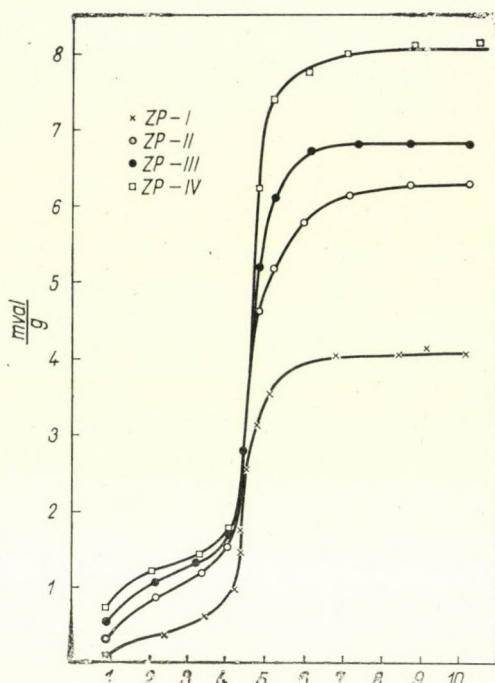


Fig. 3. Exchange capacity of zirconium phosphate as a function of the pH, measured by tracer technique

was necessary to vary the pH of the solutions, this was done by the addition of required volumes of a solution of HCl + KCl or KOH + KCl.

When measuring the distribution coefficients of the individual ions, an analogous method was applied, with the difference that the concentration of solution was chosen according to the data in Tables VIII and IX.

Table II
Measured specific surface areas

Compound	Measured specific surface area, sq. m./g			
	No. of sample			
	I	II	III	IV
CP	25.70	8.33	0.20	—
TP	96.80	8.70	0.10	—
ZP	332	2.20	0.10	<0.1

Discussion

Measurements by X-ray diffraction showed that the samples precipitated with an excess of the reagent had amorphous character, while those treated subsequently with phosphoric acid had microcrystalline structure [5].

Measurements of the specific surface areas revealed that these values markedly decreased as the PO_4 : metal ratio became higher. From this it can be concluded that within the range of amorphous substances, products of various porosity may be obtained, depending on the quantity of phosphoric acid applied. The sample prepared with stoichiometric ratio had the greatest surface area and highest porosity. It must be noted that in the case of chromium phosphate, this effect is not so well-defined as in the case of the other two phosphates partly due to the lower ratios, and partly to the smaller area of the measured surface.

The measured exchange capacities of the examined substances showed that zirconium phosphate had the higher capacity. On examining the dependence of capacities on the pH, in the case of zirconium phosphate and indefinite horizontal part was observed at pH values below 4, while a definite horizontal part began at pH 5. From a comparison of the obtained pH curves with the dissociation curve of phosphoric acid [6] it is apparent that the nearly horizontal part at pH values below 4 indicates the presence of rather small amounts of $\text{H}_2\text{PO}_4^{1-}$, while the well defined second horizontal section corresponds to the second dissociation step of phosphoric acid, i.e. to the presence of HPO_4^{2-} . Consequently, exchangeable H^+ ions may be formed by the dissociation of the above-mentioned hydrogen phosphates present in the substance. Thus, the degree of dissociation can be one of the primary factors in determining the capacity. From another aspect, this presumption might be proved by the change in the H^+ ion concentration of a solution contacted with an ion exchanger. This would practically mean that the capacity values measured by the tracer technique should fairly well agree with the data of capacity calculated indirectly from the changes in the H^+ ion concentration of the solution, provided the load of the ion exchanger is the same in both cases. According to our experimental results in this respect (cf. Table III), in the pH region below 4, deviations are found between the results of the two

Table III

*Changes in the H^+ ion concentration
at the same concentration of KCl*

Sample	Exchangeable H^+ ions, meq/g of ion exchanger	Capacity measured by tracer method, meq/g of ion exchanger	Ion exchange capacity as the percentage of total capacity %
ZP-I	0.15	0.47	32
ZP-II	0.53	0.85	62
ZP-III	0.59	0.92	64
ZP-IV	0.63	0.93	68

kinds of measurement. These deviations decrease with the rise of the PO_4/metal ratio.

This fact, and the above-mentioned relationship established in the surface area measurements lead to the conclusion that, under the given conditions, the deviations are to be attributed to the adsorptive properties

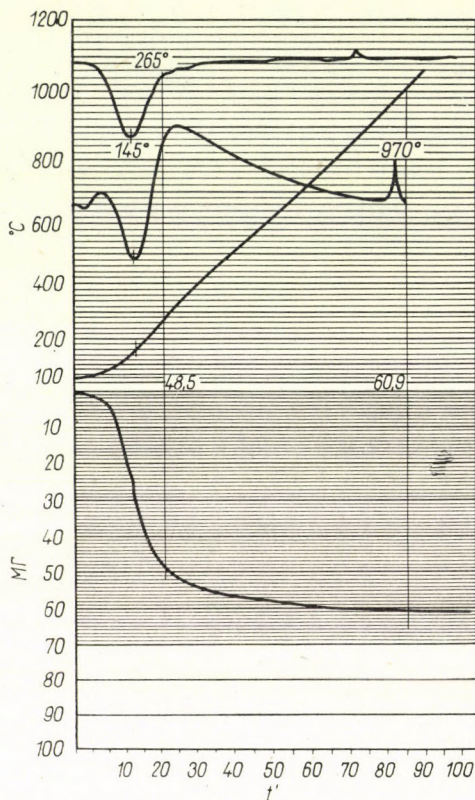


Fig. 4. Thermogram of sample ZP-I

of the substances. A reliable evaluation of the adsorption data relating to the upper step of the pH curve was impossible owing to the probable hydrolysis of the examined substances, unambiguously described also in literature [5]. However, in our opinion this does not mean that the discussed adsorptive property cannot prevail under such conditions.

In order to obtain information as regards the composition of the exchangers, and to confirm the above-mentioned hypothesis of dissociation, thermoanalytical investigations were carried out. In the thermoanalytical curves of zirconium phosphate (Figs 4–7), endothermic peaks appear at about 135 °C and then at about 460°, followed by rapid weight changes. In the case of the amorphous samples an exothermic peak is found at about

950°, which is not followed by a weight change. The observed loss of weight presumably indicates the loss of water, which consists of crystal and structure as shown by the data in Table IV. This presumption is based on the following practical experiences: on the basis of the thermograms, the samples treated at 260° and 800°, respectively, were selected, and the reversibility of their

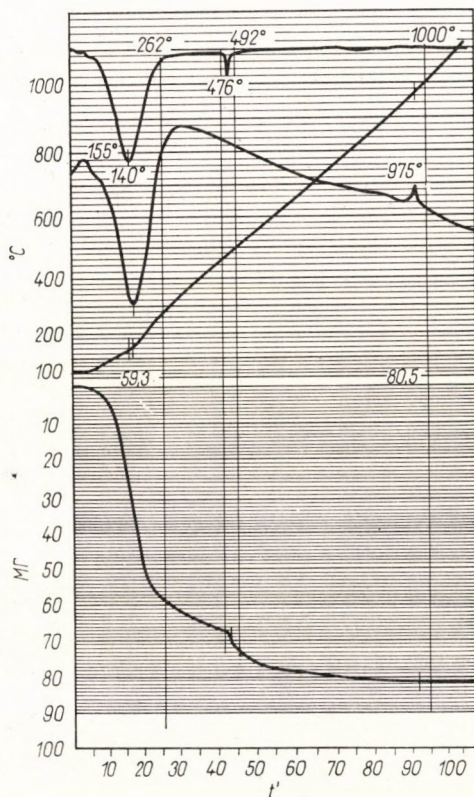


Fig. 5. Thermogram of sample ZP-II

weight losses was studied. It was found that the samples treated at 260 °C, when allowed to stand for 24 hours at room temperature, absorbed, in general, appreciable amounts of moisture, while this water uptake was negligibly low in the case of samples treated at 800 °C. Then the test samples were loaded by amounts of K^+ ions corresponding to the first and second horizontal part, respectively, of the pH curve. Weight increases due to water uptake showed a corresponding decrease. From this it follows that one part of the loss of water below 260 °C originates from the condensation of phosphate groups, while the other part, the irreversible loss of water, corresponds to the crystal water of the molecule. The loss of water between 260 and 800 °C is due to

Table IV
Data of weight loss obtained by thermogravimetry

Sample	Water of crystallization, %	a %	b %	a ₁ %	b ₁ %	s %
CP-I	14.6	0.2	0	7.0	2.4	4.8
CP-II	15.0	0.7	0.2	7.5	2.6	5.4
CP-III	14.1	0.8	0.2	7.7	2.7	5.6
TP-I	13.6	4.0	3.0	2.0	0.5	2.5
TP-II	14.2	3.8	2.4	4.2	0.8	4.8
TP-III	9.6	4.6	2.3	7.0	1.8	7.5
ZP-I	10.0	9.2	6.2	4.3	3.3	4.0
ZP-II	9.0	3.8	1.2	5.7	1.8	6.6
ZP-III	8.5	0.8	0.2	6.7	0.5	6.8
ZP-IV	8.0	5.8	2.1	7.0	2.8	7.9

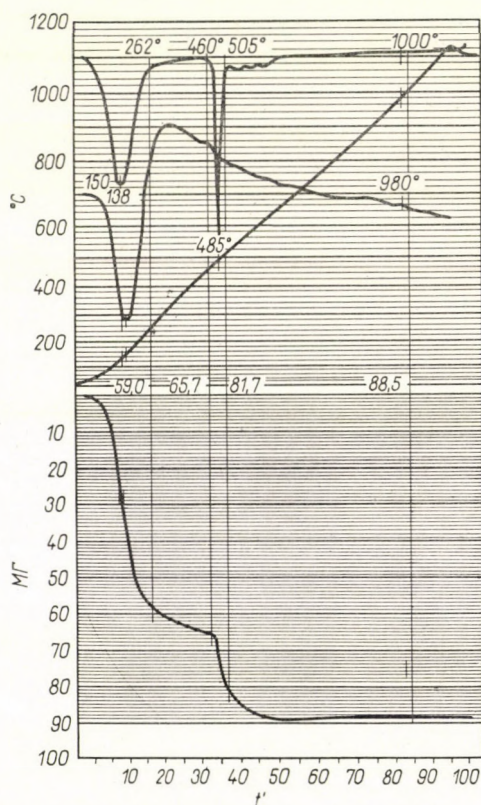
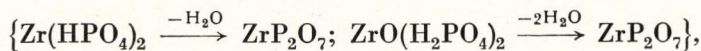
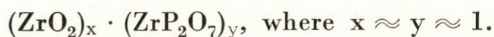


Fig. 6. Thermogram of sample ZP-III

further condensation of the phosphate groups:



while the exothermic peak appearing at 950° in the case of amorphous samples indicates the presence of a substance of the composition



On the basis of the thermoanalytical data obtained, these material compositions hold good also for titanium phosphate, while in the case of chromium phosphate the reactions

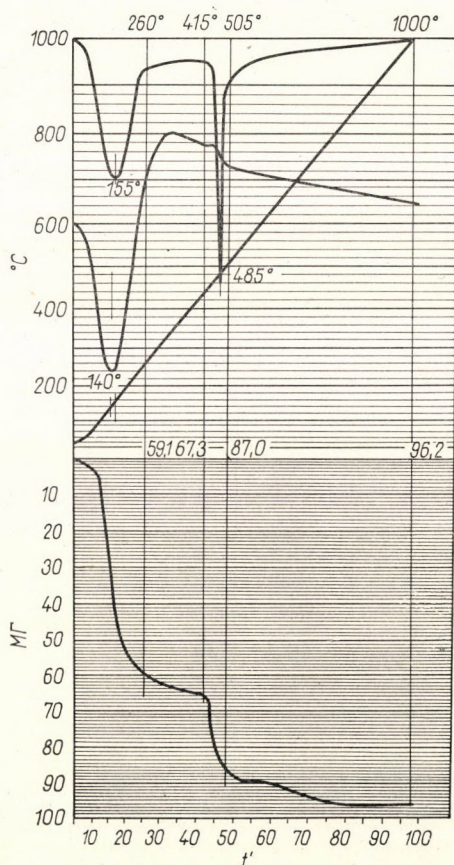
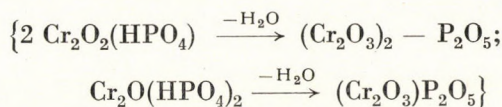
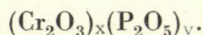


Fig. 7. Thermogram of sample ZP-IV

lead at the mentioned higher temperature to a different composition:



It is evident from the above-mentioned saturation experiments concerning the weight between 260 and 800 °C that the theoretical capacity of the ion exchangers cannot be attained, because not all places are available to the counter-ions; this also directly follows from the data given in Table IV.

On the basis of the presumption that the exchangeable H^+ ions are supplied by the dissociation of the hydrophosphate groups, the expected capacities were calculated from the above-discussed losses of water by the formula:

$$(a - b) + (a_1 - b_1) = s\%$$

where a is the percentage weight increase of the ion exchanger treated at 260 °C, not saturated by ions; b = percentage weight increase of the ion exchanger treated at 260 °C, saturated by ions; a_1 = percentage weight decrease of the exchanger treated at 800 °C, not saturated by ions; b_1 = percentage weight decrease of the ion exchanger treated at 800 °C, saturated by ions; and s = quantity of water taken into account as far as the exchange capacity is concerned (in %).

In these calculations we started with the presumption that, on the basis of what has been said before, the samples treated at 800 °C had the compositions $(\text{ZrO}_2)_x \cdot (\text{ZrP}_2\text{O}_7)_y$ and ZrP_2O_7 , respectively, depending on the PO_4/metal ratio. Thus, e.g., in the case of micro crystalline zirconium phosphate, with a $\text{PO}_4 : \text{Zr}$ ratio of 1.94 we have:



crystal water 8% = 1.16 mole H_2O molecular weight 284
 water — s % = 7.9 = 1.14 mole H_2O molecular weight 305

Consequently, the expected capacity is:

$$Q = \frac{2280}{305} = 7.5 \text{ meq/g.}$$

The capacities of the investigated samples obtained in this way are listed in Table V, together with data afforded by other methods of measurement. It is to be noted that the load of the ion exchanger was the same in all methods of measurement. The capacity values obtained by calculation from the changes in the H^+ ion concentration produced in the solution by ion exchange agreed,

within the error limits, with the capacities determined by thermogravimetry and by the tracer technique (Table V).

The correctness of the above assumption, according to which the exchangeable H^+ ions are supplied in the case of the investigated ion exchangers

Table V

Exchange capacities of ion exchangers measured by various methods

Capacity meq/g	ZP				TP			CP		
	I	II	III	IV	I	II	III	I	II	III
By the thermogravimetry ...	3.8	5.8	6.1	7.5	2.4	5.1	7.1	4.3	5.4	5.8
By tracer technique	4.7	6.3	6.8	8.1	2.4	5.0	7.7	4.7	5.7	5.9
Calculated from changes in H^+ ion concentration	4.2	5.7	6.3	7.6	2.8	5.3	7.3	4.5	5.5	6.0

by the dissociation of the hydrogen phosphate groups, is confirmed by the agreement, within the error limits, of the results given in Table V, obtained by three different methods. Accordingly, the ion exchange is conceived as a two-step process, depending on the pH, corresponding to the steps of dissociation. Thus, the hydrogen ions formed in the process



are exchanged in the first step, while those originating from the dissociation



in the second step.

Some investigations on practical application of zirconium and chromium phosphates

As it has been shown by preliminary experiments, under the given conditions titanium phosphate is unsuitable for the separation of the chosen pair of ions. Thus, further studies concerning the separation were limited to zirconium and chromium phosphates only. During this work, our purpose was to study the suitability of the examined ion exchangers for the separation of ions produced in simultaneous nuclear reactions. In order to decide this question, the capacity of samples as a function of the ionic radii, and the changes in the capacities of samples subjected to radioactive radiation were examined. The distribution coefficients for the pairs of ions chosen as models were also established as a function of the pH and concentration, and experiments with

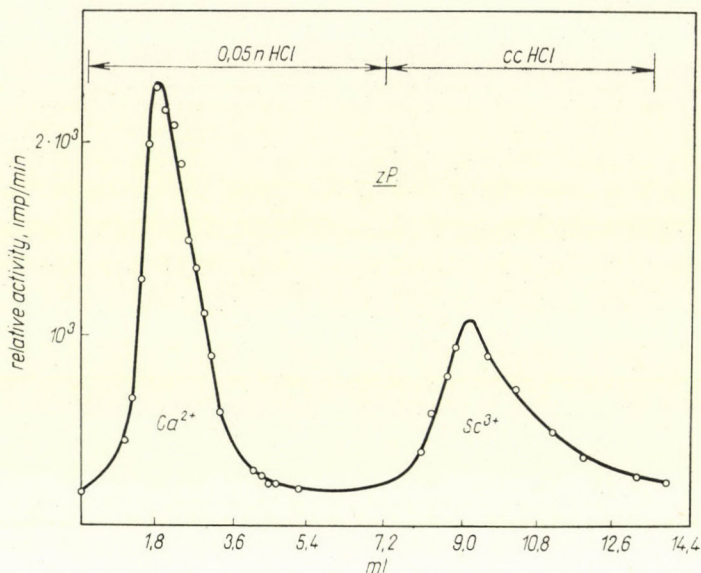


Fig. 8. Elution curve of the ion pair $\text{Sc}^{3+} - \text{Ca}^{2+}$

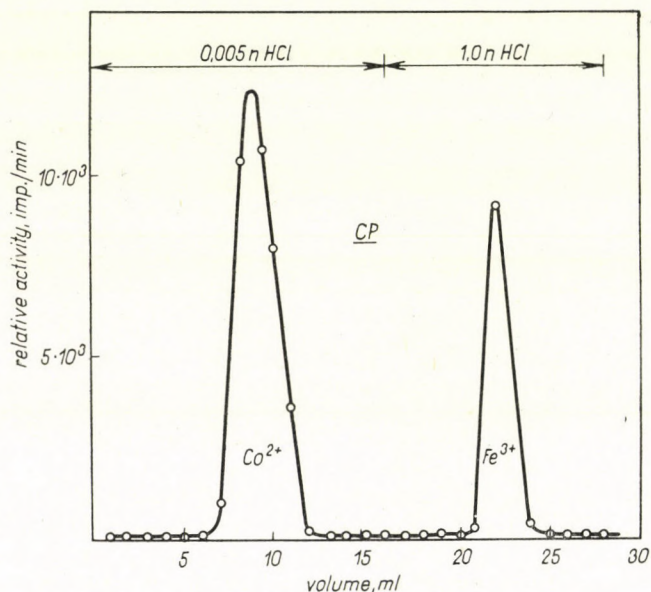


Fig. 9. Elution curve of the ion pair $\text{Fe}^{3+} - \text{Co}^{2+}$

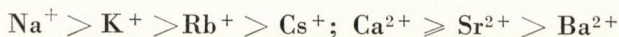
exchange columns were carried out. In the former work a tracer technique, based on identical principles as the capacity determinations, was employed, while the experiments using columns were conducted as follows. A resin bed was made employing about 3 g of the ion exchanger of 43 to 49 mesh grain size. An amount of cations representing less than a 10% load of the resin was trans-

ferred on the bed at a rate of 0.18 ml/sec. The various cations were eluted at the same rate, using hydrochloric acid solutions of various concentration. The experimental results are shown in Tables VI–IX, and in Figs 8–9.

Table VI
Exchange capacities versus the ionic radii
(at pH = 2.5)

Ion	Ionic radius [7] Å	Capacity, meq./g		
		CP-III	TP-III	ZP-III
Na ⁺	0.95	0.90	1.15	1.35
K ⁺	1.33	0.70	1.05	1.20
Rb ⁺	1.48	0.66	0.90	1.10
Cs ⁺	1.69	0.62	0.84	1.03
Ca ²⁺	0.99	0.31	0.42	0.53
Sr ²⁺	1.13	0.29	0.39	0.50
Ba ²⁺	1.35	0.23	0.32	0.40

It is seen from these data that the exchange capacity for mono- and bi-valent cations depends on the ionic radius according to the following order:



which is analogous to that observed with organic resins containing sulphonic groups.

As it is shown by Table VII simultaneous irradiation with $0.8 \cdot 10^8$ rad

Table VII
Change of the exchange capacity
on the effect of radioactive radiation
(at pH = 2.5)

Irradiation	Capacity, meq./g		
	CP-III	ZP-III	Dowex-50
Before	0.70	1.20	2.0
After	0.72	1.18	—

neutron and $7.0 \cdot 10^4$ rad γ -doses left the capacities of the samples practically unchanged, while the organic ion exchange resin *Dowex-50*, under the same conditions, suffered decomposition.

The values of the distribution coefficients (D) and the selectivity factors (α) calculated from them (*cf.* Tables VIII and IX) indicated the possibility

Table VIII

*Distribution coefficients (D) and — selectivity factors (α)
for Sc^{3+} and Ca^{2+} ions in the case of zirconium phosphate*

HCl normality	D_{Sc} meq/g of ion exchanger				D_{Ca} meq/g of ion exchanger				$\alpha_{\text{Ca}}^{\text{Sc}}$			
	0.1	0.2	0.3	0.5	0.1	0.2	0.3	0.5	0.1	0.2	0.3	0.5
Conc.	0.001	0	0	0.	—	—	—	—	—	—	—	—
1.0	1.2	0.3	0.2	0.09	—	—	—	—	—	—	—	—
0.5	4.8	0.8	0.7	0.4	—	—	—	—	—	—	—	—
0.1	5.5	0.9	0.8	0.5	0	0	0	0	—	—	—	—
0.05	8.2	1.2	0.7	0.4	0.04	0.03	0.02	0.01	205	40	35	40
0.01	4.6	1.0	0.6	0.3	0.3	0.2	0.08	0.06	15.3	5.0	7.5	5.0
0.005	2.7	0.8	0.4	0.2	0.6	0.4	0.2	0.1	4.5	2.0	2.0	2.0
0.001	1.6	0.4	0.2	0.1	0.9	0.7	0.4	0.2	1.8	0.6	0.5	0.5

of efficient separation of the chosen cations. The correctness of these indications was proved by the elution curves (Figs 8 and 9) obtained in the experiments with exchange columns and by the subsequent radiochemical examination of the purity of the fractions corresponding to the peaks of these curves.

Table IX

*Distribution coefficients (D) and selectivity factors (α)
for Fe^{3+} and Co^{2+} ions in the case of chromium phosphate*

HCl normality	D_{Fe} meq/g of ion exchanger				D_{Co} meq/g of ion exchanger				$\alpha_{\text{Co}}^{\text{Fe}}$			
	0.1	0.2	0.3	0.5	0.1	0.2	0.3	0.5	0.1	0.2	0.3	0.5
1.0	0.005	0.004	0.004	0.001	0.001	0.001	0.001	0.001	5	4	4	1
0.5	0.01	0.009	0.009	0.008	0.001	0.001	0.001	0.001	10	9	9	8
0.1	0.06	0.05	0.05	0.04	0.001	0.001	0.001	0.001	60	50	50	40
0.05	0.11	0.07	0.07	0.05	0.001	0.001	0.001	0.001	110	70	70	50
0.01	0.13	0.11	0.09	0.06	0.001	0.001	0.001	0.001	130	110	90	60
0.005	0.21	0.16	0.12	0.07	0.001	0.001	0.001	0.001	210	160	120	70
0.001	0.35	0.24	0.15	0.09	0.001	0.001	0.001	0.001	350	240	150	90
0.0005	0.7	0.34	0.20	0.11	0.001	0.001	0.001	0.001	700	340	200	110

SUMMARY

As a novel member of groups of synthetic inorganic ion exchangers, chromium phosphate has been prepared. At given ratios of PO_4/Cr , this compound can be best characterized by the formula $\text{Cr}_2\text{O}_2\text{HPO}_4$ and $\text{Cr}_2\text{O}(\text{HPO}_4)_2$, respectively. Some properties of this product were investigated and compared with those of zirconium phosphate and titanium phosphate. It was found that, though the radicals HPO_4^{2-} predominate in the prepared compounds, also the presence of the radicals H_2PO_4^- and PO_4^{3-} is to be taken into account. Further, as it follows from the close analogy between the curve of exchange capacity vs. pH, and the dissociation curve of phosphoric acid, the formation of exchangeable H^+ ions may be attributed to the dissociation of the hydrogen phosphate groups present in the ion exchanger. Consequently, the mechanism of the ion exchange process is of a two-step nature (depending on the pH); the hydrogen ions formed in the process $\text{H}_2\text{PO}_4^- \rightarrow \text{HPO}_4^{2-}$ are exchanged in the first step, while those liberated by the dissociation $\text{HPO}_4^{2-} \rightarrow \text{PO}_4^{3-}$ in the second step. Further, it has been found that when low ratios of PO_4 metal are used i.e. when substances of amorphous are formed, also the adsorption properties are of importance. On the basis of the high degree of analogy observed, these conclusions may be extended to all three substances examined. The positive results concerning practical applicability justify the use of these ion exchangers in radiochemical practice, e.g. for the separation of ions formed with different activities in the case of simultaneous nuclear reactions, such as $^{59}\text{Co}(\text{n}, \gamma) ^{60}\text{Co}$ and $^{59}\text{Co}(\text{n}, \text{p}) ^{59}\text{Fe}$ and being present in various concentrations.

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ACTIVATION ANALYSIS OF TRACE CONTAMINANTS IN GaAs SEMICONDUCTOR MATERIALS

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The maximum permissible contamination in GaAs semiconductors is of ppm or ppb order, similarly to the case of semiconductor grade silicon. The sensitivity of known chemical or instrumental methods of analysis covers in the best cases the higher values of the ppm order only, and the reliability of the determination is considerably affected by the impurities of similar order which may be present in the p. a. grade chemicals and reagents used. Thus any instrumental analysis may easily involve an error of 100 to 200%.

Since in the development of high grade semiconductors and advanced semiconductor devices the purity requirements are much higher than that which can be checked by the above methods, it has become necessary to develop an adequate technique for the activation analysis of trace contaminants in GaAs semiconductors.

HOSTE and VAN DER BERGHE [1a], BUJDOSÓ *et al.* [1b], as well as NIESE [2] have reported the determination of some trace contaminants in gallium and GaAs by activation analysis. Owing to the high activation rate of the matrix components, these authors dealt only with contaminants yielding medium or long-lived activities. The long cooling time (from 140 to 600 hours) and multistep chemical separation involved render the procedure both laborious and lengthy.

In developing the technique of the activation analysis, efforts have been made to find a procedure suitable also for the determination of contaminants generating activities with half-lives of a few hours, such as copper, by which the semiconductor parameters can be particularly affected.

Both gallium and arsenic produce high activities, and if used as matrix components, differences as high as 5 orders of magnitude may arise between the matrix and total contaminant activities even in the presence of microgram amounts of contaminant. Now, since in semiconductor GaAs monocrystal the maximum permissible impurity concentration is substantially lower, being of ppb order, the difference in activities usually amounts to 10^7 – 10^8 cps.

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The above data imply at the same time that the trace impurities in the GaAs system cannot be determined by nondestructive gamma spectrometry, but they have to be separated each time by a chemical method.

In Table I we have listed the contaminants investigated, the nuclear

Table I

Element	Nuclear Reaction	σ act (barn)	$T_{1/2}$	(Activity, dps)* 24h; μ g	$E\gamma$ MeV
Cu	$^{63}\text{Cu}(n,\gamma)^{64}\text{Cu}$	3.9	12.9 h	$2 \cdot 10^5$	0.51; 1.34
Hg	$^{196}\text{Hg}(n,\gamma)^{197}\text{Hg}$	4.4	65 h	$3.8 \cdot 10^3$	0.077; 0.191 0.279
Au	$^{197}\text{Au}(n,\gamma)^{198}\text{Au}$	93	64.8 h	$6.6 \cdot 10^5$	0.411
Cd	$^{114}\text{Cd}(n,\gamma)^{115}\text{Cd}$	0.3	55.2 h	$4.4 \cdot 10^2$	(0.335)**0.260 0.523
Co	$^{50}\text{Co}(n,\gamma)^{65}\text{Co}$	20	5.2 a	$7.2 \cdot 10^2$	1.17; 1.33
Zn	$^{64}\text{Zn}(n,\gamma)^{60}\text{Zn}$	0.4	245 d	$7.6 \cdot 10$	0.51; 1.14

* 10^{13} n/cm²sec.

** Energy of the $^{115\text{m}}\text{In}$.

reactions, and the nuclear properties of the isotopes involved in the analysis [8].

The $^{68}\text{Zn}(n,\gamma)^{69\text{m}}\text{Zn}$ reaction which reveal the presence of zinc with a sensitivity by orders of magnitude higher than that of the reaction listed in the Table, cannot be used because it is impossible to distinguish this $^{69\text{m}}\text{Zn}$ activity with 13.9 h half-life, from that produced in the reaction $^{69}\text{Ga}(n,p)^{69\text{m}}\text{Zn}$ due to fast neutron capture in the gallium matrix and exceeding many times the former. The ^{66}Cu activity produced by a (n,α) process in ^{69}Ga does not interfere with the determination of copper, since its half-life is very short (5.1 m). The ^{67}Cu activity produced by the $^{71}\text{Ga}(n,\alpha n)$ process does not disturb the evaluation of ^{64}Cu .

In principle, considering the restricted possibilities for remote controlled manipulations required for radiation protection, two methods seemed to be convenient for the separation of the matrix component from the contaminants, namely ion-exchange or solvent extraction. Since for gallium and arsenic matrix elements the ion-exchange technique is not sufficiently selective owing to difficulties presented by the remote manipulation of the necessarily large solution volumes, the solvent extraction method proved to be more suitable in practice.

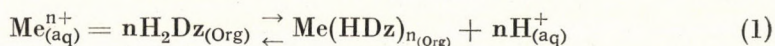
Considering the high production cost of GaAs monocrystals and the substantial shielding equipment needed for the measurement, the solvent and reagent were chosen such that it should react with a group of the contaminants to permit the simultaneous determination of several elements from a single

irradiated and processed sample. Quantitative evaluation of the extracted contaminants can be made from the measured energy spectra of the extracted activities. Since the extraction has to be performed by manipulator, no emulsion must form in the solvent; the phases should rapidly separate, and the extraction of the matrix components, even in trace amounts, has to be prevented.

Of the known chelate reagents the system dithizone/carbontetrachloride ($\text{H}_2\text{Dz}/\text{CCl}_4$) seemed to be the most suitable in our case, and the method has been developed for the use of this system.

Depending on the acidity of the solution H_2Dz forms with the metallic contaminants under investigation complexes either of primary $\text{Me}_x(\text{HDz})_y$ type or of secondary $\text{Me}_x(\text{Dz})_y$ type, extractable with carbon tetrachloride or chloroform solvent [3]. Low pH favours, in general, the formation of primary complexes of a somewhat higher solubility in carbon tetrachloride as compared with the secondary complexes produced at higher pH values. Zinc and cadmium are exceptions to this general rule in that they are known to form primary complexes only.

The formation rate of each metallic complex markedly depends on the hydrogen ion concentration of the aqueous phase. In highly dilute solutions the rate of the equilibrium reaction (1) is very slow and proportional to the metallic ion and dithizone concentrations. At higher acidities the reaction equilibrium can only be achieved after prolonged shaking.



In Table II the primary metallic complexes, the extraction and stability constants, the optimum pH value for their formation, and some other important parameters are listed.

Table II
[3, 5, 6, 7]

Element	Primary complex	$\frac{\log K_{ex}}{\text{CCl}_4}$	$\log K$	pH range	Reaction rate	Solubility M/CCl_4	Colour
Cu	$\text{Cu}(\text{HDz})_2$	10.5	23.3	1—4	moderate	10^{-3}	violet-red
Au	$\text{Au}(\text{HDz})_3$	—	—	w. H_2SO_4	slow	10^{-5}	orange
Hg	$\text{Hg}(\text{HDz})_2$	26.8	40.3	w. H_2SO_4	fast	10^{-5}	orange
Cd	$\text{Cd}(\text{HDz})_2$	2.1	—	6.5—14	fast	$1.4 \cdot 10^{-5}$	rosa
Co	$\text{Co}(\text{HDz})_2$	1.6	13.0	5.5—8.5	fast	$1.6 \cdot 10^{-4}$	purple
Zn	$\text{Zn}(\text{HDz})_2$	2.2	—	6—9.5	fast	10^{-3}	reddish violet
Ga	$\text{Ga}(\text{HDz})_3$	—1.3*	—	4.5—6	slow	10^{-5}	violet-red

* The value is given for chloroform solvent.

As it is obvious from the Table II, the contaminants of interest can be divided into two groups with respect to extractability. Copper, gold and mercury are extracted with slightly acidic, while cadmium zinc and cobalt with alkaline solutions. Thus, there is a possibility for the co-extraction of three elements in each single operation.

Experimental

The solutions and solvents used were:

1. 1 : 1 mixture of 1 : 1 diluted HNO_3 and HCl (HNO_3/HCl)
2. 25% ammonium citrate solution adjusted to pH 3 with H_2SO_4
3. 25% K-Na-tartarate solution
4. 1 : 1 mixture of diluted HCl and 1 N H_2SO_4 ($\text{HCl}/\text{H}_2\text{SO}_4$)
5. 2.5 NaOH solution
6. 1.5 mg/100 ml purified $\text{H}_2\text{Dz}/\text{CCl}_4$ solution

The schematic drawing of the extractor developed for the extraction of the contaminants from GaAs is shown in Fig. 1.

The extractor is housed in a hot chamber with concrete and lead shield and provided with a remote controlled manipulator. For the dosage of the solvent a precisely calibrated feeder of maximum 5 ml volume is used, connected by a capillary to the actual extractor. The solvent is discharged through a gooseneck capillary, the length of which is set such that on overturning the column the solvent discharges automatically and continuously while the drops can be easily counted.

The solvent container the piston serving for controlling the operation, and the speed controller of the motor driving the agitator mechanism are located outside of the hot chamber. The solvent container and the piston are connected with the extractor by a 2 meter long polyethylene tube of 3 mm inside diameter. These appliances permit the remote control and manipulation of the extractor.

For single extraction, the solvent can be fed into the extractor in volumes of 5 ml or less, and thus it is possible to extract about 95% of the contaminants. The extraction constant of the $\text{Ga}(\text{HDz})_3$ complex in chloroform ($\log K_{\text{ex}} = -1.3$) is much lower than of any dithizone complex of the contaminants we want to determine. This permits by precise dosage of the reagent to avoid the extraction of gallium even in trace amounts.

To obtain identical conditions for this co-extraction of contaminants, 10 μg of inactive carrier was added to the active sample for each of the contaminants involved, and the reagent concentration was adjusted relative to the added amounts.

For the activation analysis of trace contaminants in the GaAs system the technique was developed using samples of 0.1–0.2 g, activated in quartz ampoules with a thermal neutron flux of about $1.5 \cdot 10^{13} \text{ n/cm}^2 \cdot \text{sec}$ for 24 h in the case of copper, mercury and gold, and for 116 h in the case of cadmium, zinc and cobalt.

(a) Determination of copper, gold and mercury: After 24 h irradiation, the active sample was dissolved in HNO_3/HCl mixture using a 50-ml beaker containing 10 μg inactive carrier of copper, gold and mercury each, then evaporated. The dry residue was taken up in 5 ml of $\text{HCl}/\text{H}_2\text{SO}_4$ solution and evaporated again in order to remove the nitrous vapours. The not fully dried residue was dissolved in 5 ml of ammonium citrate buffer solution, and poured into the extractor containing the measured volume of solvent. On precise adjustment of the solution volumes, the pH of the aqueous phase was 1 ± 0.5 . The extraction was performed with $2 \times 5 \text{ ml}$ of $\text{H}_2\text{Dz}/\text{CCl}_4$, with agitation for 2 minutes. The block diagram of the arrangement for separation by extraction is shown in Fig. 2. Standards containing known amounts of the contaminants were processed simultaneously with the samples under identical conditions.

(b) Determination of cadmium, cobalt and zinc: After irradiation for 116 h, the active sample was dissolved and processed in the same way as described in (a); the not completely dried residue was then dissolved in 5 ml of 25% K-Na-tartarate solution, the acidity of which was adjusted by buffer to pH 9.4–9.7. (If necessary, the pH of the solution can be adjusted later by the addition of NaOH in a quantity checked by phenolphthalein indicator.) After addition of the solvent, the solution was poured by manipulator into the extractor, and the extraction of the contaminants was effected with $2 \times 5 \text{ ml}$ of $\text{H}_2\text{Dz}/\text{CCl}_4$. Standards of the contaminants were processed simultaneously with the samples in the same way.

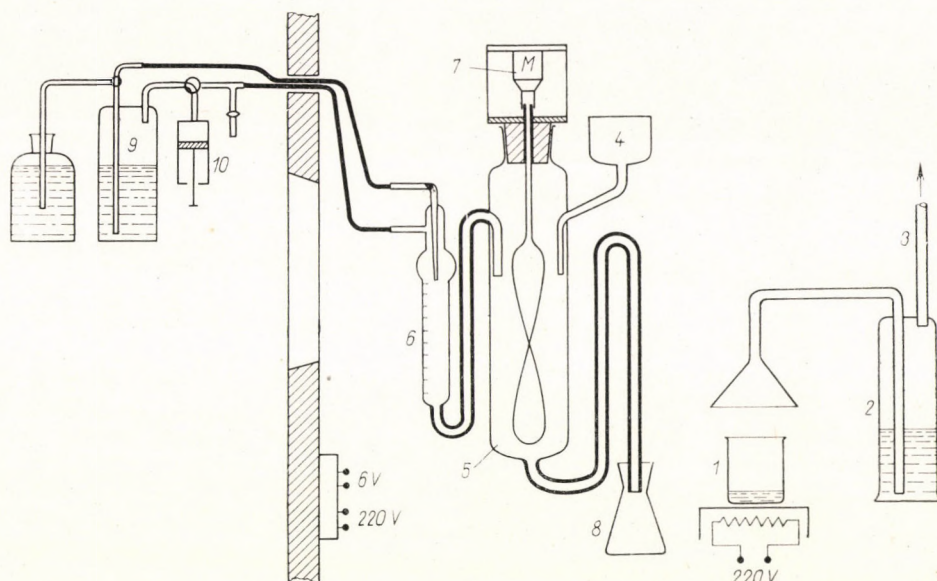


Fig. 1

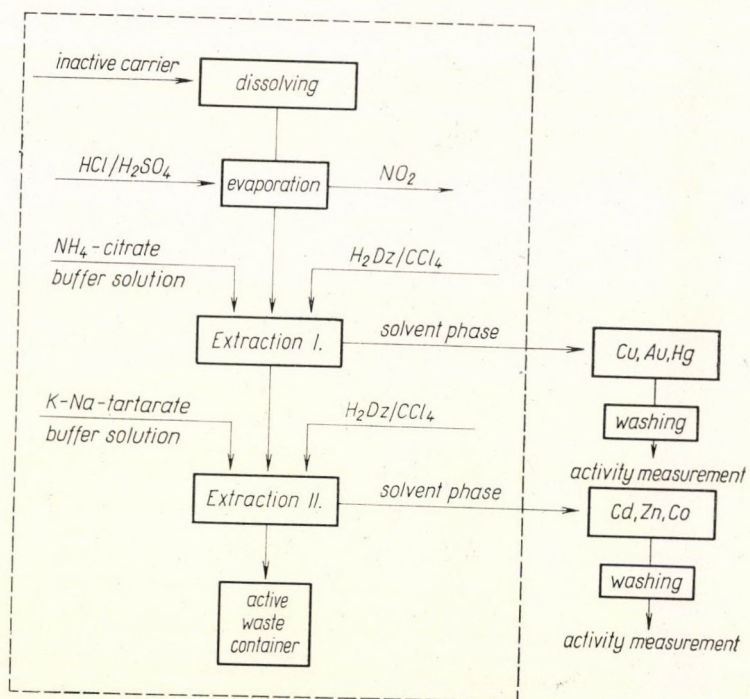


Fig. 2

Results and evaluation

For a qualitative and quantitative evaluation of the extracts gamma-spectrometric and coincidence techniques were used. The energy spectra were obtained with a *System KFKI, NTA-256* type multichannel analyzer using a $3'' \times 3''$ *Nuclear Enterprises* NaI(Tl) crystal detector.

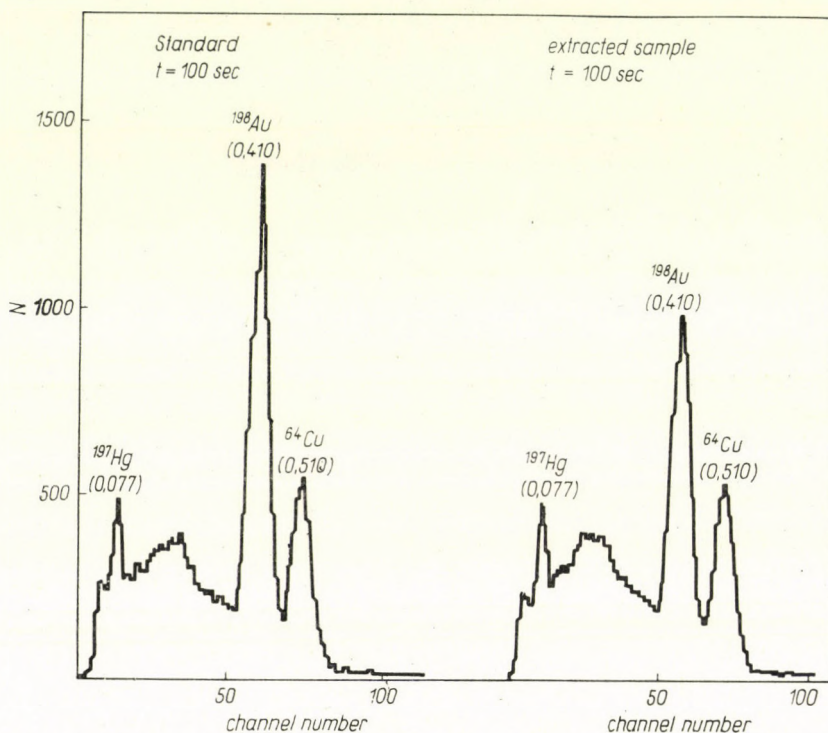


Fig. 3. Activities in the measured and the extracted standard samples. ^{64}Cu : 10^{-8} g; ^{198}Au 10^{-9} g; ^{197}Hg : $2 \cdot 10^{-8}$ g. Inactive carrier: 10^{-3} g, pH = 1, 2×5 ml $\text{H}_2\text{Dz}/\text{CCl}_4$

The distribution coefficients of the dithizone complexes, formed with individual contaminants as a function of the pH, were taken to be the values reported in the literature [3, 4]. In order to avoid partial extraction of the gallium matrix, which is possible only in the range 4.5–6, the extraction of copper, gold and mercury was made from slightly acidic (pH = 1) solution while that of the zinc, cadmium and cobalt group from alkaline (pH 9.4–9.7) medium.

The energy spectra of the extract containing copper, gold and mercury activities and of the standards taken under the same conditions are shown in Fig. 3.

Copper and mercury are extracted almost quantitatively, while the extraction of gold amounts to about 67–70%. Under identical experimental conditions the variation in the percentual extraction of gold can be kept within 10%. For a closer reproduction of the experimental conditions, the

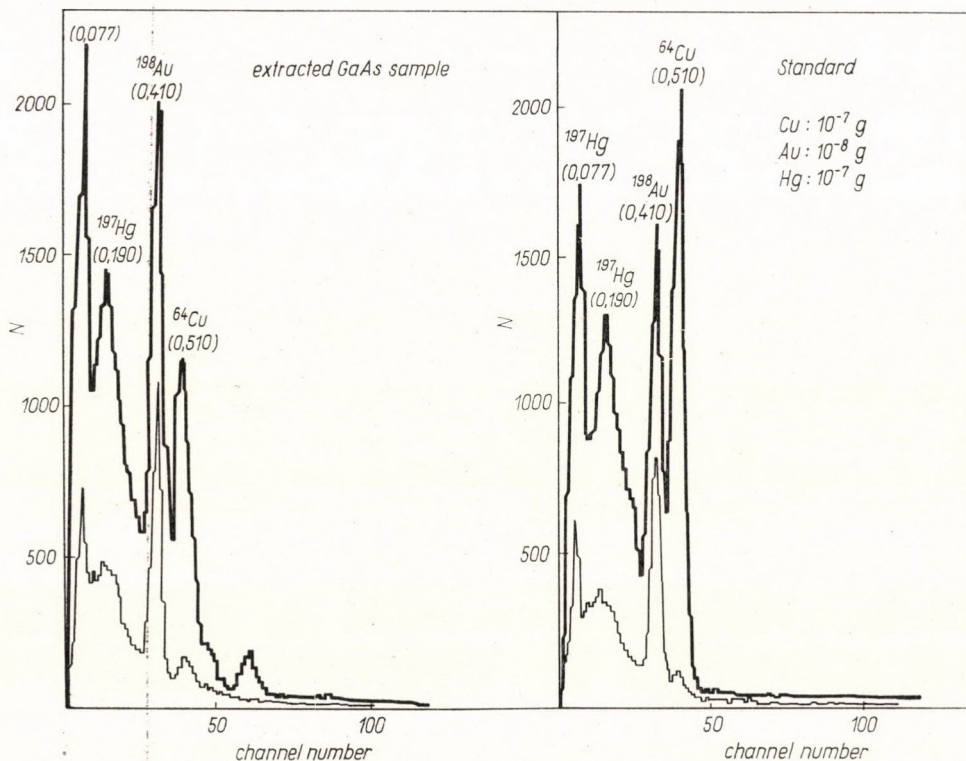


Fig. 4. Energy spectra of the extracted GaAs sample and of the standard

extraction was performed from a solution to which about 10^5 cps GaAs activity had been added.

In Fig. 4 the energy spectrum of the extract of an about 0.1 g GaAs sample, activated for 24 hours, is shown. The spectra were taken 4 and 66 hours after the end of irradiation. Simultaneously with, but in a separate operation the coincidence spectrum of ^{64}Cu was also recorded.

As it is seen in the Figure, the contaminating copper, gold and mercury activities can be well separated even from high gallium and arsenic activities and well evaluated in the energy spectrum. The method is particularly advantageous for the determination of copper, but lends itself well for the determination of contaminants, the half-life of which is close to that of ^{76}As , like gold and mercury in our case. Owing to the simplicity of the apparatus, the method can be conveniently used for the determination of long-lived activities,

such as ^{65}Zn , and ^{60}Co which yield dithizone complexes well extractable from carbon tetrachloride. The time taken by the determination is practically restricted to that of the irradiation, since there is no need for cooling time.

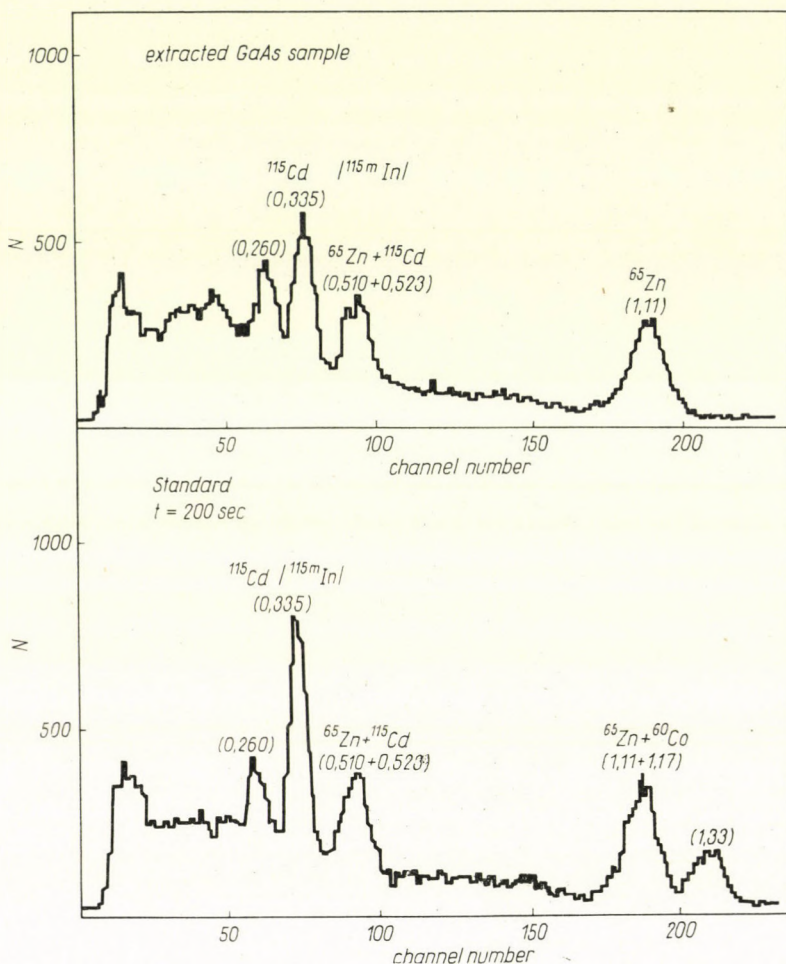


Fig. 5. Energy spectra of alkaline extracts of GaAs samples, activated for 116 hours, and of the processed standards

In Fig. 5 the gamma spectrum of the GaAs sample, activated for 116 hours and extracted from alkaline solution, is compared with the energy spectra of the extracted activities of the ^{115}Cd , ^{65}Zn and ^{60}Co standards.

In Table III the accuracy of the determination is given for various quantities of contaminants.

The data given in the Table were obtained by extracting a known quantity of each contaminant activity from GaAs-free buffer solutions in the pres-

Table III

Contaminants, μg	Cu	Au	Hg	Cd	Zn	Co
	measured μg		$\Delta m\%$			
0.5	0.525 5	0 —	0.520 4	0.480 4	0.540 8	0.470 6
0.1	0.092 8	0.091 9	0.097 3	0.093 7	0.094 6	0.088 12
0.05	0.062 24	0.047 6	0.045 10	0.053 6	—	0.044 12
0.01	0.011 10	0.011 10	0.007 30	—	—	—
0.005	—	0.004 20	—	—	—	—

ence of a suitable inactive carrier. The activities of these extracts were then used as reference for comparison with the gamma spectra of the co-extracted activities for the same amount of contaminants.

The sensitivity of the method for the different contaminants is also seen from the Table. For some of the contaminants, using adequately measuring times, the sensitivity can be improved (*e.g.*, for Cu and Au), but in this case the error may become as high as 50 to 100%.

For some contaminants the maximum detectability is by about an order of magnitude higher than the sensitivity given in Table III.

Table IV

Contaminant	Maximum detectability, g/24h	Contaminant	Maximum detectability, g/116h
Cu	10^{-9}	Cd	10^{-8}
Au	$5 \cdot 10^{-10}$	Zn	$5 \cdot 10^{-8}$
Hg	10^{-8}	Co	10^{-8}

It is seen that the method can be satisfactorily applied for the determination of the contaminants in GaAs and similar matrix elements producing multicurie activities. The chemical processing, extraction and gamma-spectrometric evaluation can be performed usually within 4 to 6 hours.

SUMMARY

A rapid activation analytical method developed for the determination of copper in GaAs monocrystals is described. The contaminant activities are separated from the activities produced in the matrix elements by remote controlled extraction. The use of dithizone as a group reagent makes possible the determination of five other contaminants (Au, Hg, Cd, Zn, Co) simultaneously with copper. The contaminants are identified by their gamma spectra with coincidence technique. The method is faster and less laborious than conventional multi-step chemical separation. The extraction and measurement of the six contaminants under investigation can be performed in about 4 to 6 hours.

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GAS CHROMATOGRAPHIC INVESTIGATION OF THE THERMAL DECOMPOSITION OF POLYDIMETHYLSILYLENE

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Introduction

Gas chromatographic and thermogravimetric results concerning the thermal decomposition of polydimethylsilylene, $[\text{Si}(\text{CH}_3)_2]_n$, have been summarized in a previous paper [1]. These investigations have shown that, in contrast to current notions, this long-chain compound containing a skeleton of many silicon atoms has considerable thermal stability in an inert atmosphere. Recent work concerning the nature of the Si—Si bond [2] has ruled out the former hypothesis, according to which the poor thermal stability of silicon analogues as compared with aliphatic carbon chains is to be explained by the much lower bond energy values. Conclusions in our previous paper [1] and reported physico-chemical properties of low molecular weight organosilylene compounds indicate that the different characteristics of silicon and carbon chemistry may be attributed only to a minor extent to differences in the energies of the C—C and Si—Si bonds and the main responsible factor is to be found in the markedly different reactivities of the two classes of compounds.

Starting these general conclusions, it appeared reasonable to make a detailed investigation of the breakdown procedure in order to obtain new information about the thermal reactions of the bonds present in this type of polymer, and about the nature of the decomposition process. It is known that in the course of the decomposition of polymer molecules (e.g., during the cracking of organic macromolecules) complex sets of chemical reactions take place simultaneously, and the obtainable chemical information is usually restricted to the observation of tendencies, identification of reaction types, and to conclusions of mainly general character.

According to our program, the technique of pyrolysis and of the characterization of the degradation products by gas chromatography have been further developed.

The depolymerization reactions were carried out in a microreactor built similarly to the one described in a previous paper [3]. A somewhat modified pyrolysis technique was employed so as to ensure access to the column of the

entire, wide-boiling mixture of degradation products. The samples were treated with heat either for a prolonged time or by instantaneous heat pulses (method of flash pyrolysis), in order to elucidate whether the degradation products of prolonged pyrolysis are formed *via* time-consuming, multistep reactions or not.

The degradation products were separated on a capillary column of linearly programmed temperature.

In order to identify the pyrolysis products, the retention indices were measured and compared with those of various organosilicon compounds determined by one of the authors in an earlier work [4]. Some peaks of the extremely complex, multicomponent pyrograms were identified by comparing them with synthetic reference compounds.

The determination of the silicon content of the degradation products, or at least the decision whether they contain silicon or not, is of paramount importance in solving the problem outlined in the introduction. A recently developed method [5, 6] has been found very helpful in detecting the silicon compounds.

Experimental

Micropyrolysis

The following two methods of pyrolysis were used:

1. Prolonged heating of the polymer sample in a closed chamber (at gradually raised temperatures) in an inert (nitrogen) gas atmosphere.

2. Instantaneous heating (flash pyrolysis) in an inert gas stream.

The original microreactor already described [3, 7] was modified as follows:

The pyrolysis unit was made of stainless steel, in contrast to the former [3] all-glass apparatus. In addition to the inlet and outlet connection for the carrier gas, the unit was provided with two further junctions. By means of these it was possible to fill the reactor chamber with any kind of reactive gas, or to flush it towards the surrounding atmosphere. The reactor chamber could be closed completely with the aid of needle valves and a stopcock. In this way the pyrolysis could be carried out in a reactive gas atmosphere even at somewhat elevated pressures. A by-pass was used in order to ensure continuous flow of the carrier gas along the chromatographic column when the microreactor was closed.

Reproducibility of the micropyrolysis experiments was guaranteed by standardizing all experimental conditions. The polymer was ground and homogenized in an agate mortar, and quantities 0.3–2.0 mg of the homogenized sample were used in the pyrolysis depending on the character of the experiment.

Cyclic polymers and some oligomers soluble in organic solvents and characterized by relatively high volatility were formed as by-products in the synthesis of the polymers used in the present investigations. These by-products were removed by repeated washings in the course of preparation. In addition, before starting the pyrolysis experiment, the polymer samples were kept at 100° in the microreactor until the complete absence of volatile components was indicated by gas chromatography.

A model mixture consisting of C_8 to C_{20} n-alkanes, made up to a known percentage composition, was used in a series of preliminary experiments in order to establish the standard working parameters of the microreactor. It was found that when the pyrolysis was carried out in a closed microreactor, the walls of the device had to be heated at least to 250°C, and the atmosphere of the reactor had to be transferred to the column by opening the stopcock permanently. In this case even the components of poorest volatility were completely transferred to the column. If the tantalum cup containing the sample was heated rapidly while passing a gas flow through the open microreactor (flash pyrolysis), additional heating of the reactor wall was unnecessary.

In the permanent pyrolysis experiments at various elevated temperatures in closed microreactor, 2.0 mg of the polydimethylsilylene was weighed into the tantalum cup. After

the removal of the volatile components, the samples were heated to 250° (by heating only the walls of the microreactor), and then, by the permanent opening of the stopcock, the entire gas contents of the reactor were flushed to the column and the chromatogram was taken. Subsequently, the reactor was closed once more, and the same sample was submitted to a repeated pyrolysis by heating the tantalum cup to 350° for one minute, and the breakdown products were chromatographed under the same conditions as before. The same procedure was repeated in other experiments at various temperatures ranging between 250 and 600°, so that four pyrolysis chromatograms were obtained from each weighed sample.

When using the flash pyrolysis method, 0.3 mg of the polymer was weighed, and the tantalum cup was heated to 350° or 450°, respectively, within 10 seconds, while the rate of the continuous carrier gas flow in the microreactor was 300 ml/sec.

Gas chromatographic recordings

Microreactor gas chromatography was carried out with the aid of a *Carlo Erba Fractovap Mod. C* type instrument. In order to meet the requirements of the different separation problems, various columns and temperature programs were used. A complete survey of reaction products and perfect separation had to be achieved at the same time. With these aims in mind, chromatograms taken on a 50 m long capillary column (i. d. 0.25 mm) coated with APL, operated with a linear program of 5 °C/min. and 3.5 °C/min., respectively, in a temperature range from 60° to 250°, were found to be most appropriate. The separation of the most volatile components was not satisfactory even under these circumstances. For this reason, the pyrolysis experiments accompanied by the formation of high amounts of volatile compounds were repeated, and separation was effected on a 50 m long (i. d. 0.25 mm) capillary column coated with squalane, either at 36° under isothermic conditions, or with a 1.25 °C/min. temperature program in the range of 36° to 120°.

Nitrogen was used as the carrier gas in all experiments. The inlet pressure was 1.77 atm. the rate of flow 2 ml/min. along the column. A splitting ratio of 150 : 1 was used before column inlet.

The analysis of the volatile pyrolysis products was also repeated on a 2m × 2 mm packed column containing styrene-divinylbenzene polymer beads as the stationary phase. The column temperature was 125°.

In order to distinguish between organosilicon and pure organic compounds in the pyrogram, dual-channel chromatography was employed, using a hydrogen- and a methane-hydrogen flame ionization detector simultaneously. Details of this method have been described previously [5, 6]. Organosilicon compounds were recognizable with the aid of this method, as the detector operated by a methane-hydrogen gas mixture indicated the presence of these components in the form of negative peaks. The column used in these experiments was 3 m long (i. d. 2 mm) and it was filled with HMDS-treated *Chromosorb W* coated with 10% APL. The column temperatures ranged from 60° to 280°, being raised at a rate of 6.5 °C/min. during separation.

Kováts' retention index of each component was determined for the characterization of the pyrolysis products. Retention index measurements were performed both on squalane and APL, under separation conditions identical to those mentioned before (see also Table I). Mixtures of C₅ to C₂₀ n-alkanes composed according to requirements were used as reference materials when determining the retention indices.

Reference compounds

Several simple organosilicon compounds were synthesized, the presence of which among the breakdown products seemed to be probable according to theoretical considerations and the experimental evidence of the chromatograms. Thus dimethylsilane, trimethylsilane and vinyltrimethylsilane were prepared from the corresponding chlorides with lithium aluminium hydride in ether. Further, hexamethyldisilane was synthesized by the methylation of hexachlorodisilane, and bis-trimethylsilylmethane was made from halomethyl-dimethyl- and trimethylchlorosilane with the Grignard procedure in the usual way.

Results

Schematic chromatograms indicating the composition of the degradation products at different pyrolysis temperatures are compared in Fig. 1.

Table I
Retention data of the products of micropyrolysis of $[\text{Si}(\text{CH}_3)_2]_n$

Product No.	Conditions of separation	t_r korr (min.)	T (°C)	I ^{Se} Squ	I ^{Pr} Squ	I ^{Pr} APL	Assumed formula
1	Squalane isothermic 36 °C	0.0473		~(274)			
2	Squalane isothermic 36 °C	0.063		~(300)			$\text{SiH}_2(\text{CH}_3)_2$
3	Squalane isothermic 36 °C	0.145		~(377)			$\text{SiH}(\text{CH}_3)_3$
4	Squalane isothermic 36 °C	0.260		~(432.7)			
5	Squalane isothermic 36 °C	0.346		~(459.5)			$\text{SiH}_2(\text{CH}_3)(\text{CH}=\text{CH}_2)$
6	Squalane isothermic 36 °C	0.400		~(473.3)			$\text{SiH}(\text{CH}_3)_2(\text{CH}=\text{CH}_2)$
7	Squalane isothermic 36 °C	1.95		624.8			
8	Squalane isothermic 36 °C	2.18		635.4			
9	Squalane isothermic 36 °C	2.42		645.0			$(\text{CH}_3)_6\text{Si}_2\text{O}$
10	Squalane isothermic 36 °C	2.90		661.8			
11	Squalane isothermic 36 °C	3.02		665.3			
12	Squalane isothermic 36 °C	3.12		668.6			
13	Squalane 36°—1.25°/min.	4.02	43.5	692.1	~700		
14	Squalane isothermic	4.26		697.6			$(\text{CH}_3)_6\text{Si}_2$
15	Squalane isothermic		48.5		~762.5		
16	Squalane 36°—1.25°/min.		60.5		~870.5		
17	Squalane 36°—1.25°/min.		64		896.3		
18	Squalane 36°—1.25°/min.		65.5		900		
19	Squalane 36°—1.25°/min.		66.2		910.3		
20	APL 60°—5°/min.		81			~(924)	
21	APL 60°—5°/min.		84			~(946)	
22	APL 60°—5°/min.		99.5			~(1048.6)	
23	APL 60°—5°/min.		106			1084	
24	APL 60°—5°/min.		109.5			1102.5	
25	Squalane also with program	100.7	112.5		1116.4	1117.5	
26	Squalane also with program		115.5			1132.5	
27	Squalane also with program	105	118		1142.5	1145	

28	Squalane also with program	106.5	120.5	1151.5	1157.5	
29	APL 60°—5°/min.		121.5		1162	
30	APL 60°—5°/min.		125		1180	
31	APL 60°—5°/min.		144		1278	
32	APL 60°—5°/min.		155		1342.4	[Si(CH ₃) ₂] ₅
33	APL 60°—5°/min.		158		1360.7	
34	APL 60°—5°/min.		160		1372.7	
35	APL 60°—5°/min.		161.5		1382	
36	APL 60°—5°/min.		162.5		1388	
37	APL 60°—5°/min.		163.5		1396	
38	APL 60°—5°/min.		164.5		1403.3	
39	APL 60°—5°/min.		166		1413.3	
40	APL 60°—5°/min.		185		1537.9	
41	APL 60°—5°/min.		191		1579.3	
42	APL 60°—5°/min.		193		1593	[Si(CH ₃) ₂] ₆
43	APL 60°—5°/min.		194		1600	
44	APL 60°—5°/min.		195.5		1614	
45	APL 60°—5°/min.		196		1618.5	
46	APL 60°—5°/min.		196.5		1622.2	
47	APL 60°—5°/min.		197.5		1629.2	
48	APL 60°—5°/min.		198.5		1637	
49	APL 60°—5°/min.		199.5		1644.4	
50	APL 60°—5°/min.		200		1648.1	
51	APL 60°—5°/min.		201		1655.5	
52	APL 60°—5°/min.		202		1662.9	
53	APL 60°—5°/min.		219		1800	
54	APL 60°—5°/min.		223		1834.7	
55	APL 60°—5°/min.		225		1852.2	
56	APL 60°—5°/min.		228.5		1882.6	

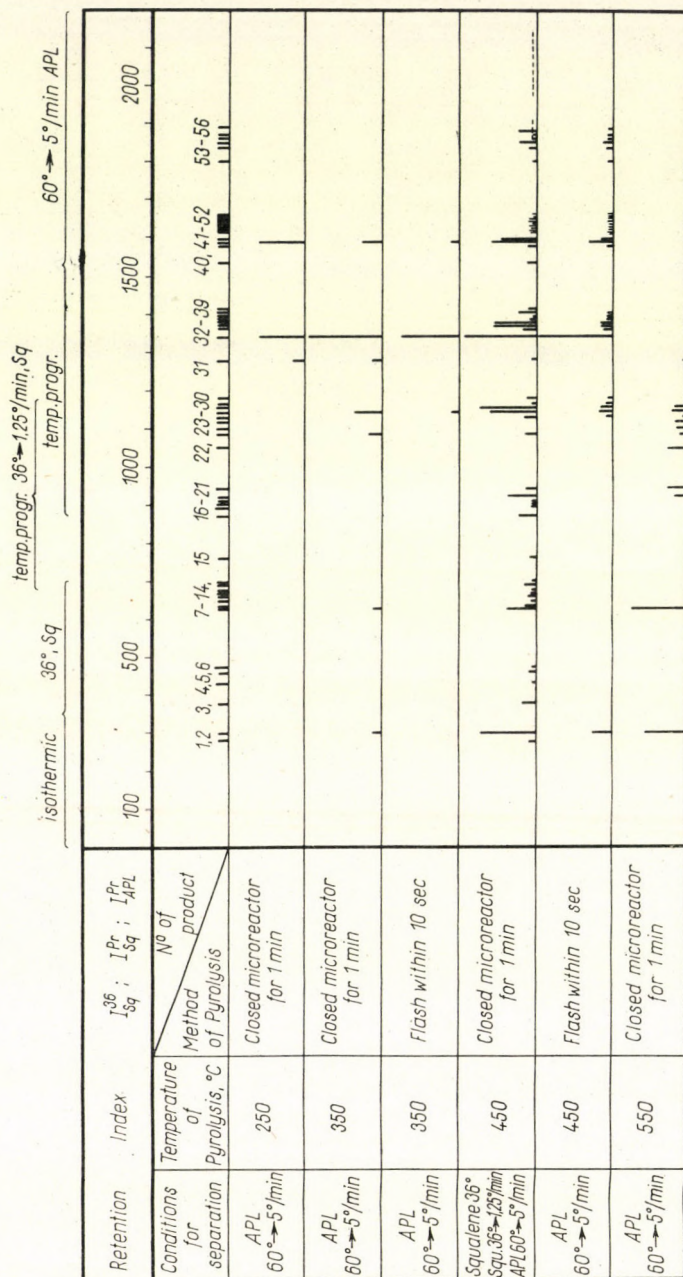


Fig. 1. Schematic drawings of pyrograms

The separation of the pyrolysis products was accomplished in all six cases shown in the diagram on a capillary column covered with APL, and, starting from 60°, the temperature was programmed linearly up to 250° at a rate of 5 °C/min. Prolonged pyrolysis at 450° was repeated connecting the microreactor to a squalane-coated capillary column. This was necessary because the products of this procedure contained the volatile components in the highest concentration. In the latter arrangement separations were also carried out at 36° (isothermic condition) and with the same starting temperature followed by a heating program of 1.25 °C/min.

The retention data of all significant pyrolysis products are shown in Table I. Attempts were made to characterize each material with retention data determined under the most suitable conditions. Data where the optimal conditions were not guaranteed and accordingly, the accuracy of the retention indices were not satisfactory, are shown in parentheses.

As the conditions of separation of the most volatile components (1–6) were disadvantageous on squalane even at an isothermic column temperature, of 36°, the separation of both the pyrolysis products and the reference compounds was repeated on a column packed with styrene-divinylbenzene polymer. A good separation of the compounds in question was possible in this column at 125°. The results obtained on the polystyrene column were in agreement with those of capillary chromatograms. Therefore, and for the sake of a uniform discussion, retention indices of the volatile components — although these values are of limited accuracy — have also been based on capillary chromatograms.

As it is seen in Table I, the retention data obtained by the three different methods of separation (squalane isothermic, squalane programmed, and APL programmed) were overlapping. This circumstance rendered possible the unambiguous recognition and identification of all components, and the simultaneous demonstration of the three chromatograms of prolonged pyrolysis at 450° (see Fig. 1).

The physical meaning represented by the I_{APL}^{Pr} values is essentially the same, since squalane and APL are chemically very similar materials. This is also verified by the experience that the differences between the values I_{Squ}^{Pr} and I_{APL}^{Pr} were not greater than those between I_{Squ}^{36} and I_{Squ}^{Pr} . Slight deviations in both cases are due to the temperature dependence of the retention indices.

Fig. 1 representing the four investigated pyrolysis temperatures shows significant differences in some respect.

The product of prolonged pyrolysis at 250° consists but of three components. Two of them (No. 32 and 42) are present in about equal concentrations, while the amount of the third component (No. 31) is considerably less. This component is absent on the chromatogram of instantaneous pyrolysis, giving rise to the assumption that it is formed as a product of multistep reactions.

At 350° the total amount of pyrolysis products as well as the number of components is higher. New components of increased volatility appear in considerable amounts (e.g., peaks No. 23 and No. 27). The ratio of peaks No. 42 is shifted significantly in favour of the former.

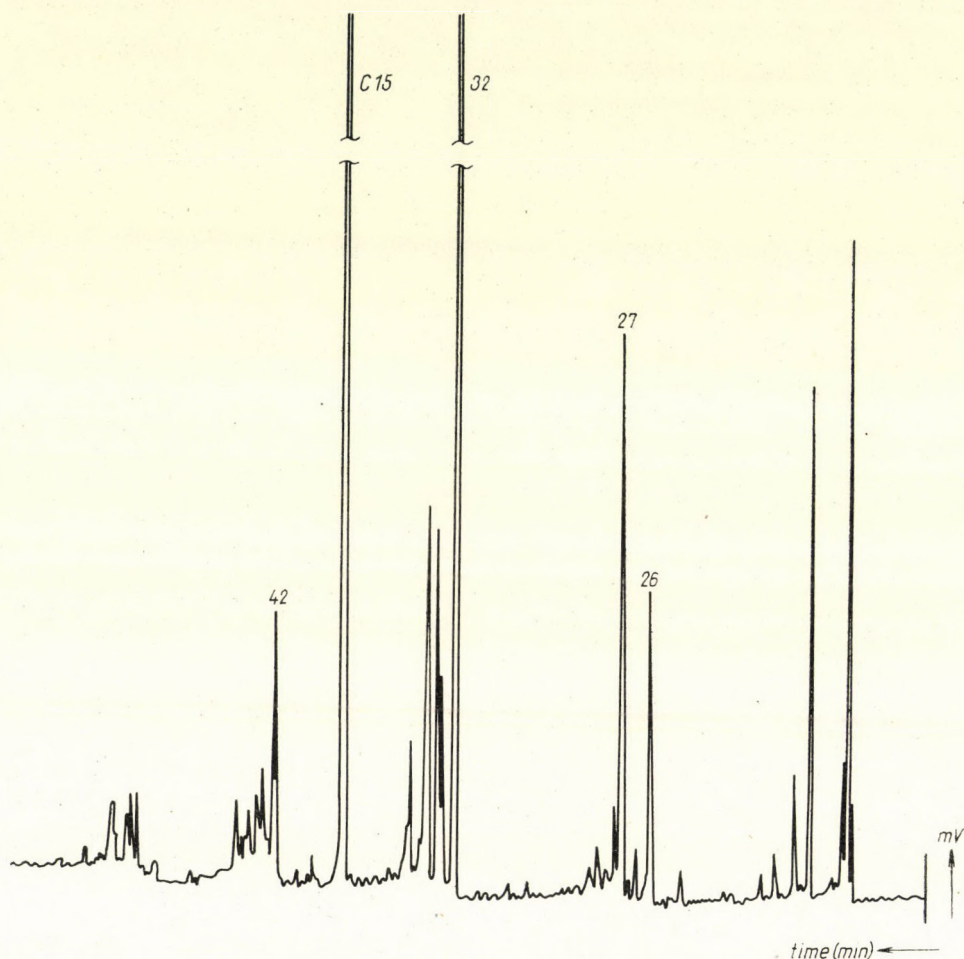


Fig. 2. Micropyrolysis chromatogram (pyrogram) at 400 °C
Column: 50 m $\times$ 0.25 mm capillary coated with Temperature program: 5 °C/min.,
starting from 60 °C
Internal standard: $C_{15}H_{32}$

Pyrolysis at 450° resulted in the appearance of all those components that had been dominant at lower pyrolysis temperatures, with the exception of peak No. 31. At the same time numerous new peaks were found in the vicinities of the peaks observed earlier. The number and the total amount of the more volatile breakdown products increased markedly, but new peaks were observed

among the components of minor volatility as well. The 450° pyrogram is endowed with a conspicuous structure by the fact that peaks are assembled in seven groups, separated rather well from one another. This is clearly seen in Fig. 2 where one of the chromatograms used in the construction of Fig. 1 is presented.

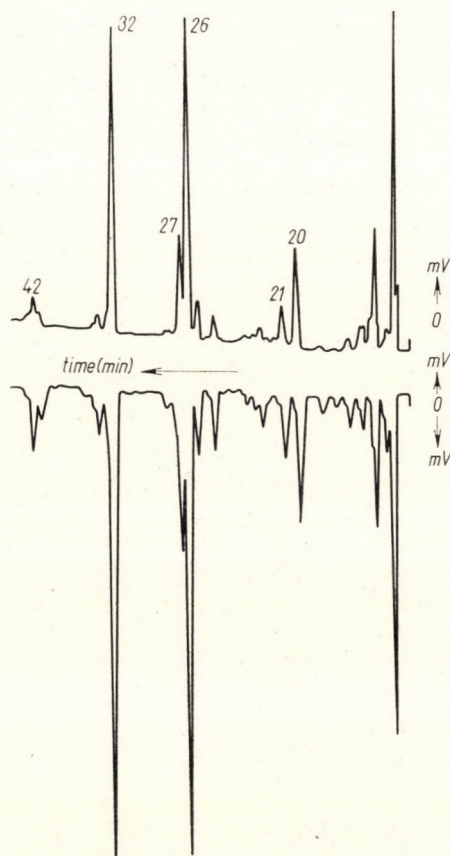


Fig. 3. Pyrogram taken by the dual-channel detection method
 Column: 3 m $\times$ 2 mm, packed with HMDS-treated Chromosorb W, coated with 10% APL
 Temperature program: 6.5 °C/min., starting from 60 °C
 Hydrogen flame ionization (upward peaks) and methane-hydrogen flame ionization, (downward peaks) dual-channel detection

Prolonged micropyrolysis at 550° is characterized partly by the complete absence of peaks No. 32 and No. 42, that were characteristic up to this point. On the other hand, a lot of new characteristic peaks appear in the index range 1000–1140. Similarly, new peaks — although in small amounts — are observed in the retention index range of 1200–1300, which region was desolate at lower pyrolysis temperatures. Though the amounts of the individual components

above index number 1150 are negligible, they represent a considerable proportion of the pyrolysate owing to their high number.

Concerning the results of the flash pyrolysis experiments, Fig. 1 reveals that the structures and characteristics of the products are highly resembling those of the prolonged pyrolysis. The only peaks that are completely missing are Nos 23 and 31, and the total amount of breakdown products is naturally less. Based on these findings it has been concluded that the complex sets of reactions provoked by instantaneous (of some seconds duration) and prolonged heat treatment are essentially the same. Consequently, it is unnecessary to take into account the formation of long reaction chains in the condensed phase. As far as consecutive reactions are concerned, they may take place with the participation of volatile components arising from the condensed phase.

In order to test the heat resistance of the components formed in the pyrolysis process, and to clarify the relation of their breakdown products to those of the original polymer, a microreactor experiment was performed using dimethylcyclohexasilylene, $[(CH_3)_2Si]_6$, prepared synthetically, but also formed in considerable amounts in the course of polymer pyrolysis (Table I.). The compound was treated at 550°. The product composition was similar to that of the polymer pyrolyzed at the same temperature. Peaks indicating products in considerable amounts were situated below index number 1150, but the total amount of compounds beyond this region was not negligible in this case either. It was striking many of the low-molecular components present in high amounts proved to be identical with some of the breakdown products of the polymer molecules. At the same time many of the significant degradation products of the polymer — e.g. the starting hexacyclic compound itself — was absent in the destruction products of dimethylcyclohexasilylene.

Identification of the pyrolysis products

The chromatogram of a 400° pyrolysis, obtained with a packed column with APL as the stationary phase, and detected simultaneously by a hydrogen flame ionization detector and methane-hydrogen flame ionization detector is presented in Fig. 3. As it is seen, the breakdown products consist solely of organosilicon compounds (the signals are exclusively negative when using the methane-hydrogen detector). At 500° and at higher pyrolysis temperatures, peaks corresponding to organic compounds containing no silicon were also present in the starting region of the chromatogram. The evaluation of the chromatograms led to a further observation. It was found that apart from the early peaks representing highly volatile components, the ratio of C/Si in the molecules of the breakdown products was approximately 2.

The retention indices of those substances which were supposed to have some bearing on peak identification are listed in Table II.

On comparing these data to those in Table I, it is evident that small quantities of $(\text{CH}_3)_6\text{Si}_2\text{O}$ and $(\text{CH}_3)_6\text{Si}_2$ are present among the products of

Table II
Retention data of the reference compounds

Compound	Conditions of separation	t_R korr. (min.)	T_R (°C)	I ^{sq} Squ	I ^{Pr} Squ	I ^{Pr} APL
$\text{SiH}_2(\text{CH}_3)_2$	Squalane iso- thermic 36 °C	0.063		~(300)		
$\text{SiH}(\text{CH}_3)_3$	Squalane iso- thermic 36 °C	0.142		~(377)		
$\text{Si}(\text{CH}_3)_4$	Squalane iso- thermic 36 °C	0.220		~(419)		
$\text{SiH}_2(\text{CH}_3)(\text{CH}=\text{CH}_2)$...	Squalane iso- thermic 36 °C	0.340		~(459)		
$\text{SiH}(\text{CH}_3)_2(\text{CH}=\text{CH}_2)$...	Squalane iso- thermic 36 °C	0.410		~(475)		
$\text{Si}_2(\text{CH}_3)_6\text{O}$	Squalane iso- thermic 36 °C	2.47		645.7		
$\text{Si}_2(\text{CH}_3)_6$	Squalane iso- thermic 36 °C	4.33		699		
$\text{Si}_2(\text{CH}_3)_6\text{CH}_2$	Squ. isoth. and programmed	11.98	50	792.9	~ 788	
$\text{Si}_3(\text{CH}_3)_8\text{O}_2$	Squ. isoth. and programmed		55	832.0	~ 829.7	
$\text{Si}_4(\text{CH}_3)_{10}\text{O}_3$	Squalane progr. 36 °C—1.25°/ min.		81.5		1003	
$[\text{Si}(\text{CH}_3)_2]_6$	APL progr. 60 °C—5°/ min.		193			1593

pyrolysis, but $(\text{CH}_3)_8\text{Si}_3\text{O}_2$ and $(\text{CH}_3)_{10}\text{Si}_4\text{O}_3$ are not detectable. It is worth mentioning that in the synthesis of methylpolysilylenes only the corresponding siloxanes were obtained instead of $(\text{CH}_3)_8\text{Si}_3$ and $(\text{CH}_3)_{10}\text{Si}_4$, owing to the extreme sensitivity to oxidation of the latter compounds. The absence of the mentioned siloxanes point to the fact that fully methylated di- and trisilanes have not been formed in the course of pyrolysis. $\text{Si}(\text{CH}_3)_4$ and $(\text{CH}_3)_6\text{Si}_2\text{CH}_2$ are not present among the products of pyrolysis either.

The retention data have indicated that one of the dominant components among the highly volatile breakdown products (peak No. 2) is $\text{SiH}_2(\text{CH}_3)_2$, while $\text{SiH}(\text{CH}_3)_3$, $\text{CH}_3\text{SiH}_2 \cdot \text{CH}=\text{CH}_2$ and $(\text{CH}_3)_2\text{SiH} \cdot \text{CH}=\text{CH}_2$ are also

found among the neighbouring peaks. The other dominant component of this group (peak No. 7) has not been identified so far.

Results of the experiments carried out with different temperature programs showed unambiguously that peak No. 42 in the pyrolysis chromatograms represented the cyclic oligomer $[\text{Si}(\text{CH}_3)_2]_6$.

The substance corresponding to peak No. 32 was separated by preparative gas chromatography, using the product of the macropyrolysis of polydimethylsilylene as starting material. Subsequent mass spectrometric investigations confirmed its identity with $[\text{Si}(\text{CH}_3)_2]_5$, i.e. an oligomer of cyclic structure.*

It was already mentioned that the C/Si ratio in the breakdown products was approximately 2, estimated by the dual-channel gas chromatographic method. This fact and the general comparison of the retention indices of the peaks, arranged in groups in the pyrogram, with the retention indices of the reference substances justify the following assumption (see Fig. 1) characterized by $I < 500$ (peaks No. 1 to No. 6) contain a single atom of silicon, peaks of $I = 600-800$ correspond to components containing two atoms of silicon; similarly $I = 850-1050$ means components containing three, $I = 1050-1300$ components containing four silicon atoms, while the next groups of peaks represent, in turn, compounds containing five, six and seven silicon atoms.

Conclusions

In the light of the experimental results presented in this paper and on the basis of data of our previous communication, it seems possible to draw a schematic picture on some of the main characteristics of the decomposition process of polydimethylsilylene.

A depolymerization of relatively simple character, accompanied by cleavages of the Si—Si bonds takes place in the first stage of pyrolysis (250—350). This process resembles the splitting of analogous carbon chains, although the end products are naturally different (see, e.g. [8]). The simple nature of this process is reflected by the small number of components in the pyrogram, further by the fact that the two main products are simple dimethylsilylenes with cyclic structures as it has been proved in the case of components No. 32 and No. 42.

A number of volatile (low-molecular) organosilicon compounds appear in the next phase of thermal decomposition (350—500°), which cannot have cyclic structures because of the small number of silicon atoms present. At the

* A communication on the separation and mass spectrometric investigation of $[\text{Si}(\text{CH}_3)_2]_5$ is in preparation.

same time, the close vicinity of the components absolutely prevailing at low pyrolysis temperatures is overflowed by new components which are very similar one to another with respect to polarity and volatility. Taking into account both observations, we come to the assumption of a multifold intramolecular rearrangement (migration of methyl groups and hydrogen), taking place in this 350–500° temperature range. Further it should be noted that besides methyl substituents, vinyl groups have also been observed in the breakdown products. This points to the fact that reactions characterized by radical mechanism and by the previous cleavage of the C—Si bond, may also play a definite role at these temperatures. Moreover, the real existence of such processes is proved by the appearance of compounds containing Si—H bonds, such as $(\text{CH}_3)_2\text{SiH}_2$ and $(\text{CH}_3)_3\text{SiH}$ in the starting region of the chromatogram.

The observation that bis-trimethylsilylmethane, $(\text{CH}_3)_6\text{Si}_2\text{CH}_2$, has not been traceable among the volatile components, although hexamethyldisiloxane $[(\text{CH}_3)_6\text{Si}_2\text{O}]$ and hexamethyldisilane $[(\text{CH}_3)_6\text{Si}_2]$ are disclosed in the same region of the chromatogram, indicates that in the stage of the reaction when Si— CH_3 groups are split by heat (to give, e.g., vinylsilane or silicon hydride), there is no possibility for a chemical reaction between the product of this decomposition and free radicals containing silicon atoms with odd electrons [such as $(\text{CH}_3)_2\text{Si}$, $(\text{CH}_3)_3\text{Si}$].

Reactions involving the cleavage of Si—C bonds also afford organic components above 500°, that is in the third phase of reactions. On the other hand, simple oligomers disappear, as they are cracked under such conditions of high temperature pyrolysis. This type of reaction has also been demonstrated in the case of the cyclic hexamer (*cf.* Experimental).

When the thermal decomposition of polydimethylsilylene is compared with that of organic polymers, no fundamental difference is found either in the thermal stability of the basic chain or in the character of the first phase of the breakdown process. Thus, the results do not furnish evidence for the lability of Si—Si bonds, which has been a current view so far. The differences, which are more marked in the stage of total destruction, are to be attributed partly to the lower electronegativity of silicon (there is no possibility for double bond formation and no aromatization processes can take place) and partly to the existence of empty d-orbitals (tendency for intramolecular rearrangement), and cannot be explained in terms of chemical bond energies.

SUMMARY

The thermal decomposition of polydimethylsilylene has been investigated by means of microreactor gas chromatography. The polymer was exposed to prolonged or instantaneous heat treatment at various temperatures, and the chromatograms of the breakdown products were determined.

Using a dual-channel detection method (hydrogen flame ionization and methane-hydrogen flame ionization detectors, respectively), the approximate C/Si atomic ratios charac-

teristic of the products of decomposition were estimated. Based on the Kováts' retention indices, some of the breakdown products could be identified with simple organosilicon compounds prepared synthetically.

Three stages dependent on the temperature of pyrolysis have been distinguished in the thermal decomposition process of the polymer. The first stage is characterized by a depolymerisation process accompanied by the formation of organosilicon oligomers, few in number and of medium molecular weight. Cleavage of chemical bonds in the second stage is followed by an intramolecular rearrangement resulting in the formation of numerous medium- and low-molecular organosilicon compounds. The third stage is characterized by destruction of the oligomers and the formation of mainly low-molecular organosilicon and organic compounds.

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ОПРЕДЕЛЕНИЕ ДЛИНЫ ПЕРИОДА ИНГИБИРОВАНИЯ В РАДИКАЛЬНОЙ ПОЛИМЕРИЗАЦИИ

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1. Введение

В наших предыдущих сообщениях мы теоретически подробно рассматривали кинетику ингибирования термополимеризации стирола [1] и и правильность теоретических выводов проверяли на примере ингибированной хинонами термополимеризации стирола [2]. В дальнейшем мы рассмотрели также разные, часто встречающиеся на практике, более сложные случаи ингибирования, где кроме элементарной реакции ингибирования наблюдаются такие побочные реакции, как, например, регенерация цепи, побочное инициирование ингибитором, вторичное замедление и т. д. Одновременно были также разработаны методы для точного определения параметров ингибирования. В связи с этими проблемами — краткости ради — мы ссылаемся только на обзоры [3, 4].

Одним из самых важных параметров ингибирования является длина периода ингибирования, которая находится в непосредственной связи со стехиометрией реакции ингибирования. В работе [1] было показано, что экстраполяция кривых конверсия-время (или, что более точно, экстраполяция зависимости $\lg m_0/m = f(t)$) не дает истинную длину периода ингибирования (t_i), а только его кажущуюся длину (t'). Эти две величины связаны соотношением:

$$t' = t_i F^*(\varphi_0) \quad (1)$$

где $F^*(\varphi_0)$ — поправочная функция и φ_0 — параметр ингибирования. (Большинство обозначений идентично или вполне аналогично применяемым в работах [1 и 5].) Точная функция $F^*(\varphi_0)$ была получена в работе [5], для случая термического инициирования.

Целью настоящей работы является решение проблемы одноступенчатого ингибирования и сопоставление разных методов определения длины периода ингибирования, в случае любого инициирования.

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2. Анализ кинетики ингибирования

Для рассмотрения возьмем самый простой случай, когда механизм ингибирования состоит только из следующих четырех элементарных реакций:

1. Инициирование



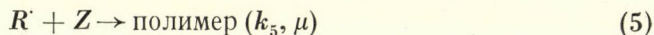
2. Рост цепи



3. Бимолекулярный обрыв цепей



4. Обрыв цепей ингибитором



где M означает молекулу мономера, $R^{\cdot}$ — радикала, носителя цепи, Z — ингибитора. В скобках указаны константы скорости соответствующих реакций, μ — стехиометрический коэффициент ингибитора. В этой схеме W_1 — скорость инициирования, которую мы принимаем везде постоянной:

$$W_1 = \text{const} \quad (6)$$

Вследствие этого, получаемые здесь результаты имеют общее значение, так как не зависят от способа инициирования.

Систему дифференциальных уравнений для данного механизма можно дать в следующей форме:

$$-\frac{dm}{dt} = k_2 rm \quad (7)$$

$$-\frac{dz}{dt} = k_5 rz \quad (8)$$

и

$$\frac{dr}{dt} = W_1 - \mu k_5 rz - k_4 r^2 \quad (9)$$

где концентрации обозначены соответствующими маленькими буквами.

Из уравнений (7) и (8), при начальных условиях $t = 0$, $m = m_0$, $z = z_0$ получаем одно из основных уравнений

$$\log \frac{m_0}{m} = \frac{k_2}{k_5} \log \frac{z_0}{z} \quad (10)$$

Это уравнение дает возможность определения относительной реакционной способности ингибитора.

Как это было раньше подробно обсуждено [1], для активных центров с большой точностью действителен принцип стационарного состояния, т. е.

$$\frac{dr}{dt} = 0 \quad (11)$$

С учетом этого условия, дифференциальное уравнение (9) переходит в алгебраическое, из которого можно выразить стационарную концентрацию радикалов:

$$r = \frac{r_{st}}{\varphi + \sqrt{1 + \varphi^2}} \quad (12)$$

где

$$\varphi = \beta z = \frac{\mu k_5}{2 \sqrt{W_1 k_4}} z \quad (13)$$

и r_{st} — стационарная концентрация радикалов в отсутствие ингибитора ($= \sqrt{W_1/k_4}$). Соотношение (12) имеет большую важность, поскольку оно связывает концентрацию радикалов с концентрацией ингибитора. Относительную концентрацию радикалов ($r_{rel} = r/r_{st}$) в зависимости от безразмерного параметра ингибирования φ , мы поместили в таблице I. (Следует от-

Таблица I

φ	r_{rel}	φ	r_{rel}	$1/2 \varphi$
0	1	1	0,4142	0,5000
0,1	0,905	1,3	0,3401	0,3846
0,13	0,878	1,6	0,2868	0,3125
0,16	0,852	2	0,2361	0,2500
0,20	0,820	2,5	0,1926	0,2000
0,25	0,781	3	0,1623	0,1667
0,30	0,744	4	0,1231	0,1250
0,40	0,677	5	0,0990	0,1000
0,50	0,6180	6,3	0,07887	0,07937
0,60	0,566	8	0,06226	0,06250
0,80	0,4806	10	0,04988	0,05000

метить, что в целях общности, мы старались привести все зависимости к безразмерному виду.) Если $\varphi > 10$, то приближение

$$r_{rel} \approx 1/2 \varphi \quad (14)$$

выполняется достаточно хорошо, как это видно из таблицы I. Это условие физически означает то, что при этом бимолекулярным обрывом (4) можно пренебречь, по сравнению с реакцией (5).

Следует рассмотреть, как меняется концентрация ингибитора во времени. Для этой цели, сокращая уравнения (8) и (12), приходим к дифференциальному уравнению:

$$-\frac{d\varphi}{dt} = B \frac{\varphi}{\varphi + \sqrt{1 + \varphi^2}} \quad (15)$$

где

$$B = k_5 r_{st} = \text{const} \quad (16)$$

Интегрирование уравнения (15), при начальных условиях $t = 0$ и $\varphi = \varphi_0$, приводит к функции $F(\varphi)$:

$$F(\varphi) = \varphi + \sqrt{1 + \varphi^2} - \log \frac{1}{\varphi} \{1 + \sqrt{1 + \varphi^2}\} = F(\varphi_0) - Bt \quad (17)$$

При больших значениях φ , $F(\varphi)$ сильно упрощается:

$$F(\varphi) \approx 2\varphi \quad (18)$$

Приближенная функция:

$$F(\varphi) \approx 2\varphi - \frac{1}{2\varphi} \quad (19)$$

при $\varphi = 1$ дает ошибку всего лишь в 2%. Используя самое простое приближение ($F(\varphi) \approx 2\varphi$), мы приходим к очень простому соотношению:

$$2\varphi = 2\varphi_0 - Bt \quad (20)$$

которое, после упрощения, принимает вид

$$z = z_0 - \frac{W_1}{\mu} t \quad (21)$$

Следовательно, в некотором времени, $t = t_i$, φ и z становятся равными нулю; этот момент времени, соответственно из (20):

$$t_i = \frac{2\varphi_0}{B} \left(= \frac{\mu z_0}{W_1} \right) \quad (22)$$

В дальнейшем это выражение принимаем как теоретическое определение для длины периода ингибирования.

На самом же деле, условия процесса являются более сложными. Наш предыдущий вывод — из-за принятых грубых пренебрежений — действителен только как первое, грубое приближение. Как только по ходу реакции φ становится меньше 3, концентрация ингибитора начинает уменьшаться медленнее, чем это следует из линейной зависимости (21). Дело в том, что при этом условии все более значительную роль начинает играть бимолекулярный обрыв радикалов (4), который тоже уменьшает концентрацию носителей цепи, но который, однако, не расходует ингибитор.

Совершенно строгий анализ процесса, поэтому, следует провести следующим образом. По уравнениям (17) и (22), при $t = t_i$ и $\varphi = \varphi_i$ мы имеем:

$$F(\varphi_i) = F(\varphi_0) - 2\varphi_0 \quad (23)$$

Если условие $\varphi_0 \gg 3$ выполняется, то учитывая уравнение (18) мы получаем:

$$F(\varphi_i) = 0 \quad (24)$$

Корень этого трансцендентного уравнения:

$$\varphi_i = 0,4478 \quad (25)$$

т. е. при этих условиях φ_i является постоянной величиной. Если, однако, условие $\varphi_0 \gg 3$ не выполняется, то значение φ_i определяется из точного уравнения (23). Очевидно, что при этом φ_i перестает быть постоянной, а зависит от φ_0 , и может принимать значения в пределах:

$$0 \leq \varphi_i \leq 0,4478 \quad (26)$$

Из всего сказанного следует, что $t = t_i$, $z_i \neq 0$, как это следует из приближенного уравнения (21); более точно, $z_i = \varphi_i/\beta > 0$. Можно также показать, что концентрация ингибитора становится равной нулю только тогда, когда $t \rightarrow \infty$ (т. е. она ведет себя асимптотически). Как было показано (1), $F(\varphi)$ тоже сильно упрощается при маленьких значениях φ и принимает вид:

$$F(\varphi) \simeq \log \frac{e}{2} \varphi \quad (27)$$

Если $\varphi < 0,1$, то это приближение уже мало отличается от точного значения, как это видно из таблицы II. Здесь мы собрали данные для точной функции $F(\varphi)$, а также данные разных приближенных функций.

Если в уравнение (10) поставим выражение φ из (27), с учетом равенства $z_0/z = \varphi_0/\varphi$, то мы получаем асимптотическую форму зависимости (10):

$$\log \frac{m_0}{m} = k_2 r_{st} + \frac{k_2}{k_5} \left\{ \log \frac{e}{2} \varphi_0 - F(\varphi_0) \right\} \quad (28)$$

Как видно, (28) не что иное, как уравнение прямой, производная которой

$$\frac{d}{dt} \log \frac{m_0}{m} = k_2 r_{st} = W_{st} = \text{const} \quad (29)$$

Следовательно, процесс полимеризации на этом участке ($\varphi < 0,1$) идет уже с «нормальной» скоростью, несмотря на то, что в системе еще присутствует — хотя и в небольшой концентрации — ингибитор.

Таблица II

φ	$F(\varphi)$	по (18)	по (19)	по (27)
20	39,975	40	39,975	—
10	19,950	20	19,950	—
5	9,901	10	9,900	—
4,5	8,890	9	8,889	—
4,0	7,876	8	7,875	—
3,5	6,858	7	6,857	—
3,0	5,835	6	5,833	—
2,5	4,803	5	4,800	—
2,0	3,755	4	3,750	—
1,5	2,678	3	2,667	—
1,0	1,533	2	1,500	—0,307
0,5	0,175	1	0	—0,386
0,4478	0	—	—	—0,497
0,4	—0,170	—	—	—0,609
0,3	—0,574	—	—	—0,898
0,2	—1,093	—	—	—1,996
0,1	—1,915	—	—	—1,996
0,05	—2,662	—	—	—2,689
0,02	—3,595	—	—	—3,605
0,01	—4,288	—	—	—4,298
0	—	—	—	—

Какраз из уравнения (28) следует то, что длина периода ингибирования, определяемая экстраполяцией зависимости $\lg m_0/m = f(t)$ к значению $\lg m_0/m = 0$, является только кажущейся длиной. Именно, в этот момент времени t' , мы имеем:

$$k_2 r_{st} t' + \frac{k_2}{k_5} \left\{ \log \frac{e}{2} \varphi_0 - F(\varphi_0) \right\} = 0 \quad (30)$$

из которого, после несложных преобразований:

$$t' = t_i F^*(\varphi_0) \quad (1)$$

где функция $F^*(\varphi_0)$ определяется уравнением:

$$F^*(\varphi_0) = \frac{1}{2} \left\{ 1 + \frac{1}{\varphi_0} (\Phi_0 - 1) - \frac{1}{\varphi_0} \log \frac{1 + \Phi_0}{2} \right\} \quad (31)$$

где вспомогательная функция, Φ_0 :

$$\Phi_0 = \sqrt{1 + \varphi_0^2} \quad (32)$$

Поправочная функция $F^*(\varphi_0)$ обладает некоторыми интересными свойствами. В силу того, что

$$\lim_{\varphi_0 \rightarrow \infty} \left\{ \frac{1}{\varphi_0} (\Phi_0 - 1) \right\} = 1 \quad (33)$$

и

$$\lim_{\varphi_0 \rightarrow \infty} \left\{ \frac{1}{\varphi_0} \log \frac{1 + \Phi_0}{2} \right\} = 0 \quad (34)$$

следует, что

$$\lim_{\varphi_0 \rightarrow \infty} F^*(\varphi_0) = 1 \quad (35)$$

С другой стороны:

$$\lim_{\varphi_0 \rightarrow \infty} \left\{ \Phi_0 - 1 - \log \frac{1 + \Phi_0}{2} \right\} = 0 \quad (36)$$

и поэтому

$$\lim_{\varphi_0 \rightarrow \infty} F^*(\varphi_0) = \frac{1}{2} \quad (37)$$

Соответственно, эта функция может принимать значения в пределах $0,5 \leq F^*(\varphi_0) \leq 1$. Следовательно, величина t' всегда меньше t_i (за исключением предельной величины $\varphi_0 = \infty$), причем, при маленьких значениях φ_0 , мы имеем 100%-ное расхождение. Значения $F^*(\varphi_0)$ помещены в таблице III. Если $\varphi_0 < 0,1$, то достаточно хорошее приближение дается уравнением:

$$F^*(\varphi_0) \approx 0,5 + \frac{1}{8} \varphi_0 \quad (38)$$

Как видно из таблицы, если $\varphi_0 > 10^2$, то $F^*(\varphi_0) \approx 1$, и практически $t_i = t'$. Однако, для того, чтобы это условие выполнялось, необходимо, чтобы ингибитор обладал очень высокой реакционной способностью (β и k_3 должны

Таблица III

φ_0	$F^*(\varphi_0)$	φ_0	$F^*(\varphi_0)$
0,1	0,51240	10	0,8666
0,13	0,51642	13	0,8881
0,16	0,51978	16	0,9028
0,2	0,52488	20	0,9168
0,25	0,53096	25	0,9291
0,3	0,53711	30	0,9369
0,4	0,54905	40	0,9499
0,5	0,56070	50	0,9577
0,63	0,75601	63	0,9646
0,8	0,59350	80	0,9707
1	0,6130	100	0,9754
1,3	0,6394	130	0,9801
1,6	0,6624	160	0,9832
2	0,6887	200	0,9860
2,5	0,7159	250	0,9883
3	0,7382	300	0,9900
4	0,7728	400	0,9921
5	0,7984	500	0,9935
6,3	0,8233	630	0,9946
8	0,8470	800	0,9956
—	—	1000	0,9964

иметь очень большие значения). Это обычно выполняется в случае ингибиторов-стабильных свободных радикалов, но очень редко действительно для ингибиторов-молекул. Следовательно, указанными поправками обычно нельзя пренебрегать.

На основе зависимости $\log m_0/m = f(t)$ можно определить t_i и другим образом, а именно, по уравнению (10) при $t = t_i$ мы имеем:

$$\log \frac{m_0}{m} \Big|_{t=t_i} = \frac{k_2}{k_5} \log \frac{\varphi_0}{\varphi_i} \quad (39)$$

Однако, этим выражением можно пользоваться удобно только тогда, если выполняется условие $\varphi_0 > 3$. В этом случае уравнение (39) можно дать в более простой форме:

$$\log \frac{m_0}{m} \Big|_{t=t_i} = \frac{k_2}{k_5} \{ \log \varphi_0 - \log 0,4478 \} \quad (40)$$

Следует отметить, что, с точки зрения точности, этот способ определения ничем не уступает экстраполяционному методу.

В отличие от предыдущих двух «интегральных» методов, Бамфордом и Дженкинсом был предложен «дифференциальный» метод. Последний основывается на том, что при $t = t_i$, $\varphi_i = \text{const}$, и согласно уравнению (12)

$$r_{\text{rel}, t_i} = \frac{r}{r_{st}} \Big|_{t=t_i} = \frac{k_2 m r}{k_2 m r_{st}} \Big|_{t=t_i} = W_{\text{rel}, t_i} \quad (41)$$

тоже должна быть постоянной. Более конкретно:

$$W_{\text{rel}, t_i} = \frac{1}{0,4478 + \sqrt{1 + (0,4478)^2}} = 0,648 \quad (42)$$

Ясно, однако, что этот метод может применяться только тогда, когда выполняется условие $\varphi_0 > 3$. В противном же случае, в силу неравенства (26) мы имеем:

$$1 > r_{\text{rel}, t_i} = W_{\text{rel}, t_i} > 0,648 \quad (43)$$

и значение W_{rel, t_i} будет меняться от опыта к опыту (в зависимости от φ_0). Скорость полимеризации определяется обычно несколько менее точно, чем конверсия, и поэтому этот метод дает несколько менее точные результаты. Тем не менее, этот метод может быть очень полезен в тех случаях, когда при больших концентрациях ингибитора обнаруживаются разного рода побочные реакции.

Точно также можно использовать зависимость $r = f(t)$ для определения t_i , по-крайней мере, принципиально. В настоящее время, однако, этот способ еще не может применяться на практике, поскольку соответствующие концентрации радикалов (порядка 10^{-7} — 10^{-9} моль/л) еще не поддаются точному измерению.

Кроме рассмотренных до сих пор методов [т. е. использование зависимостей $\log m_0/m = f(t)$, $r = f(t)$] можно использовать также зависимость $z = f(t)$ или же равноценную зависимость: $\varphi = f(t)$, для определения t_i . Это делается очень просто: экстраполяцией линейного участка кривой $z = f(t)$. На практике, при этом, определяют не t_i , а равноценную ему величину $W_{1/\mu}$, из наклона прямого участка кривой. Следует обратить внимание на то обстоятельство, что при такой экстраполяции получают непосредственно значения t_i (а не t'). Но для того, чтобы кривая $z = f(t)$ поддавалась точной экстраполяции, следует соблюдать условие $\varphi_0 \gg 3$.

При использовании зависимости $z = f(t)$, для определения t_i можно использовать уравнение (13). При $t = t_i$ мы имеем $z_i = 0,4478/\beta$. Неудобство, однако, состоит в том, что для этого мы должны знать значение β .

Последнее же определяется отдельно dilatометрическим способом, по уравнениям (12) и (13). С другой стороны, для измерения концентрации ингибитора мы должны всегда иметь соответствующий аналитический метод определения ингибитора. Это требование часто трудно выполнять.

Следует еще отметить, что аналогично зависимости (42), для ингибитора мы имеем:

$$\left(\frac{dz}{dt}\right)_{t=t_i} = 0,290 \left(\frac{dz}{dt}\right)_{t=0} \quad (44)$$

Наконец, следует еще упомянуть следующий метод (7). Дифференцированием зависимости $\log m_0/m = f(t)$ мы можем из точки в точку определять $W_{\text{rel}} = f(t)$, а из последней, по уравнению (12), зависимость $\varphi = f(t)$. Зная φ , мы можем рассчитать $F(\varphi)$ по уравнению (17). (На практике последний шаг производится с помощью графика, построенного по данным таблицы 2.) Таким образом, мы приходим к графику $F(\varphi) = f(t)$, который должен быть строго линейным. Экстраполяция данного графика к $F(\varphi) = 0$ непосредственно дает значение t_i . Этот метод оказался очень полезным в случае слабых ингибиторов (вплоть до значения $k_3/k_2 = 1$).

Из всего анализа вытекает, что за исключением экстраполяции $\lg m_0/m = f(t)$, а также его дифференциального варианта, о котором только что говорилось, для применения всех остальных методов требуется выполнение условия $\varphi_0 > 3$. Поэтому, именно эти два метода следует считать наиболее общими методами определения длин периода ингибирования, так как они одинаково пригодны как в случае сильных, так и в случае слабых ингибиторов.

В заключение следует отметить, что данные выводы либо без изменения, либо с небольшими формальными изменениями можно распространять на все, неразветвленные цепные реакции.

РЕЗЮМЕ

В данном сообщении мы провели точный анализ кинетики ингибирования для случая, когда ингибирование происходит в одном электронном акте. Была установлена формула для определения длины периода ингибирования на основе dilatометрических измерений. Анализировались и критически сопоставлялись также другие методы определения периода ингибирования.

SUMMARY

An exact analysis of the kinetics of inhibited free radical polymerization has been made for the most simple case, when inhibition is represented by a single elementary reaction. A formula for the determination of the length of the inhibition period, based on dilatometric data, has been derived. Other methods for the determination of the length of the inhibition period have also been critically evaluated and compared.

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ЭНЕРГИИ СВЯЗЕЙ АТОМОВ-ОРГАНОГЕНОВ С МЕТАЛЛАМИ-КАТАЛИЗАТОРАМИ

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Численные значения энергии связи атомов реагирующих молекул с поверхностью катализаторов имеют значение с точки зрения предсказания величин энергии активации каталитических процессов [1]. Они характеризуют сродство катализатора к тем атомам реагирующих молекул, которые принимают участие в данном каталитическом процессе.

Термохимические и спектроскопические методы определения приведут к величинам, не тождественным со значениями энергий связей, образующихся между реагирующими молекулами и катализатором в ходе реакции.

Величины энергии связей, образующихся на каталитической поверхности, состоят из двух частей [2]:

$$Q_{XK} = Q_{XK}^0 + \lambda \quad (1)$$

где Q_{XK} — энергия связи между поверхностным атомом катализатора (K) и атомом реагирующего вещества (X),

Q_{XK}^0 — энергия связи X с K в соединении, содержащем эти атомы,

λ — сублимационный член — слагаемое, передающее все влияние соседних атомов поверхности.

Величины λ , о более точном значении которой см. [3], могут значительно повлиять на величины Q_{XK} , как это было показано на примере никелевых катализаторов различного приготовления [4]. Из этого следует, что для предсказания каталитической активности имеют первостепенное значение энергии связей, образованных между субстратом и поверхностными атомами катализатора.

Баландиным был развит [5] кинетический метод определения энергий связей, образующихся на каталитической поверхности. С помощью этого метода, используя величины энергий активации каталитической реакции, можно рассчитать искомые величины энергии связей. Этот метод был про-

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верен [6] и обширно использовался [7] для окисных катализаторов. Гораздо меньше имеется данных относительно металлических катализаторов [4, 8, 9]. Эти данные относятся к катализаторам Ni, Pt. Кроме этого были рассчитаны энергии связей на Ni, Pt, Pd и Fe [10] с использованием данных по энергиям активации различных реакций, опубликованных разными авторами, применявшими катализаторы различного метода приготовления. Однако при расчете энергии связей более желательно — если возможно — пользоваться данными по энергиям активации различных реакций, проведенных на одном и том же образце катализатора.

А. А. Баландиным и автором [11—13], а также автором с сотрудниками [14—19] проводились исследования, касающиеся каталитической активности 18 различных металлов в процессе дегидрогенизации и дегидратации спиртов, а также дегидрогенизации циклогексана и циклогексена. В результате исследований определялись энергии активации этих реакций на ряде металлов. Эти данные позволяют рассчитать энергии связей водорода, углерода и кислорода с металлическими катализаторами.

Принцип расчета основывался на выдвинутом А. А. Баландиным методе [5]. Составлялась система уравнений, выражающих энергию активации вышеуказанных трех реакций через энергии связей, разрывающихся (Q_{CH} , Q_{OH} и Q_{CO}) и образующихся (Q_{HMe} , Q_{CMe} и Q_{OMe}) при взаимодействии катализатора с реагирующим веществом. Решением этой системы были получены искомые величины Q_{HMe} , Q_{CMe} и Q_{OMe} .

Такой метод расчета может применяться только при условии, что в случае всех трех исследованных реакций одна и та же часть поверхности является активной, т. е. все три реакции проходят на одинаковых центрах катализатора. Было найдено [18, 19], что параметр распределения активных центров, величина « h » в уравнении

$$k_0 = ae^{h\epsilon}, \quad (2)$$

выражающем компенсацию [20] между константами уравнения Аррениуса* в случае трех исследованных реакций очень мало различаются друг от друга:

$$\text{дегидрогенизация циклогексена: } h = 7,50 \cdot 10^{-4}$$

$$\text{дегидрогенизация изо-пропанола: } h = 8,10 \cdot 10^{-4}$$

$$\text{дегидратация третичного бутанола: } h = 8,40 \cdot 10^{-4}$$

На основе близости величин « h » можно предположить, что все три реакции проходят на одинаковой части каталитической поверхности.

* k_0 — предэкспоненциальный множитель уравнения Аррениуса
 e — энергия активации

Анализ изменения каталитической активности металлов показывает [21], что при дегидрогенизации углеводородов происходит разрыв С—Н, при дегидрогенизации спиртов разрыв С—Н и О—Н, и при дегидратации спиртов разрыв С—Н и С—О связей. Было установлено также, что дегидрогенизация циклических углеводородов происходит посредством постепенного отрыва атомов водорода. Учитывая все это, для энергии активации трех исследованных реакций получаем следующие выражения.

Дегидрогенизация циклогексена:

$$\varepsilon_1 = 2Q_{\text{CH}} - 2Q_{\text{CMe}} - 2Q_{\text{HMe}} \quad (3)$$

Дегидрогенизация спирта:

$$\varepsilon_2 = Q_{\text{CH}} + Q_{\text{OH}} - Q_{\text{CMe}} - 2Q_{\text{HMe}} - Q_{\text{OMe}} \quad (4)$$

Дегидратация спирта:

$$\varepsilon_3 = Q_{\text{CH}} + Q_{\text{CO}} - 2Q_{\text{CMe}} - Q_{\text{HMe}} - Q_{\text{OMe}} \quad (5)$$

На основе литературных данных принимаем следующие значения для энергий связей в молекуле*:

Q_{CH} (в спиртах) = 99 ккал [22]

Q_{CH} (в циклических углеводородах) = 89 ккал [23]

Q_{CH} (первая реагирующая связь в циклогексене) = 77 ккал [23]

$Q_{\text{OH}} = 111$ ккал [23]

$Q_{\text{CC}} = 83$ ккал [22]

$Q_{\text{CO}} = 86$ ккал [23]

$Q_{\pi} = 60$ ккал [22]

$Q_{\text{HH}} = 104$ ккал [22].

Решением системы и используя указанные значения для связей внутри молекул, получаем следующие формулы для расчета искомых энергий связей:

$$\begin{aligned} Q_{\text{HMe}} &= 55 + \frac{1}{2} \left(-\frac{1}{2} \varepsilon_1 - \varepsilon_2 + \varepsilon_3 \right) \\ Q_{\text{CMe}} &= 29 + \frac{1}{2} \left(-\frac{1}{2} \varepsilon_1 + \varepsilon_2 - \varepsilon_3 \right) \\ Q_{\text{OMe}} &= 72 + \frac{1}{2} \left(\frac{2}{3} \varepsilon_1 - \varepsilon_2 - \varepsilon_3 \right) \end{aligned} \quad (6)$$

* Данные по энергиям связи и по энергиям активации во всей статье подразумеваются ккал/моль, но ради простоты пишутся лишь в ккал.

По поводу уравнений (3)—(5) необходимо отметить, что при их составлении был предположен полный разрыв связей внутри молекул при их адсорбции на поверхности катализаторов. Это предположение кажется в случае металлов более правдоподобным, чем использование коррекционного множителя $4/3$ для пересчета опытных значений энергии активации. Такой множитель применялся для окисных катализаторов на основе представления о частичном только разрыве связей в молекулах при образовании поверхностного комплекса реагирующего субстрата с катализатором.

Необходимо далее отметить, что уравнения (3)—(5) основываются на предположении, по которому энергии активации образования поверхностного соединения равны тепловому эффекту этого процесса, т. е., что образование этого комплекса не требует собственной энергии активации. Это предположение основывается на представлении, что поверхностные атомы имеют свободные валентности, а собственные энергии активации реакций, происходящих с участием свободных валентностей, например свободных радикалов, вообще незначительны. Все же кажется, что такое предположение вносит некоторую условность в расчеты. Поэтому рассчитанные по формулам (6) величины можно принять как параметры, характеризующие сродство между катализатором и атомами-органогенами, но можно их называть энергиями связей только условно.

Таблица I содержит сводные данные по энергиям активаций, определенным в наших, цитированных уже работах. Методы получения катализаторов и характеризующие их данные приведены в работах [11—14, 18]. Методика проведения экспериментов находится в работах [11, 15].

На основе данных, содержащихся в Таблице I, с помощью формул [6] рассчитывались величины Q_{HMe} , Q_{CMe} и Q_{OMe} , приведенные в Таблице II.

В вышеприведенных расчетах использовались энергии активации дегидрогенизации циклогексена, так как на примере никеля было установлено, что кажущаяся энергия активации в этом случае не сильно отличалась от истинной [24]. В случае же дегидрогенизации циклогексана механизм процесса более сложен, в скорости реакции играет значительную роль скорость адсорбции исходного вещества и скорость поверхностной химической реакции. Энергии активации этих двух процессов значительно различаются друг от друга [25, 26]. Анализ кинетических данных и результатов исследования механизма показывает [24], что при адсорбции происходит диссоциация первой C—H связи циклогексана и образуется поверхностный комплекс $C_6H_{11} \cdot Me$. В течение поверхностной реакции происходит разрыв второй связи C—H и образование циклогексена, удельная скорость дальнейшего превращения которого намного больше, чем предыдущие стадии реакции.

Таблица I

Энергия активации дегидрогенизации циклогексана (ϵ_1), изопропанола (ϵ_2) и третичного бутанола (ϵ_3) на различных металлах

Катализатор	ϵ_1 ккал	ϵ_2 ккал	ϵ_3 ккал
Железо	9	20	17
Кобальт	25	12	18
Никель	8	10	22
Медь	15	11	18
Рутений	9	9	19
Родий	10	13	23
Палладий	10	18	25
Серебро	11	20	26
Иридий	6	11	22
Платина	11	17	25
Золото	18	16	22

Значительно большее значение энергии активации адсорбции циклогексана по сравнению с энергией активации последующего поверхностного процесса, несмотря на то, что в течение обеих стадий реакции происходит разрыв одной С—Н связи, является показателем того, что эта адсорбция требует значительной собственной энергии активации. Поэтому для расчета энергий связей можно использовать только энергию активации поверхностной дегидрогенизации, которая — на основе вышеизложенного представления о механизме процесса — выражается следующим образом:

$$\epsilon_1 = Q_{CH} - Q_{CMe} - Q_{HMe} \quad (7)$$

Решив систему, состоящую из уравнений (4), (5) и (7) и используя вышеприведенные значения энергий связей Q_{CH} , Q_{OH} и Q_{CO} , приходим к следующим расчетным формулам:

$$\begin{aligned} Q_{HMe} &= 58 + \frac{1}{2}(-\epsilon_1' - \epsilon_2 + \epsilon_3) \\ Q_{CHe} &= 32 + \frac{1}{2}(-\epsilon_1' + \epsilon_2 - \epsilon_3) \\ Q_{OMe} &= 62 + \frac{1}{2}(3\epsilon_1' - \epsilon_2 - \epsilon_3) \end{aligned} \quad (8)$$

Величины энергии активации для поверхностной стадии дегидрогенизации циклогексана были определены [25] в случае никеля, платины и родия (10, 13 и 10 ккал, соответственно). Используя эти значения, а также

величины энергии активации дегидрогенизации и дегидратации спиртов (Таблица I), были рассчитаны энергии связей для этих трех катализаторов (Таблица III).

Сравнение данных в Таблицах II и III позволяет установить, что имеются лишь небольшие различия между значениями энергий связей, рассчитанных по формулам (6) и (8). Это говорит в пользу применимости этих формул для расчета.

В Таблице IV приводятся некоторые литературные данные по энергиям связи, полученные термохимическим, спектральным или расчетным путем, и сравниваются с данными, полученными кинетическим методом.

Сравнение энергии связей по данным Таблиц II и IV показывает, что полученные кинетическим методом величины не отличаются в значительной мере от данных, полученных термохимическим, спектральным или расчет-

Таблица II

Энергии связей атомов водорода, углерода и кислорода с металлическими катализаторами, рассчитанные по формулам [6]

Катализатор	Q_{HMe} ккал	Q_{CMe} ккал	Q_{OMe} ккал
Железо	50	28	57
Кобальт	52	24	61
Никель	59	21	58
Медь	55	21	62
Рутений	58	22	61
Родий	58	22	57
Палладий	56	23	54
Серебро	55	23	53
Иридий	59	22	57
Платина	56	22	55
Золото	53	21	59

Таблица III

Энергии связей атомов водорода и кислорода с металлическими катализаторами, рассчитанные по формулам [8]

Катализатор	Q_{HMe} ккал	Q_{CMe} ккал	Q_{OMe} ккал
Никель	59	21	61
Родий	58	22	59
Платина	56	22	60

ным путем. Это подтверждает реальность кинетического метода. Нельзя, конечно, ожидать полного совпадения, поскольку кинетический метод, как было указано выше, дает энергии связей на поверхности, а другие методы — энергии связей в химических соединениях.

Таблица IV

Литературные данные по энергиям связи водорода, углерода и кислорода с металлами

Металл	Q_{HMe}° ккал		Q_{CMe}° ккал		Q_{OMe}° ккал	
	расч. ²⁷	эксп.	расч. ²⁷	эксп.	расч. ²⁷	эксп.
Железо	53		14		52	46 ²⁸
Кобальт	57		15		57	49 ²⁸
Никель	54	55 ²²	14	18 ²⁹	53	
Медь	47	62 ²⁸	12		43	67 ²⁸
Рутений	65		16		50	
Родий	60		14		45	
Палладий	50		12		45	
Серебро	45	58 ²⁸	12		49	32 ²⁸
Иридий	66		16		47	
Платина	56		14		44	
Золото	47	72 ²⁸	11		34	

Результатом этого обстоятельства является повидимому то, что Q_{CMe} и Q_{OMe} (Таблица II), как правило, больше, чем Q_{CMe}° и Q_{OMe}° , что находится в согласии со смыслом выражения (1). В случае же величин Q_{HMe} и Q_{HMe}° такое явление не наблюдается, что требует дальнейшего рассмотрения. Возможно, что в этом случае играет роль вышеуказанное исходное предположение при расчетах, об отсутствии собственной энергии активации в процессе образования поверхностных соединений. Это приводит к пониженным значениям энергии связей в сравнении с настоящими.

При сравнении данных в Таблице II с другими значениями Q_{HMe} , Q_{CMe} и Q_{OMe} , полученными кинетическим путем [10], наблюдается довольно хорошее совпадение. Значительные отличия оказываются только в случае Q_{OPt} и Q_{OPd} . Эти величины, рассчитанные с использованием энергии активации разложения муравьиной кислоты, оказываются значительно, на 10—20 ккал меньшими, чем данные в Таблице II. Здесь может оказывать влияние прохождение двух реакций, — дегидрогенизаций и дегидратаций — при распаде муравьиной кислоты. Как было установлено [30], соотношение продуктов не поддается стехиометрическим коэффициентам, что говорит о реакции продуктов между собой в условиях разложения муравьиной кис-

лоты. Это может привести к значительным искажениям величин энергии активации.

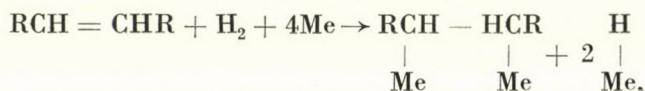
Полученные нами данные можно успешно использовать для расчета энергии активации других реакций, не служивших для расчета энергии связей.

К. Шехтер в нашей лаборатории определила кажущуюся энергию активации крекинга кумола в присутствии никеля: 35 ккал. Энергия активации для этой реакции выражается следующим образом:

$$\varepsilon_k = Q_{\text{C-C}} + Q_{\text{C-H}} - 3Q_{\text{C-Me}} - Q_{\text{H-Ni}} \quad (9)$$

Учитывая, что в этом случае $Q_{\text{C-H}} = 77,5$ ккал [23], и используя данные из Таблицы II для $Q_{\text{H-Ni}}$ и $Q_{\text{C-Ni}}$, получается для энергии активации 39 ккал, величину, довольно хорошо совпадающую с экспериментальными данными.

Полученные данные могут применяться также для приближенной оценки энергии активации гидрирования двойной связи. Предположив, что при гидрировании происходит сначала процесс:



для энергии активации получаем выражение:

$$\varepsilon_{\text{H}} = Q_{\pi} + Q_{\text{H-H}} - 2Q_{\text{C-Me}} - 2Q_{\text{H-Me}} \quad (10)$$

Принимая приведенные выше и в Таблице II величины, для энергии активации гидрирования двойной связи на никеле по формуле (10) получаем величину 4 ккал. Проведенные в нашей лаборатории исследования *Л. Гуци* [31] дали следующие величины для энергии активации гидрирования; этилена: 2,4, пропилена: 3,7, бензола: 4 и циклогексена: 8 ккал. Опыты проводились с никелем того же приготовления, как при дегидрогенизационных реакциях. Близость рассчитанной и определенной опытным путем энергий активации говорит в пользу применимости кинетического метода определения энергий связей.

При рассмотрении данных приведенных в Таблице II, обращает на себя внимание следующее обстоятельство.

Величины энергии связей меняются не очень значительно при переходе с одного металла к другому. Изменения величин энергии связей в объемных химических соединениях (Таблица IV) гораздо более значительны, чем в случае поверхностных образований. Это особенно наглядно выражается, если мы рассматриваем сумму

$$Q_{\text{H-Me}} + Q_{\text{C-Me}} + Q_{\text{O-Me}}$$

Эта сумма меняется очень незначительно в случае различных металлов. Ее значение колеблется между 131 и 141 ккал, всего на 7—8%.

Несмотря на небольшие изменения в энергиях связей, скорости различных реакций меняются очень значительно в зависимости от природы металла [14, 18, 19, 21].

Незначительное влияние природы металла на энергии связей поверхностных образований можно объяснять исходя из неоднородности металлической поверхности. Неоднородность была доказана, например, адсорбционными измерениями водорода с никелем [32] и платиной [33]. Очень вероятно, что каталитическая реакция происходит не на всей поверхности катализатора, а только на тех местах, которые энергетически выгодны для нее. Реакция как будто «выбирает» для себя ту часть поверхности, которая наиболее выгодна для ее протекания. Поэтому энергетические показатели данной реакции на различных металлах отличаются незначительно. Однако число активных мест, величина той части поверхности, на которой проходит реакция, естественно зависит от природы и от метода приготовления катализатора. Поэтому в скорости каталитических реакций, в каталитической активности металлов наблюдаются очень значительные различия, несмотря на сравнительную близость параметров, характеризующих активность катализаторов с энергетической стороны.

РЕЗЮМЕ

На основе кинетических данных энергий активации различных каталитических реакций были рассчитаны энергии связей водорода, углерода и кислорода с 11 различными металлами. Показана реальность этих значений и возможность оценки с их помощью величины энергии активации для других каталитических реакций. Отмечено, что на численные значения энергий связей сравнительно мало влияет природа металла.

SUMMARY

From the energy of activation of different catalytic reactions, the bond energies between hydrogen, carbon, oxygen and eleven different metals have been calculated. The reality of these values and the way in which the energy of activation for other catalytic reactions may be estimated have been shown. It is pointed out that the numerical values of the bond energies are influenced by the nature of the metal to a relatively small extent.

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VIBRATIONAL SPECTRA OF SILACYCLOHEXANE DERIVATIVES AND THE Si-C STRETCHING FREQUENCIES OF VARIOUS-MEMBERED SILACYCLOALKANES

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Introduction

OSHESKY and BENTLEY published the infrared spectra of 21 different 1,1-silacyclohexane derivatives in 1957 [1]. By comparing these spectra, it has been established that the most suitable bands to identify the heteroring in these compounds are to be found in the ranges $909-915\text{ cm}^{-1}$ and $480-495\text{ cm}^{-1}$.

One of the objects of the present research has been to make a more detailed study of the skeletal vibrations of silacyclohexane. Normal coordinate analysis was performed by the well-known method [20, 21], while the internal modes of the CH_2 and SiH_2 groups were neglected. In order to facilitate the solution of the assignment problem, the vibrational spectra of some derivatives were also examined. Another aim of the present work has been to obtain information about the strain of the ring introduced by the angle CSiC ; this could be done by comparing the so far uninvestigated spectra of various-membered rings.

Experimental

The compounds investigated were prepared in the *Institute for Petrochemistry of the Academy of Sciences of USSR*. 1,1-Dichlorosilacyclohexane was made from SiCl_4 and $\text{Br}(\text{CH}_2)_5\text{Br}$ according to [22]. Methylation of the above compound gave 1,1-dimethylsilacyclohexane. 1,1-Dihydrocyclohexane was prepared from the dichloro derivative by means of LiAlH_4 . All the above-mentioned compounds were purified by rectification on a column having a theoretical plate number of 20, and their purity was checked by gas chromatography. The properties of the products were in good agreement with the literature data [23].

The so far unknown compound, 1,1-dideuterosilacyclohexane, was prepared by the reaction of LiD , AlBr_3 and $\text{Cl}_2\text{Si}(\text{CH}_2)_5$ without isolation of the intermediary product LiAlD_4 . The compound was purified by preparative gas chromatography. The boiling point, refractive index and specific gravity are practically the same as those of silacyclohexane. 1,1-Dimethylsilacyclobutane and 1,1-dimethylsilacyclopentane were synthesized according to [24] and [22]; the products were purified using a distillation column, and the purity was checked by gas chromatography.

The vibrational spectra were recorded at the *Inorganic Research Group of the Hungarian Academy of Sciences*. The infrared spectra were obtained in solution with a *Hilger H 800* spectrom-

Table I
*Raman frequencies of silacyclohexane (a), dimethylsilacyclohexane (b)
 and dichlorosilacyclohexane (c)*

(a)		(b)		(c)	
cm ⁻¹	Int.	cm ⁻¹	Int.	cm ⁻¹	Int.
115	m	111	w	140	s
150	m	146	s	200	w
300	m	204	s	229	m
353	w	240	m	259	w
450	vw	340	m	309	vs
525	vw	371	w	347	w
571	s	483	w	375	w
600	m	529	w	411	vw
656	vs	586	vs	472	vs
734	m	635	w	490	m
797	m	695	m	579	w
863	w	725	w	634	vw
892	m	798	m	658	vw
909	m	836	vw	694	s
946	s	907	m	781	w
983	m	1005	m	799	m
1008	s	1077	w	908	m
1083	m	1102	w	982	m
1105	m	1133	w	1005	m
1116	m	1181	m	1044	vw
1162	m	1194	m	1076	w
1180	m	1250	m	1103	w
1197	m	1270	m	1128	w
1265	m	1290	m	1182	m
1289	m	1334	w	1200	m
1343	m	1405	s	1258	w
1409	s	1446	s	1272	w
1451	s	2229	w	1297	m
2140	vs	2460	m	1335	w
2500	s	2492	s	1349	m
				1400	m
				1454	s
				2237	w
				2467	m
				2500	s

w — weak m — medium s — strong v — very

eter, while the Raman spectra were recorded using liquids and a *Hilger* type recording equipment. It may be noted that the deuterated derivative contained a small amount of silacyclohexane but this did not interfere with the evaluation of the spectrum. For the compounds whose infrared spectra have been reported by OSHESKY [1], only the Raman spectra are given in this paper.

Table II

Infrared spectra of silacyclohexane and 1,1-dideuterosilacyclohexane

$C_6H_{10}SiH_2$		$C_6H_{10}SiD_2$		$C_6H_{10}SiH_2$		$C_6H_{10}SiD_2$	
cm^{-1}	Int.	cm^{-1}	Int.	cm^{-1}	Int.	cm^{-1}	Int.
450	vw	413	vw	1266	w	1261	w
569	m	517	m	1289	vw	1286	vw
598	w	545	m			1305	vw
652	w	637	w	1341	w	1339	m
		671	m	1408	m	1402	m
738	m	698	s	1442	m	1445	s
791	m	773	vs	1458	w	1456	m
		819	w			1533	vs
		843	w			1550	vs
865	vs			2120	vs		
887	s					2300	vw
909	s	907	s	2660	vw	2640	w
925	w					2780	w
946	vs			2850	m	2840	s
997	m	990	s	2915	s	2900	vs
1006	w	1006	w				
1046	w	1039	vw				
1075	vw	1073	vw				
		1100	vw				
1180	s	1180	s				
1195	w	1195	w				

Calculations

With respect to the geometry of the silacyclohexane skeleton it has been assumed that it corresponds to the chair form of cyclohexane. In this geometry all angles are tetrahedral but the form of the ring deviates somewhat from that of cyclohexane owing to the difference between the C—C and C—Si bond lengths. Irrespective of the chair, or boat form, the molecule belongs to point group C_s , so that the spectra of the two conformations may be expected to differ much less than those of the cyclohexane conformers. Owing to the low

symmetry of the molecule, all normal modes are infrared and Raman active. The geometrical data and the force constants of the molecule have been adopted from dimethylsilane and cyclohexane [2, 3] and they are listed in Tables III and IV. The mass of the groups CH_2 and SiH_2 were taken as the sum

Table III

Parameters of the molecule

$$\begin{aligned} R_{\text{CC}} &= 1.54 \text{ \AA} & R_{\text{CSi}} &= 1.86 \text{ \AA} \\ \Phi_{\text{CCC}} &= \Phi_{\text{CSiC}} = \text{tetrahedral angle} \\ m_{\text{SiH}_3} &= 30.1 & m_{\text{CH}_2} &= 14.0 \end{aligned}$$

Table IV

The F matrix in internal coordinate representation

	r_1	r_2	r_3	r_4	r_5	r_6	φ_1	φ_2	φ_3	φ_4	φ_5	φ_6
r_1	K'_Q	H_ϵ^*	0	0	0	H_ϵ^*	c'_ϵ	c_ϵ^*	0	0	0	0
r_2		K_Q	H_ϵ	0	0	0	0	c_ϵ^{**}	c_ϵ	0	0	0
r_3			K_Q	H_ϵ	0	0	0	0	c_ϵ	c_ϵ	0	0
r_4				K_Q	H_ϵ	0	0	0	0	c_ϵ	c_ϵ	0
r_5					K_Q	H_ϵ^*	0	0	0	0	c_ϵ	c_ϵ^{**}
r_6						K'_Q	c'_ϵ	0	0	0	0	c_ϵ^*
φ_1							k'_ϵ	$l_{\epsilon\epsilon}^*$	0	0	0	$l_{\epsilon\epsilon}^*$
φ_2								k_ϵ^*	$l_{\epsilon\epsilon}^{**}$	0	0	0
φ_3									k_ϵ	$l_{\epsilon\epsilon}$	0	0
φ_4										k_ϵ	$l_{\epsilon\epsilon}$	0
φ_5											k_ϵ	$l_{\epsilon\epsilon}^*$
φ_6												k_ϵ^*

$$\begin{aligned} K_Q &= 4.24 \cdot 10^5 & k_\epsilon &= 1.15 \cdot 10^{-11} & H_\epsilon &= 0.25 \cdot 10^5 \\ l_{\epsilon\epsilon} &= 0.24 \cdot 10^{-11} & c_\epsilon &= 0.34 \cdot 10^{-3} & K'_Q &= 2.98 \cdot 10^5 \\ k'_\epsilon &= 0.65 \cdot 10^{-11} & k_\epsilon^* &= 0.95 \cdot 10^{-11} & H'_\epsilon &= 0.032 \cdot 10^5 \\ H_\epsilon^* &= 0.15 \cdot 10^5 & l_{\epsilon\epsilon}^* &= 0.10 \cdot 10^{-11} & l_{\epsilon\epsilon}^{**} &= 0.20 \cdot 10^{-11} \\ c'_\epsilon &= 0.21 \cdot 10^{-3} & c_\epsilon^* &= 0.25 \cdot 10^{-3} & c_\epsilon^{**} &= 0.30 \cdot 10^{-3} \end{aligned}$$

Dimensions: K, H — $\text{dyn} \cdot \text{cm}^{-1}$ k, l — $\text{dyn} \cdot \text{cm}$ c — dyn

Table V

Symmetry coordinates

$$\begin{aligned} A' \quad S_1 &= 1/\sqrt{2} (r_1 + r_6) & S_2 &= 1/\sqrt{2} (r_2 + r_5) \\ S_3 &= 1/\sqrt{2} (r_3 + r_4) & S_4 &= \varphi_1 \\ S_5 &= 1/\sqrt{2} (\varphi_2 + \varphi_6) & S_6 &= 1/\sqrt{2} (\varphi_3 + \varphi_5) \\ S_7 &= \varphi_4 \\ A'' \quad S_8 &= 1/\sqrt{2} (r_1 - r_6) & S_9 &= 1/\sqrt{2} (r_2 - r_5) \\ S_{10} &= 1/\sqrt{2} (r_3 - r_4) & S_{11} &= 1/\sqrt{2} (\varphi_2 - \varphi_6) \\ S_{12} &= 1/\sqrt{2} (\varphi_3 - \varphi_5) \end{aligned}$$

of the corresponding atomic masses. The numbering of the groups and the internal coordinate choice is given in Fig. 1. The symmetry coordinates are given in Table V. The eigenvalues and eigenvectors of the secular equation were calculated with a *National Elliott 803 B* digital computer by the co-workers of the *Computation Centre of the Hungarian Academy of Sciences*. The results of the calculations are summarized and compared with the experimental values in Table VI. It is to be noted that not WILSON's L matrix itself, but its transpose is given.

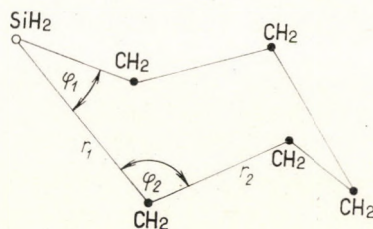


Fig. 1. Internal coordinates

Table VI

Normal vibrations, calculated and observed frequencies of silacyclohexane

A'	s ₁	s ₂	s ₃	s ₄	s ₅	s ₆	s ₇	calc. cm ⁻¹	obs. cm ⁻¹
Q ₁	-0.229	1	-0.585	0.178	-0.262	-0.236	0.454	1035	1046 (IR)
Q ₂	-0.278	0.549	1	0.150	0.096	-0.512	-0.436	890	887-892 (IR, R)
Q ₃	1	0.189	0.080	-0.081	-0.648	0.266	-0.079	660	652-656 (IR, R)
Q ₄	-0.137	0.011	-0.009	0.327	-0.457	-0.745	-0.745	525	525? (IR,R)
Q ₅	-0.031	-0.003	0.054	0.397	0.831	0.812	1	440	450 (IR, R)
Q ₆	-0.134	-0.033	0.033	1	-0.962	-0.107	0.523	280	294-300 (IR, R)
Q ₇	0.013	-0.007	-0.033	1	0.386	-0.210	-0.287	160	150 (R)

A''	s ₈	s ₉	s ₁₀	s ₁₁	s ₁₂			calc. cm ⁻¹	obs. cm ⁻¹
Q ₈	0.154	-0.670	1	0.228	-0.196			1083	1082 (R)
Q ₉	-0.415	1	0.715	-0.022	-0.777			970	983-997 (R, IR)
Q ₁₀	1	0.234	0.054	-0.647	0.043			736	734 (IR, R)
Q ₁₁	-0.095	0.023	0.047	-0.748	1			385	353-365 (R, IR)
Q ₁₂	0.081	0.041	0.024	1	0.531			232	—

Assignment of the vibrational frequencies of silacyclohexane

The data of Table VI show that the approximate calculations reported here can be well in the assignment of the bands. Owing to the great number of bands appearing between 850 and 1100 cm^{-1} it was not possible, however, to assign the bands belonging to the normal coordinates Q_1 , Q_2 , Q_8 and Q_9 on the basis of the calculations alone. In this case it was especially important to compare the spectra of the derivatives. This comparison rendered possible to assign also such bands which are not skeletal motions. The likely assignment of these bands is the following:

571, 600 cm^{-1}	SiH and/or CSiH deformation
797, 909, 1006 cm^{-1}	CH_2 deformations
863, 946 cm^{-1}	SiH_2 deformations

According to the assignments, the frequency values assigned to the individual normal coordinates are in agreement with expectation in the low frequency region, too. The bands which had been considered to be characteristic for the [1], correspond according to our assignments to a CH_2 rocking mode (908 cm^{-1}) and to a skeletal motion having mainly CCC bending character (450 cm^{-1}).

It is interesting to compare the spectra of silacyclohexane and its 1,1-dideutero derivative. As it is shown by the data of Table II, the two spectra are rather similar, as expected. In the lower frequency region the deuterio derivative has, in general, lower frequency values than silacyclohexane. The very intense bands at 863 and 946 cm^{-1} corresponding to the SiH_2 deformation vibrations are not found in the spectrum of the deuterio derivative, although the corresponding SiD_2 bands could not be identified. Above 1000 cm^{-1} the two spectra are practically identical, apart from the SiH stretching frequency (2120 cm^{-1}) and the SiD stretching frequencies (1550 and 1533 cm^{-1}). The symmetric and antisymmetric stretching modes of the SiH_2 group are not split, while those of the SiD_2 group are.

The Si—C stretching frequency and the strain of the CSiC angle

The Si—C stretching frequencies have been separately examined in the course of this work, and they have been compared with the analogous frequencies of the monosilane derivatives [4–8]. According to the data of Table VII there are not great differences between the corresponding values of a silane derivative and a silacyclohexane derivative. The analogy is most conspicuous in the case of dimethylsilacyclohexane and tetramethylsilane. The position of the infrared inactive A_1 band of tetramethylsilane is practically

Table VII

Si—C stretching frequencies of silacyclohexane derivatives and the corresponding silane derivatives [4—8]

Compound	C ₆ H ₁₀ SiH ₂	Me ₂ SiH ₂	C ₆ H ₁₀ SiCl ₂
symm. cm ⁻¹	655	658	690
asymm. cm ⁻¹	734	732	799

Compound	Me ₂ SiCl ₂	C ₃ H ₁₀ SiMe ₂	Me ₂ SiMe ₂
symm. cm ⁻¹	688	587	594
asymm. cm ⁻¹	805	693	695

the same also in dimethylsilacyclohexane, but it is no longer inactive. The agreement of the SiC frequencies of silane and silacyclohexane derivatives supports our original assumption about the strainless structure of the ring. As to four-membered and five-membered rings, they are probably strained, i.e. the valence angles differ from the tetrahedral values. This problem has been thoroughly studied in the case of the analogous cycloalkanes, still it cannot be considered completely clarified. Spectroscopical evidence has shown that cyclopentane is almost planar and the valence angles are only slightly distorted ($\angle \text{CCC} = 108^\circ$; $\angle \text{HCH}$ is tetrahedral)[9, 10, 17], while the potential energy distribution calculations [11, 12] suggested a non-planar (puckered) arrangements. The electron diffraction data of cyclobutane render probable that the ring is puckered [13], although the vibrational spectrum can be fairly well interpreted also in this case by assuming a planar geometry of symmetry D_{4h} [14]. As the valence angles within the ring decrease, the HCH angles are increasing. In cyclobutane the HCH angle is $114 \pm 8^\circ$ [13], while in cyclopropane it is $116\text{--}120^\circ$ [15, 16, 17]. This fact is in agreement with the hybridization theory, according to which any increase in the p-character of the C—C bonds must result in an increase of the s-character of the C—H bonds. An increase of the s-character leads to the strengthening of the bonds [18] thus the corresponding frequencies are shifted towards higher values, the CH stretching frequency region being $2800\text{--}3000\text{ cm}^{-1}$ for the alkanes, and $3000\text{--}3100\text{ cm}^{-1}$ for cyclopropane. Assuming that the geometry of silacycloalkane rings is similar to that of cycloalkanes, it may be expected by analogy that the SiC stretching frequencies belonging to the exocyclic methyl groups are shifted upward on passing from silacyclohexane to silacyclopentane and silacyclobutane. In order to examine this problem, the infrared and Raman spectra of 1,1-dimethylsilacyclopentane and 1,1-dimethylsilacyclobutane have been recorded, and the symmetric SiC stretching frequencies of the dimethylsilacycloalkanes are listed in Table VIII.

Table VIII

Symm. Si—C stretching frequencies of silacycloalkanes

Compound	C ₆ H ₁₀ SiMe ₂	C ₄ H ₈ SiMe ₂	C ₃ H ₆ SiMe ₂
Frequency, cm ⁻¹	586	598	612

The identification of these bands has been facilitated by their high Raman intensities. The exocyclic and endocyclic SiC stretching frequencies are degenerate in the case of a six-membered ring, while in the case of five-, and four-membered rings they are split. As it is seen, the frequency shifts are such as expected, and they suggest strain in both the five-, and four-membered rings. It may be pointed out that strain appears already in the five-membered ring, indicating that the distortion of the CSiC angle is higher in silacyclopentane than that of the corresponding CCC angle in cyclopentane. This result is in agreement with the only relevant measurement that has been obtained by the electron diffraction method [19].

SUMMARY

The infrared and Raman spectra of some silacyclohexanes have been investigated. On the basis of an approximate normal coordinate analysis, the assignments of the skeletal vibrations of the silacyclohexane molecule are given. The SiC stretching frequencies of the corresponding silacyclohexane and silane derivatives have been compared, and the changes of the SiC stretching frequencies in the six-membered, five-membered and four-membered heterocycles have been studied. On this basis, information has been obtained concerning the strain prevailing in the rings of these compounds.

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CHANGES IN THE DEHYDROCYCLIZING ACTIVITY OF NICKEL CATALYSTS DURING USE

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Catalytic activity is, as a rule, not a constant value during an experiment. In industrial practice as well as in kinetic measurements it is desired to restrict the variations of activities to the possible minimum. On the other hand, a careful examination of the changes of catalytic activity, *i.e.* of the so-called transient states of catalyst functioning may greatly contribute to a better understanding of catalytic phenomena.

One of the authors investigated the variations of the activity of chromia-alumina catalysts in the process of dehydrocyclization [1]. It has been stated, that maximum activity of the regenerated catalyst is reached only after a "development" process; this effect is caused by a partial oxidation of Cr(III) during regeneration by air to Cr(VI); Cr(VI) is reduced to Cr(III) by the first portions of hydrocarbons. Maximum activity is attained only when the water formed during reduction has been desorbed from the catalyst surface.

Carbonaceous deposits on aromatizing catalysts containing platinum should be removed by means of air, too, but in order to attain maximum activity, hydrogen is required. After hydrogenation, the catalyst possessed maximum activity without delay (in 1-2 minutes) [2].

The aromatizing activity of nickel catalysts has been known for a relatively long time [3], but little if any detailed studies have been made on the behaviour of catalysts with different nickel contents in the process of dehydrocyclization and regeneration.

Of several nickel-on-alumina catalysts, maximum catalytic activity in cyclohexane dehydrogenation was found with the sample in which the molar ratio of Ni and Al_2O_3 corresponded to 1:1 [4]. In nickel-alumina catalysts nickel-meta-aluminate promoting the activation of nickel with hydrogen has been supposed to be present [5].

In our previous publications characteristics of the aromatization reactions of *n*-heptene and *n*-hexene in the presence of nickel-alumina as well as of nickel metal were reported [2, 6]. Measurements were performed in a pulse technique apparatus, which proved to be an excellent tool to investigate chan-

ges in the activities of catalysts with different nickel contents. Such results are reported in the present communication.

The catalysts were prepared by precipitation of the hydroxides by means of ammonium hydroxide from aqueous solutions of nickel nitrate and aluminium nitrate, or from that of nickel nitrate alone, followed by reduction with hydrogen at 360 °C [6, 7]. The properties of the catalysts obtained are listed in Table I.

Table I
Properties of catalysts

Property	Catalyst		
	Ni/Al ₂ O ₃ , No. 1	Ni/Al ₂ O ₃ , No. 2	Ni, No. 3
Nickel content in crude catalyst	18.62%	28.16%	52.5%
after reduction	32.80%	50.3%	100%
Molar composition of crude catalyst	Ni(OH) ₂ 2.22 Al(OH) ₃ 1.6 H ₂ O	Ni(OH) ₂ 1.13 Al(OH) ₃ 1.47 H ₂ O	Ni(OH) ₂ 1.1 H ₂ O
Molar ratio of Ni : Al ₂ O ₃ in re- duced catalyst	0.90	1.74	
Specific surface after reduction	266 m ² /g	220 m ² /g	3.5 m ² /g

n-Hexane and *n*-heptane were used as the starting materials. Entirely analogous behaviour was observed with both hydrocarbons.

The first hydrocarbon pulses introduced to a freshly reduced catalyst were quantitatively cracked. When further pulses were introduced, the quantity of cracked products was decreasing, and that of unchanged paraffinic hydrocarbons was continuously increasing; at the same time aromatics appeared among the products. These facts show that nickel catalysts exhibited an aromatizing activity only after a kind of development process. In order to obtain quantitative data, both nickel-alumina catalysts samples containing equal amounts of nickel metal (0.13 g) were measured. Fig. 1 indicates the product compositions obtained in the presence of these catalyst samples as a function of the quantity of hydrocarbon introduced.

The different character of the curves obtained with the two types of catalysts is obvious. Cracking activity of Catalyst No. 1 containing less nickel decreased much more rapidly (after an initial period showing a large cracking effect) than that of Catalyst No. 2; the former had at the same time a considerably larger aromatizing activity (*cf.* Curves 1-A and 2-A-I). The quantity of aromatics could be characterized with a maximum curve in case of both catalysts. After the amount of aromatics had attained the maximum, the aro-

matizing activity decreased rather slowly; thus it could be regarded in first approximation as stationary, in spite of a considerably larger parallel change in the quantity of cracked products.

In several cases small quantities of olefins were also detected among the products; their amount was slightly larger in the presence of deactivated

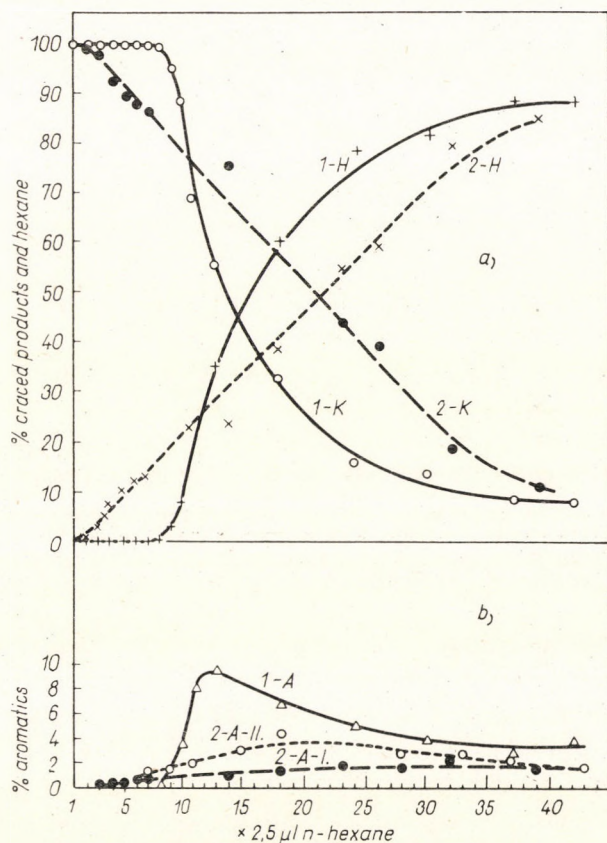


Fig. 1. Development of nickel-on-alumina catalysts in the process of dehydrocyclization of *n*-hexane ($t = 360^\circ \text{C}$; carrier gas: He)
Catalysts: 0.67 g of crude No. 1; 0.46 g of crude No. 2 (= 0.13 g of Ni) The numbers of curves are identical to the No's of the catalysts
K — cracked products; H — recovered *n*-hexane; A — aromatics
I — results on freshly reduced catalyst;
II — results on regenerated catalyst

catalysts, but relative experimental errors did not allow a quantitative evaluation. Parallel to the aromatizing activity, the catalysts also had alkylating and dealkylating effects [6]. At a typical temperature of the experiments (360°) toluene was extensively demethylated by both nickel-alumina catalysts. Using hexane as the starting hydrocarbon, a detectable amount of toluene

was formed only in the presence of Catalyst No. 1; in this case aromatics consisted of 10–20% toluene and 80–90% benzene. In evaluating the results, (Fig. 1) the amounts of these two compounds were added. Toluene formation in the presence of the other two catalysts cannot be precluded either, but the quantity of this product was at any rate less than the detection limit.

Since the nickel metal catalyst had a relatively small specific surface, in the presence of a sample containing 0.13 g of pure metal, *i.e.* the quantity equivalent to that of Ni in the nickel-alumina samples, no detectable aromatization was observed. Therefore, an arbitrary greater sample (corresponding to 0.36 g of pure metal) was used. This catalyst also showed a development process, which was more rapid, but otherwise entirely analogous to that of the nickel-alumina catalysts; our sample became totally deactivated after introducing about 15 pulses 2.5 μ l's of *n*-hexane each. The aromatic contents of the product had maximum in pulses 2–3, amounting, however, only to 0.3% of the total catalysate. These data are not suitable to make a quantitative evaluation of the development process of the pure nickel catalyst having a very small specific surface. The results prove, however, unambiguously that the observed process takes place irrespective of the presence of the alumina carrier, thus it is due to the nickel itself.

After introducing about 100 μ l of *n*-hexane, a hydrogen stream was passed over each catalyst at 360° for 1.5 hours. After this treatment the catalysts showed an analogous behaviour to the freshly reduced samples: in the course of a progressive dosing of hydrocarbon pulses the process of development was repeated. The curves showing the amounts of individual components retained their shapes characteristic of a given catalyst. The curves of the second development are rather near to those of Fig. 1; for the sake of clarity they are not indicated in the Figure. At the same time there were also differences between the primary and secondary developments; the latter took place slightly more rapidly. Some typical data are shown in Table II. Curve 2-A-II indicates an interesting difference between the two development processes of Catalyst No. 2; a much larger aromatizing activity is observed after regeneration than with the freshly reduced catalyst. No such phenomenon was experienced in case of Catalyst No. 1. Only an incomplete regeneration was achieved in case of Catalyst No. 3, where irreversible changes were greater due to its small specific surface.

The observations listed above show that the nature and extent of the activity of nickel catalysts depend primarily on their hydrogen contents. This is additional evidence to show the important role played by hydrogen in the individual — sorption and reaction — steps of dehydrogenation and dehydrocyclization. The hydrogen content of a catalyst has an optimum value from the point of view of dehydrocyclization; nickel containing much hydrogen favours the hydrocracking reaction, *i.e.* the breaking of C—C linkages. Thus,

Table II

*Product composition of the dehydrocyclization reaction
of n-hexane in the presence of catalysts treated in different ways*
Catalyst: 0.46 g of crude Ni/Al₂O₃, No. 2.

Pre-treatment of catalyst	No. of n-hexane pulse after treatment	Product composition, % (w/w)			
		Cracked products	Hexane	Benzene	Others
Freshly reduced	1.	99.8	0.15	—	—
	7.	86.4	13.1	0.5	—
	18.	60.1	38.7	1.2	—
	39.	11.2	84.6	1.5	hexene: 0.5
40 ml of H ₂ (in pulses)	1.	60.3	38.2	1.5	—
H ₂ stream at 360 °C for 1.5 hrs.	2.	99.5	0.5	—	—
	7.	88.7	10.2	1.1	—
	18.	48.6	47.0	4.1	hexene: 0.3
	37.	15.3	82.2	2.1	hexene: 0.4
	50.	5.8	92.7	1.5	—
Oxidized by air at 360 °C	1.	51.0	10.0	—	unidentified lower products: 37.7
	2.	44.2	35.6	2.1	unidentified lower products: 18.1
	5.	48.9	34.7	2.9	unidentified lower products: 13.5
20 ml of H ₂ (in pulses)	1.	84.1	14.5	1.4	—
	8.	19.5	77.5	2.5	hexene: 0.5
4 ml of H ₂ (in pulses)	1.	47.3	48.4	2.3	—
5 μ l of H ₂ O	1.	67.8	30.0	2.1	—
	2.	56.8	40.2	2.9	—

over-hydrogenating of the catalyst — though it may lead to a full conversion of *n*-hexane — results in a harmful selectivity from the point of view of aromatization.

Carbonaceous surface deposits formed during reaction can be removed by hydrogenation much easier than in case of platinum catalysts [2]; also a pulse-like introduction of hydrogen may be effective (Table II). This fact makes possible to maintain catalyst activity at the desirable maximum level for a longer period by the careful dosage of hydrogen.

The differences between the two types of nickel-alumina catalysts may be explained by different dispersity of nickel particles or by different interactions between the nickel and the alumina carrier in some way, *e.g.* as reported

in the literature [5]. These interactions affect the strength of the hydrogen-nickel bonds. After the removal of one part of surface hydrogen from Catalyst No. 1 the higher aromatizing activity of its nickel particles becomes effective [4]. On the other hand, surface nickel particles in Catalyst No. 2 retain their relatively lower cracking activity for a longer period. The precise interpretation of the catalytic activity of different nickel catalysts as a function of their structures needs more detailed experimental studies.

In addition to recognizing the decisive role of surface hydrogen, we also investigated the possible influence of other processes playing a part in the development (maturing) of chromia-alumina catalysts [1], which, in principle, are not to be precluded in this case either, owing to the common carrier and reduction process. These processes, *i.e.* the possible incomplete reduction of the catalyst as well as the adsorption of water on the catalyst surface, were studied by using Catalyst No. 2. The corresponding data are compiled in Table II.

When the catalyst was partially oxidized by introducing air, the next hydrocarbon pulse was not aromatized. The beginning of the chromatogram was considerably different from that obtained for the reduced catalysts. The peak of cracked products increased, and it was followed by a long tail which consisted of unidentified products. This tailing gradually decreased as further amounts of hydrocarbons were introduced; at the same time the catalyst aromatized the next hexane pulse to a larger extent than in its deactivated state before oxidation, indicating that oxygen had removed most of the carbonaceous deposits, too. Thus, partial oxydation of the catalyst surface affected the overall aromatizing activity only slightly; the difference between the chromatograms obtained with oxidized and reduced catalysts also showed that the primary reduction of the catalyst had been practically complete.

If water was introduced to the surface of the catalyst, the quantity of cracked products from *n*-hexane slightly increased, while that of benzene slightly decreased. Water was desorbed from the catalyst surface before introducing the next hexane pulse; the product composition from the latter was similar to that of the first pulse fed before water desorption, indicating that also the presence of water affected the dehydrocyclizing activity of nickel-alumina catalysts only to a relatively minor extent, in comparison to chromia-alumina catalyst.

The influence of repeated heating and cooling of the catalyst and of the size of the pulse and the period between pulses has not been investigated although preliminary data show that they have some effect on catalytic activity, too. These phenomena may constitute the subject of another study.

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SUMMARY

Nickel-alumina and nickel metal catalysts attain their maximum level of dehydrocyclizing activity only after a "development" process, in the course of which surface hydrogen is removed. The duration and extent of development has been found different with two nickel-alumina catalysts of different nickel contents. The extent and selectivity of catalytic activity is decisively determined by the hydrogen content of the catalyst surface, and to a lesser extent by its incomplete reduction and possible water content.

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ИЗУЧЕНИЕ КАТАЛИТИЧЕСКОГО ГИДРИРОВАНИЯ (ДЕЙТЕРИРОВАНИЯ) ЦИКЛОГЕКСЕНА НА ПЛАТИНОВОМ КАТАЛИЗАТОРЕ, I

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Гидрирование ненасыщенных углеводородов в газовой фазе на металлических катализаторах изучалось многими авторами. Опубликованные данные, однако, указывают на то, что кинетика и механизм этого процесса ещё далеко не выяснены, так как экспериментальные результаты отдельных авторов, а также сделанные на их основе выводы отличаются друг от друга [1—10].

Эти противоречия обусловлены, по всей вероятности, различными способами получения катализатора и различной степенью старения, наблюдаемой в каждом отдельном случае. Подобное положение, по существу, наблюдается и при гидрировании в жидкой фазе на контактных катализаторах, где степень старения и предварительная обработка катализатора сильно влияют не только на кинетику, но даже и на относительный вес отдельных ступеней процесса [11].

В данном сообщении приводятся экспериментальные результаты, относящиеся к каталитическому гидрированию (дейтерированию) циклогексена. При этом будет рассматриваться изменение кинетической структуры реакции и относительный вес отдельных стадий процесса гидрирования в зависимости от степени старения катализатора.

При интерпретации экспериментальных данных мы будем опираться, в первую очередь, на данные по распределению дейтерия в исходном субстрате и в продукте, а также на изменение скорости реакции. Данная работа является продолжением кандидатской диссертации одного из авторов (*Дэжэ Могер*), выполненной в МГУ под руководством академика *Н. Н. Семёнова* [12].

Общая схема процесса

При каталитическом гидрировании — как вообще при газовых реакциях на контактных катализаторах — с физической точки зрения нужно считаться с двумя фазами, а именно, с газовой и адсорбционной фазами.

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С химической точки зрения нужно учитывать следующие частицы: водород (дейтерий), непредельный углеводород, промежуточный продукт гидрирования и предельный углеводород, являющийся конечным продуктом гидрирования. Различные химические и физические процессы протекают с участием этих частиц и физических фаз. В согласии с такой классификацией принципиальная система реакций показана на схеме 1, предполагая при этом, что гидрирование протекает с участием водорода, адсорбированного в атомном состоянии, и что непредельный углеводород содержит одну двойную связь.

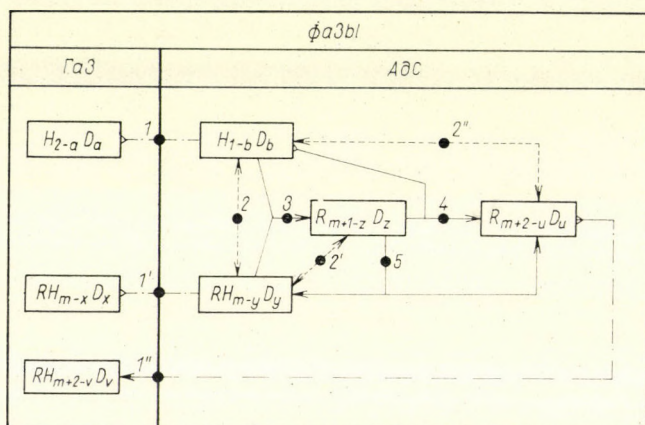
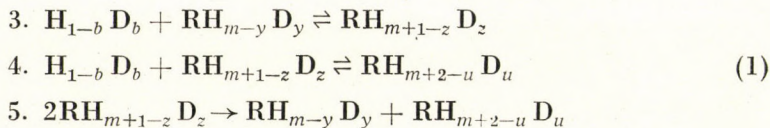


Схема 1. Принципиальная схема процесса гидрирования

В схеме 1 применялись следующие обозначения: $H_{2-a}D_a$ — дейтерированный водород в газовой фазе, где $0 \leq a \leq 2$; $RH_{m-x}D_x$ — непредельный углеводород, где $0 \leq x \leq m$; R — углеродный скелет, соответствующий данному соединению; m — целое число, зависящее от углеводорода; $RH_{m+2-v}D_v$ — предельный углеводород, $0 \leq v \leq m+2$; $H_{1-b}D_b$ — дейтерированный водород, адсорбированный в атомном состоянии $0 \leq b \leq 1$; $RH_{m-y}D_y$ — адсорбированный непредельный углеводород, $0 \leq y \leq m$; $RH_{m+1-z}D_z$ — полугидрированный промежуточный продукт, $0 \leq z \leq m+1$; $RH_{m+2-u}D_u$ — адсорбированный предельный углеводород, $0 \leq u \leq m+2$.

Отдельные процессы имеют следующий характер: 1, 1' и 1'' — процессы адсорбции и десорбции компонентов; 2, 2' и 2'' — реакции, приводящие к изотопному обмену; 3, 4 и 5 — химические реакции:



При условиях опыта (что касается давления и температуры) реакции 4 и 5 являются необратимыми, так как реакция гидрирования практически необратима.

Согласно схеме 1 реакция гидрирования может протекать по двум путям: А) 1 — 1' -3 -4 -1'' или Б) 1 — 1' -3, -5 -1'', а также через их комбинацию. Среди реакций изотопного обмена (2, 2' и 2'') 2'', т. е. обмен Н—D между продуктом и водородом, может быть изучена отдельно, что позволяет решить, какую роль будет играть этот процесс.

Пути А) и Б), в благоприятном случае, можно различать друг от друга, определяя изотопное распределение как в исходном углеводороде, так и в продукте реакции.

Экспериментальная установка

Каталитический реактор, использованный для измерений, является, по существу, закрытым циркуляционным газовым реактором. При отборе образцов через определённые интервалы времени с помощью газовой хроматографии можно следить за степенью превращения, а с помощью масс-спектроскопического анализа — за изменением изотопного распределения в исходном и конечном продуктах. Скорость реакции определяется путём измерения уменьшения давления газовой смеси в циркуляционном пространстве реактора, причём предполагается, что протекает только реакция гидрирования.

В качестве непредельного углеводорода применялся циклогексен, который на основе газо-хроматографического анализа содержал лишь 0,1% бензола и циклогексана. D₂ был получен электролизом 99,5%-ной тяжёлой воды и подавался в реактор через палладиевый фильтр. Катализатором служила платиновая проволока, длиной 20 см и диаметром 0,2 мм, которая была платинирована электрохимическим путём.

Схема каталитического реактора показана на рис. 1. Реактор приводится в операцию следующим образом: сосуд с приготовленным катализатором припаивается к установке согласно рис. 1. При соответствующих положениях вентилей в установке создаётся вакуум 10^{-4} мм рт. ст., затем при закрытых вентилях 9/1 и 9/2, сосуд с катализатором отключается от циркуляционной системы. Закрывается также вентиль 9/7, который служит для эвакуирования. Компоненты подаются в систему через вентили 9/6 и 9/8. Парциальные давления измеряются с помощью манометра 4. Для полного смешения компонентов начинаем циркуляцию, открывая вентиль 9/3. После 10—15 минутной циркуляции и при достижении желаемой температуры в термостатирующем сосуде, открываются краны 9/1 и 9/2, а вентиль 9/3 закрывается. Вследствие этого газовая смесь циркулирует через катализатор. Этот момент времени принимается за начало реакции. Образцы

берутся так, что заранее эвакуированный участок трубки между вентилями 9/4 и 9/5 в данный момент заполняется реакционной смесью, открывая и закрывая вентиль 9/4.

Изотермические условия обеспечиваются термостатирующим сосудом 3 ($\pm 1^\circ\text{C}$), а также формой сосуда для катализатора, представленной на рис. 1. Мощность насоса равна 6—8 л/мин., а объём сосуда с катализа-

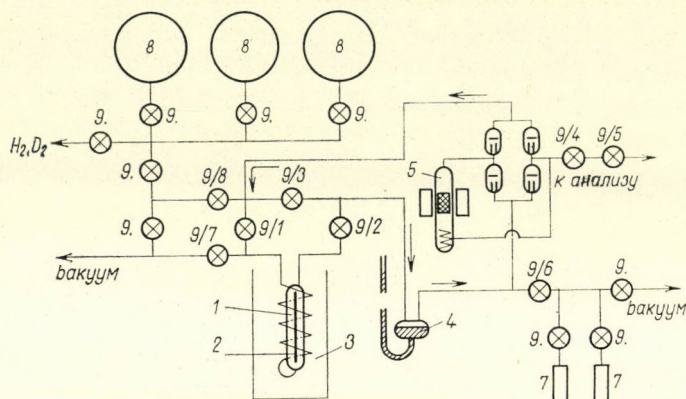


Рис. 1. Принцип построения каталитического реактора. 1. Резервуар для катализатора; 2. Катализатор (платиновая проволока); 3. Термостатирующая рубашка; 4. Манометр; 5. Циркуляционный насос с магнитом; 6. Клапаны; 7. Ампулы для хранения жидких компонентов; 8. Стекланные шары для хранения газообразных компонентов; 9. Вентили

тором 20—25 мл. Таким образом, время пребывания в сосуде (τ_0) будет

$$\tau_0 = \frac{20.60}{6000} \text{ s} = 0,2 \text{ sec}$$

Учитывая экспериментальные значения скорости реакции, этот промежуток является довольно коротким для того, чтобы концентрацию газовой смеси в любом месте циркуляционной системы можно было считать постоянной.

Анализ образцов проводился с помощью газового хроматографа, сконструированного специально для данной цели. Газом-носителем служил водород. Колонка длиной 250 см со внутренним диаметром 5 мм была заполнена зёрнами термолитного кирпича диаметром 0,25—0,5 мм, содержащего 20% трикрезилфосфата. С помощью воздушного термостата рабочая температура колонки поддерживалась при 75°C . Детектором служила ячейка теплопроводности с платиновой проволокой диаметром 0,015 мм, подключённая как мостик Уитстона. Ток нагревания составлял 100—120 мА. Ток в мостике измерялся регистрирующим потенциометром типа ЭПП—09 советского производства. Для количественного определения циклогексена и циклогексана снималась калибровочная кривая. Для оценки исполь-

зовались высоты хроматографических пиков. Образцы из реактора подавались в газовый хроматограф с помощью вентиля, показанного на рис. 2.

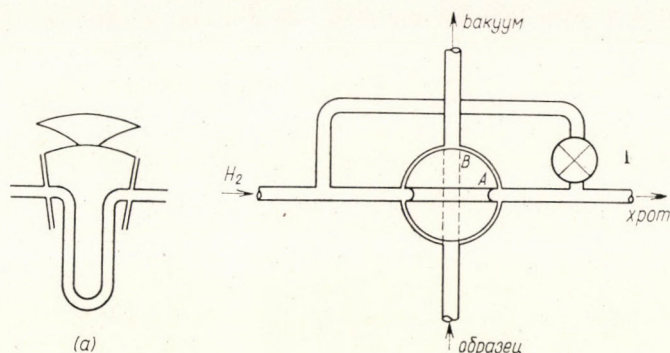


Рис. 2. Вентиль для отбора образцов

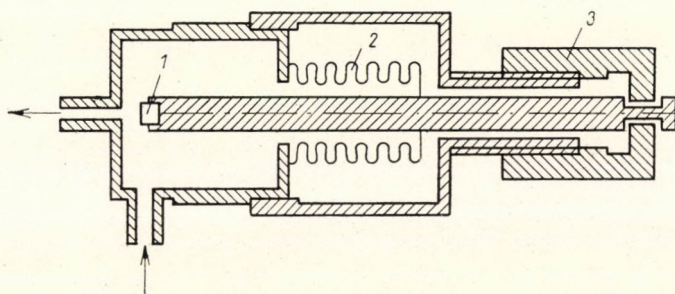


Рис. 3. Металлический клапан. 1. Полиамидная шайба; 2. Упругая медная мембрана; 3. Винт для закрытия и открытия

Внутренний, U-образный мостик вентиля для отбора образцов присоединялся к реактору способом В). Погружая этот участок в жидкий воздух и при положении вентиля В, присутствующие в образце циклогексен и циклогексан могут быть выморожены; при этом участок реактора для отбора образцов необходимо откачивать. Поворачивая вентиль для отбора образцов в положение А и закрывая вентиль I, газ-носитель H_2 вымывает теперь нагретые циклогексен и циклогексан и, таким образом, подаёт их на хроматографическую колонку. Содержание дейтерия в циклогексене и циклогексане определялось с помощью модифицированного [13] советского масс-спектрометра типа МИ—1305 таким образом, что выходящие из колонки циклогексен и циклогексан анализировались отдельно.

Согласно нашим наблюдениям, пары смазки сильно отравляют катализатор. Поэтому мы не приняли стеклянных кранов со смазкой, а заменяли их на металлические вентили, сохраняющие надёжно вакуум, схема которых представлена на рис. 3.

Результаты экспериментов

Первая серия измерений была выполнена при 30°C с парциальными давлениями циклогексена и водорода 20 и 40 мм рт. ст., соответственно, следя за изменением давления во времени. После того, как реакция прошла примерно на 50%, реактор откачивался диффузионным ртутным насосом в протяжении 30 минут, а затем измерение повторялось.

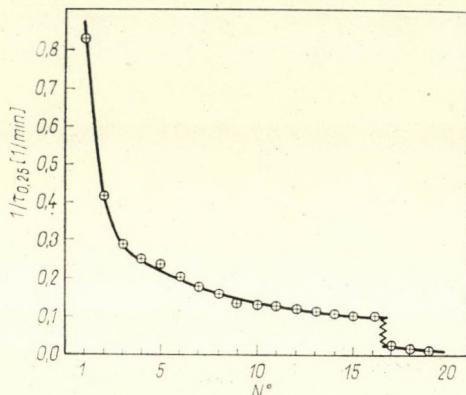


Рис. 4. Изменение активности катализатора при последовательном гидрировании

Измерения показали, что имеет место старение катализатора, т. е. его активность постоянно уменьшается. Поэтому нами и не использовались кривые конверсия-время для определения уравнения скорости, а активность катализатора и скорость реакции были охарактеризованы временами реакции, соответствующими степени превращения, равной 0,25 ($\tau_{0,25}$). Результаты этой серии показаны на рис. 4, где на абсциссу наносили порядковый номер опыта, а на ординату $1/\tau_{0,25}$. Из рисунка видно, что активность катализатора сначала резко падает (опыты 1—4), затем уменьшение замедляется (опыты 5—16), но не достигает постоянного значения. При опытах 17—19, в отличие от остальных серий, катализатор откачивался при 200°C на протяжении 2 часов. Как можно видеть, эта термическая обработка приводит к дальнейшему уменьшению активности. Были сделаны попытки разработать стандартный метод приготовления катализатора, для того чтобы хотя бы экстраполированные к 0-времени значения скоростей реакций можно было использовать для установления кинетического уравнения. Однако, эти попытки не оказались успешными, и значения активности свежеприготовленных катализаторов совпадали с точностью одного порядка. Были сделаны попытки использовать различные способы регенерации, причём, отчасти получились удовлетворительные результаты следующим путём. После отдельных опытов объём реактора откачивался при 300°C до 10^{-3} мм

рт. ст. Затем, в реакции циркулировал сначала O_2 при давлении 50 мм рт. ст., а потом H_2 при давлении 50 мм рт. ст. на протяжении 30 минут. После этого катализатор откачивался ртутным насосом при $300^\circ C$ на протяжении 1 часа, и только потом приступали к новому опыту гидрирования.

Воспроизводимые кривые скорости процесса получились с помощью этого метода регенерации, но всё-таки активности свежего катализатора достичь не удалось. Экспериментальные результаты представлены на рис. 5 в виде кривых конверсия (φ) — время (τ).

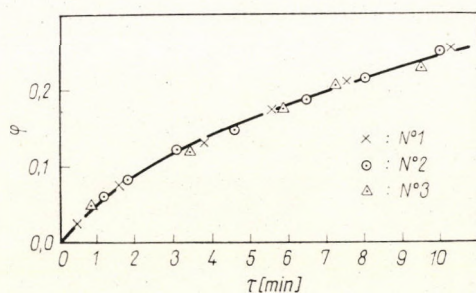


Рис. 5. Зависимость конверсии от времени в случае регенерированных катализаторов

Опыты повторялись и для дейтерия, дополняя их при этом масс-спектроскопическим определением содержания дейтерия в циклогексене и циклогексане. Экспериментальные результаты иллюстрируются рис. 6., на котором, подобно рис. 4, представлены значения $1/\tau_{0,25}$, а также средние числа атомов дейтерия, соответствующие превращению $\varphi = 0,25$ в циклогексене ($\bar{x}$) и в циклогексане ($\bar{v}$). На рисунке также показано число атомов дейтерия ($\Sigma \bar{D}$), приведённое к одному молю циклогексана, вступивших или в циклогексен или в циклогексан. Согласно вышесказанному, величина $\Sigma \bar{D}$ определяется следующим уравнением:

$$\Sigma \bar{D} = \bar{v} + \frac{1 - \varphi}{\varphi} \bar{x} \quad (2)$$

Если величина $\Sigma \bar{D}$ выше 2, то это указывает на появление водорода в газообразном дейтерии во время реакции.

На основе кривых рис. 6 результаты опытов можно подразделить на 3 категории:

I) Активность катализатора, $\bar{v}$ и $\Sigma \bar{D}$ быстро падают. Величина $\Sigma \bar{D} > 2$, т. е. в газообразном дейтерии появляется водород. Циклогексен также подвергается H—D обмену, т. к. $\bar{x} > 0$.

II) Активность катализатора уменьшается медленнее, величины $\bar{v}$ и $\Sigma \bar{D}$ практически постоянны. $\Sigma \bar{D} \approx 2$, т. е. водород не появляется в газо-

образном дейтерии. И здесь наблюдается обмен $H-D$ в циклогексене ($\bar{x} > 0$), но в меньшей степени, чем в I) категории.

III) Активность катализатора гораздо меньше, чем в категориях I) и II), а $\bar{v}$ и $\Sigma \bar{D}$ снова возрастают. $\Sigma \bar{D} > 2$, т. е. водород и здесь появляется в газообразном дейтерии. В циклогексене обмен $H-D$ практически не происходит, $\bar{x} \approx 0$.

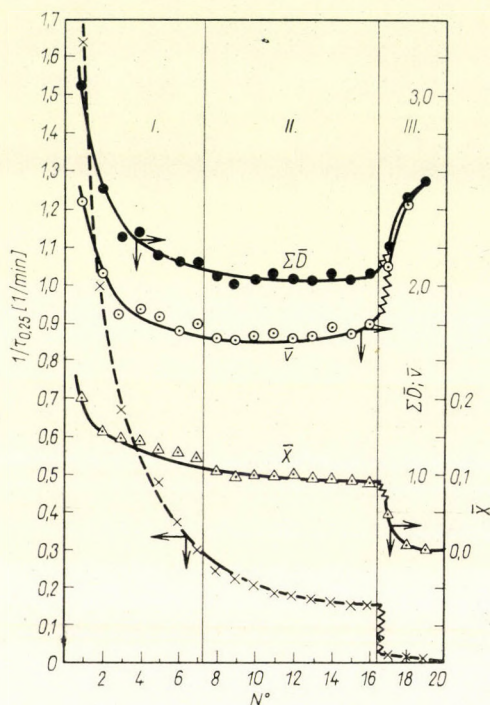


Рис. 6. Изменение активности катализатора ($1/\tau_{0,25}$), $\Sigma \bar{D}$ и среднего содержания дейтерия в циклогексене ($\bar{x}$) и циклогексане ($\bar{v}$) при последовательном гидрировании

Для дальнейшей характеристики измерений, относящихся к этим категориям, на рис. 7, 8 и 9 представлены результаты масс-спектроскопического анализа опытов, характерных для отдельных категорий.

На рис. 7 представлено процентное распределение молекул циклогексана, содержащих различное число атомов дейтерия, при различных значениях степени превращения. Значения для нулевой конверсии являются результатом экстраполяции. Исходя из рис. 7, кажется характерным, что в случае всех трёх категорий фракции, содержащие 0—7 атомов дейтерия, появляются уже при нулевой конверсии. Максимум кривой распределения для реакций, относящихся к I) категории, лежит в области фракций с 1 и 2 атомами дейтерия. В категории II) максимум смещается в сторону фракций

циклогексана с 0 и 1 атомами дейтерия. В реакциях III) категории процентное содержание недейтерированной фракции снова падает, и максимум находится в области циклогексана с 1 и 2 атомами дейтерия.

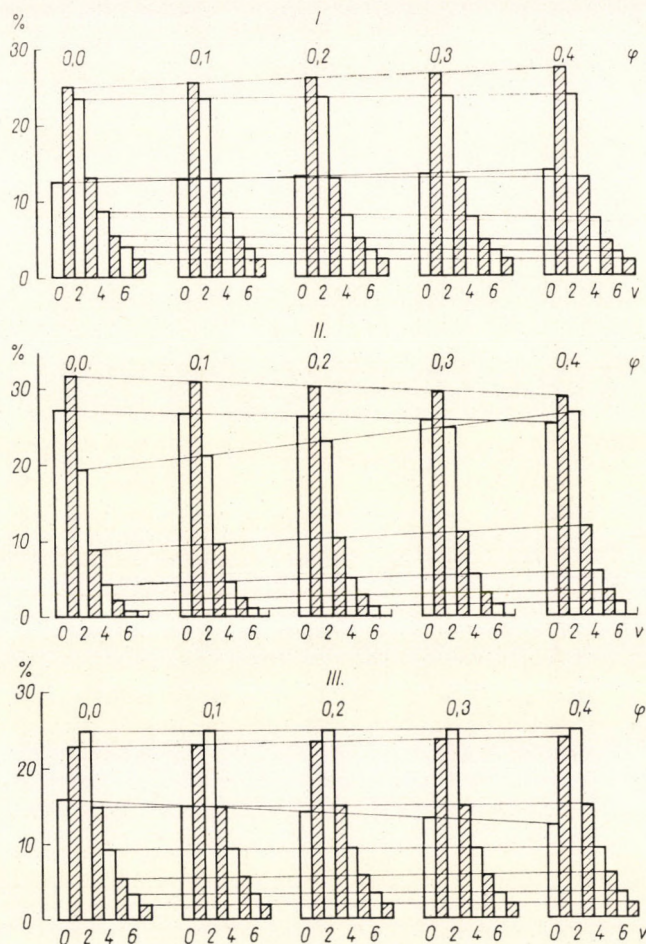


Рис. 7. Изменение процентного количества фракций циклогексана, содержащих различное количество дейтерия (v) с конверсией (ϕ) в случае катализаторов различной активности ($I > II > III$)

Как видно из рис. 8, на котором изображены кривые процентного распределения фракций циклогексана, содержащего дейтерий, в зависимости от конверсии для реакций гидрирования, относящихся к категориям I и II, не наблюдается характерной разницы между двумя категориями (в реакциях категории III циклогексен не содержит дейтерия). Во всяком случае, можно установить, что спектр распределения дейтерия в циклогексене гораздо уже, чем в случае циклогексана, и процент фракций циклогексана, содержащих дейтерий, тоже ниже.

Зависимость величин $\bar{v}$, $\bar{x}$ и $\Sigma \bar{D}$ от конверсии для трёх категорий представлена на рис. 9. Из рисунка видно, что в категории I как $\bar{v}$, так и $\Sigma \bar{D}$ уменьшаются с конверсией. В категории II, хотя $\Sigma \bar{D}$ не зависит от конверсии (≈ 2), $\bar{v}$ не уменьшается, как в категории I, а наоборот, увеличивается с конверсией. В категории III $\bar{x}$ равно нулю, в отличие от категорий I и II,

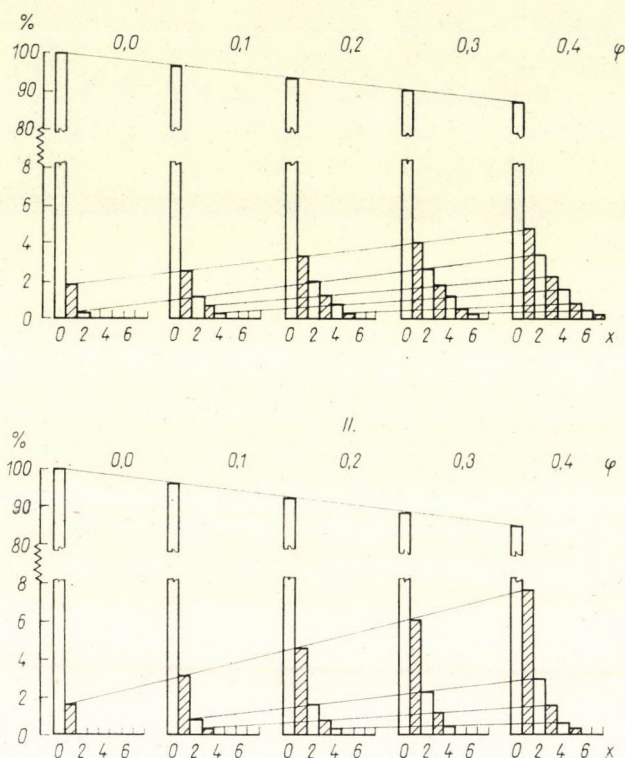


Рис. 8. Изменение процентного количества фракций циклогексена, содержащих различное количество дейтерия (x), с конверсией в случае катализаторов различной активности ($I > II$)

где его величина монотонно возрастает с конверсией. Величины $\bar{v}$ и $\Sigma \bar{D}$ ($\bar{v} \approx \Sigma \bar{D}$) растут с конверсией.

Было также изучено влияние отношения D_2/C_6H_{10} на содержание дейтерия в полученном циклогексане. Описанным способом регенерации удачно воспроизводится катализатор средней активности, соответствующий реакции категории II. Поэтому влияние отношения D_2/C_6H_{10} на содержание дейтерия в продукте изучалось на таком катализаторе. Парциальное давление циклогексена, как и в предыдущих опытах, равнялось 20 мм рт. ст., а давление дейтерия изменялось. Экспериментальные результаты для конверсии, равной 0,1, показаны на рис. 10 для $v = 0, 1$ и 2.

На основе рис. 10 можно заключить, что при увеличении давления D_2 в области II процентное содержание фракций с 0 атомами дейтерия в образующемся циклогексане быстро уменьшается. Также падает, но в мень-

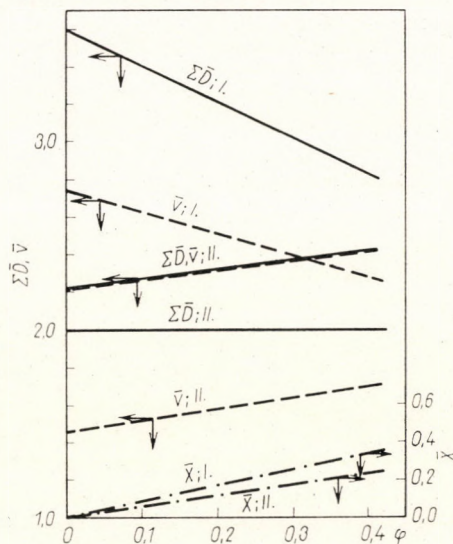


Рис. 9. Изменение $\bar{\nu}$, $\Sigma\bar{D}$, и $\bar{x}$ с конверсией в случае катализаторов различной активности (I > II > III)

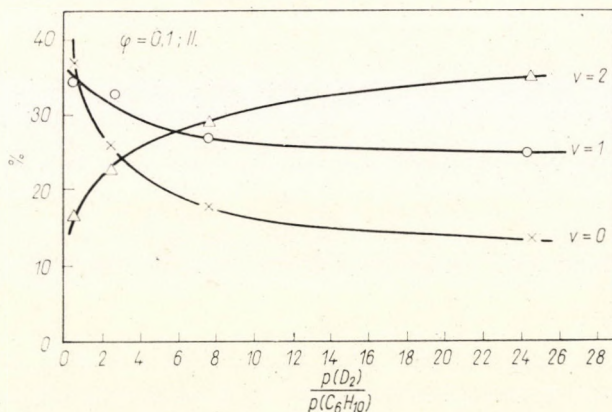


Рис. 10. Зависимость процентного распределения фракций циклогексана, содержащих различное количество дейтерия (v), от парциального давления дейтерия и циклогексена

шей мере, относительное количество фракций с $v = 1$. Процентное содержание фракции с $v = 2$ растёт по мере увеличения отношения D_2/C_6H_{10} .

Изучалась также реакция изотопного обмена водорода на дейтерий в циклогексане, являющемся конечным продуктом. Согласно опытам, обмен

H—D за время гидрирования наблюдается только на катализаторе, относящемся к I категории. В категориях II и III нельзя было обнаружить обмен при условиях реакции гидрирования.

Обсуждение экспериментальных результатов

Для выяснения реальности отдельных ступеней общей схемы реакции, показанной на схеме 1, а также для установления их относительного веса имеются в нашем распоряжении следующие характерные экспериментальные результаты.

а) Обмен H—D наблюдается и в циклогексене ($X > 0$). Глубина этого превращения уменьшается с уменьшением активности катализатора, т. е. с его старением.

б) Обмен H—D, наблюдаемый в газообразном дейтерии, имеет минимум в зависимости от активности катализатора. В точке минимума — при катализаторе средней активности — обмен H—D в газообразном дейтерии практически равен нулю ($\Sigma \bar{D} \approx 2$).

в) Обмен H—D между циклогексаном и D_2 независимо от реакции гидрирования наблюдается лишь в случае наиболее активных катализаторов.

г) Как в циклогексене, так и в циклогексане присутствует полный спектр молекул с различным числом атомов дейтерия.

д) Процентное отношение молекул циклогексана с различным числом атомов дейтерия меняется лишь незначительно с конверсией.

е) При увеличении отношения D_2/C_6H_{10} растет относительный вес фракций с более высоким числом атомов дейтерия в циклогексане.

Рассмотрим роль отдельных ступеней в общей схеме 1 с точки зрения вышеупомянутых экспериментальных данных. Исходя из предположения, что активные центры катализатора являются энергетически однородными, старение, обусловленное сильной адсорбцией продуктов побочных реакций, рассматривается как уменьшение числа этих активных центров. Из-за старения, протекающего с измеряемой скоростью за время отдельных реакций, нельзя было установить кинетическое уравнение. Поэтому экспериментальные результаты можно интерпретировать лишь качественно, судя по той или иной тенденции кинетических эффектов.

Последовательные процессы должны протекать во всех случаях, и их следствия можно обнаружить опытным путем. Результаты непоследовательных процессов наблюдаются лишь тогда, когда их значения не равны нулю и их скорость соизмерима с общей скоростью реакции. Т. е., если скорость непоследовательного процесса обозначать через W_p , а общую скорость —

через W , то

$$W_p \neq 0; \quad \frac{W_p}{W} \ll 1$$

Ступени 1, 1' и 1'' являются последовательными процессами адсорбции и десорбции, поэтому их протекание необходимо для гидрирования. Опытные данные а), б) и в) можно интерпретировать только в том случае, если эти процессы являются обратимыми. Если отдельные скорости обозначить через $\bar{W}_1, \bar{W}_{1'}, \dots$, то для Н—D обмена в циклогексене, согласно вышеуказанному, необходимо, чтобы

$$\bar{W}_{1'} \neq 0; \quad \frac{\bar{W}_{1'}}{W} \ll 1 \quad (3)$$

Так как $\bar{x}$ монотонно падает со старением катализатора, то то же самое следует полагать и для $\bar{W}_{1'}/W$. Для того, чтобы в газообразном циклогексене появился D, условие (3) является лишь необходимым, но не достаточным. Для этого необходимо также, чтобы D попал в адсорбированный циклогексен, т. е., согласно схеме 1:

$$\begin{array}{cccc} W_2 \neq 0 & \bar{W}_3 \neq 0 & W_{2'} \neq 0 & \bar{W}_5 \neq 0 \\ \frac{W_2}{W} \ll 1; \text{ или } \frac{\bar{W}_3}{W} \ll 1; \text{ или } \frac{W_{2'}}{W} \ll 1; \text{ или } \frac{\bar{W}_5}{W} \ll 1 & & & \end{array} \quad (4)$$

Первым необходимым условием появления водорода в газообразном дейтерии, на подобии условия (3), является:

$$\bar{W}_1 \neq 0; \quad \frac{\bar{W}_1}{W} \ll 1 \quad (5)$$

Разумеется, что для этого необходимо предполагать и соответствующий относительный вес других реакций, т. е.

$$\begin{array}{ccc} W_2 \neq 0 & \bar{W}_3 \neq 0 & W_{2''} \neq 0 \\ \frac{W_2}{W} \ll 1; \text{ или } \frac{\bar{W}_3}{W} \ll 1; \text{ или } \frac{W_{2''}}{W} \ll 1 & & \end{array} \quad (6)$$

Тот экспериментальный факт, что появление водорода в газообразном дейтерии в зависимости от старения катализатора описывается кривой с минимумом, можно интерпретировать либо подобным поведением отношения $\bar{W}_1/W$, либо результирующей тенденцией изменения относительных весов процессов в (6) при старении.

Для интерпретации фактов г) и д), наблюдавшихся экспериментально, необходимо, чтобы какая-либо или все реакции обмена Н—D имели место, т. е.:

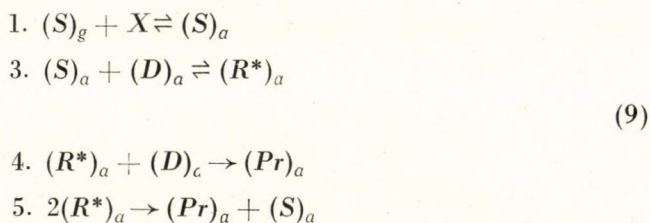
$$\begin{array}{ccc} W_2 \neq 0 & W_{2'} \neq 0 & W_{2''} \neq 0 \\ \frac{W_2}{W} \ll 1; \text{ или } \frac{W_{2'}}{W} \ll 1; \text{ или } \frac{W_{2''}}{W} \ll 1 & & \end{array} \quad (7)$$

Химическая реакция 5 вместе с 3 также приводит к Н—D обмену как в адсорбированном циклогексане, так и в адсорбированном циклогексене, так как в результате этих процессов дейтерий, принимавший участие в процессе 3, как бы снова «примешивается» к адсорбированному циклогексену. Одна эта реакция, однако, не может приводить к кривым распределения, наблюдавшимся экспериментально, особенно в случае циклогексана. Причиной этого является то, что реакция 5 приводит и к гидрированию, и поэтому относительное количество дейтерированных фракций циклогексана должно было бы зависеть от степени конверсии, что согласно пункту д) не наблюдается (см. рис. 7).

Как уже было упомянуто, мы исходим из предположения, что активные центры имеют однородную активность. Обозначим активный центр через X , а поверхностную концентрацию отдельных компонентов (моль/единицу поверхности) через

$$\theta_X, \theta_S, \theta_D, \theta_{R^*}, \theta_{Pr} \quad (8)$$

где X означает активный центр, S — циклогексен, D — дейтерий, R^* — «полугидрированный» промежуточный продукт, а Pr — циклогексан, являющийся конечным продуктом. Согласно нашим ранним исследованиям [14], при гидрировании в жидкой фазе старение оказывает лишь незначительное влияние на способность платинового катализатора адсорбировать водород. Поэтому адсорбция дейтеро-водорода и десорбция продукта не являются стадиями, лимитирующими скорость. При данных экспериментальных условиях не наблюдается адсорбции продукта в измеряемой степени. Таким образом, стехиометрические уравнения ступеней, лимитирующих скорость, в соответствии со схемой 1 можно представить следующим образом:



где индекс g обозначает газовую фазу, а a — адсорбированную фазу. Приводя скорости реакций циклогексана, из системы уравнений (9) можно получить следующие зависимости:

$$-\frac{1dn_s^g}{F d\tau} = W = \vec{W}_1' - \vec{W}_1'; \quad \frac{d\theta_{R^*}}{d\tau} = \vec{W}_3 - \vec{W}_3' - \vec{W}_4' - 2\vec{W}_5'$$

$$\frac{d\theta_s}{d\tau} = \vec{W}_1' - \vec{W}_1' - \vec{W}_3' + \vec{W}_3 + \vec{W}_5 \quad (10)$$

где F — поверхность катализатора, n_s^g — число молей субстрата (циклогексена) в газовой фазе.

В стационарном или квазистационарном состоянии, согласно принципу Боденштейна

$$\frac{d\theta_s}{d\tau} \approx 0 \quad \frac{d\theta_{R^*}}{d\tau} \approx 0 \quad (11)$$

На основе системы уравнений (10) и (11):

$$W = \vec{W}_1' - \vec{W}_1' = \vec{W}_3 - \vec{W}_3' - \vec{W}_5' = \vec{W}_4 + \vec{W}_5 \quad (12)$$

Обозначая равновесные концентрации на поверхности через θ_S^0 , θ_D^0 , θ_{Pr}^0 и θ_X^0 , на основе системы уравнений (9) можно получить следующие кинетические уравнения для отдельных ступеней:

$$\vec{W}_1' - \vec{W}_1' = k_1' (\theta_S^0 - \theta_S); \quad \vec{W}_3 = \vec{k}_3 \theta_D^0 \theta_S$$

$$\vec{W}_3 = \vec{k}_3 \theta_{R^*}; \quad \vec{W}_4 = \vec{k}_4 \theta_D^0 \theta_{R^*}; \quad \vec{W}_5 = \vec{k}_5 \theta_{R^*}^2;$$

$$W = k_1' (\theta_S^0 - \theta_S) = \vec{k}_3 \theta_D^0 \theta_S - \vec{k}_3 \theta_S - \vec{k}_5 \theta_{R^*}^2 = \vec{k}_4 \theta_D^0 \theta_{R^*} + \vec{k}_5 \theta_{R^*}^2 \quad (13)$$

где, если адсорбция D и S происходят на разных активных центрах, то

$$k_1' = \vec{k}_1' p_S^g + \vec{k}_1'; \quad \theta_S^0 = \frac{K_S p_S^g}{1 + K_S p_S^g} \theta_*^0; \quad K_S = \frac{\vec{k}_1}{\vec{k}_1} \quad (14)$$

Символ p_S^g обозначает давление субстрата в газообразном состоянии.

На основе схемы I, аналогично выражениям (13) получаем следующие кинетические уравнения для реакций обмена:

$$W_2 = k_2 \theta_D^0 \theta_S; \quad W_2' = k_2' \theta_S \theta_{R^*}; \quad W_2'' = k_2'' \theta_D^0 \theta_{Pr} \quad (15)$$

Рассмотрим, каким образом можно интерпретировать экспериментальные результаты на основе кинетических уравнений (12) — (15).

Как уже было отмечено, активные центры считаются энергетически однородными, в результате чего константы скорости в кинетических уравнениях (13) — (15) должны быть постоянными, не зависящими от старения. Согласно системе уравнений (13) уменьшение W (старение катализатора) обязательно связано с уменьшением θ_S , θ_{R^*} . Это, в свою очередь, вызвано уменьшением θ_S^0 , что, согласно (14), равноценно уменьшению $\theta_{X,T}^0$, т. е. понижению поверхностной концентрации активных центров в согласии с представлениями о старении катализатора.

На основе системы уравнений (13)

$$\theta_{R^*} = \frac{1}{2\vec{k}_5} \left[-\vec{k}_4 \theta_D^0 + \sqrt{(\vec{k}_4 \theta_D^0)^2 + 4\vec{k}_5 W} \right] \quad (16)$$

откуда

$$\frac{\partial \theta_{R^*}}{\partial W} = \frac{1}{\sqrt{(\vec{k}_4 \theta_D^0)^2 + 4\vec{k}_5 W}} > 0 \quad (17)$$

$$\theta_S = \frac{1}{\vec{k}_3 \theta_D^0} [(\vec{k}_3 + \vec{k}_4 \theta_D^0) \theta_{R^*} + 2\vec{k}_5 \theta_{R^*}^2] \quad (18)$$

и принимая во внимание зависимость (17)

$$\frac{\partial \theta_S}{\partial W} = \frac{1}{\vec{k}_3 \theta_D^0} [(\vec{k}_3 + \vec{k}_4 \theta_D^0) + 4\vec{k}_5 \theta_{R^*}] \frac{\partial \theta_{R^*}}{\partial W} > 0 \quad (19)$$

Относительная скорость ступеней 4 и 5, приводящих к образованию продукта, на основе системы уравнений (13) будет

$$\frac{\vec{W}_4}{\vec{W}_5} = \frac{\vec{k}_4 \theta_D^0}{\vec{k}_5 \theta_{R^*}} \quad (20)$$

Как уже отмечалось, ступень (4) приводит к образованию продукта, содержащего, по меньшей мере, 1 атом дейтерия, т. е. величина отношения $\vec{W}_4/\vec{W}_5$ отражает увеличение относительного веса продуктов с большим числом атомов дейтерия. Согласно зависимости (2), увеличение отношения $\vec{W}_4/\vec{W}_5$ может быть вызвано либо увеличением θ_D^0 , либо уменьшением θ_{R^*} , т. е. увеличением давления дейтерия или старением катализатора. Это находится в согласии с экспериментальными результатами (рис. 7 и 10), а также указывает на наличие реакций 4 и 5.

Как уже отмечалось, для того, чтобы образовался дейтерированный, циклогексен, соотношение (3) должно быть справедливым, а также одна из реакций 2, 2', 3, 5 должна протекать. Реакции 2' и 5 уже были рассмотрены

было показано, что обе они протекают при гидрировании. Согласно этому, монотонное уменьшение $\bar{x}$ со старением катализатора можно только объяснить уменьшением отношения $\bar{W}_1/W$.

На основе уравнений (13) и (19)

$$\frac{\partial}{\partial W} \left(\frac{\bar{W}_1}{W} \right) = k_1' \frac{\partial}{\partial W} \left(\frac{\theta_S}{W} \right) = \frac{k_1' \bar{k}_5}{\bar{k}_3 \theta_D^0 \theta_{R^0}} \frac{2W - \bar{k}_3 \theta_D^0 \theta_S}{(\bar{k}_4 \theta_D^0 + \bar{k}_5 \theta_{R^0})^2} \frac{\partial \theta_{R^0}}{\partial W} \quad (21)$$

Это соотношение находится в согласии с экспериментальными результатами только в том случае, если

$$2W > \bar{k}_3 \theta_D^0 \theta_S \quad (2W > \bar{W}_3) \quad (22)$$

Так как при таких условиях из (21) вытекает, что

$$\frac{\partial}{\partial W} \left(\frac{\bar{W}_1}{W} \right) = k_1' \frac{\partial}{\partial W} \left(\frac{\theta_S}{W} \right) > 0 \quad (23)$$

Иными словами, относительный вес процесса 1 падает со старением катализатора, что приводит к уменьшению $\bar{x}$, в согласии с опытом (см. рис. 6).

Не рассматривалось ещё изменение $\Sigma \bar{D}$ вследствие старения катализатора, которое описывается кривой с минимумом, и в минимуме $\Sigma \bar{D} \approx 2$. Как уже отмечалось, условие $\Sigma \bar{D} > 2$ равноценно тому, что происходит обмен H—D в газообразном дейтерии. Для этого в первую очередь необходимо, чтобы, согласно вышеуказанному, процесс 1 имел место. Предполагалось, что адсорбция дейтерия не лимитирует скорость, и процесс 1 протекает с относительно высокой скоростью. Однако, необходимо ещё, чтобы какой-либо из процессов 2, 2'' и 3, имел место, т. к. они «поставляют» водород в фазу, содержащую адсорбированный дейтерий. В связи с процессом 2'' уже отмечалось, что он наблюдается только на наиболее активных катализаторах. Вследствие этого этот процесс не должен вызывать появление водорода в газовом дейтерии заново по мере старения катализатора. Относительный вес процесса 2., согласно (13) и (15)

$$\frac{W_2}{W} = k_2 \theta_D^0 \frac{\theta_S}{W} \quad (24)$$

т. е. учитывая и выражение (23)

$$\frac{\partial}{\partial W} \left(\frac{W_2}{W} \right) = k_2 \theta_D^0 \frac{\partial}{\partial W} \left(\frac{\theta_S}{W} \right) > 0 \quad (25)$$

Это значит, что отношение W_2/W также уменьшается со старением катализатора, и поэтому процесс 2, подобно процессу 2'', приводит лишь к уменьшению $\Sigma \bar{D}$ с уменьшением активности катализатора.

Относительный вес процесса $\tilde{3}$ на основе выражения (13) даётся следующим образом:

$$\frac{\tilde{W}_3}{W} = \frac{\tilde{k}_3}{\tilde{k}_4 \theta_D^0 + \tilde{k}_5 \theta_{R^0}} \quad (26)$$

откуда, учитывая соотношение (17),

$$\frac{\partial}{\partial W} \left(\frac{\tilde{W}_3}{W} \right) = - \frac{\tilde{k}_3 \tilde{k}_5}{(\tilde{k}_4 \theta_D^0 + \tilde{k}_5 \theta_{R^0})^2} \frac{\partial \theta_{R^0}}{\partial W} < 0 \quad (27)$$

Это значит, что относительный вес процесса $\tilde{3}$ растёт со старением катализатора. В результате двух процессов, действующих в противоположных направлениях, может осуществиться условие $\Sigma \bar{D} \approx 2$.

Согласно опытным данным (рис. 6) мы пришли к выводу, что величина $\Sigma \bar{D}$ уменьшается со старением катализатора вследствие уменьшения относительного веса процессов 2 и 2'', а затем увеличивается вследствие роста относительного веса процесса $\tilde{3}$.

На основе общей реакционной схемы 1 удалось интерпретировать все экспериментальные факты.

РЕЗЮМЕ

В связи с механизмом гидрирования циклогексена на платиновом катализаторе и с влиянием старения катализатора на механизм было установлено следующее:

1) Гидрирование протекает в двух ступенях. Первая ступень является присоединением одного атома водорода к циклогексену. Вторая ступень может протекать двояким образом: происходит либо диспропорционирование полугидрированного продукта, либо присоединение второго атома водорода.

2) Скорость реакции лимитируется адсорбцией циклогексена.

3) Влияние старения сказывается в первую очередь на уменьшении адсорбции циклогексена. Механизм реакции остаётся неизменным, а изменяется лишь относительный вес отдельных ступеней.

SUMMARY

In connection with the mechanism of catalytic hydrogenation of cyclohexene in the presence of platinum catalyst, and concerning the effect of decreasing activity on the reaction mechanism, the following facts have been established:

1. The hydrogenation takes place in two steps. In the first step one hydrogen atom is taken up. In the second step either a second hydrogen atom is transferred, or the semi-hydrogenated product suffers disproportionation.

2. The rate determining step is the adsorption of cyclohexene.

3. The influence of ageing is reflected primarily by the diminished adsorption of cyclohexene. During ageing the reaction mechanism remains unaltered, and only the relative importance of the elementary processes is changed.

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ХИМИЯ СВОБОДНЫХ РАДИКАЛОВ, VI

ИССЛЕДОВАНИЕ НЕКОТОРЫХ СВОБОДНЫХ РАДИКАЛОВ, ТИПА ОКИСИ АЗОТА, МЕТОДОМ ЭПР

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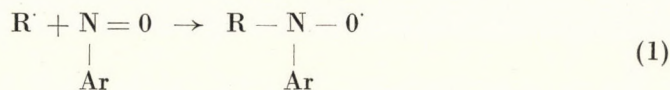
(Центральный Исследовательский Институт Химии, АН Венгрии, Будапешт)

Поступило 27 июля 1967 г.

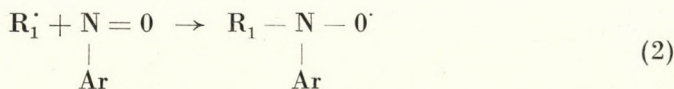
1. Введение

Исследуя изменение во времени концентрации промежуточных радикалов, образующихся из ингибитора в ходе радикальной полимеризации, а также изучая их структуру, можно судить о таких элементарных процессах ингибированной полимеризации, которые не могут быть вообще или с полной уверенностью изучены с помощью макрокинетических исследований. Исследования такого рода начали проводиться нами совместно с сотрудниками Института Химической Физики АН СССР, В. В. Воеводским и С. Солодовниковым. В нашем раннем сообщении [1] приводятся некоторые новые методы определения параметров ингибирования, а также обсуждаются условия кинетического исследования промежуточных радикалов. На нескольких примерах иллюстрировалась пригодность промежуточных радикалов, образующихся из нитрозо-соединений, в качестве моделей вышеупомянутых исследований методом ЭПР.

В последующие годы проводились многосторонние исследования влияния нитрозо-соединений на радикальную полимеризацию [2, 3, 4]. Было установлено, что такие сильно реакционноспособные ингибиторы, как изученные ароматические нитрозо-соединения, реагируют не только с радикалами-носителями цепи ($R\cdot$):



а также и с первичными радикалами, образующимися при распаде инициатора ($R_1\cdot$):



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В зависимости от соотношения концентраций, эти два радикала могут появляться в системе одновременно. С помощью макрокинетических исследований нельзя разделить эти два процесса. Однако, на основе различия в сверхтонкой структуре спектров ЭПР этих двух типов радикалов, можно провести различие между этими двумя процессами.

В ходе дальнейших исследований оказалось, что в отдельных случаях, нитрозо-соединения непосредственно реагируют также с виниловыми мономерами, в результате чего образуются дальнейшие промежуточные продукты радикального характера, которые препятствуют исследованию процессов (1) и (2) радикального присоединения [5].

Для более обстоятельного изучения конкурентных реакций, описываемых уравнениями (1) и (2), а также для исключения вышеупомянутых мешающих влияний, сперва казалось целесообразным изучение реакции нитрозо-соединений с первичными радикалами по уравнению (2). На основе сверхтонкой структуры спектров исследовались электронная структура образующихся радикалов, типа окиси азота, и влияние заместителей.

Синтез радикалов, типа окиси азота, на основе реакций (1) и (2) обладает некоторыми преимуществами перед другими препаративными методами. Метод не трудоемок, и, принимая во внимание доступность большого числа разнообразных инициаторов и нитрозо-соединений в настоящее время, этот метод можно считать довольно общим.

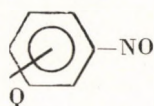
Необходимо упомянуть, что в последние годы большое число радикалов диарил-, диалкил- и арил-алкил-производных окиси азота изучались методом ЭПР [6, 7, 8], в результате чего было сделано много интересных заключений.

Публикуемые здесь исследования предоставляют дальнейшие результаты относительно структуры и свойств радикалов, типа арил-алкил-производных окиси азота.

2. Экспериментальная часть

В ходе исследований использовались тщательно очищенные азо-бис-изобутиронитрил, в некоторых случаях перекись бензоила, и бензол в качестве растворителя. Необходимые для исследований производные нитрозо-бензола синтезировались, как правило, из соответствующего нитробензола через гидроксил-амин. Во избежание получения ненужных изомеров, исходные нитросоединения также тщательно очищались [9]. Исходный нитрозо-бензол очищался перегонкой с водяным паром и повторной перекристаллизацией. Температуры плавления использованных веществ даны в таблице I.

Таблица I



где Q- заместитель в фенильном кольце соединения:

Заместитель	Темп. плавл.		Синтез
	литер. (°C)	эксп. (°C)	
H	68	68	[15]
<i>o</i> -F	60—61	60—61	[10]
<i>o</i> -Cl	56	55,5	[10]
<i>o</i> -Br	97	96—98	[10]
<i>o</i> -J	117	118	[10]
<i>o</i> -CH ₃	72	71—72	[10]
<i>o</i> -C ₂ H ₅	61,5	60,5—61	[11]
<i>o</i> -OCH ₃	101,5	102	[12]
<i>m</i> -F	—	60—61	—
<i>m</i> -Cl	72	72	[13]
<i>m</i> -Br	78	77—78	[13]
<i>m</i> -CH ₃	55	53—54	[14]
<i>p</i> -F	39—40	40	[13]
<i>p</i> -Cl	87—89	87—88	[14]
<i>p</i> -Br	95	95	[13]
<i>p</i> -CH ₃	48,5	46—48	[16]
<i>p</i> -OH	126	125—127	[17]
<i>p</i> -OCH ₃	22	22	[18]
<i>p</i> -CO ₂ C ₂ H ₅	83—84	83	[19]

Необходимые для ЭПР исследований образцы готовились следующим образом. Раствор двух компонентов с соответствующими концентрациями (АИБН $\approx$ 0,1 моль/л, нитрозо-соединение $\approx$ 0,1—0,01 моль/л) вводился в ЭПР ампулу и освобождался от кислорода, точно также, как и в случае полимеризационных образцов [20], методом вымораживания с последующим эвакуированием. Ампулы перед их использованием хранились в темноте, при -10°C . Для достижения желаемой концентрации промежуточных радикалов, ампулы нагревались в течение нескольких минут при $50\text{--}70^\circ\text{C}$. Соответствующим подбором этих параметров, а также концентрации веществ мы стремились достигнуть такую концентрацию свободных радикалов, при которой соотношение сигнал-шум, а также расщепление спектров были бы одновременно оптимальными. Тщательным освобождением от кислорода и подбором параметров измерения удалось достигнуть значи-

тельно более лучшего сверхтонкого расщепления, чем в подобных исследованиях, приведенных в литературе [6, 7, 8]. Следует упомянуть, что ампулы можно было хранить в холодильнике в течение нескольких недель и даже месяцев без значительного уменьшения при этом концентрации свободных радикалов. Измерения проводились на спектрометре типа JES-P-10, производства JEOL, при $+5 - +10^\circ \text{C}$.

3. Результаты измерений

Для всех исследованных промежуточных радикалов, типа окиси азота, характерным является то, что основным расщеплением их спектров является триплет. Очевидно, что это имеет место вследствие взаимодействия неспаренного электрона с атомом азота связи $\text{N}-\text{O}$. На основе дальнейшего сверхтонкого расщепления основного триплета, которое зависит от качества и места заместителя, исследованные радикалы могут быть подразделены на три основных группы:

1) В первую группу входят радикалы, образующиеся из орто-замещенных производных нитрозобензола.

2) Ко второй группе относятся такие мета- и паразамещенные производные, где заместители не вызывают или никакого или только простое дальнейшее расщепление.

3) К третьей группе относятся радикалы, образующиеся из производных п-нитрозоанилина, в случае которых заместители вызывают дальнейшее сложное расщепление.

Внутри первой группы исследовалось влияние следующих заместителей: $-\text{CH}_3$, $-\text{C}_2\text{H}_5$, $-\text{OCH}_3$, $-\text{F}$, $-\text{Cl}$, $-\text{Br}$ и $-\text{I}$. Для всех орто-замещенных производных характерным является вышеупомянутое расщепление на триплет; однако, кроме этого, наблюдаются две такие особенности, которые отличают их от мета- и пара-замещенных производных. Одна из них: при комнатной температуре отдельные линии триплета при наилучших разрешающих условиях или вообще не показывают, или только в незначительной мере имеют дальнейшее сверхтонкое расщепление. Вторая особенность заключается в том, что ширина отдельных линий триплета значительно больше, чем в случае мета- и пара-замещенных производных: в случае орто-замещенных ширина линии составляет 2 Ое, в то время как в случае соединений 2-ой и 3-ей групп ширина отдельных линий является величиной порядка 0,5 Ое.

Для иллюстрации сказанного на рис. 1 дан спектр радикала, образующегося из о-нитрозо-этилбензола.

Из рисунка, который характерен для всех представителей этой группы, видно, что спектр содержит три хорошо разделенных линии одинаковой интенсивности.

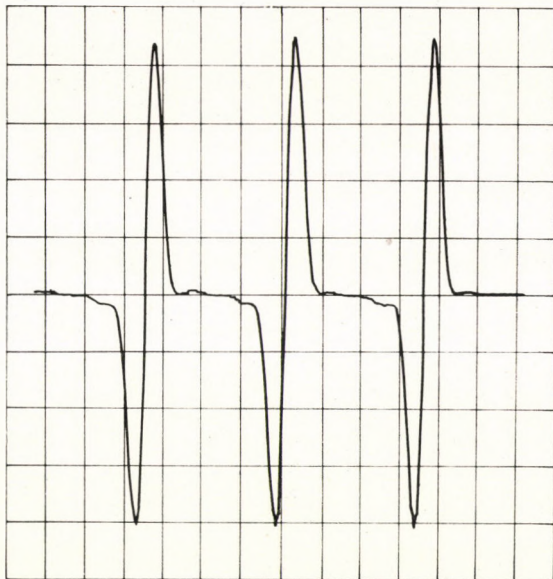


Рис. 1. Спектр ЭПР радикала, образующегося из о-нитроэтилбензола

Эти свойства спектра могут быть хорошо объяснены, если принять во внимание стерические условия радикалов, входящих в данную группу. В этом случае, вследствие орто-замещения, группа $\text{N}-\text{O}^\bullet$ не копланарна с ароматическим кольцом. Значительное уменьшение вторичного сверхтонкого расщепления может быть результатом именно такого отсутствия сопряжения. Этот вывод подтверждается также сравнением спектров $\text{o}-\text{F}$, $\text{o}-\text{Cl}$, $\text{o}-\text{Br}$ и $\text{o}-\text{I}$ производных. Как видно из рис. 2, в случае атома фтора, который имеет относительно меньший объем, с ядерным спином $I = 1/2$, линии триплета, хотя и в небольшой степени, но все же дают определенную сверхтонкую структуру.

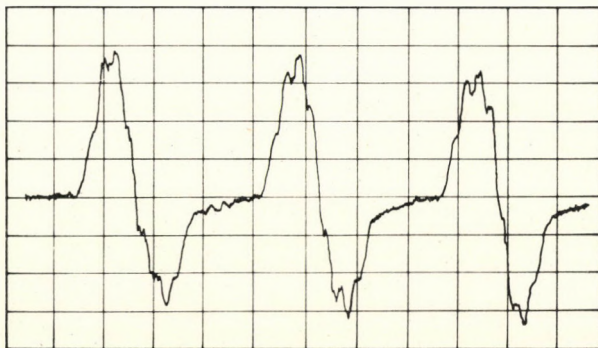


Рис. 2. Спектр ЭПР радикала, образующегося из о-нитрофторбензола

В противоположность этому $-\text{Cl}$, $-\text{Br}$ и $-\text{I}$ производные не показывают уже никакой сверхтонкой структуры, в интервале температур исследования. В случае этих соединений, следовательно, появляющаяся возможно лишь в незначительной степени сверхтонкая структура сливается в одну огибающую кривую. На основании этого, можно ожидать зависимость между шириной линии и стерическим эффектом орто-заместителей. Исследуя с этой точки зрения данные для производных с галогенными заместителями в орто-положении, вытекает, что ширина линии радикала, образующегося из фтор-нитрозобензола равна 3,5 Ое, а для $-\text{Cl}$, $-\text{Br}$ и $-\text{I}$ производных имеет величину около 2 Ое. Таким образом, вероятно, что переход от фтор-замещенных к соответствующим хлор-замещенным производным, в отличие от других галоген-замещенных производных, еще приводит к заметному изменению угла поворота и степени сопряжения.

Эти заключения, одновременно, находятся в хорошем согласии с данными, относящимися к реакционной способности. Из кинетических исследований вытекает, что радикалы орто-замещенных производных окиси азота, в противоположность соответствующим мета- и пара-замещенным производным, с большей или меньшей скоростью присоединяются к двойной связи более реакционноспособных виниловых соединений [3, 4, 21]. Это означает, что орто-замещенные производные являются значительно более реакционноспособными. На основании сказанного, это вполне понятно, так как уменьшение сопряжения должно приводить к увеличению реакционной способности промежуточного радикала.

В связи с соединениями первой группы, необходимо обратить внимание еще на одно интересное обстоятельство. Вследствие относительно хорошего расщепления линий триплета в случае этих соединений, мы имели возможность, при специальных условиях измерения, наблюдать линии изотопа ^{13}C . Принимая во внимание соотношение интенсивностей линий, а также природную распространенность изотопа ^{13}C (1,1%), можно установить, что ответственными за появление этих линий являются оба атома углерода, соседние с азотом. Один из характерных примеров этих измерений приводится на рис. 3.

Далее переходим к рассмотрению спектров радикалов, типа окиси азота, относящихся ко второй группе. Сюда относятся радикалы, образующиеся из нитрозобензола и его производных, замещенных в мета- и пара-положениях следующими группами: $-\text{F}$, $-\text{Cl}$, $-\text{Br}$, $-\text{I}$, $-\text{CH}_3$, $-\text{C}_2\text{H}_5$, $-\text{OH}$, $-\text{OCH}_3$ и $-\text{CO}_2\text{C}_2\text{H}_5$.

Эту группу соединений иллюстрируем двумя типичными спектрами. На рис. 4 представлен спектр радикала, образующегося при взаимодействии нитрозобензола с циан-изопропильным радикалом.

Линии триплета (1:1:1), происходящие от атома азота группы $\text{N}-\text{O}$, полностью расщепляются, так что вторичное расщепление представляет

собой квадруплет с отношением интенсивностей 1:3:3:1. Расщепление с таким отношением интенсивностей могут вызывать только три эквивалентных протона. Принимая во внимание возможные предельные структуры и квантово-химические расчеты, проведенные методом молекулярных орбит,

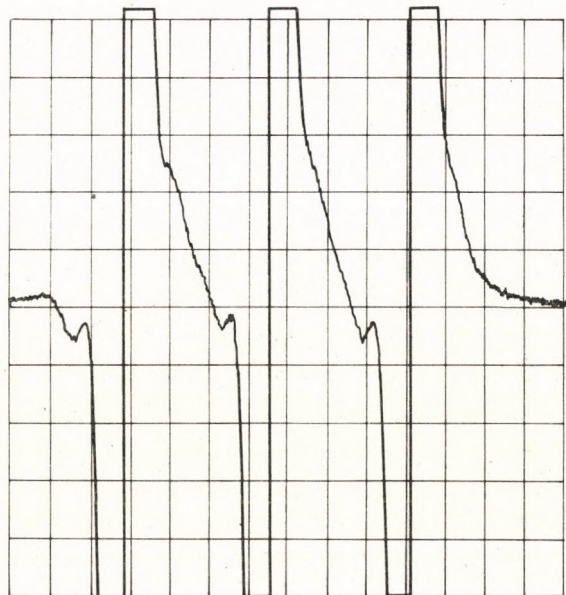


Рис. 3. Изотопные линии ^{13}C радикала, образующегося из о-нитрозо-иодбензола, в спектре ЭПР

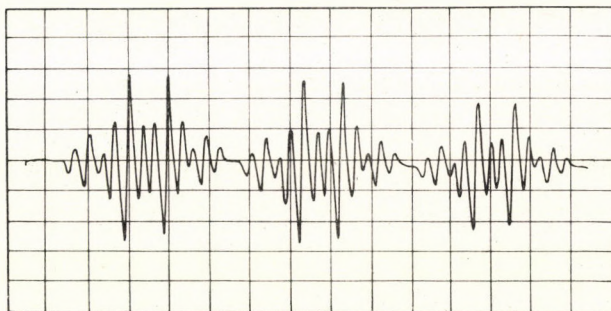


Рис. 4. Спектр ЭПР радикала, образующегося из нитрозобензола

можно заключить, что плотность неспаренного электрона является максимальной в орто-, и пара-положениях ароматического кольца, так что вторичное расщепление вызвано двумя орто- и одним пара-протоном. Отметим, что орто- и пара-протоны могут рассматриваться эквивалентными с точностью 1—2%. Такое высокое равенство является несколько неожиданным, так как, принимая во внимание симметрию молекулы, даже оба орто-протона нельзя считать полностью эквивалентными.

Наблюдающееся в дальнейшем третичное расщепление представляет собой триплет с соотношением интенсивностей 1:2:1, который обусловлен двумя эквивалентными протонами, очевидно, двумя мета-протонами. На рис. 5 приводится спектр радикала, образующегося из м-нитрозо-фторбензола. Из рисунка видно, что основным расщеплением является триплет (1:1:1), вторичным — квадруплет (1:3:3:1). Дальнейшее расщепление представляет собой два дублета, больший из которых соответствует мета-фтору, а меньший — мета-протону. Несмотря на то, что часть линий сливается и,

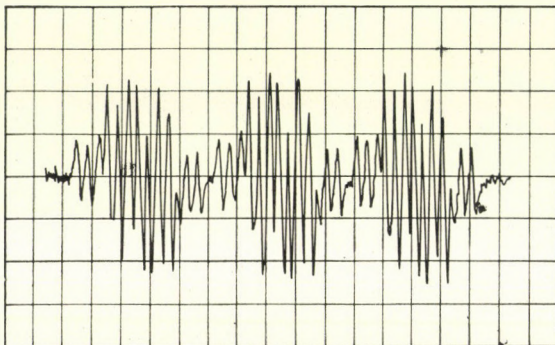


Рис. 5. Спектр ЭПР радикала, образующегося из м-нитрозо-фторбензола

таким образом, общее число линий меньше теоретического ($3 \times 4 \times 2 \times 2 = 48$), спектр является полностью однозначным, и константы расщепления могут быть измерены из него непосредственно.

В случае производных, содержащих такой заместитель в мета-положении, который не вызывает расщепления, вторичное расщепление спектров представляет собой квадруплет с отношением интенсивностей (1:3:3:1), (вызванный орто-, орто'- и пара-протонами), каждая линия которого расщепляется мета-протоном на дублет, с относительными интенсивностями 1:1.

Относительно простым является дальнейшее расщепление в случае $-\text{CH}_3$ и $-\text{C}_2\text{H}_5$ заместителей. Протоны метильной и метиленовой групп вызывают расщепление, эквивалентное протонам ароматического кольца в подобном положении.

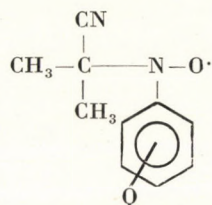
Спектры радикалов, образующихся из производных п-нитрозоанилина, относящихся к 3-ей группе, уже были иллюстрированы нами несколькими примерами в предыдущих сообщениях [1, 22], где также было показано, что при формировании сверхтонкой структуры, кроме азота в пара-положении, необходимо учесть и влияние метиловых и этиловых групп, обладающих эффектом сверхсопряжения. Хотя в ходе настоящих исследований нам удалось достичь намного лучшее разрешение, чем ранее [1], объяснение этих сложных спектров возможно будет лишь на основе изучения систематически дейтерированных производных.

Применение в качестве инициатора перекиси бензоила приводит к хорошо известным радикалам, типа дифенил-окиси азота. Это в свою очередь указывает на то, что молекулы ингибитора реагируют не с бензилокси-радикалами, а с фенильными радикалами, образующимися при декарбок-силровании.

4. Обсуждение констант расщепления

Выше была изучена структура спектров промежуточных радикалов. В дальнейшем рассмотрим количественную оценку констант расщепления. Константы расщепления мета- и пара-замещенных производных собраны в таблице II. Второй столбец таблицы содержит константы расщепления на азоте, а последующие столбцы константы расщепления на о- и п-протонах, м-протонах ароматического кольца. В пятом столбце приведены электро-фильные константы заместителей.

Таблица II



Q	a_N (Oe)	$a_{N_{o,p}}$ (Oe)	a_{H_m} (Oe)	σ^+	a_o/a_m
<i>p</i> -ОН	11,87	2,26	0,78	-0,920	2,90
<i>p</i> -ОСН ₃	11,63	2,18	0,79	-0,778	2,76
<i>p</i> -СН ₃	11,29	2,38 ¹	0,86	-0,311	2,77
<i>m</i> -СН ₃	11,28	2,22	0,74 ²	-0,066	3,00
<i>p</i> -F	11,53	2,28 ³	0,84	-0,073	2,70
H	11,25	2,28	0,87	0	2,62
<i>p</i> -Cl	10,94	2,35	0,95	0,114	2,48
<i>p</i> -Br	10,84	2,24	— ⁴	0,150	—
<i>m</i> -F	10,83	2,32	0,82 ³	0,352	2,83
<i>m</i> -Cl	10,94	2,31	0,82	0,399	2,82
<i>m</i> -Br	10,87	2,28	0,82	0,404	2,78
<i>p</i> -СО ₂ С ₂ Н ₅	10,54	2,36	0,91	0,482	2,60

¹ $a_{CH_3} = a_{H_{o,p}}$

² $a_{CH_3} = a_{H_m}$

³ Атом фтора вызывает расщепление в виде большого дублета, $a_{Fp} = 5,22$ Ое и $a_{Fm} = 1,81$ Ое. Следующие отношения $a_{Fp}/a_{H_o} = 2,29$ и $a_{Fm}/a_{H_m} = 2,21$, в согласии с ожидаемым, являются постоянными.

⁴ Нельзя измерить вследствие недостаточного расщепления.

Известно, что с помощью констант сверхтонкого расщепления можно получить информацию о распределении неспаренного электрона в системе сопряженных связей. Г. М. МакКоннел [23] установил, что константа расщепления на протоне ароматического кольца пропорциональна плотности неспаренного электрона, на связанном с ним атоме углерода, т. е. имеет место следующее соотношение:

$$a_j = Q \rho_j \quad (3)$$

В этом уравнении a_j обозначает константу расщепления на протоне, связанном с j -тым углеродным атомом, а ρ_j плотность неспаренного электрона на том же атоме углерода. Большинство авторов — в согласии с экспериментальными данными — предполагает, что значение Q для одного и того же типа связи постоянно.

В случае изученных радикалов, типа окиси азота, заместители, благодаря своим индуктивным и мезомерным эффектам, модифицируют распределение спиновой плотности на атомах углерода ароматического кольца. Из табл. 2 видно, что хотя и константы расщепления на орто-, пара- и мета-протонах изменяются несколько, однако, они не показывают однозначной тенденции в зависимости от констант σ^+ . Это все же не означает, что заместители, в действительности, не влияют на плотность неспаренного электрона на атомах углерода ароматического кольца, а дело просто в том, что точность определения в данном случае не превышает 0,05 Ое, и поэтому изменения в несколько процентов не могут быть замечены.

В связи с константами расщепления следует указать еще на одно обстоятельство. В случае фенил-трет.-бутил-окиси азота, а также ее многих производных, замещенных в пара-положении, значение отношения a_o/a_m приблизительно равно двум [7]. В случае же изученных нами радикалов, отличающихся от предыдущих лишь тем, что одна из метильных групп трет.-бутильной группы замещена нитрильной группой, значение этого отношения равно примерно 2,8. Это увеличение является, прежде всего, следствием повышения значения a_o (и a_p). Эти факты указывают на то, что изменения такого рода в электронной плотности ароматического кольца вызваны сильным индуктивным (электронно-акцепторным) эффектом циано-пропильной, точнее нитрильной группы последней.

Нами были сделаны попытки найти корреляцию между константами расщепления на азоте и электрофильными константами σ^+ заместителей. Зависимость $a_N = f(\sigma^+)$ изображена на рис. 6.

Как видно из рисунка, корреляция является хорошей и линейной. С другой стороны, видно, что электронно-акцепторные заместители снижают значение a_N .

Подобная зависимость была установлена ранее Колкером, Стоуном и Ватерсом [24] в ряду радикал-анионов нитробензола. Было показано, что

значение a_N находится в отличной линейной корреляции с парциальными факторами скорости нитрования. Аналогичным образом, значения a_N , установленные Ригером и Френкелем [25] для радикал-анионов замещенного нитробензола, можно привести в корреляцию с электрофильными константами заместителей. Следует, однако, отметить, что системы термов ради-

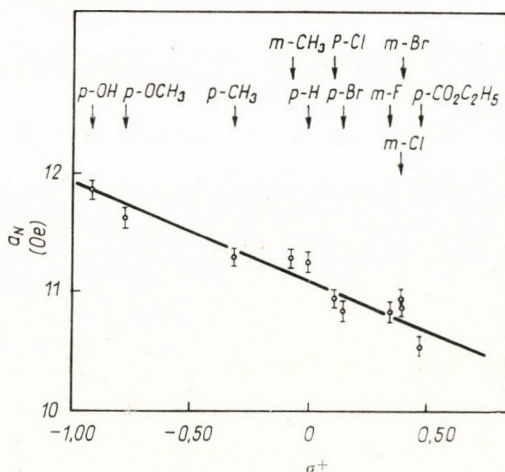


Рис. 6. Зависимость констант расщепления на азоте от электрофильных констант заместителей

кал-анионов и нейтральных радикалов коренным образом отличаются, так что эта аналогия довольно поверхностна.

Среди нейтральных радикалов такую зависимость можно обнаружить в ряду замещенных радикалов Бэнфильда [26]. Подобная хорошая корреляция была установлена для константы a_N Лёмером и сотрудниками [7]. Отметим, что в настоящее время не имеется точного теоретического обоснования для этих зависимостей, и выбор из принимаемых во внимание различных рядов констант заместителей (напр., σ , σ^+ , σ_1) проводится на основе подчинения линейности. Уточнение этого важного вопроса возможно будет лишь на основе гораздо более широкого исследования влияния заместителей.

Ассигнация константы расщепления на азоте к электронной плотности неспаренного электрона на азоте требует большой осмотрительности.

Хеннинг [27] исследовал различные радикал-ионы, содержащие азот, с целью изучения зависимости между a_N и распределением спиновой плотности. Согласно исследованиям этого автора, константа расщепления ^{14}N (a_N) зависит не только от спиновой плотности на азоте (ρ_N) но, хотя и в меньшей степени, и от спиновых плотностей на соседних атомах углерода (ρ_{C_1} , ρ_{C_2}), согласно следующему уравнению:

$$a_N = Q_{NN} \rho_N + Q_{CN} (\rho_{C_1} + \rho_{C_2}) \quad (4)$$

где величины Q_{NN} и Q_{CN} равны $19,1 \pm 1,7$ и $9,1 \pm 1,7$ Ое, соответственно.

В том случае, если к атому азота присоединяется не только атом углерода, но также и другой гетероатом, то последний может тоже оказывать влияние на величину константы расщепления на азоте. Относительно этого мы располагаем данными о радикал-анионах нитробензола. Для последних, на основе исследований Карплуса и Френкеля [28], a_N может быть описана следующей зависимостью:

$$a_N = Q_{NN} \rho_N + Q_{CN} \rho_C + 2Q_{NO} \rho_O \quad (5)$$

где ρ_N , ρ_O , ρ_C означают спиновую плотность π -электрона на атоме азота, кислорода и углерода, соседних с атомом азота. $Q_{NN} = \pm 99,0 \pm 10,2$; $Q_{NO} = \pm 35,8 \pm 5,9$ гаусс. Из этих исследований выяснилось, что вторым фактором в правой части уравнения можно пренебречь, по сравнению с другими, т. е. из факторов, влияющих на константу расщепления на азоте, решающая роль принадлежит спиновой плотности на азоте и кислороде.

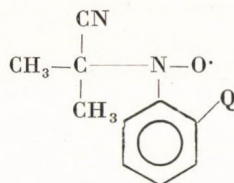
На основании сказанного можно предположить, что в случае радикалов, образующихся из нитрозо-соединений, зависимость Гаммета для констант расщепления может быть объяснена либо изменением ρ_N или ρ_O , либо одновременным изменением этих двух величин. Независимо от того, какую из альтернатив мы принимаем в данном случае, речь идет об изменении спиновой плотности центра N—O.

Эти рассуждения, между прочим, приближают нас к возможности объяснения зависимости Гаммета для фактора регенерации цепи. Наши ранние исследования показали [9], что реакционная способность радикалов, образующихся из нитросоединений (которые в противоположность радикалам, образующимся из нитрозо-соединений, обладают гораздо большей склонностью к регенерации цепи), увеличивается с введением электронно-донорных заместителей. Данные исследования, с другой стороны, показывают, что опять-таки электронно-донорные заместители увеличивают спиновую плотность реакционного центра промежуточных радикалов. Однако, увеличение спиновой плотности означает, что делокализация неспаренного электрона уменьшается, вследствие чего реакционная способность радикала должна возрасть. Это влияние в исследованной реакции вызывает именно увеличение фактора, характеризующего регенерацию цепи.

Продолжая ход этих размышлений, рассмотрим константы расщепления радикалов, образующихся из о-нитрозо-соединений, величины которых собраны в табл. III. В третьем столбце таблицы приведены радиусы Ван дер Вальса для галоген-заместителей.

При качественном обсуждении спектров ЭПР было показано, что уменьшение копланарности группы N—O и ароматического кольца приводит к полному или частичному исчезновению линий сверхтонкой структуры.

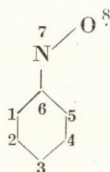
Таблица III



Q Заместитель	a_N (Oe)	Радиус Ван дер Вальса (Å)
—F	13,37	1,35
—Cl	13,44	1,80
—Br	13,69	1,95
—J	13,65	2,15
—CH ₃	13,24	—
—C ₂ H ₅	13,39	—
—OCH ₃	13,87	—

Вследствие уменьшения взаимодействия неспаренного электрона с ароматическим кольцом, константы расщепления на водороде, в случае этих радикалов, уже не могут быть определены.

При сравнении величин a_N , приведенных в табл. 2 и 3, можно видеть, что в случае орто-замещенных производных наблюдается значительный рост этих величин, по сравнению с пара- и мета-замещенными производными. На основе предыдущей дискуссии (т. е. $a_N = f(\varrho_N, \varrho_O)$) это означает, что с выворачиванием N—O· группы из плоскости кольца, параллельно должны возрастать величины спиновой плотности ϱ_N и ϱ_O . Для изучения этой проблемы проводились расчеты спиновой плотности с помощью метода ЛКАО—МО с вариантом «открытой оболочки», на примере нижеследующей восьмицентровой модели:



Зависимость величин ϱ_N , ϱ_O , и ϱ_C , относящихся к различным углам поворота, от угла поворота показана на рис. 7.

Вследствие приближенного характера метода, данные не могут быть приняты за абсолютные величины. Однако, однозначно наблюдается та тенденция, что стерический эффект в данном случае проявляется в возрастании величин ϱ_N и ϱ_O , а также в уменьшении ϱ_C . Следовательно, эти результаты

согласуются с тем экспериментальным, уже упомянутым фактом, что радикалы, образующиеся из о-нитрозо-соединений, в противоположность мета- и пара-замещенным производным, обладают значительной способностью к реакции регенерации цепи. Из этих исследований однозначно вытекает, что параллельно с увеличением спиновой плотности реакционного центра возрастает реакционная способность рассматриваемых радикалов.

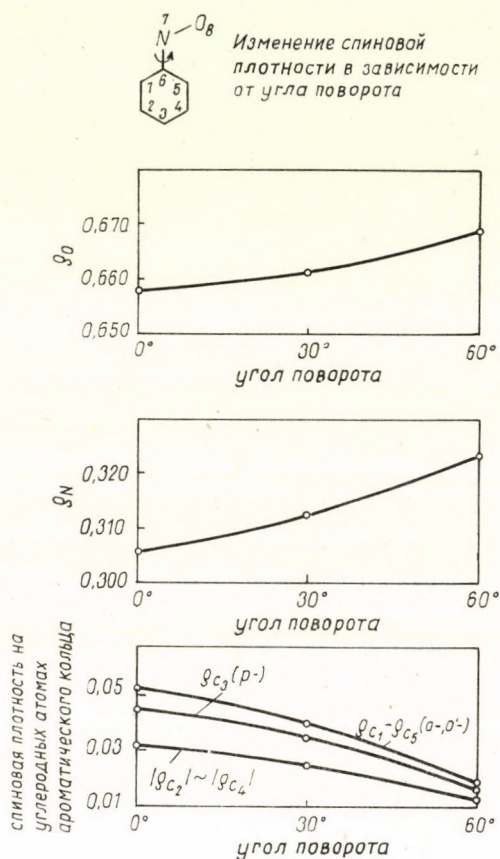


Рис. 7. Зависимость изменения ρ_N , ρ_O и ρ_C от угла поворота

Наконец, упомянем, что влияние заместителей на электронную структуру радикала изучается нами на большом числе дальнейших примеров. О результатах этих исследований будет сообщено позднее.

Приносим благодарность Я. Хейдт и Л. Йокаи за синтез нитрозо-соединений, др. Я. Ладику и Г. Бицо за помощь, оказанную в квантово-химических расчетах, а также Б. Мохошу за помощь, оказанную в ЭПР исследованиях. За участие в экспериментальной работе приносим благодарность Э. Рокенбауэр, Ю. Тимар и К. Йокаи.

РЕЗЮМЕ

Были синтезированы и изучены методом ЭПР стабильные свободные радикалы фенил-(2-циан-2-пропил)-окиси азота, а также 18-ти ее различных замещенных производных. Были определены константы расщепления спектров ЭПР и объяснялись на основе молекулярной структуры. Было установлено, что в случае орто-замещения эти системы не являются копланарными, вследствие чего неспаренный электрон, в основном, концентрируется на связи N—O. Обсуждалось влияние мета- и пара-заместителей на электронную структуру, и была установлена линейная корреляция между константой расщепления на азоте (a_N) и электрофильными константами заместителей (σ^+).

SUMMARY

The phenyl-(2-cyano-2-propyl)-nitrogen-oxide stable free radical and its 18 derivatives substituted in different positions were prepared and investigated by ESR method. The coupling constants of ESR spectra were determined and interpreted on the basis of molecular structure. It was stated that in the case of o-substitution these systems are not coplanar, and, as a consequence, the odd electron is concentrated chiefly on the NO bond. The effect of substituents in m- and p-positions on the electron structure of the radicals was discussed and it was demonstrated that the coupling constants of nitrogen (a_N) are in linear correlation with the electrophilic substituent constants (σ^+).

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STUDY OF THE NATURE OF ACTIVE CENTRES INITIATING THE LOW TEMPERATURE RADIATION POLYMERIZATION OF ACRYLONITRILE

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At usual temperatures the radiation polymerization of vinyl monomers proceeds according to free radical mechanism [1—3].

For a long time it was accepted as a fact that the ions, which are the primary products of radiolysis, can play no role in the initiation of the polymerization process. Later, however, it was proved that at sufficiently low temperatures (-80°C) ions formed under the influence of high energy radiation might also initiate the polymerization of vinyl monomers thus the earlier negative results were due to the unfavourable temperature conditions of the polymerization process. It has been proved experimentally that isobutylene, known to be one of the few monomers which do not polymerize according to the free radical mechanism, polymerizes under the influence of radiation at -78°C at a well measurable rate [4]. Several authors have shown that under high energy radiation several vinyl monomers polymerize at low temperatures according to cationic mechanism [5—8]. The possibility of initiation of radiation polymerization according to anionic mechanism was first demonstrated by ABKIN *et al.* on the example of the low temperature radiation polymerization of acrylonitrile [9, 10].

On the basis of the pertaining literature, some conclusions may be drawn as to the fundamental laws of ionic radiation polymerization, but the experimental data available give no unequivocal answer concerning the nature of the ions which initiate the polymerization process.

It is a known fact that when the polymerization of vinyl monomers is initiated with catalysts which act according to ionic mechanism, the "catalyst" ion and the counter-ion with the opposite charge are located in the vicinity of each other during the entire chain growth process. This might be the case even when the difference between the ionization potential and electron affinity of the medium can be compensated by the free solvation energy.

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Under the influence of gamma radiation, however, it might be supposed that the positively and negatively charged particles in the irradiated material are distributed evenly throughout the entire volume of the substance. The distance between the charged particles might probably be sufficiently great to exclude the role of electrostatic forces in the deactivation of the ions, thus the deactivation process must be dependent on diffusion. This means that the useful life of the ions formed will be comparable to the useful life of the free radicals formed under identical conditions. Thus it might be supposed that under suitable temperature conditions radiation polymerization will be initiated not by ion pairs, but by ions with free charges. In the present work we aim at the experimental proof of this conception.

We have assumed that the active centre which initiates the polymerization of acrylonitrile is an anion with "free charge". If this is in fact so, then if radiation polymerization is performed between electrodes, a direct current voltage applied to the electrodes should affect the kinetics of polymerization.

Experimental

The reactor for investigating the polymerization of acrylonitrile consisted of a soluble-wall cylindrical vessel (5 in Fig. 1). The reactor was cooled by liquid or gaseous nitrogen. The net volume of the vessel was 60 ml. The inner cylindrical vessel was gold-plated, serving as one electrode for the d. c. electric field. The other electrode was a vibrating agitator (6 in Fig. 1), gold-plated, too. Each electrode had a surface of 150 cm². The distance between the electrodes was 5 mm, the current flowing through the specimen at 12 V was about 1 mA.

The vibrating electrode ensured a good stirring of the monomer. Thus, near the vibrating electrode, the fluid was being continuously changed during polymerization.

The mixture should be stirred at such a rate, that no double layer may form on the electrode. The vibrating electrode is operated by an electromagnet (1 in Fig. 1). The frequency of the vibrations could be varied from 7 cycle/sec to 26 cycle/sec, using an impulse generator. At maximal frequency the amplitude of the vibration was 5 mm. The voltage was connected to the vibrating electrode by means of a phosphor-bronze spring (10 in Fig. 1), well insulated from the reactor body. In order to avoid the precipitation of atmospheric moisture on the inner surface of the reactor, it was filled with deoxygenated dry nitrogen at a pressure of 1.5 atm.

Temperature measurements in the reactor were made by means of copper-constant thermoelements (12 in Fig. 1). The temperature of the reactor could be kept constant within $\pm 0.5^\circ$ in the temperature range of -10 to -120° C. For cooling the reactor an automatic nitrogen cryostat was designed, which could maintain a constant temperature for several hours, consuming from 2 to 8 litres/hr of liquid nitrogen.

The monomer and the solvent (dimethylformamide) were carefully purified and dried. After drying, the monomer was de-aerated by successive freezing, evacuating and melting. Two sets of experiments were carried out to investigate the effect of the d.c. field on the polymerization rate and on the molecular weight of the polymer:

- (a) polymerization under a d.c. voltage of 12 V
- (b) polymerization without a d.c. field.

The vibrating electrode served as the anode in both cases. Each experiment was carried out by letting purified dry nitrogen flow through the reactor for 15–20 minutes. After the desired temperature had been reached, the monomer was injected into the reactor. The injection did not take more time than a few tenths of a second. The polymerization was continued to attain 1–10% conversion. The reactor was irradiated by a ⁶⁰Co source, type K-60,000 having a radium equivalent activity of 60,000. The construction of the cobalt source [8] made possible a fairly homogeneous irradiation over the whole area of the reactor. Irradiation doses were measured by the ferrous sulphate method [9].

The polymer was filtered through a G4 glass filter and washed several times on the filter with acetone. When polymerizing in solution, the polymer was precipitated by acetone. The filtered and washed polymer was then dried in vacuum (10^{-6} mmHg) to constant weight. Conversions were measured gravimetrically. The molecular weights were determined viscosimetrically in dimethylformamide solutions at 20° C.

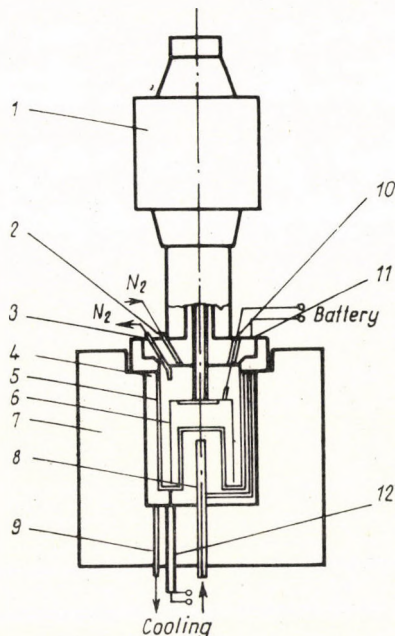


Fig. 1. Reactor for investigating the low-temperature radiation polymerization of acrylonitrile. 1 = Electromagnet, 2 = Nitrogen inlet tube, 3 = Nitrogen outlet, 4 = Reactor body, 5 = Covering of cooler, 6 = Vibrating electrode, 7 = Thermal block, 8 = Cooling agent inlet tube, 9 = Cooling agent outlet, 10–11 = Sockets for the electric voltage, 12 = Thermocouples. Distance between the electrodes: 5 mm

Experimental results and discussion

According to literature data [9, 10], the low temperature radiation polymerization of acrylonitrile proceeds predominantly according to ionic mechanism. When the temperature of polymerization is increased, the role of the free radical processes gains more and more in importance, and near room temperature the polymerization process can be actually regarded as a free radical reaction.

Our experimental data are in complete agreement with the above described conceptions on the mechanism of the radiation polymerization of acrylonitrile. It can be seen from Fig. 2 that at -80°C the acrylonitrile content of the copolymer obtained from the monomer pair acrylonitrile styrene approaches the acrylonitrile content of the copolymer produced by an ionic catalyst. When the temperature of the polymerization process is gradually increased, the styrene content of the copolymer gradually increases, and

finally the composition of the copolymer obtained at -10°C approaches the composition of the copolymer obtained by free radical polymerization mechanism. Similar results were obtained for the kinetics of bulk polymerization. The overall activation energy of the process at -80°C is 1.5 kcal/mole, and

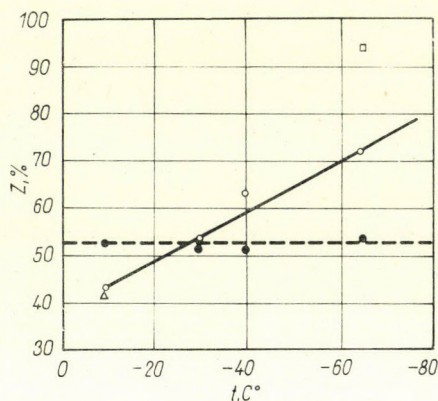


Fig. 2. Acrylonitrile contents of copolymers, obtained by the radiation block polymerization of the acrylonitrile-styrene monomer pair, as a function of temperature. (Styrene: acrylonitrile = 1 : 6. Dose rate: 372 rad/sec. Time of irradiation 60 min.)

- o — copolymer prepared without voltage
- x — copolymer prepared under voltage
- z — acrylonitrile content of the copolymer in mole-%
- Δ — acrylonitrile content of the acrylonitrile-styrene copolymer prepared according to free radical mechanism
- $\square$ — acrylonitrile content of the acrylonitrile-styrene copolymer prepared according to anionic mechanism

near room temperature it is 5.35 kcal/mole (Fig. 3). A series of experiments was devised to study in detail the mechanism of radiation polymerization and to distinguish between the ionic and free radical processes. In these experiments the polymerization was carried out between electrodes (12 V) in a reactor provided with a vibratory stirrer as described in an earlier communication [10]. It could be expected that the discharge of the ions on the electrodes might have a considerable damping effect on the ionic processes, and consequently there will be a chance for the closer study of the role of the radical processes in polymerization. Further, some interesting supplementary data on the mechanism of initiation of radiation polymerization were also expected from this method.

Indeed, under the influence of direct voltage, the electrodes considerably resuppress the ionic processes, and the polymerization proceeds, in the entire temperature range investigated (between $+20^{\circ}\text{C}$ and -80°C), fundamentally according to free radical mechanism. In this case the radiation block polymerization of acrylonitrile has an overall activation energy of 5.00 kcal/mole in the entire temperature range studied (Fig. 3). It is interesting to note that

at temperatures below -30°C the polymer formed is located on the vibrating electrode (anode).

A comparison of the values of the polymerization rates observed under direct voltage and without applying a voltage (Fig. 4) shows that above -30°C

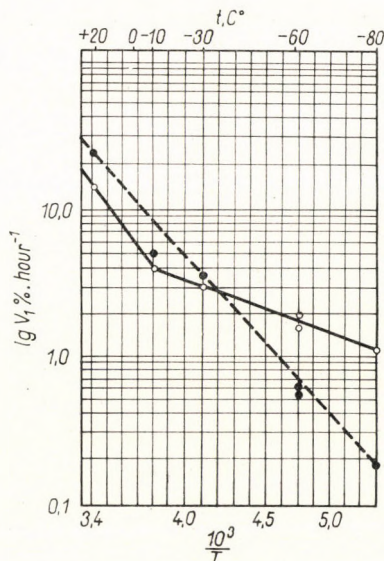


Fig. 3. The rate of polymerization $\lg V$ as a function of $1/T$ in acrylonitrile block polymerization

o — polymerization without voltage
x — polymerization under voltage

the polymerization rate is considerably increased under the influence of the voltage, while in the range of lower temperatures (between -30°C and -80°C) the rate somewhat decreases. The molecular weights of the polymers formed are also slightly reduced as an effect of the voltage applied. Increase in the rate of polymerization with a simultaneous decrease in the molecular weight of the polymeric product bear proof to the fact that the increase in the rate of polymerization is caused by an increase in the rate of initiation. In order to explain the experimental data obtained, and especially to understand the increase in the rate of initiation under the influence of voltage, it is indispensable to subject to a detailed analysis the mechanism of the processes which take place during the radiation polymerization of acrylonitrile.

During the radiolysis of the monomer, two primary processes may take place:

Dissociation of the monomer molecule into free radicals:



and ionization of the monomer molecule:

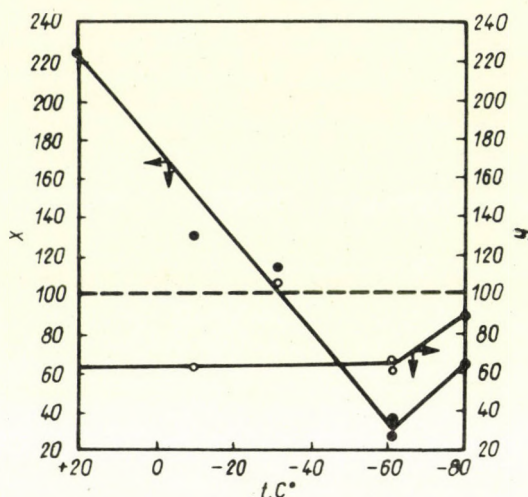


Fig. 4. Effect of voltage on the rate of the radiation block polymerization of acrylonitrile in the temperature range between $+20^\circ$ and -80°C . (The polymerization rate and limiting viscosity number for the polymerization without voltage were deliberately chosen as 100%).

$$x = \frac{V_1}{V_2} \cdot 10^2 y = \frac{[\eta]_1}{[\eta]_2} \cdot 10^2$$

V_1 = rate of polymerization under voltage

V_2 = rate of polymerization without voltage

$[\eta]_1$ = limiting viscosity number of polymers obtained by polymerization under voltage

$[\eta]_2$ = the limiting viscosity number of polymers obtained by polymerization without voltage

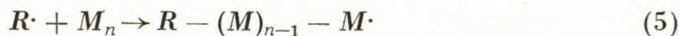
The electron removed from the molecule — after having lost its excess energy — may be captured by a monomer molecule which has an electron acceptor group. This process leads to the formation of a so-called anion-radical:

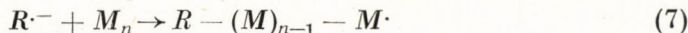
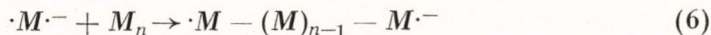


A similar process occurs between the free radicals — which have, as it is well known, a high electron affinity — and the thermalized electrons. This process leads to the formation of anions:

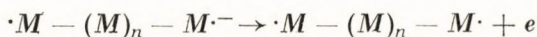


In the polymerization system the anion-radicals and anions formed react with the monomer units and procedure chains with one or two active centres:





The capture of electrons by monomer molecules or by free radicals is assumed to be a reversible process. The splitting off of the electron from the anion-radical should lead to the regeneration of the monomer molecule. If, however, the primary anion-radical had captured, already up to the time of the splitting off of the electron, one or more monomer molecules, then the loss of the electron leads to the formation of a so-called bi-radical.



It is known from the literature [11] that bi-radicals in which the active centres lie close to each other are inclined to ring formation and therefore unable to initiate the polymerization process. If, however, up to the moment when the electron is split off, the active centres in the anion-radical are sufficiently removed from one another, the active centres in the bi-radical formed are able to initiate the polymerization process as entirely independent units.

Bearing in mind that a dynamic equilibrium exists in the polymerization system, namely: anion-radical (or di-anion) $\rightleftharpoons$ bi-radical, it becomes quite obvious that the stationary concentration of the active centres with an ionic or free radical character is determined solely by the formation rate of the primary radicals or anion-radicals produced by irradiation and by the decomposition rate of the kinetic chains (through recombination or disproportionation), or by the rate of neutralization of the free charge of the anions (on the positively charged particles in the system), but this stationary concentration is also strongly influenced by the prevailing position of the above mentioned dynamic anion radical $\rightleftharpoons$ bi-radical equilibrium.

On the basis of the aforesaid it is quite clear that all factors (e.g., the rate of chain propagation) furthering the growth of the anion-radical to dimensions which will hinder cyclization, produce an increase in the concentration of the active centres in a given polymerization system, consequently they promote the increase of the rate of initiation. At low temperatures the anion-radical $\rightleftharpoons$ bi-radical equilibrium is shifted in the direction of the charged active centres. Bearing in mind the fact that with a decrease of the temperature the rate of radical polymerization is strongly lowered, it becomes understandable that polymerization proceeds nearly entirely according to the ionic mechanism. With an increase in the temperature the equilibrium is shifted more and more in the direction of the radical product. At a sufficiently high temperature (according to experimental data at room temperature) the polymerization process proceeds entirely according to free radical mechanism.

If a direct voltage is applied on the electrodes, the probability of the discharge of the anion-radicals, that is to say the transformation rate of the anion-radicals into bi-radicals suddenly rises, and thereby the equilibrium is shifted in the directions of the formation of active centres of radical character. The adsorption of bi-radicals on the surface of the positively charged electrodes hinders the cyclization process, and consequently a possibility arises for the bi-radicals to grow to dimensions at which the active centres of the bi-radicals become independent of each other, which again leads to an increase in the rate of initiation.

In the case of copolymerization, the equilibrium concentration of the polar component (in our case that of acrylonitrile) will be greater on the surface of the electrode, because of the greater adsorption than within the reaction mixture. Consequently, the copolymer formed on the surface of the electrode will be richer in acrylonitrile than the copolymer formed within the mixture. Thus, in the entire temperature range investigated the copolymer produced under the influence of direct voltage will be richer in the acrylonitrile component than the usual radical copolymer (Fig. 2).

The degree and nature of the voltage effect on the polymerization rate is greatly dependent on the temperature (Fig. 4). This temperature dependence is in all probability related to the polymer layer which is formed on the surface of the electrode and which is insoluble in the monomer. The density of the polymer layer formed on the electrode surface, and consequently the permeation rate of the anion-radicals and bi-radicals through this layer, is absolutely dependent on the polymerization temperature.

The higher the polymerization temperature, the greater the electrode voltage on effect the polymerization rate. At very low temperatures, when the entire quantity of the polymer formed precipitates on the electrode and the macro bi-radicals are occluded together with the inactive polymer chains, there is a marked decrease in the polymerization rate, owing to the low diffusion rate of the monomer molecule.

There is also another explanation for the decrease in the polymerization rate caused at low temperatures by the voltage applied:

As an effect of the voltage applied, the dynamic anion-radical $\rightleftharpoons$ bi-radical equilibrium in the system shifts toward the formation of radical products, for which the activation energy of chain growth is considerably higher than for ionic products, and this — disregarding the increase of the rate of initiation — results in a lower polymerization rate.

With the aim to check our above assumption, we have investigated the effect of voltage on the kinetics of the radiation block polymerization of the acrylonitrile-styrene monomer pair (acrylonitrile : styrene = 6 : 1), on the copolymerization kinetics of acrylonitrile-styrene in dimethylformamide solution (acrylonitrile : styrene = -2 : 1) over a wide temperature range

(when the copolymer is soluble in the reaction mixture), and on the polymerization kinetics of acrylonitrile in dimethylformamide solution at -60°C (monomer concentration 2 to 15 moles/litre). The experimental data obtained (Fig. 5) prove that the character and degree of the voltage effect on the polymerization rate is independent of the temperature.

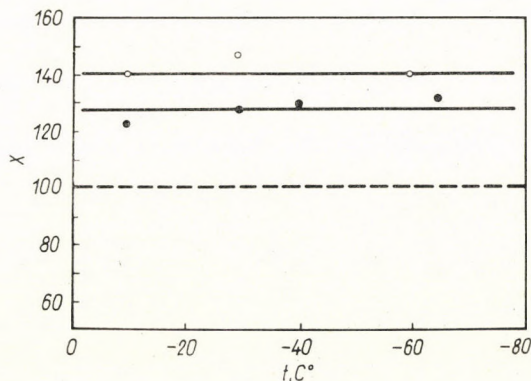


Fig. 5. Polymerization rate as a function of applied voltage in the radiation-induced block and dimethylformamide solution polymerizations of the acrylonitrile-styrene monomer pair.

x = block copolymerization

o = copolymerization in solution

$$x = \frac{V_1}{V_2} \cdot 10^2$$

V_1 = polymerization rate under voltage

V_2 = polymerization rate without voltage

The measurements which served to study the effect of voltage on the kinetics of the radiation polymerization of acrylonitrile in dimethylformamide solution (Fig. 6 and Table I) have shown that at monomer concentrations which lead to the precipitation of the polymer formed on the anode, a voltage applied on the electrodes reduces the rate of polymerization. At lower monomer concentrations (4 to 10 moles/litre) the polymerization rate increases as a result of the voltage. The maximum effect was observed at 6 moles/litre concentration. (At concentrations higher than this, the polymer formed is only partly soluble in the reaction mixture, and with increasing concentration it is deposited more and more on the vibrating electrode.)

The decrease of the voltage effect on the polymerization rates at concentrations below 6 moles/litre, moreover the blocking effect of voltage at concentrations below 4 moles/litre can be explained as follows: The most fundamental reason for the increase of the polymerization rate can be found in the stabilization of the bi-radicals on the electrode surface, which results in the bi-radical reaching a critical chain length, at which cyclization is no

Table I
*Effect of direct voltage on the radiation polymerization
 of acrylonitrile in dimethylformamide solution*
 Dose rate: 372 rad/sec; temperature: -60°C

No.	Monomer concentration, mole/litre	Voltage, V	Polymerization rate, % · hour ⁻¹
1	2.00	—	1.12
2	2.00	12	0.67
3	3.50	—	1.33
4	3.50	12	1.00
5	4.35	—	4.00
6	4.35	12	5.21
7	6.00	—	2.90
8	6.00	12	4.47
9	8.00	—	3.88
10	8.00	12	4.20
11	13.60	—	3.19
12	13.60	12	1.94
13	15.10	—	1.88
14	15.10	12	0.52

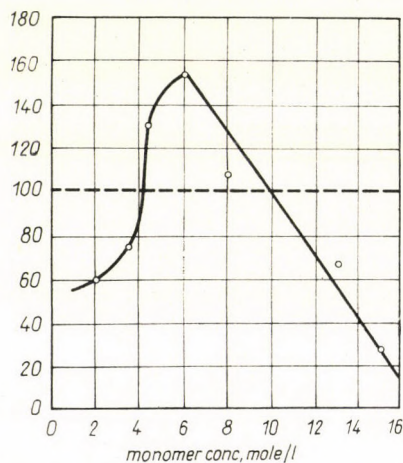


Fig. 6. Polymerization rate under the influence of direct voltage in the radiation polymerization of acrylonitrile in dimethylformamide solution, as a function of the monomer concentration. (Monomer concentrations: 2 to 16 moles/litre. Polymerization temperature: -60°C . Dose rate 372 rad/sec.)

$$x = \frac{V_1}{V_2} \cdot 10^2 \quad y = \frac{M_1}{M_2} \cdot 10^2$$

V_1 = polymerization rate under voltage

V_2 = polymerization rate without voltage

M_1 = molecular weight of the polymer obtained by polymerization under voltage

M_2 = molecular weight of the polymer obtained by polymerization without voltage

longer possible, prior to the beginning of the desorption process. A decrease of the monomer concentration in the reaction mixture reduces the probability that the bi-radicals can grow to a suitable length, and thus the desorption and chain termination (cyclization) of the bi-radicals consisting of a few monomer units lead to a reduced accelerating effect of the voltage, and to a decrease of the polymerization rate.

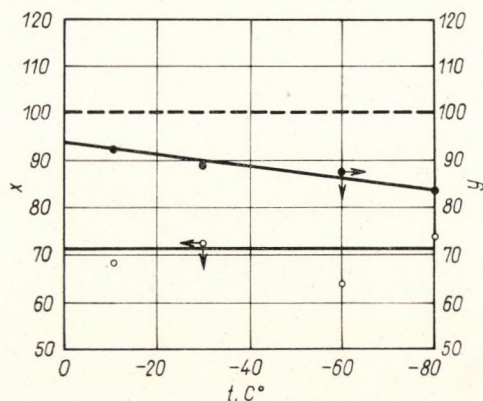


Fig. 7. Polymerization rate under the influence of direct voltage in the radiation polymerization of acrylonitrile in trimethylamine solution as a function of temperature in the range between -10 and -80°C . (Monomer concentration: 2 moles/litre. Dose rate: 372 rad/sec.)

V_1 = polymerization rate under voltage

V_2 = polymerization rate without voltage

M_1 = molecular weight of the polymer obtained by polymerization under voltage

M_2 = molecular weight of the polymer obtained by polymerization without voltage

Summing up what has been said before, when a direct voltage is applied to the electrodes, this results in a shifting of the anion-radical $\rightleftharpoons$ bi-radical equilibrium in the direction of the radical product; the adsorption of the bi-radical on the electrode reduces the probability of ring formation and leads to an increase in the concentration of the active centres. If the monomer formed is insoluble in the polymerization system, the polymer precipitated on the electrode will induce an essential change in the character of the voltage effect on polymerization kinetics.

It might be assumed that if the cations present in the polymerization system are stabilized (e.g., by forming complexes with the solvent), this results in a sharp rise of the anionic polymerization rate and is capable of changing the nature and degree of the voltage effect. Our experimental data (Fig. 7 and Table II) prove that if polymerization is carried out in trimethylamine (monomer concentration 2 moles/litre), the polymerization rate is considerably higher than under the same conditions in dimethylformamide solution. In the entire temperature range studied the voltage applied to the

Table II

Effect of direct voltage on the polymerization rate and on the molecular weight of the polymers in the radiation polymerization of acrylonitrile in triethylamine solution

Monomer concentration: 2 moles/litre. Dose rate: 372 rad/sec

No.	Temperature, °C	Voltage, V	Conversion, %	Polymerization rate, % · hour ⁻¹	M
1	-80	12	2.10	3.14	1420
2	-80	—	2.83	4.25	1710
3	-60	12	2.10	3.14	1470
4	-60	—	3.30	4.95	1686
5	-30	12	3.65	4.60	1512
6	-30	—	4.24	6.36	1700
7	-10	12	4.00	6.00	1620
8	-10	—	5.89	8.83	1750

electrodes reduces the polymerization rate and the molecular weight of the polymer formed.

Therefore, in order to check on the possibility of free radical polymerization mechanism at low temperatures, we carried out a series of experiments in which the polymerization of acrylonitrile was initiated in the presence of DPPH and without DPPH by irradiation with ultraviolet light (303–313 mμ). The experimental results show (Table III) that radical polymerization proceeds without DPPH even at -70°C at a rate which can be readily measured.

Table III

Polymerization of acrylonitrile initiated by ultraviolet (303–313 mμ) radiation in the temperature range between +20° and -70°C with and without DPPH

No.	Temperature, °C	Irradiation time, min.	DPPH concentration, mole/litre	Polymerization rate, % · hour ⁻¹
1	+20	240	—	1.14
2	0	180	—	0.28
3	-20	300	—	0.20
4	-36	300	—	0.11
5	-50	300	—	0.07
6	-60	300	—	0.04
7	-70	300	—	0.03
8	+20	300	10 ⁻³	—
9	-50	300	10 ⁻³	—
10	-70	300	10 ⁻³	—

Conclusions

1. We have shown that the polymerization of acrylonitrile initiated by γ -radiation at low temperatures mainly proceeds according to anionic mechanism because of the shifting of the anion-radical $\rightleftharpoons$ bi-radical equilibrium in the direction of the formation of active centres with ionic character. With an increase in the polymerization temperature, the equilibrium is shifted in the direction of active centres of radical character, and thus products with a radical nature become predominant in the initiation of the polymerization process.

2. As an effect of the direct voltage applied on the electrodes, the anion-radical $\rightleftharpoons$ bi-radical equilibrium is shifted in the direction of the formation of active centres of radical character in the entire temperature range. There is a simultaneous increase in the reaction rate which is probably the result of a concentration increase of the active centres due to the adsorption and stabilization (reduced probability of ring formation) of the bi-radicals on the electrode surface.

3. The deposited polymer layer hinders the diffusion of the monomer and of the active centres to the electrode, and thus it reduces the effect of voltage on the rate of polymerization.

4. Stabilization of the cations through complex formation with the solvent (trimethyl-amine) leads to an increase of the polymerization rate. In this case a direct voltage applied to the electrodes will reduce the polymerization rate.

Only the fate of free radical and anionic products have been studied in the present work. It has been assumed that, at least in first approximation, the effect of positive ions and that of electrons should be small in comparison with that of negative ions. Positive ions are considered to combine readily with electrons to give inactive centres.

SUMMARY

The polymerization of acrylonitrile, induced by γ -irradiation, has been studied in an electrical field, in the temperature range between -80° and $+20^{\circ}\text{C}$. It has been concluded from the experimental data that the polymerization is indicated at low temperatures by free anion-radicals. There is an equilibrium state between the anion-radical form and the bi-radical form; the actual state of this equilibrium is responsible for the anionic or free radical mechanism of the polymerization.

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THE PREPARATION AND PROPERTIES OF AN ACENAPHTHYLENE-DIVINYLBENZENE CATION EXCHANGE RESIN

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In recent years, ion exchange resins have found increasing application in various fields of industry, and accordingly, the requirements to be met by these resins have become more and more differentiated. The production of nuclear power, *e.g.* raises the problem of purifying waste waters contaminated by radioactive fission products. This problem requires the preparation of ion exchange resins whose ion exchange capacities and mechanical properties are not worse than those of other commercial resins, while at the same time their resistance to high-energy radiation must be essentially higher.

The styrene-divinylbenzene sulfocation exchange resin tolerates radiations up to -10^8 rad relatively well [1, 2]. This favourable feature is due to the presence of benzene rings in the polymeric skeleton *i.e.* to the presence of a system of conjugated double bonds. We presumed that acenaphthylene, containing two more conjugated double bonds in addition to those present in styrene, is likely to lend a still higher resistance to radiation to the ion exchanger prepared from it. It is known from the literature [3, 6] that the capacity of acenaphthylene cation exchange resins (6 mg-equivalents per gram) exceeds that of other known cation exchangers. At the same time, it is also known that this type of resin is not produced yet on industrial scale, and it has not found use in industrial practice. This can be explained by the fact that, in the copolymerization of acenaphthylene and divinylbenzene, 21% of the acenaphthylene applied remains unchanged, or is retained in the pearl polymer as a homopolymer. This homopolymer, together with the unaltered monomer, is removed from the pearl polymer on sulfonation. By this process the structure of beads is weakened, and the mechanical strength of the resin is impaired. Considering the importance of the above-mentioned problem and the fact that acenaphthylene is a cheap initial substance available in large quantities, we set ourselves the task to find such optimum conditions for the copolymerization of acenaphthylene and divinylbenzene which will allow the preparations of a cation exchange resin of adequate mechanical strength. The questions investigated in the present study are as follows.

- (a) Optimum conditions of the synthesis of an acenaphthylene-divinylbenzene copolymer, suitable for the preparation of a sulfocation exchanger.
- (b) Optimum conditions of the synthesis of copolymers of various degrees of porosity, suitable for preparing cation exchange resins with a high rate of ion exchange.
- (c) Conditions of the sulfonation of the copolymers prepared.
- (d) The properties of the cation exchange resins.

The applied experimental technique has been described in detail in earlier communications [7, 9].

Experimental results and their evaluation

It is known [10] that the conversion rates of polymerization are essentially affected by the employed conditions of copolymerization (nature of the initiator, temperature, *etc.*). Under the reaction conditions known from literature (100°C; benzoyl peroxide), in the copolymerization of acenaphthylene and divinylbenzene the diffusion of acenaphthylene molecules to the macro radicals is strongly inhibited, presumably due to rapid gel formation [11, 12]. Thus, the reaction proceeds at a very slow rate or it is completely stopped. We assumed that under suitable experimental conditions it would be possible to prepare a copolymer whose composition is identical with that of the initial monomer mixture.

The initiators investigated as regards their influence on the conversion of the copolymerization of the pair of monomers acenaphthylene and divinylbenzene, are listed in Table I.

The experimental data (Table I) show that of the initiators and initiator mixtures examined the best results have been obtained with tertiary butyl perbenzoate or a mixture of *t*-butyl perbenzoate and benzoyl peroxide. In the presence of *t*-butyl peroxide or cumyl peroxide, the conversion was insignificant, no pearl polymer was formed. This is readily understandable since at 100°C both initiators decompose at minimum rate [13]. When the polymerization was initiated by mixtures of benzoyl peroxide with *t*-butyl peroxide, or cumyl peroxide or *t*-butyl peracetate, the quantity of the material extractable from the copolymer was approximately the same as that extractable in the case of initiation solely benzoyl peroxide. These data clearly indicate that the synergic effect [10] observed in the peroxide-initiated polymerization of some monomers is absent in the copolymerization of acenaphthylene and divinylbenzene. This can be interpreted by the fact that acenaphthylene, notwithstanding its symmetrical structure, has high activity and thus readily reacts with both kinds of free radicals formed from the two peroxides, inhibiting in this way the recombination of the active centres prior to the chain-

Table I

*Effect of initiator on the appearance of copolymer
and on the amount of components which can be extracted from the copolymer*

No.	Initiator	Appearance of copolymer	Extractable components, %
1.	<i>t</i> -Butyl peroxide	oil	—
2.	Dicumyl peroxide	oil	—
3.	<i>t</i> -Butyl perbenzoate	pearl	2.3—3.3
4.	<i>t</i> -Butyl peracetate	pearl	8.6—11.3
5.	Benzoyl peroxide	pearl	8.9—11.3
6.	1 : 1 (w/w) mixture of benzoyl peroxide and <i>t</i> -butyl peroxide	pearl	14.6—15.0
7.	1 : 1 (w/w) mixture of benzoyl peroxide and dicumyl peroxide	pearl	11.4
8.	1 : 1 (w/w) mixture of benzoyl peroxide and <i>t</i> -butyl perbenzoate	pearl	3.7—4.4
9.	1 : 1 (w/w) mixture of benzoyl peroxide and <i>t</i> -Butyl peracetate	pearl	10.8—18.1

initiating action. The validity of this interpretation follows from an analysis of Fig. 1 where the courses of the reactions initiated by *t*-butyl benzoate, benzoyl peroxide and by the mixture of both peroxides are presented.

It appears from a comparison of Curves 1 and 2 in Fig. 1 that the initial rate of copolymerization initiated by benzoyl peroxide essentially exceeds that observed in the polymerization initiated by *t*-butyl perbenzoate. When benzoyl peroxide is used for initiation, an insoluble copolymer is formed only after the elapse of 8 hours. At the same time, conversion was 45% in the first, and 96% in the second case.

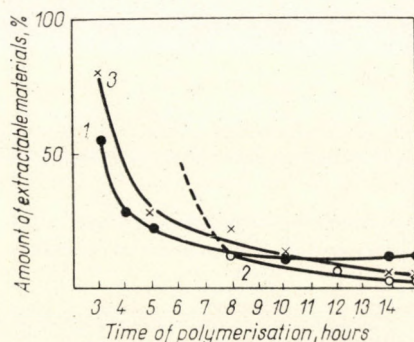


Fig. 1. Contents of soluble substances in the acenaphthylene-divinylbenzene copolymers as a function of the time of polymerization 1: benzoyl peroxide; 2: *t*-butyl perbenzoate; 3: mixture of benzoyl peroxide and *t*-butyl perbenzoate

Curve 3 runs between Curves 1 and 2; the shapes of the curves clearly reflect the course of the initiation process. In the first hours of the reaction, predominantly the radicals formed from benzoyl peroxide are responsible for the initiation of polymerization. It follows from this that the initiators do not react with each other in this case.

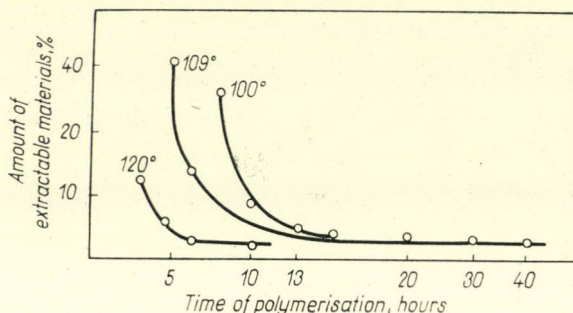


Fig. 2. Course of the pearl polymerization process of the pair of monomers acenaphthylene and divinylbenzene at 100, 109 and 120°C

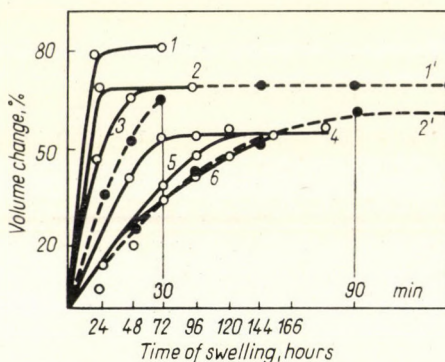


Fig. 3. Kinetics of the swelling of an acenaphthylene-divinylbenzene copolymer prepared at 109°C. 1: time of polymerization 8 hours; 2: 10 hours; 3: 12 hours; 4: 14, 20 hours; 5: 30 hours; 6: 41 hours; 1': 10, 12 hours; 2': 14, 20, 30 and 40 hours. From 1 to 6: not extracted; 1' and 2': extracted

The influence of temperature on the pearl polymerization of acenaphthylene and divinylbenzene was studied at 100° and 120° C.

It is seen (Fig. 2) that higher temperatures result in higher polymerization rates. For the formation of an insoluble copolymer, 3 hours were required at 120°, while 6 hours were needed at 109° and 8 hours at 100° C.

Sweilling tests of the prepared copolymers have shown that shorter polymerization periods result in stronger swelling power of the copolymer, and the limit values of swelling are attained more rapidly (Fig. 3).

On comparing Curves 4, 5 and 6 in Fig. 3 we find that copolymers polymerized for various periods show the same swelling limit values, though their swelling rates are different. However, if the same copolymers had been previously extracted with benzene, their swelling rates were also identical (Curves 1' and 2' in Fig. 3). Taking into account these results and the observation that the amount of extractable substance remains constant after a given period of time, the conclusion can be drawn that at 109° C copolymerization

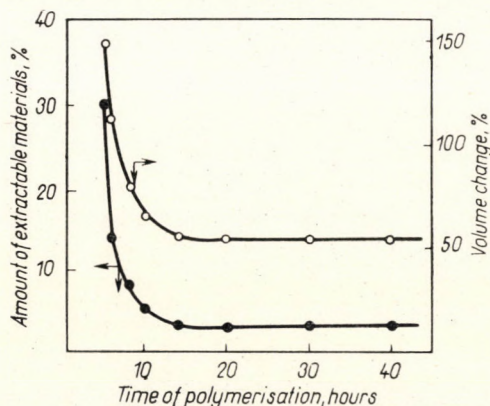


Fig. 4. Kinetics of the copolymerization of acenaphthylene and divinylbenzene at 109° C.

is completed in 14 hours, and subsequently only the homopolymerization of acenaphthylene is continued. The density of distribution of the polymer chains is increased by the homopolymer formed in the cross-linked structure, and thus, on swelling, the diffusion of solvent molecules into the inside of the pearl polymer is rendered more difficult (Fig. 4).

The presented experimental data show that the conversion is decisively affected by the initial rate of copolymerization. Optimum effects can be attained by employing *t*-butyl perbenzoate as initiator. No synergic effect can be observed when the polymerization of the pair of monomers acenaphthylene-divinylbenzene is initiated by peroxide mixtures.

Several methods are known for the preparation of macroporous ion exchanger skeletons [14–19].

The porous acenaphthylene-divinylbenzene copolymer has been prepared in the presence of *n*-nonane. In this solvent the monomers are readily dissolved while the copolymer does not swell. On varying the ratio of the diluent and cross-linking component, the appearance of copolymers changed from a transparent glassy state to an opaque, porcelain-like structure (Table II, and a, b, c in Fig. 5).

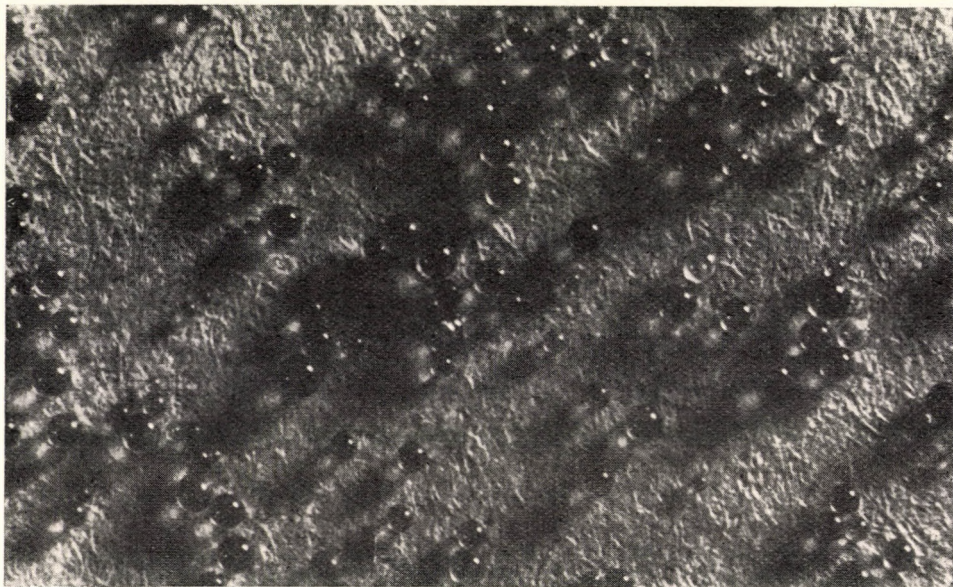
The study of the optimum conditions for the production of porous copolymers required a quick method of measuring the degree of porosity.

Table II

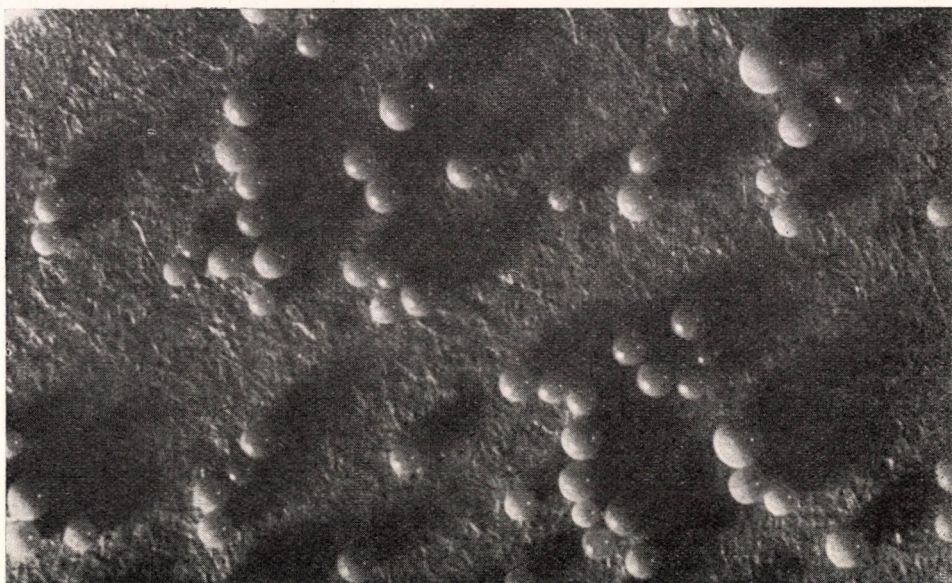
Properties of acenaphthylene-divinylbenzene phaneroporous pearl-copolymers depending on the degree of cross-linking and the quantity of inert solvent

No.	Solvent	Degree of cross-linking	Apparent density	External appearance
1	20	24.4	0.617	Transparent beads
2	30	24.4	0.520	Slightly opalescent beads
3	40	24.4	0.430	Opalescent beads
4	50	24.4	0.400	Opalescent beads
5	20	30.6	0.620	Transparent beads
6	40	30.6	0.330	Opalescent beads
7	50	36.3	0.295	Opalescent beads
8	60	41.4	0.288	Opalescent beads

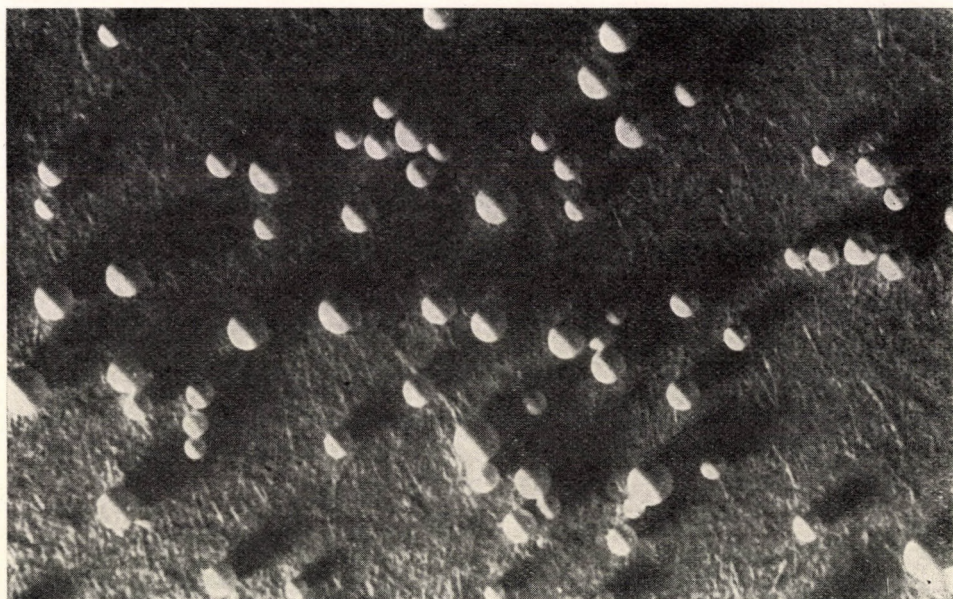
Several such methods have been reported in the literature, however, these are rather complicated [20, 21] and require special instruments. Thus, under the conditions prevailing in a conventional synthetic laboratory, such measurements would encounter difficulties. Therefore, a method has been evolved for the quick measurement of the degree of porosity of polymers. This is based on the following principle. The volume increase of the copolymer and the quantity of solvent taken up are measured in a swelling solvent and in a non-



(a) common copolymer



(b) semi-microporous copolymer;



(c) phaneroporous copolymer

Fig. 5. External appearance of acenaphthylene-divinylbenzene copolymers

swelling one. Toluene and cyclohexane were used as the swelling and non-swelling solvents, respectively.

In Figures 6 and 7, the volume changes and solvent take-up capacities of the copolymers are plotted against the degree of cross-linking and the quantity of solvent used. It appears from Curves 1 and 2 that, on raising the quantity of inert solvent and the divinylbenzene content of the copolymer,

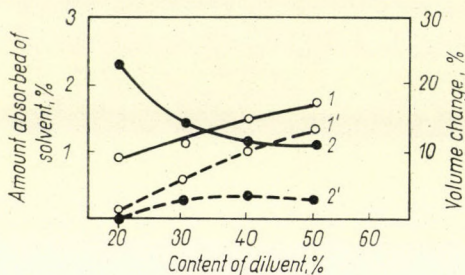


Fig. 6. Solvent absorption capacity and volume of the copolymer as a function of the quantity of inert solvent used

Cross-linking: 24.4%

Curve 1: Absorption of toluene; Curve 2: Volume changes in toluene; Curve 1': Absorption of cyclohexane; Curve 2': Volume change in cyclohexane

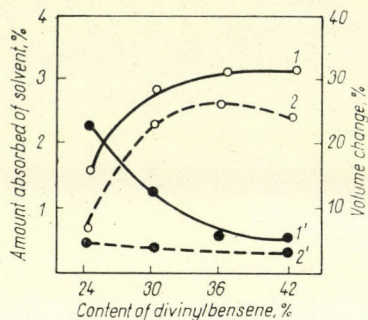


Fig. 7. Solvent absorption capacity and volume of the copolymer as a function of the degree of cross-linking. The monomer mixture contained 50% solvent

Curve 1: Absorption of toluene; Curve 2: Absorption of cyclohexane; Curve 1': Volume change in toluene; Curve 2': Volume change in cyclohexane

also the amounts of toluene and cyclohexane taken up by the copolymer increase. However, the uptake of cyclohexane begins to decrease at a cross-linking of 38%. On increasing the degree of cross-linking and the amount of inert solvent, the relative volume increase in toluene of all copolymers examined show a decreasing trend (Curves 1'), while cyclohexane gives rise to a slight swelling of the copolymers (Curves 2'). These experimental facts indicate that the macroporosity of the copolymer is essentially affected by both factors: the degree of cross-linking and the quantity of inert solvent applied.

The volume of toluene taken up by the copolymer (Q_T) is always higher than the volume of absorbed cyclohexane (Q_{ch}), and the copolymer undergoes also in cyclohexane a slight but measurable volume change. These observations lead to the conclusion that the porosity of the copolymer is not homogeneous, i.e. pores of different volumes exist in the copolymer.

Pores can be classified in three groups:

1. Macropores which are capable of absorbing both toluene and cyclohexane without any volume change. (The volume of such macropores will be denoted by V_{macro})

2. Micropores (whose volume denoted by V_{micro}) which appear in the polymer due to swelling on the effect of toluene.

3. Pores of medium size (whose volumes will be denoted by V_{med}) which absorb both toluene and cyclohexane, and undergo volume increase in both solvents. (Their volume changes are conditionally denoted both in toluene and in cyclohexane by V_{med} for the sake of simplicity.)

The quantity of toluene absorbed by the porous copolymer is equal to the combined sum of pores in the swollen copolymer:

$$Q_T = V_{\text{macro}} + V_{\text{med}} + \Delta V_{\text{med}} + V_{\text{micro}} \quad (1)$$

Since cyclohexane is absorbed only by the macropores and the pores of medium size, the volume of absorbed cyclohexane will be:

$$Q_{\text{ch}} = V_{\text{macro}} + V_{\text{med}} + \Delta V_{\text{med}} \quad (2)$$

The volume increase of the copolymer in toluene is due to the volume increase of pores of medium size and to the formation of micropores, while in cyclohexane only the volume increase of the copolymer is the responsible factor. Thus, the following equations can be written:

$$V_{\text{med}} + V_{\text{micro}} = V_T - V_0 \quad (3)$$

$$V_{\text{med}} = V_{\text{ch}} - V_0 \quad (4)$$

where V_0 is the volume of the dry copolymer, while V_{ch} and V_T denote the volumes of copolymers swollen in cyclohexane and toluene, respectively.

Consequently, the total volume of micropores can be calculated from Eq. (5), and that of the macropores and pores of medium size together from Eq. (6) as follows:

$$V_{\text{micro}} = Q_T - Q_{\text{ch}} \quad (5)$$

$$V_{\text{macro}} + V_{\text{med}} = Q_{\text{ch}} - \Delta V_{\text{med}} \quad (6)$$

The solvents employed in the present measurements are also absorbed by micropores and pores of medium size. Thus, it is impossible to calculate separately the volumes of these pores by the above method. Therefore, the degree of phaneroporosity is expressed by the formula

$$Q_{\text{ph}} = \frac{V_{\text{macro}} + V_{\text{med}}}{Q_T} \quad (7)$$

where Q_{ph} is the specific phaneroporosity, i.e. the volume of phaneropores referred to the volume attained on complete swelling.

The curves shown in Figs 8 and 9 were calculated and constructed by means of the above equations. These curves correctly indicate the role of the degree of cross-linking and of the quantity of inert solvent in the formation of porous copolymers. The increase of the quantity of the inert solvent and of divinylbenzene (Fig. 8) results in the rise of the integral degree of porosity and, within this, that of the number of macropores, while the number of micropores diminishes with the increase of the volume of solvent.

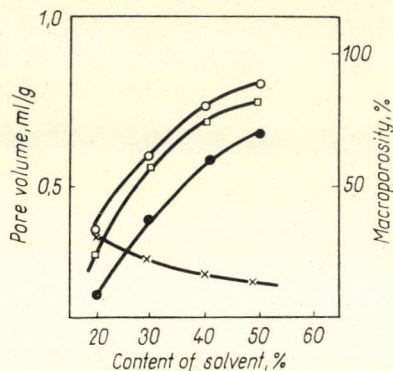


Fig. 8. Degree of porosity of the copolymer as a function of the quantity of inert solvent used (Divinylbenzene content of the copolymers: 24.4%)

x—x—x: volume of micropores, ml/g; — — —: volume of macropores and of medium-size integral pores; o—o—o: integral volume of pores, ml/g; □—□—□: macroporosity, %

The situation may also occur (Fig. 9) when the degree of cross-linking attains such a high level that the amount of inert solvent is unsatisfactory, and thus the integral volume increase of the pores of the copolymer is due to the increase of the total volume of micropores. For the production of a porous resin containing 38% of divinylbenzene, an amount of inert solvent exceeding 50% is necessary. On the basis of the experimental data it is justified to state that the degree of porosity of the copolymer depends on the degree of cross-linking and on the nature of inert solvent employed. For the production of phaneroporous acenaphthylene-divinylbenzene copolymers, at least 24 to 36% of divinylbenzene and 45 to 60% of *n*-nonane are required.

In the sulfonation of the copolymer, the sulfonating action of the following substances have been examined: 20% oleum, 60% oleum monohydrate, and chlorosulfonic acid. For the sulfonation of the copolymer, 20% oleum proved to be the agent of optimum effect. The properties of the obtained cation exchange resin are listed in Table III. It appears from these data that the properties of the resins depend to a great extent on their content of divinylbenzene. Thus, an increase of the degree of cross-linking, *i.e.* of the density of the copolymer may lead to the decrease of swelling capacity which eventually results in a decrease of the exchange capacity of the resin. With the rise of the

degree of cross-linking, also the resistance to nitric acid, together with the resistance to hydrolysis increase, and the mechanical strength slightly improves.

In Table III, the properties of the ion exchange resin KU-2 (a styrene-divinylbenzene resin most widespread in practice) [23] are compared with those of the resin prepared by us. It can be seen that the capacity of the latter exceeds that of resin KU-2, while the other physico-chemical indices differ only to a slight extent.

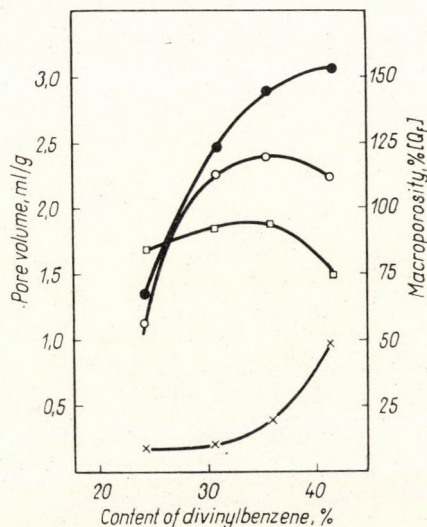


Fig. 9. Influence of the quantity of divinylbenzene used on the total volume of pores (Concentration of inert solvent: 50%)

x—x—x: volume of micropores, ml/g; o—o—o: integral volume of macropores and of medium-size pores ml/g. —.—: integral volume of all pores, ml/g □—□—□: degree of macroporosity, %

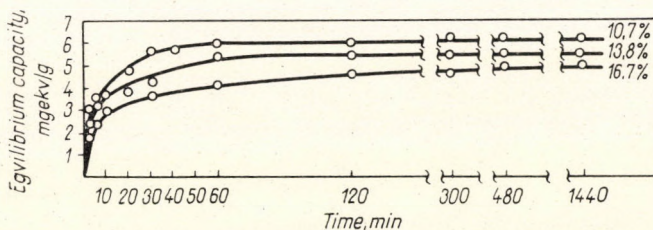


Fig. 10. Kinetics of the ion exchange of acenaphthylene-divinylbenzene cation exchange resins of various degrees of cross-linking

The rate of ion exchange depends on the degree of cross-linking, since this latter determines the capability of the resin to swell which is finally responsible for the rate of diffusion of the ions into the inside of the resin particles. *E.g.*, only one hour is required for the 100% saturation of a resin cross-linked to 10.7%. Resins of 13.8 and 16.7% cross-linking are completely saturated in 5 and 8 hours, respectively (Fig. 10).

Table III

Physico-chemical properties of the cation exchange resin KU-4

No.	Degree of cross-linking, %	Oxidizability, O ₂ mg/g	Dynamic capacity, meq./g	Chemical 5N		Stability 1N 10%		Resistance to thermal hydrolysis,		Oxidizability of aqueous filtrate, after heat stability test	Mechanical strength, %
				NaOH	H ₂ SO ₄	HNO ₃	H ₂ O ₂	NaOH	CaCl ₂		
1	10.70	1.85	1239.9	100	100	73.4	100	96.5	91.0	5.17	92.0
2	13.80	1.60	1610.2	98	98	82.7	100	100.0	97.6	4.76	92.0
3	16.70	1.36	1560.0	98	98	95.0	100	100.0	98.5	4.00	94.5
4	KU-2—10*	1.5	1350.0	100	100	100.0	100	100.0	100.0	0.00	96.0

The porous copolymer was sulfonated with 20% oleum for 5 hours at 85—90°C. On completing the sulfonation, the resin was separated from the mother liquor, and washed with distilled water until neutral. During washing, the phaneroporos "porcelain" resin did not crack, and the beads remained intact. Data on our sulfonation experiments are summarized in Table IV.

From Table IV it appears that with the rises of the porosity of the resin (Experiments 1—4, where the amount of inert solvent was constant, but the content of divinylbenzene was increased) and in the experiments where the

Table IV

Properties of the porous cation exchange resin KU-4

No.	Divinylbenzene, %	Solvent, %	Stat. capacity, meq./g		Spec. volume 0.1 N	Dynamic capacity, meq./g		Mechanical strength, %
			0.1 N	0.1 N		0.1 N	0.1 N	
			NaOH	CaCl ₂	NaOH and CaCl ₂ ml/g	NaOH	CaCl ₂	
1	24.4	50	4.02	3.75	2.8	1430	1340	98.6
2	40.6	50	3.78	3.8	3.2	1180	1180	98.0
3	36.3	50	3.61	2.86	3.5	1030	814	86.0
4	41.4	50	5.7	5.34	3.85	1470	1370	93.0
5	24.4	20	5.46	5.25	1.8	3000	2920	94.0
6	24.4	30	4.9	4.8	2.47	1970	1940	98.0
7	24.4	40	4.5	4.08	2.6	1730	1570	93.0
8	24.4	50	4.02	3.75	2.8	1430	1340	93.6
9	30.6	20	0.42	0.3	—	—	—	—
10	30.6	40	4.7	4.1	3.5	1340	1170	95.2
11	30.6	50	3.78	3.8	3.2	1180	1190	98.1

divinylbenzene content of the resin was kept constant and the amount of inert solvent was varied (Experiment 5—7, 8 and 10—11), the capacity diminished, and was markedly different from the theoretical capacity values.

This can be explained by some essential alterations which take place with the increase of porosity in the inner structure of the copolymer beads. Instead of a more or less uniform density of the beads (a characteristic feature of common copolymers), pores and voids vary at random with more compact places. The increase of the degree of porosity leads to an increase of the density of the non-porous parts of the pearl polymer, whether it has been due to the

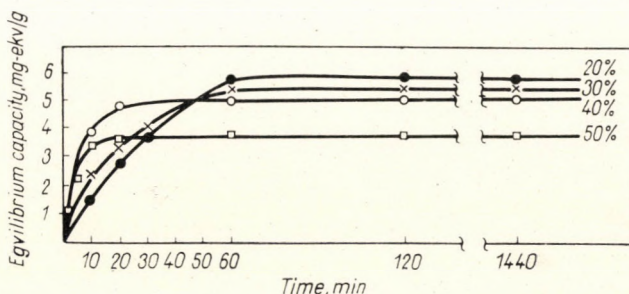


Fig. 11. Kinetics of the ion exchange of porous resins prepared in the presence of various quantities of inert solvent. (Divinylbenzene content 24%)

increase of divinylbenzene content or to the inert solvent, consequently in all probability only the pore walls or the parts lying near the walls are sulfonated, and this obviously results in a higher capacity of the resin.

It also appears from Table IV that the mechanical strength of porous resins does not exceed that of common resins of low degree of cross-linking. However, one must take into account the advantage offered by porous resins, namely, that on swelling or on changes of the pH they undergo but a slight volume change, and the beads do not crack. This is just the reason why the bead polymers may be washed with water right after sulfonation, without any risk of cracking.

The kinetics of ion exchange on porous resins are presented in Figs 11 and 12. It is seen that with the rise of the degree of macroporosity, the rate of ion exchange of the resins increases. In the series where the amount of inert solvent was kept constant, the resin cross-linked to 36.3% ($Q_{PH} = 97\%$) had the highest ion exchange capacity (Experiments 1—4 in Table IV). Saturation was complete in ten minutes.

In the series where the amount of divinylbenzene was kept constant (Experiments 5—8 in Table IV), the maximum rate of ion exchange (10 minutes) was shown by the resin prepared with 50% of inert solvent.

It appears from these data that in the case of porous resins, a fair resistance to the effect of pH fluctuation and the high ion exchange capacity, is accompanied by a hazard of capacity decrease.

The resistance to radiation effects was investigated in co-operation with the *Kurchatov Research Institute for Nuclear Energy*. The detailed examination of the resistance to radiation effects of the acenaphthylene-divinylbenzene resin KU-4 is in progress in the Physico-chemical Research Institute of the USSR, under the direction of Academician K. V. CHUMTOV [23].

The capacities of resins of various degrees of cross-linking prior to and after irradiation are shown in Table V.

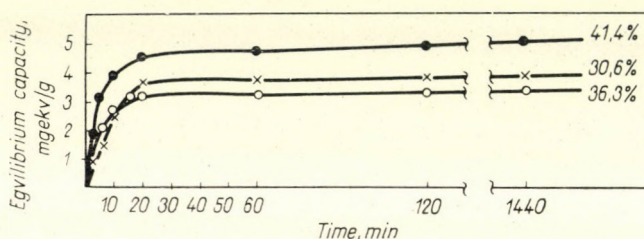


Fig. 12. Kinetics of the ion exchange of porous resins of various degrees of cross-linking (Content of inert solvent 50%)

To facilitate the evaluation of the experimental results, the radiation resistance of the cation exchange resin KU-2 (made of styrene-divinylbenzene) is also given in the Table on the basis of literature data.

From Table V it appears that the radiation resistance of the resin increases with the degree of cross-linking. With more advanced cross-linking *i.e.* at a higher density of the resin, the degree of solvation of the $-\text{SO}_3\text{H}$ groups and consequently the possibility of secondary reactions with the $\text{OH}-$

Table V

Comparison of the resistance to radiation
of the cation exchange resins KU-2 and KU-4

No.	Type of resin	Degree of cross-linking, %	Integral dose, 10^2 Mrad	Stat. capacity eq./g		Decrease of capacity, %
				prior to irradiation	after	
1	KU-2	8.0	1.92	4.90	2.45	50.0
2	KU-2	12.0	1.92	4.90	2.50	49.0
3	KU-2	16.0	1.92	4.75	2.60	45.0
4	KU-4	10.7	2.00	5.90	4.96	16.0
5	KU-4	13.8	2.00	5.45	4.68	14.2
6	KU-4	16.7	2.00	4.96	4.54	8.6

or H^+ ions formed in the radiolysis of water decrease. These reactions would result in the cleavage of the sulfo groups from the polymer skeleton. It is also seen from the data that while cation exchange resins of type KU-2 lose 45 to 50% of their original capacity on irradiation, the KU-4 resin prepared by us loses only 15%. Thus, the resistance to radiation effects of the latter resins is three times as high as that of KU-2 ion exchangers.

SUMMARY

It has been found that the conversion in the copolymerization of acenaphthylene and divinylbenzene depends on the conditions of the reaction (type of initiator, its concentrations and temperature).

A copolymer suitable for the preparation of a sulfocation exchange resin (with an extractable content of 3%) can be prepared at 109°C in 14 hours, using 1% of *t*-butyl perbenzoate (referred to the weight of the monomer mixture) as initiator.

Acenaphthylene-divinylbenzene copolymers of phaneroporos structure have been prepared.

A new method has been evolved for the quick measurement of the degree of porosity of the copolymers. It was found by this method that the degree of porosity depends on the ratio of inert solvent and the cross-linking component used. Phaneropores are formed in the copolymer only at a definite ratio of inert solvent to cross-linking component.

Copolymers of the required mechanical strength and degree of porosity are obtained at degrees of cross-linking of 24–36% and in the presence of 40 to 50% inert solvent.

It has been shown that porous copolymers can be sulfonated less readily than the common, non-porous copolymers, and the degree of sulfonation decreases with increasing porosity.

The resistance to heat and chemical agents, mechanical strength, and the resistance to radiation of the new sulphocation exchange resins have also been examined. The first three parameters of the resin differ only slightly from those of the resin KU-2, while its radiation resistance has been found three times as high.

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ON THE CROSS-LINKING MECHANISM OF EPOXY COMPOUNDS

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The practical application of epoxy resins has a past of more than twenty years, and today these resins find widespread use in various fields of industry. Nevertheless, the cross-linking process, which is the theoretical basis of processing, has not been fully clarified up to the present, and owing to the characteristic complexity of cross-linking systems, this field of investigation poses many difficult problems for researchers.

The chemical mechanism of the elementary processes occurring at the beginning of cross-linking has been known for a relatively long time. In the early fifties, the reactions of the epoxy group were studied by several authors.

They used monofunctional model compounds (unsuitable for cross-linking) to investigate by traditional methods of analysis all those main reactions which occur in the synthesis of epoxy resins and in their cross-linking effected with various reagents.

The work of SHECHTER and WYNSTRA [1, 2], FISCH and HOFMANN [3], NARRACOT [4], DEARBORN [5], GREENLEE [6], *etc.* must be considered without doubt fundamental, since even our present knowledge as regards the elementary processes is based on this work. These researches were instrumental in showing that in the cross-linking of the chief representatives of epoxy resins — the diepoxides on bisphenol A basis — three types of cross-linkages may be formed depending on the reagent used:

in cross-linking with amine: $C-N-C$



in cross-linking with anhydride: $C-O-C$



in catalytic cross-linking: $C-O-C$

* Candidate of Chemical Sciences, the dissertation was made in the *Mendeleev Institute for Chemical Technology* (Moscow) under the leadership of Prof. M.S. AKUTYN.

It is evident, however, that experiments with non-cross-linking model substances could not cover every aspect of the whole complicated process which, as it is well known, involves the interaction of chemical, physicochemical and physical processes. They could not furnish information, *e.g.*, on such important problems as the relation between the network structure and the properties, afterreactions, *etc.*

The application of modern physicochemical methods in the field of epoxy research began in the late fifties. Among these methods, IR spectroscopy has a prominent place. The first publications by DANNENBERG and co-workers [7-9] appeared in 1958-60, and were followed later by those of LISSNER [10] and PIROZHNAJA [11]. These authors investigated the changes of the epoxy and other functional groups during the cross-linking reaction by IR spectroscopy. These works showed the correctness of the reaction mechanism that had been established earlier by chemical methods. Further development of these methods resulted in recent years in two publications, in which also the kinetics of the cross-linking process were followed by IR spectroscopy, and quantitative conclusions were drawn on the conversion of the epoxy groups. One of these publications is the work of MORIMOTO and co-workers [12], who effected the cross-linking with amines, and the other that of BLAGONRAVOVA and co-workers [13], who used boron trifluoride diethyl etherate as cross-linking reagent.

Of the methods used recently for the investigation of the cross-linking reaction of epoxy resins, the work of KOVARSKAJA, AKUTYN and co-workers should be mentioned [14-17]. These authors obtained useful information by recording the thermomechanical curves, and checked the degree of cross-linking by the determination of the high elasticity-modulus at equilibrium.

Though development in methodics has been of great help in overcoming the difficulties presented by the complex character of the investigated process, the evaluation of experimental results is rendered difficult by the further fact that epoxy compounds are complicated substances whose chemical structures cannot be always unequivocally defined.

The fundamental concept of the present work was that the investigation by more advanced methods of simple, well defined diepoxides of regular structure, which are at the same time capable of cross-linking, may furnish additional information.

Therefore, the cross-linking process was studied with chemically pure model compounds, and some properties of the cross-linked product were investigated.

Bisphenol A-diglycidyl ether, the basic compound of industrial epoxy resins was selected as model compound, and aliphatic diglycidyl ethers, which have become known in recent years, as reactive diluents.

The study of this latter group of compound is interesting also owing to the fact that aliphatic diglycidyl ethers (used in practice as flexibilizers) participate as components of epoxy systems in the cross-linking process, however, no systematic investigation on the cross-linking of aliphatic diglycidyl ethers has been reported so far.

Model compounds and experimental methods

Aliphatic diglycidyl ethers of various chain length (C_6-C_{12}) and bisphenol A-diglycidyl ether were synthesized. The diglycidyl ethers used in this work and their characteristic data are listed in Tables I and II.

Table I

Compound	Short name	Symbol
Bis-(2,3-epoxypropyl) ether	Diglycidyl ether	DG
Ethyleneglycol-di(2,3-epoxypropyl) ether	Ethyleneglycol diglycidyl ether	EDG
1,3-Propyleneglycol-di-(2,3-epoxypropyl) ether	Propyleneglycol diglycidyl ether	PDG
1,6-Hexamethyleneglycol-di-(2,3-epoxypropyl) ether	Hexamethylene-glycol-diglycidyl ether	HDG
4,4'-Isopropylidene-phenol-di-(2,3-epoxypropyl) ether	Bisphenol A diglycidyl ether	DDG

Table II

Diglycidyl ether	Epoxy equivalent		Boiling point, °C/torr	Refractive index, 20 °C	Viscosity, (cP) 20 °C	Melting point, °C	Spec. weight 20 °C
	Calcd.	Found					
DG	65	68—69	90°/9	1.4461	4.2	—	1.119
EDG	87	89—90	122°/0.7	1.4535	6.3	—	1.121
PDG	94	98—100	127°/0.6	1.4528	8.0	—	1.089
HDG	115	118—119	132°/0.2	1.4550	9.8	—	1.030
DDG	170	171—172	232°/0.19	1.5711	—	41.8	—

Diglycidyl ether, the first member of the series, was prepared from epichlorohydrin in the presence of boric acid with dimethylaniline catalyst.

The other aliphatic diglycidyl ethers were synthesized from epichlorohydrin and the corresponding diols, in the presence of boron trifluoride-etherate catalyst.

Bisphenol A-diglycidyl ether was prepared from low molecular weight epoxy resin by vacuum fractionation.

The following distilled, chemically pure aliphatic amines were used as cross-linking agents:

ethylenediamine (EDA) and hexamethylenediamine (HMDA), which have an identical number of functional groups, but differ in chain-length;

diethylenetriamine (DETA) and triethylenetetramine (TETA), which form cross-linked structures with identical chain-length between the nodes of the network, but differ from each other in secondary amine group content.

The reaction components were mixed in stoichiometric ratio, and determinations were made within the temperature range 20–60°, in each case at 4 different temperatures.

By systematic combination of the starting materials, cross-linked systems of different chemical structures were obtained.

Infrared spectroscopy

The course of cross-linking was followed by IR spectroscopy. A ZEISS UR 10 Type instrument, equipped with a special, thermostated cell holder was used for the investigations. The progress of the reaction was indicated by a change in the concentration of the epoxy group that is to say by observing the optical density change of the epoxy band. The reaction components were mixed and placed into the cell, and the spectrum of the absorption band was recorded, at the given temperatures at certain intervals (10 min). The spectrum was obtained at the wave number 4520 cm^{-1} .

Physicomechanical measurements

The progress of cross-linking in the model mixtures was also checked on the basis of changes in the physicomechanical properties of the system. Curing, leading from the liquid to the solid state through a gel condition, was assumed to proceed in two stages. The first stage, ranging from the start of the process to the beginning of gel formation, is characterized by a change in the viscosity of the reaction mixture. The second stage, from the beginning of the rubber-elastic state up to solidification, is characterized by a change of the value of reversible deformation. Viscosity in the first stage was measured periodically at 10 minutes intervals with a Höppler Rheoviscosimeter and plotted against time. The decrease in reversible deformation in the second stage was determined with a Höppler Konsistometer. Measurements were commenced, when the sample placed into the metal cell attained a rubber consistency as a result of cross-linking, and repeated each 10 minutes, subjecting the sample for 10 seconds to a pressure load of 5 kg/cm^2 . The deformation values obtained at equal intervals were plotted against time. The curves are characteristic of the last stage of cross-linking under the given experimental conditions.

Thermomechanical measurements

Thermomechanical measurements were carried out on samples of the obtained cross-linked products with the double purpose to characterize these products, and to detect possible subsequent cross-linking processes. The thermomechanical curves were recorded in the usual way with a Höppler Konsistometer at a load of 10 kg/cm^2 and a heating rate of 1 °C/min. After solidification and before the thermomechanical measurements the samples were subjected to various aftereffects. Some of the samples allowed to stand at 25°C for 48 hours, 14 days and 30 days, respectively, after solidification, to observe the effect of the time factor. The rest of the samples was exposed to heat treatment for 6 hours at 100°C, after standing for 48 hours and 30 days, respectively, from the time of solidification.

Derivatography

The cross-linked samples were tested also by derivatography. The aim of these tests was a qualitative comparison of the products of different structures obtained by different methods of cross-linking, from the point of view of thermal stability, and the detection of subsequent cross-linking by means of observing possible thermal effects. In consideration of the aspects of practical applicability, the derivatographic tests were made in air stream. The heating program was 6°C/min., and the upper temperature limit was 600°C.

Discussion of the results

During our experiments all combinations of the previously mentioned diepoxides and polyamines were studied at various temperatures. The aim of the work was to obtain information about the influence of the starting components and temperature on the reaction rate and degree of conversion.

The kinetic curves recorded by IR spectroscopy show, in general, the character of the course of the reactions to be similar in all cases investigated. The process starts without any considerable induction period, it has self-accelerating character, and it markedly slows down after 60–70% of the epoxy groups have reacted. Maximum reaction rate is observed, in general, at a conversion of 25–50%. The reaction rate and degree of conversion are very sensitive to the reaction conditions. In the different experiments, the conversion varied between 50 and 100%.

In order to evaluate the reaction rate, expediently the half-period of the process, that is to say the time during which 50% of the epoxy groups have reacted, was chosen as the basis for comparison. Half-periods measured in the experiments are listed in Table III. These data show that of the three investigated factors, the diglycidyl ether component exerts the decisive effect on the course of the reaction, in other words, under otherwise identical conditions the diglycidyl ethers determine certain required reaction times.

This is also the reason why the reaction could be examined in a relatively wide temperature range (20–60°C) only in the case of ethyleneglycol-diglycidyl ether; with the other diglycidyl ethers the excessive violence or slowness of the reaction made work at certain temperatures impracticable. The influence of the structural differences of diglycidyl ethers on the kinetics of cross-linking is shown in Fig. 1. From this the following conclusions may be drawn: among the aliphatic diepoxides, diglycidyl ether reacts at the highest rate to be followed by ethyleneglycol, propyleneglycol and finally hexamethyleneglycol diglycidyl ethers. This shows that the reactivity of aliphatic diglycidyl ethers can be arranged unequivocally in an order, according to which the reactivity decreases with the increase of the chain length.

Moreover, the experimental results show that the degree to which the reaction will proceed *i.e.* the conversion of the epoxy groups, depends also fundamentally on the chemical structure of the diglycidyl ether used; under the given reaction conditions illustrated in the diagram, this value varies between 80 and 100%. As it is to be expected, the aromatic member of the diepoxide series studied, bisphenol A-diglycidyl ether, presents a different behaviour. As shown in the figure, this compound has a very high reactivity at the beginning. However, the reaction slows down considerably after about 50% of the epoxy groups have reacted, and the total conversion is relatively poor. The low conversion as compared to the relatively high reaction rate of

Table III

Diglycidyl ether	Amine	20 °C	30 °C	35 °C	40 °C	50 °C	60 °C
DG	EDA	134	55	36	27	—	—
	DETA	114	56	38	31	—	—
	TETA	180	92	55	33	—	—
	HMDA	152	88	60	34	—	—
EDG	EDA	170	65	47	22	—	—
	DETA	150	68	56	46	22	12
	TETA	250	108	90	61	—	—
	HMDA	230	120	85	51	—	—
PDG	EDA	—	—	—	—	—	—
	DETA	285	142	95	73	—	—
	TETA	—	—	—	81	—	—
	HMDA	—	—	—	55	—	—
HDG	EDA	—	203	—	84	65	39
	DETA	—	255	165	110	—	—
	TETA	—	200	—	136	59	35
	HMDA	—	205	—	67	59	41
DDG	EDA	240	105	—	41	26	—
	DETA	217	93	—	48	24	—
	TETA	305	105	—	54	28	—
	HMDA	225	100	—	45	23	—

bisphenol A-diglycidyl ether seems to be indicative of the fact that the aromatic ring constitutes a steric hindrance to cross-linking.

The influence of the amines, the other components of the system, on the course of the reaction was also studied. Exact relationships, similar to those found for diglycidyl ethers, could not be established. It is to be assumed

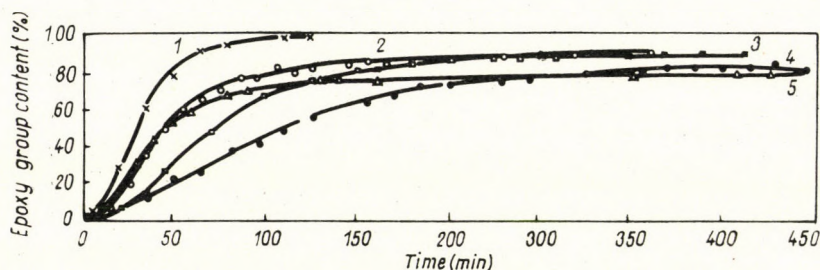


Fig. 1. Kinetical curves of the cross-linking of various diglycidyl ethers as determined from the change in optical density of the epoxy groups (Cross-linking: DETA, 40 °C)

1 — DG; 2 — EDG; 3 — PDG; 4 — HDG; 5 — DDG

that differences in the structure of the amines investigated influence but to a smaller degree the cross-linking process, and thus, only trends could be observed.

Nevertheless, the evidence of numerous experiments permits to conclude that the rate of cross-linking increases with the decrease of both the chain length and the secondary amine group content of the amine compound.

On the basis of the curves plotted at various temperatures, the overall activation energy of the process was determined by a graphical method, to obtain a value of 12–17 kcal/mole.

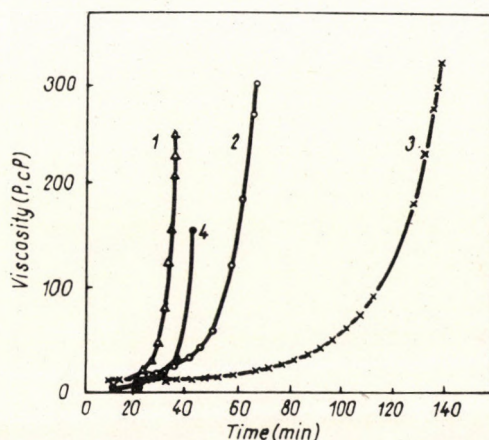


Fig. 2. The change in viscosity of the mixtures of various diglycidyl ethers and DETA in the initial stage of cross-linking (Cross-linking: 40°C) -
1 - EDG; 2 - PDG; 3 - HDG; 4 - DDG

Parallel with the IR investigations, the process of cross-linking was also examined by a combined method of viscosity and deformation measurements. It was found that the physicomechanical behaviour of the macroscopic system reflects, well indeed, the findings obtained by IR spectroscopy.

The viscosity curves plotted for the first stage of the cross-linking process present viscosity values which increase very slowly in the beginning, and then very rapidly. This jump is connected with the beginning of gel formation. Therefore the perpendicular drawn to the abscissa from the intersection of the tangents traced to the lower and upper branches of the curve will give the gelation time. The gelation time was considered by us as a characteristic value of the viscosity curves. This value, besides having a practical importance in the processing of epoxy resins, may serve as a basis of comparison of the rates of cross-linking processes.

Fig. 2 shows, for various diglycidyl ethers, the curves of the change of viscosity under identical conditions of cross-linking. Gelation times derived

from these curves give the same order of activity for diglycidyl ethers, as obtained by means of IR spectroscopy.

When these gelation times are compared with the kinetic curves determined by IR spectroscopy, it can be established that the beginning of gel formation occurs at a time when about 30–50% of the epoxy groups has been converted. It may be concluded from this that about 40% of the epoxy groups is utilized in the initial period of the reaction for chain growth.

The regularities discussed above appear in the second stage of the cross-linking process in the same way as shown by the viscosity curves. The

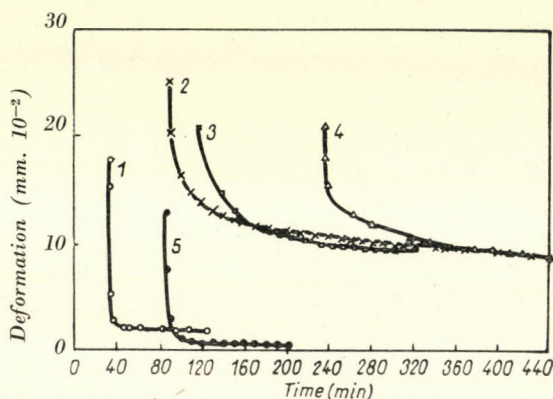


Fig. 3. The change of deformation in systems formed by various diglycidyl ethers with DETA in the terminal stage of cross-linking (Cross-linking: 40 °C)

1 — DG; 2 — EDG; 3 — PDG; 4 — HDG; 5 — DDG

curves plotted for the second section (see Fig. 3) indicate the diminishing of reversible deformation, and represent the combined change of the rubber-elastic and elastic deformation of the solidifying system. Obviously, rubber-elastic deformation will be predominant in values of the initial section of the curve.

The time of the starting point of the curves corresponds to that time of the cross-linking process, when the system attains a rubber-elastic state in the course of solidification. When the value of reversible deformation becomes constant with time, cross-linking may be regarded as terminated at the given temperature and load. On the basis of the curves, two characteristic values can be read from the coordinates: the total time of the cross-linking process, and the value of permanent deformation. Measured under identical conditions, this latter is indicative of the elasticity of the cross-linked system.

When the termination of the cross-linking processes is established on the basis of these curves, and the times obtained are evaluated for the various

diglycidyl ethers, the same order of activity is obtained as before. The shortest period is found for diglycidyl ether, to be followed by bisphenol A-diglycidyl ether, etc. and finally by hexamethyleneglycol diglycidyl ether requiring the longest time to react.

Moreover, it may be seen from the diagram that the solidified products obtained from diglycidyl diether and bisphenol A-diglycidyl ether present the lowest reversible deformation, while this value is considerably higher with the other three members of the series. This means that diglycidyl ethers having longer aliphatic chains yield structures of higher elasticity, as it was indeed to be expected.

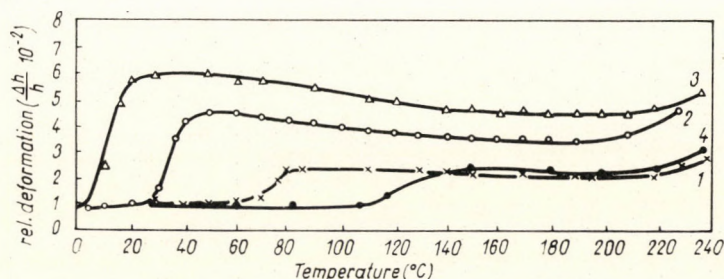


Fig. 4. Thermomechanical curves of various cross-linked diglycidyl ethers
(Cross-linking: DETA, 30 °C)

1 — DG; 2 — EDG; 3 — HDG; 4 — DDG

The cross-linked systems were studied with respect to their thermomechanical behaviour and thermal stability.

These investigations showed the structure of the starting materials to influence substantially the thermomechanical properties of the cross-linked product. However, this statement holds true primarily for the diglycidyl ether component, as the role of the amine components used in our experiments was found to be inferior.

As regards the diglycidyl ether component, marked differences are presented between compounds of aliphatic and aromatic character, furthermore, within the aliphatic group depending on the chain-length. In aliphatic systems of diglycidyl ether basis, the glass-transition temperature (T_g) is considerably lower than for systems with bisphenol A-diglycidyl ether. With systems of aliphatic structure, this value is between 3° and 76°C, while for those with aromatic structure between 71° and 115°C. A comparison within the group of aliphatic systems shows higher T_g values to belong to shorter carbon chains, and vice versa. These relations can be readily seen from Fig. 4, which shows the thermomechanical curves plotted for various diglycidyl ethers of aliphatic and aromatic structure after cross-linking under identical conditions. The T_g values and the amplitudes of rubber elasticity show that the use of aliphatic diglycidyl ethers results in structures of higher elasticity than obtainable with

the aromatic compounds, and this difference is the more marked, the longer is the aliphatic chain.

The cross-linked products were examined also by derivatography. Test carried out in air stream showed thermal destruction and oxidation to proceed simultaneously, and this stimulates well thermal conditions met within practical applications. The general character of the derivatograms obtained is almost identical for all samples, and can be characterized by the fact that

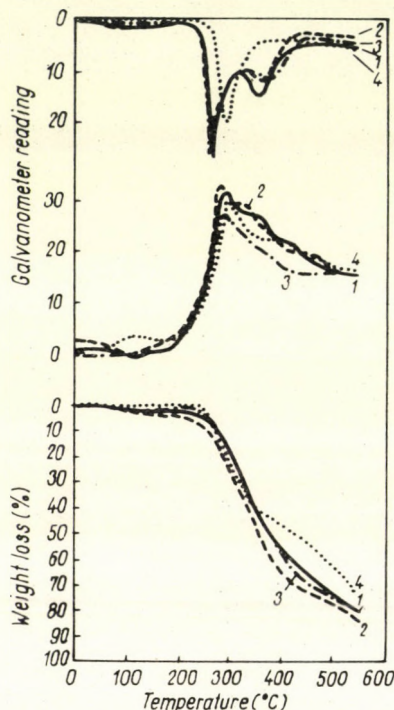


Fig. 5. Derivatograms of various cross-linked diglycidyl ethers
(Cross-linking: HMDA, 30 °C)

1 — DG; 2 — EDG; 3 — HDG; 4 — DDG

under these conditions decomposition begins, in general, above 200°C, and is completed for the most part within the range of 250–350°C.

A detailed analysis of the derivatograms shows that products of aliphatic and aromatic structure present differences also in respect of thermal stability. Fig. 5 shows the derivatograms of the investigated diglycidyl ethers, cross-linked under identical conditions, as a function of temperature. It can be seen that the decomposition temperature and the temperature of the maximum decomposition rate are higher for bisphenol A-diglycidyl ether than for the aliphatic compounds, as contrary to the weight loss on decomposition, which is lower. The curves on the diagram were obtained for samples cross-linked

with hexamethylenediamine at 30°C, and tested after standing for 14 days. In this case — as it may be seen from the figure — the decomposition temperature of the aliphatic products is 249°C, and that of the aromatic products 260°C. The temperature corresponding to the maximum decomposition rate ranges with aliphatics between 252 and 254°C, while this value for the aromatic product is 285°C. Weight losses were as follows: 85% for ethyleneglycol diglycidyl ether, 81% for hexamethyleneglycol diglycidyl ether, 80% for diglycidyl ether, and 73% for bisphenol A-diglycidyl ether. It is of interest to mention that the number of the peaks on the DTG curves indicates the decomposition of aliphatic diglycidyl ethers to proceed in two or three steps, and that of bisphenol A-diglycidyl ether in a single step.

The evaluation of the DTA curves is very difficult, because analysis in air stream results in a high heat of combustion which masks other heat effects. It should be mentioned, however, that a rather small exothermic effect is clearly visible on the diagram of the DTA curve of the aromatic diglycidyl ether in the temperature range between 100 and 105°C, which is absent on the DTA curves of the aliphatic compounds. This effect will be interpreted later on.

The conclusions drawn from the cases presented in Figs 4 and 5 are of general validity, and also apply to samples cross-linked under other conditions. Numerical data characteristic of our thermal analyses are summarized in Table IV. These results unequivocally that the heat resistance of aliphatic diglycidyl ethers, both in the chemical and mechanical sense, is lower than that of products with aromatic structure.

Table IV

Structure of diglycidyl ether	T_g , °C	Decomposition temperature, °C	Temperature of max. decomposition rate, °C	Weight loss, %
Aromatic	71—115	250—270	267—300	66—73
Aliphatic	3—76	225—250	250—275	78—89

The thermal tests were evaluated also from the point of view of the amines. Derivatography showed practically no differences, while the evaluation of the thermomechanical tests is complicated. This is due to the fact that many factors are playing a part in the development of the ultimate properties of cross-linked systems. The two principal factors in this complex effect are: the degree of cross-linking and the molecular structure of the segments. Naturally, this latter depends on both components, ether and amine. Products from diglycidyl ether cross-linked with different amines permit to conclude that

the elasticity of the structured system has a decreasing trend with a decrease in amine chain length, and with an increase in secondary amine group content. However, in the case of bisphenol A-diglycidyl ether, the T_g values of the products formed with ethylenediamine, diethylenetriamine and triethylenetetramine fall within a very narrow range (110–114°C), and only the product of

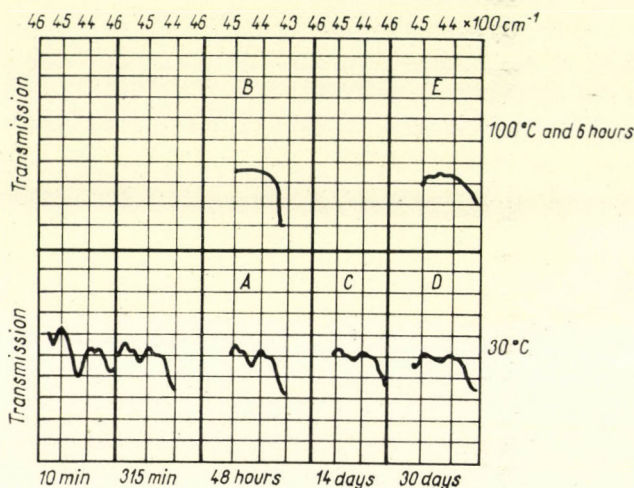


Fig. 6. Changes in the IR absorption of the epoxy groups as a function of aftertreatment

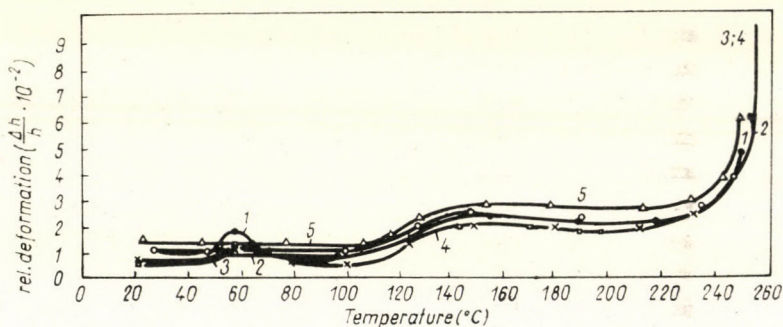


Fig. 7. Thermomechanical curves of cross-linked DDG
(Cross-linking:DETA, 30 °C, with aftertreatment)

- 1, 3, 4 — allowed to stand for 48, 336 and 720 hours, respectively, at room temperature
2, 5 — treated at 100 °C after standing for 48 and 720 hours, respectively

hexamethylenediamine, having a long aliphatic chain, differs from the others in respect of elasticity. This may be explained by the fact that the segments between the nodes of the three-dimensional network produced by ethylenediamine, diethylenetriamine or triethylenetetramine have identical dimensions, and also the differences in flexibility are slight. In case of the relatively simple molecule of diglycidyl ether even these slight differences may come into

display. When bisphenol A-diglycidyl ether, a relatively complicated molecule, is used, the effect of the ether component is predominant in determining the thermomechanical properties, and it masks the mentioned relatively small differences, so that only hexamethylenediamine, having a much longer aliphatic chain, can exert an effect promoting elasticity.

An analysis of the thermomechanical curves allows further conclusions, too. In most cases, cross-linking below 50–60°C does not produce final structures. The thermomechanical curves indicate that subsequent cross-linking takes place between 60 and 100°C. For samples with aliphatic basis, this temperature range is higher than the T_g value, and is manifested by a gradual decrease of the degree of rubber-elastic deformation with increasing temperature. For samples with bisphenol A-diglycidyl ether basis, this temperature interval comes to lie below the T_g values, and is represented by a smaller peak ("pre-deformation") on the thermomechanical curves. It may be assumed that subsequent cross-linking processes occur, at least partly, *via* the reaction of the residual epoxy groups. Fig. 6 shows for example the change in epoxy group content upon the action of aftertreatment, followed by IR spectroscopy. It can be seen that the residual epoxy group content diminishes as a function of the efficiency of after-treatment, but it vanishes completely only when subjected to heat treatment.

Naturally, the reaction of the residual epoxy groups is accompanied by heat release. However, this exothermic effect can be observed on the DTA curves of Bisphenol A diglycidyl ethers only, where the relatively small heat content released in the afterreaction is concentrated within a short time to a narrow temperature range. This explains the DTA peak, mentioned earlier, occurring at about 100 °C on the derivatogram of bisphenol A-diglycidyl ethers. Fig. 7 shows the thermomechanical curves for cross-linked bisphenol A-diglycidyl ethers, one part of which has been subjected to aftertreatment, and the other part has not. The temperature of the base point of the peak occurring on the DTA curve is the same as the temperature at which the small peak of the thermomechanical curve — *i.e.* the elastic deformation — begins to diminish as a consequence of after-cross-linkage. Fig. 7 shows that "pre-deformation" is absent on the curves of those samples which have been subjected to thermal aftertreatment. In the same way, also the small exothermic peak mentioned is absent on the DTA curves of heat-treated samples.

SUMMARY

The cross-linking process of various aliphatic diglycidyl ethers and of bisphenol A diglycidyl ether has been investigated. It has been found that the initially self-accelerating process slows down after the conversion of 60–70% of the epoxy groups. With aliphatic diglycidyl ethers the reactivity diminishes with increasing chain length. Maximum reaction rate occurs at a conversion of 25–50% of the epoxy groups, and this coincides with the beginning of gel formation. The reactivity of bisphenol A-diglycidyl ether is very high in the

initial stage of the process, however, the conversion is lower than for aliphatic diepoxides. Presumably, this may be ascribed to steric hindrance of the aromatic ring. The overall activation energy of cross-linking was found to be 12–17 kcal/mole. Cross-linked products from bisphenol A-diglycidyl ether are less elastic but more resistant to heat than products with aliphatic basis. It has been shown that complete development of the network structure requires subsequent heat treatment, and this cross-linking occurs by the reaction of the residual epoxy groups.

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INVESTIGATION OF THE REACTIVITY OF ORGANIC COMPOUNDS IN LIQUID PHASE FREE-RADICAL REACTIONS

AN INTRODUCTION

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A frequently occurring type of organic chemical reactions is the abstraction of the bounded hydrogen atom from a molecule. As a rule, hydrogen abstraction reaction presents itself in practice as elementary step of a complicated chemical reaction. The knowledge of the rate constant of this elementary reaction is significant for the explanation of the relationship between reactivity and molecular structure, as well as for the examination of complicated chemical processes.

Since 1962, the *Department for Free-radical Kinetics of the Central Research Institute for Chemistry of the Hungarian Academy of Sciences* has been engaged in a research an essential part of which takes place within the scope of a scientific co-operation agreement between the Academies of Sciences of Hungary and the USSR, concerning "The Investigation of Elementary Free-radical Reactions in the Liquid Phase". As a result of this work, eight papers have been published, or are in the press in Soviet scientific journals; six lectures have been delivered at international scientific conferences. For investigation of elementary free-radical reactions, we have employed the liquid phase model reaction: $\text{RH} + \text{CH}_3 \cdot \rightarrow \text{CH}_4$.

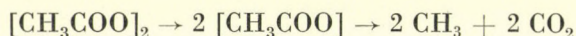
Where the possibility of methane formation has been investigated depending on the sterical and polar factors, further on the C—H bond orders of the molecule. For an investigation of the effect of the structural parameters of the molecule, different types of organic compounds have been reacted with methyl radical. The types used were as follows:

- a) Aliphatic and alicyclic hydrocarbons,
- b) Aliphatic monocarboxylic acids,
- c) Aliphatic amines,
- d) Aliphatic alcohols,
- e) Amino acids and peptides.

In Chapter I, II and III we report the experimental results of hydrogen abstraction reactions with methyl radicals from hydrocarbons and mono-

* Candidate of Chemical Sciences, the dissertation was made at the *Lomonosov State University of Moscow* under the leadership of Prof. N. M. EMANUEL.

carboxylic acids, and about our investigations concerning the structure and reactivity of alcohol-water mixture. In the reactions with compounds of this type, mainly diacetyl peroxide was employed as the source of methyl radicals. Diacetyl peroxide, when dissolved in an organic solvent or solvent mixture at low concentrations ($>5 \cdot 10^{-2}$ mole/l), dissociated during the experiment into free methyl radicals between 60 and 90°C, according to the following reaction, at a conveniently measurable rate:



The kinetics and mechanism of the decomposition was examined by SZWARC *et al.* [1]. It has been found that this homolytic decomposition takes place at low peroxide concentrations according to first order kinetics when different hydrocarbons or acetic acid are used as solvents, the decomposition rate constant is practically the same [1, 2, 3]. The acetyl radicals formed in the first step of the decomposition dissociate so quickly (the dissociation rate constant of the acetyl radical is 10^{10} sec $^{-1}$ at 60 °C, its activation energy 5 kcal/mole) that their stationary concentration in the system is insignificant as compared with the stationary concentration of the methyl radicals [4].

In addition to methane, the formation of a small quantity of ethane can also be observed in the system, depending on the composition of the reaction mixture; that is, parallel with the process of hydrogen abstraction, the recombination of the methyl radicals takes place as well. The addition of 1–2 mole-% of a free-radical scavenger to the reaction mixture does not influence the quantity of ethane formed. This fact, further the dependence of the ratio of the formed ethane/methane on the nature of the solvent used show that the recombination of methyl radicals takes place only in the immediate environment of the dissociating diacetyl peroxide molecule, that is, recombination is the result of the so-called "cage-effect", which is one of the characteristic features of the condensed phase. Therefore, a particular phase effect has also to be taken into consideration in the elementary process of hydrogen abstraction in the liquid phase, in addition to the structural factors of the reacting molecule.

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INVESTIGATION OF THE REACTIVITY
OF ORGANIC COMPOUNDS
IN LIQUID PHASE FREE-RADICAL REACTIONS, I
THE REACTIVITY OF HYDROCARBONS IN LIQUID PHASE FREE-RADICAL
REACTIONS

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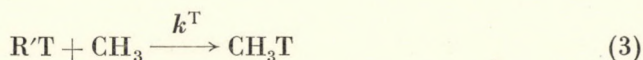
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The rate of a free-radical reaction involving hydrogen atom transfer is a function of the chemical structure of both the stable RH molecule and the attacking R $\cdot$ radical. Thorough and systematic experimental results can be found in the literature primarily concerning the influence of the molecular structure, mainly in the works of STEACIE [1] and TROTMAN-DICKENSON [2], but these investigations deal with the gaseous phase.

In our present work the abstraction of hydrogen from hydrocarbon molecules with free methyl radicals in liquid phase and the kinetics of this elementary reaction molecules have been investigated. Since the direct measurement of the reaction rate is especially difficult in case of liquid phase rapid radical reactions, the so-called isotope-kinetical method [3, 4] was chosen, which is relatively simple and affords adequate data for the elucidation of the relationship between molecular structure and reactivity.

The isotope-kinetical method essentially consists in running a so-called "standard" reaction; the hydrogen of the reacting "standard" molecule is partially labelled with tritium in a given position. Thus, from the methodical point of view such conditions are given, that the free methyl radicals generated in the system may react simultaneously in two or three directions to the same product, but one pathway leads to methane labelled with tritium. In the case of low conversions (<1 mole%) the following basic reactions have to be taken into consideration in the system:



* Candidate of Chemical Sciences, the dissertation was made at the Lomonosov State University of Moscow under the leadership of Prof. N. M. EMANUEL

where RH is the investigated hydrocarbon, and R'H and R'T are the labelled and non-labelled forms of the "standard" compound.

The subordinated role of possible side-reactions has been checked experimentally [5].

When the radioactivity of the formed methane and the initial concentration ratio $[R'H]/[RH]$ are known, the relation of the rate constants $k_{\sigma}^H/k_{\sigma st}^H$ can be calculated. The relations $k_{\sigma}^H/k_{\sigma st}^H$ obtained for the different examined hydrocarbons have been used to characterize the reactivity of the different hydrocarbons in a given reaction type. The index " σ " refers to the so-called "molecular" reactivity, thus k_{σ}^H means the reactivity of all C—H bonds of the given hydrocarbon molecule.

Since *n*-heptane labelled with tritium in position 4 and labelled cyclohexane were employed as "standard" compounds in our measurements, their molecular rate constants could easily be written as the sum of the partial rate constants (k_i^H) of the bond types C—H, according to the following equation:

$$k_{\sigma st}^H = \sum_{i=1}^{i=r} n_i k_i^H \quad (1)$$

where r = number of bond types,

n = number of identical bond types in the given molecule.

The term identical bond types means structurally equivalent bonds whose reactivity is, with known approximation, identical.

According to Eq. (1), if we take one secondary C—H bond to be equal to unity, cyclohexane and *n*-heptane contain 12 and 10.5 secondary C—H bonds, respectively, of about identical reactivity [6]. Therefore, the molecular reactivity of the investigated hydrocarbons was related to the reactivity of one secondary C—H bond of the *n*-heptane or cyclohexane molecule.

Taking into consideration what has been said above, the method can be employed in two variations:

1. The relative reactivities of the C—T bonds of different character can be determined within one compound [7], when only Reactions (2) and (3) are taking place in the system; this can be done if the specific radioactivity of the formed methane ($I_{CH_4}^0$) and that of the labelled compound (I_T) are known. When labelled and unlabelled C—H bonds of the same bond order are reacting in the system, the reciprocal of the ratio of the partial rate constants (k^H/k^T) corresponds to the kinetic isotope effect:

$$\frac{k^H}{k^T} = \frac{I_T}{n \cdot I_{CH_4}^0} \quad (2)$$

2. The molecular reactivity of a compound, related to the reactivity of one secondary C—H bond, can be determined according to the following

expression, taking into consideration the isotope effect:

$$\frac{k_{\sigma}^H}{k_{st}^H} = n \frac{I_{CH_4}^0 - I_{CH_4}}{I_{CH_4}} \cdot \frac{[R'H]}{[RH]} \quad (3)$$

where I_{CH_4} is the specific radioactivity of the formed methane, when it is also present in the system.*

In order to investigate the reactivity of C—H bonds of different types, such aliphatic alicyclic hydrocarbon molecules were selected as models which contained primary, secondary and tertiary C—H bonds, further isolated and

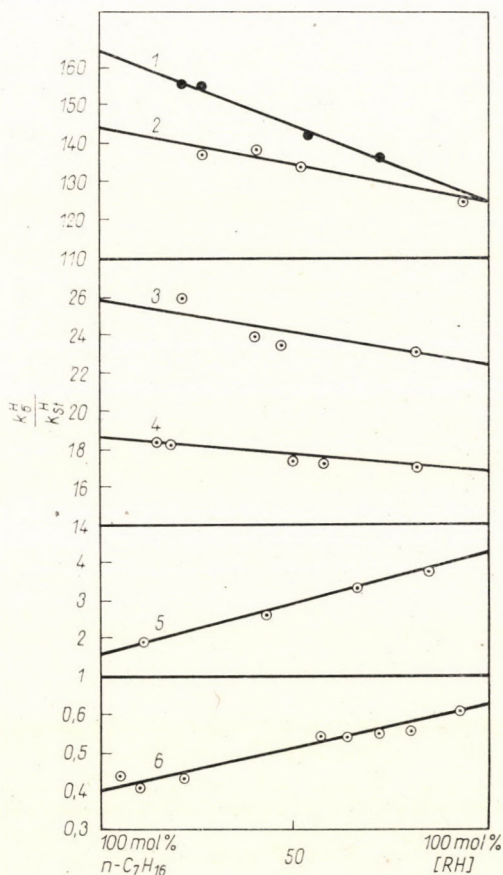


Fig. 1. Dependence of the ratio of rate constants on the composition of the reaction mixture at 80 °C. 1. Me-Cyclopentene-1; 2. Cyclohexane; 3. Me-Cyclopentane; 4. Me-Cyclohexane; 5. Isooctane; 6. Benzene

* As for the exact mathematical deduction of Equations (2) and (3) and concerning the limits of their applicability, see the paper by O. DOBIS, I. NEMES, and G. SZENTGYÖRGYI, to be published later.

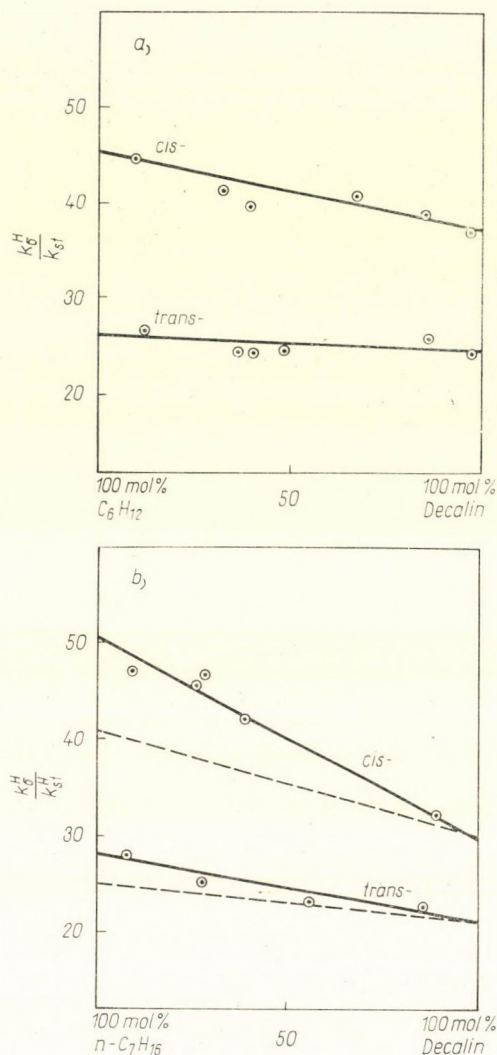


Fig. 2. Dependence of the ratio of the rate constants on the composition of reaction mixture (a) Decalin and cyclohexane; (b) Decalin and *n*-heptane at 80 °C

conjugated C=C bonds. The results obtained by varying the composition of the reaction mixture show that the ratio of the rate constants calculated from Eq. (3) depends linearly on the mole per cent composition of the mixture of hydrocarbons. This dependence on the concentration will be discussed later in detail. Fig. 1 shows the rate constants of hydrogen abstraction from the different hydrocarbons related to the reactivity of one secondary C—H bond of *n*-heptane, as a function of the mole per cent of the components. Fig. 2 shows the dependence of the reactivity of *cis*- and *trans*-decalin on the com-

position of the reaction mixture, in relation to one secondary C—H bond of cyclohexane and *n*-heptane, respectively. It is seen that altering the components of the system results in a change of the slope of the linear dependence.

In the experiment carried out with benzene, the accuracy of the measurements was not satisfactory in case of low benzene concentrations, owing to the low reactivity of the hydrogens of the benzene ring in the system of *n*-heptane and labelled benzene. Therefore, at low benzene concentrations, the measurements were also carried out in a system of benzene and labelled *n*-heptane; the results obtained in the latter system allow a more precise calculation of the relative reactivity of benzene, by means of the transformation of Eq. (3):

$$\frac{k_{\sigma}^H}{k_{st}^H} = 10.5 \frac{I_{CH_4}}{I_{CH_4}^0 - I_{CH_4}} \frac{[C_7H_{16}]}{[C_6H_6]} \quad (3a)$$

where $I_{CH_4}^0$ is the specific radioactivity of the methane formed in the pure labelled benzene system.

As shown in Fig. 1, the reactivities of benzene calculated from the kinetic data of two systems labelled in different ways are in good agreement. This result supports the correctness of the basic hypothesis of the applied kinetic method, namely, that k^T/k_{σ}^H is independent of nature of the medium, that is, Reactions (1) and (3) are the true parallel reactions.

Since a linear relation was found between the reactivity and the mole-% composition of the reaction mixture, the reactivity values extrapolated to zero concentration were taken as the basis of comparison of the reactivities of the hydrocarbon molecules. The k_{σ}^H/k_{st}^H values extrapolated to zero and 100 mole-% concentrations of the investigated hydrocarbons are summarized in Table I.

The k_{σ}^H/k_{st}^H values extrapolated to zero mole-% were divided into the partial rate constants according to Eq. (1). The partial reactivities obtained in this way are given in Table II.

The data in Table II show a certain conformity to the results of BROOK [9], and BROOKS *et al.* [10]. These authors investigated the reactivity of hydrocarbons in the process of hydrogen abstraction with free *t*-butoxy radicals in liquid phase. At the same time, certain deviations can also be found which may probably be attributed to the kinetical difference between the methyl and *t*-butoxy radicals, and to a difference in the experimental temperatures.

At the same time, the conclusions drawn from the data of the Table may be supported by the results of SZWARC *et al.* [11, 12, 13] as well.

Table II affords information about the effect of the molecular structure on the reactivity of the C—H bond types. Particularly high effect is exerted on the reactivity of a given C—H bond by a neighboring C=C bond or a benzene ring. Thus, it is seen from a comparison of the reactivities of the primary C—H bonds of *n*-heptane and toluene that the reactivity of the α C—H bond

Table I*Values of reactivity, extrapolated to 0 and 100 mole-% of n-heptane at 80 °C*

Hydrocarbon	$\frac{k^H/k_{st}^H}{[C_7H_{16}] = 100 \text{ mole-\%}}$	$\frac{k^H/k_{st}^H}{[RH] = 100 \text{ mole-\%}}$
Cyclohexane	10.7 ± 0.3	11.2
Me-Cyclohexane	18.7 ± 1	16.6
Me-Cyclopentane	25.4 ± 2	23.0
<i>trans</i> -Decalin	27.5 ± 1	21.0
<i>cis</i> -Decalin	50.5 ± 1.5	30.0
Cyclohexene	144.0 ± 6	124.0
Me-Cyclopentene-1	168.0 ± 5	107.0
Isooctane	1.6 ± 0.1	4.2
Benzene	0.4 ± 0.05	0.61
Cyclohexadiene-1,3	380.0 ± 20.0	—
Cyclopentane	14.2 ± 0.2	—

Table II*Partial rate constants of hydrogen abstraction at 80 °C*

Type of C—H bond	Hydrocarbon	k^H/k_{st}^H
Primary bond character	<i>n</i> -Heptane	0.1
	Toluene	3.7
Secondary bond character	<i>n</i> -Heptane	1.0
	Cyclohexane	0.89
	Cyclopentane	1.42
Secondary reduced α C—H bond character	Cyclohexene	35.1
	Me-Cyclopentene-1	38.5
	Cyclohexadiene-1,3	95.0
Tertiary bond character	Me-Cyclohexane	8.6
	Me-Cyclopentane	13.7
	<i>trans</i> -Decalin	6.65
	<i>cis</i> -Decalin	17.9
Aromatic C—H bond	Benzene	0.067
	Toluene (<i>para</i> C—H bond)	0.068

is increased 37 times on substitution of the aliphatic group with benzene ring. The reactivity ratio of the secondary C—H bonds in cyclohexane and cyclohexene, further in cyclopentane and methyl cyclopentene-1 show that the reactivity of the α C—H bond is increased 27–39 times by the presence of a C=C bond in the aliphatic ring. On the other hand, the presence of a conjugated C=C bond in the ring causes a 100-fold increase in the reactivity of the α C—H bond.

Similar results are obtained concerning the partial reactivities from the experimental data of SZWARC *et al.*, who calculated the reactivity of unsaturated hydrocarbons as compared with the reactivity of the isooctane molecule, from the decrease of methane product, caused by methyl radical addition reactions [11]. With the aid of the data measured by us in the system *n*-heptane-isooctane, the results of SZWARC *et al.* can be expressed as compared to the reactivity of one secondary C—H bond of *n*-heptane. According to these calculated data, the ratio of the reactivities of the primary C—H bonds of toluene and *n*-heptane is 39, whereas the reactivity-increasing effect of the C=C bond for the secondary α C—H bonds in propylene and butylene is 16–34-fold at 65°C [12, 13]. It is remarkable that the reactivity of the α C—H bonds is increased at 65°C 84 times by the C=C bonds of the pentadiene-1,4 molecule separated by σ -bonds [13], similarly to the case of the conjugated butadiene type C=C bonds of the cyclohexadiene-1,3 molecule, measured by us.

According to the partial rate constants, the character of the C—H bonds has a strong influence on the reactivity. Taking the average value of the partial reactivities of tertiary C—H bonds, the following approximate ratio is obtained at 80°C for the reactivity of C—H bonds according to the character of the saturated C—C bonds:

$$k_I^H : k_{II}^H : k_{III}^H = 0.1 : 1 : 12 \quad (4)$$

From a recalculation of similar gas-phase data [1, 2] to 80° this ratio is:

$$k_I^H : k_{II}^H : k_{III}^H = 0.1 : 1 : 10$$

Besides the molecular structure, a well-perceivable influence is exerted on the reactivity of the molecule by its conformation and by the strain of the aliphatic ring. In the case of the compounds investigated by us this effect is not strong and can be retraced basically to the *cis* and *trans* positions of the neighboring C—H bonds. From a comparison of the reactivities of cyclohexane and cyclopentane it can be seen that the reactivity of a C—H bond in *cis* position is 1.6 times greater in the cyclopentane molecule, than the C—H bond of the same character in *trans* position in the cyclohexane molecule. About the same increase of reactivity, 1.86 and 1.43-fold, is found when

the reactivities of the tertiary C—H bonds of *cis*-decalin, or methyl cyclopentane are compared with the reactivity of the C—H bond of the same character in methylcyclohexane.

The difference in the reactivities of *cis* and *trans* hydrogen atoms is the kinetical manifestation of the torsional strain of the C—H bonds. For example, the torsional strain in the cyclopentane molecule is so strong, that one of the carbon atoms lies beyond the plane of the ring [14]. If one of the hydrogen atoms is eliminated, the original tetragonal configuration of the carbon atom becomes trigonal. This configurational transition permits energetically and sterically the change of the bond angles of the carbon skeleton in a direction leading to a decrease of the torsional repulsion between the hydrogen atoms. The release of energy connected with the change of the bond angles of the carbon skeleton is not great, however, the effect exerted upon the torsional strain of the hydrogen atoms is significant. Therefore, the decomposition of the transition complex formed during the reaction is shifted by the torsional strain of cyclopentane in the direction of the formation of methane. This appears kinetically as an increase of the reactivity of the cyclopentane molecule in the given reaction.

The reactivity of *cis*-decalin compared to the *trans* compound is greater than expected. If the difference of energy between the two configurational isomers is the consequence of a torsional strain of the tertiary C—H bonds in the *cis* compound, then the enthalpy difference should be ~ 1 kcal/mole. However, the real enthalpy difference is as high as 2.72 kcal/mole [15]. Therefore, probably another energetical effect exists, as consequence of which the tertiary C—H bond of *cis*-decalin is more reactive than could be expected on the basis of a simple sterical model. Let us suppose that the partial reactivities of the tertiary C—H bonds of *cis*- and *trans*-decalin, related to each other, can be calculated on the basis of the POLÁNYI rule, using the value of the above enthalpy difference. Since after splitting off the hydrogen of the tertiary C—H bond the final states are identical in both isomers, the difference in the reaction heat equals the initial enthalpy difference:

$$\Delta E = \alpha \cdot \Delta Q = 0.25 \cdot 2.72 = 0.68 \text{ kcal/mole}$$

Supposing the same action constant for the reaction of both isomers:

$$\frac{k_{cis}^H}{k_{trans}^H} = \exp (680/353R) = 2.62$$

This ratio, calculated from the corresponding data of Table II is $17.9/6.65 = 2.69$. Consequently, the experimental data are in good agreement with the reactivities calculated theoretically with certain assumptions.

In the case of cyclohexane the influence of the conformation is weak, consequently, the reactivity of the C—H bonds is approximately identical with that of the secondary C—H bonds in *n*-heptane. In the liquid phase practically only the energetically more stable chair conformation is present under the temperature conditions employed.

According to literature data, the difference in the heat of formation between the chair and boat conformations of the cyclohexane molecule is 5.5–5.9 kcal/mole [16, 17], and the entropy change is practically due to the change in the symmetry numbers of the two conformers, *i.e.* $\Delta S = 2.16$ e.u. Thus, the change of free-energy is 5 kcal/mole at 80°, corresponding to the concentration ratio $[\text{chair}]/[\text{boat}] \approx 10^3$. As the activation barrier of the transition is about 10 kcal/mole [18], the above equilibrium distribution of the conformers is rapidly attained at 80°.

The kinetical data in Table I show at the same time that the solvent has significant influence on the reactivity of the different hydrocarbons. The solvent used frequently affects chemical reactions of various types which can be well explained by polar and ionic interactions, or by the formation of complexes [19].

Complex formation with π -bonds or unshared electron pairs of the molecules may considerably influence free-radical and atomic reactions. RUSSEL [20–23], for example, observed a 10-fold change in reactivity in the reaction of chlorine atoms when aromatic or other inert molecules were present in the system. A similar, but much smaller effect was found by RUSSEL also in the case of the reaction of *t*-butyl radicals [24]. According to SZWARC [25], free-radicals form an unstable complex with the molecules of the solvent, this may affect the kinetics of the free-radical reaction.

Thus, in the above types of reactions the interaction of the reacting free-radical with the solvent has a certain effect upon the reaction kinetics. It may be assumed that in a similar way the solvent can exert an influence on the reaction kinetics from the side of the molecular component as well, especially when the reacting molecule contains functional groups prone to dipole or other intermolecular interactions. However, it is difficult to give an explanation for the influence of the solvent in the case of practically apolar, saturated hydrocarbons, such as *cis*- and *trans*-decalin, or isooctane.

In certain cases, the extrapolated values of the straight lines in Figs 1 and 2, and the slopes of the curves can be well explained with changes in population of the conformers, or by the close packing of the liquid molecules depending on the mixture composition. For example, in the case of isooctane, the reactivity extrapolated to zero concentration is 1.6, which is practically equal to the reactivities of the 15 primary C—H bonds present in the molecule. Thus it seems that the highly reactive tertiary and secondary C—H bonds of isooctane fail to react with the methyl radicals. Therefore, it can be assumed

that at low isooctane concentrations the molecule has such conformation in which the C—H bonds of great reactivity are shielded by the steric effect of the methyl groups. However, with the increase of isooctane concentration the conditions of close packing of the molecules are changed in the mixture in a way that the conformation corresponding to less shield reactive C—H bonds may exist as well.

It can be calculated from reported data [26] that the reactivity ratio between the tertiary C—H bond and one secondary C—H bond in isooctane is $k_I^H/k_{II}^H = 0.6$ measured at 80°C in pure isooctane.

If it is assumed that in the pure isooctane system the molecule exists in such a conformation where only the tertiary C—H bond is hindered, the molecular reactivity ($1.5 + 2 + 0.6 = 4.1$) calculated on this basis and from Eq. (4) is in good agreement with the value extrapolated for 100 mole-% isooctane (see Table I).

The influence of the mixture composition on the reactivity in the case of *cis*- and *trans*-decalin can be explained similarly: these molecules have several different conformers. *cis*-Decalin may exist in more energetically and kinetically different conformations than *trans*-decalin. This is the probable explanation of the experimental fact that the reactivity of the *cis*-isomer depends on the composition much more markedly than that of the *trans* compound.

The close packing of the molecules of a mixture depends to a large extent on the geometrical congruence of the molecules present. The greater the resemblance of the two substances forming the mixture the less sensitive the system to the substitution of one substance by the other and, presumably, the smaller the dependence of the molecular reactivity on the composition. This relation can be seen in Fig. 2, where, owing to the nearly identical ring symmetry of decalin and cyclohexane, the slope of the straight line is smaller, than in the case of the system *n*-heptane-decalin. The reactivities of the decalin isomers measured in two different systems may furnish further indirect evidence for the conformational coherence of the molecules in the mixture. In Table I, the reactivity of cyclohexane is shown related to a secondary C—H bond of *n*-heptane, measured in the system *n*-heptane-cyclohexane. Using this result, the reactivities measured in cyclohexane-decalin were recalculated for system *n*-heptane-decalin. The data obtained indirectly by calculation and in direct experiment are shown in Fig. 2b (dotted line). As it is seen the reactivity values extrapolated to 100 mole-% decalin concentration practically coincide for both decalin configurations. Significant differences between the calculated and directly measured values are observed at low decalin concentrations only, especially in the case of the *cis* isomer. Fig. 2b may carry the meaning that the equilibrium of the energetically different conformational isomers of *cis*- and *trans*-decalin is different in cyclohexane and in *n*-heptane.

By increasing the molar ratio of decalin, this equilibrium is shifted toward a given limit, irrespective of the other component of the mixture.

The dependence of the reactivities on the composition in the cases of methylcyclopentane, methylcyclohexane, methylcyclopentene and cyclohexene may be interpreted similarly. As there is no great difference in energy between the conformational isomers in these compounds, the dependence of the reactivities on the composition is small. The influence of the composition on the reactivity of unsaturated hydrocarbons can partly be explained by the appearance of a steric resonance effect as well.

The dependence of the reactivity of benzene on the composition is connected with the addition reaction of methyl radicals in the benzene ring. The methane yield of this reaction is directly proportional to the benzene concentration and this results in an apparently increased reactivity in the process of hydrogen removal.

However, it has to be noted that the dependence of the equilibrium of the conformers on the composition, owing to the lack of direct experimental data, can only be considered an assumption by which the results concerning the change of reactivities can be interpreted.

The relative reactivity constants of the hydrocarbons were also measured at 60, 70 and 90°C, at a given composition of the reaction system. The logarithm of the rate constants showed good agreement for all hydrocarbons when represented according to the ARRHENIUS equation for all hydrocarbons. The ARRHENIUS parameters of the relative rate constants, as well as the mole-% compositions of the different mixtures of hydrocarbon pairs are summarized in Table III.

The former experiments made at 80°C have shown that in those cases when the ratio of the rate constants depend but slightly on the mixture composition, the results are practically independent of the fact whether the reaction of cyclohexane or *n*-heptane has been selected as the "standard" reaction. Namely, the ratio of rate constants obtained in the systems *n*-heptane ($k_{\sigma_1}^H$) — cyclohexane (k_2^H) and cyclohexane ($k_{\sigma_2}^H$) — *n*-heptane (k_1^H) is theoretically:

$$\frac{k_{\sigma_1}^H}{12 k^H_2} \cdot \frac{k_{\sigma_2}^H}{10,5 k^H_1} = 1$$

where 12 and 10.5 are the proportional "n" factors calculated for the molecules of cyclohexane, and *n*-heptane, respectively, according to Eq. (1).

In the calculation of this relation from the experimental data, employing only the corresponding pre-exponential factors of Table III owing to the equality of the exponential factors, a good agreement has been obtained

Table III
Temperature dependence of the ratio of rate constants

Hydrocarbon	"Standard" hydrocarbon	$\frac{A_{\sigma}^H}{A_{st}^H}$	$E_{\sigma} - E_{st}$ cal/mole	Mixture composition, [RH]mole-%
<i>n</i> -Heptane	Cyclohexane	2.3 $\pm$ 0.4	1130 $\pm$ 130	45.61
<i>cis</i> -Decalin	Cyclohexane	0.44 $\pm$ 0.05	3190 $\pm$ 80	31.68
<i>trans</i> -Decalin	Cyclohexane	0.038 $\pm$ 0.007	4540 $\pm$ 110	40.00
Cyclohexane	<i>n</i> -Heptane	56.5 $\pm$ 4.8	-1130 $\pm$ 130	54.39
Cyclopentane	<i>n</i> -Heptane	754	-2730 $\pm$ 240	—
<i>cis</i> -Decalin	<i>n</i> -Heptane	1.8 $\pm$ 0.08	2260 $\pm$ 280	28.08
<i>trans</i> -Decalin	<i>n</i> -Heptane	0.17 $\pm$ 0.07	3480 $\pm$ 250	27.84
Me-Cyclohexane	<i>n</i> -Heptane	35.7 $\pm$ 8.1	-480 $\pm$ 50	50.31
Me-Cyclopentane	<i>n</i> -Heptane	6.1 $\pm$ 1.8	950 $\pm$ 70	40.35
Isooctane	<i>n</i> -Heptane	0.31 $\pm$ 0.15	1500 $\pm$ 1000	43.44
Cyclohexene	<i>n</i> -Heptane	9.0 $\pm$ 1.5	1930 $\pm$ 120	40.42
Me-Cyclopentene-1 ...	<i>n</i> -Heptane	12.4 $\pm$ 2.6	1780 $\pm$ 140	25.00
Cyclohexadiene-1,3 ..	<i>n</i> -Heptane	1620.0 $\pm$ 125.0	-1950 $\pm$ 120	23.91

within the limits of experimental error:

$$\frac{2.3}{12} \cdot \frac{56}{10.5} = 1.02$$

The temperature dependence of rate constants measured in the system cyclohexane-*n*-heptane can also be calculated from the data measured in the systems *trans*-decalin-cyclohexane and *trans*-decalin-*n*-heptane. The result of this calculation

$$\frac{k_{\sigma_1}^H}{k_2^H} = 2.68 \exp (1040)/RT$$

is in approximate agreement with the temperature dependence derived from the direct experimental values.

If the temperature dependence of the ratio $k_{\sigma_1}^H/k_2^H$ is calculated from the two systems containing *cis*-decalin, a less good agreement is obtained:

$$\frac{k_{\sigma_1}^H}{k_2^H} = 1.7 \exp (1300)/RT$$

This is probably caused by the significant concentration dependence of the k_{σ}/k_{st}^H values (see Fig. 2).

As it is evident from the data of Table III, such regularities which could be explained by the structures of the reacting molecules can be found neither

in the change of the activation energy differences, nor in that of the ratio of pre-exponents. The change of these factors is essentially greater than the change of the rate constants which latter could be well interpreted by the structure and fine structure of the molecule. At the same time, there is a linear relation, shown in Fig. 3, between the activation energy and entropy differences, where the saturated and unsaturated hydrocarbons lie along two lines with different slopes. This characteristic function of the Arrhenius parameters, the so-called effect of compensation, can frequently be found in chemical and physical processes of similar types, taking place in condensed systems [27—32]. In the present case the activation energy differences are in a range of about 6,500 cal/mole. In the system employed by us, the maximum error of this range is 1,600 cal/mole; consequently, in the given case the relation shown in Fig. 3 cannot be due to experimental errors [33].

According to the thermodynamic function of the free-energy of the system, the slope of Fig. 3 is a temperature, which is known in the literature as the "isokinetic temperature".

Our results, however, did not reveal any relation between the "isokinetic temperature" of the system and the isokinetic rate of the process [34].

ROGINSKI and KHAIT [32] made a theoretical investigation of the origin of the compensation effect and they found that the probability of the process of activation in condensed phase does not depend on the average temperature of the system, but on the local temperature of the elementary cells belonging to the reacting particles. This local temperature, in turn depends on the activation energy, and thus the double dependence leads to the mentioned compensation effect. However, the equations obtained theoretically by ROGINSKI and KHAIT are not suitable for the analytical calculation of the slope of the function shown in Fig. 3.

Furthermore it is well known that in processes which take place in microstructurally co-ordinated systems, the compensation effect generally occurs. For example, the viscosity of liquids described by the equation

$$\eta = B \exp(E_{\eta}/RT)$$

gives a straight line for of identical type when represented as the function in $B = f(E)$. This is caused by the circumstance that the pre-exponent as well as the energy is proportional to the same quantity on the first and second power, respectively, *i.e.* $B = f(\nu)$ and $E_{\eta} = F(\nu^2)$, where ν is the frequency of the molecules of the liquid in the quasi-crystalline system.

Let us suppose on the basis of the work of WARING and BECHER [28] that the process of activation takes place in such a liquid the lattice sites execute simplified harmonic oscillatory vibrations about their equilibrium positions. The energy per mole of the vibrational system is equal to the ac-

tivation energy of the process of fluidity (E_φ):

$$E_\varphi = 2\pi M \nu^2 q^2 = \mathcal{J} \nu^2 \quad (5)$$

where ν is the frequency, q = amplitude of vibration, and M = molecular weight. Vibrations exceeding a certain critical q_c amplitude lead to collisions;

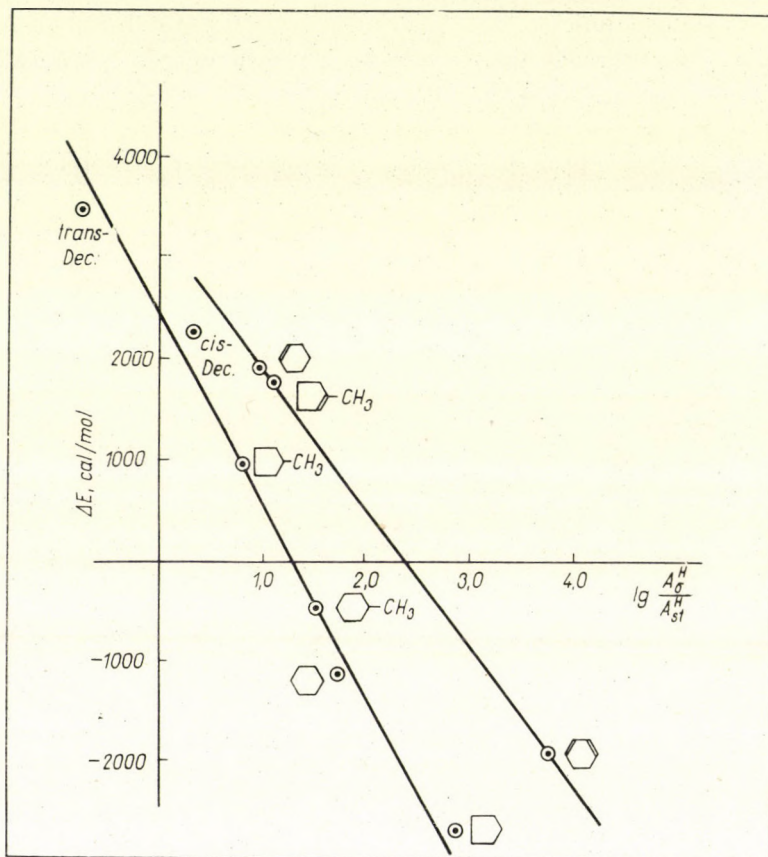


Fig. 3. Dependence of the activation energy differences on the logarithm of the pre-exponents

the number of collisions will be:

$$Z_{ab} = \frac{a, b}{c} n \nu \cdot \exp(-E_\Phi(RT))$$

where a and b denote the concentrations of the reacting particles, and c that of the solvent; n is the number of particles forming an elementary cell.

Using the above principles, for the rate of methane formation according to reaction equations 1 and 2 we get:

$$W_1 = \frac{[RH] \cdot [CH_3]}{R'H} n \nu_\sigma \exp(-E_\phi^\sigma(RT)) \exp(-E_\sigma(RT)) \quad (6)$$

$$W_2 = \frac{[R'H] \cdot [CH_3]}{[RH]} n \nu_{st} \exp(-E_\phi^{st}(RT)) \exp(-E_{st}(RT)) \quad (7)$$

where E_σ is the activation energy of Reaction 1, and E_{st} that of Reaction 2. From Eqs (6) and (7) the ratio of the rate constants of the two reactions is as follows:

$$\frac{k_\sigma^H}{k_{st}^H} = \frac{[RH]}{[R'H]} \cdot \frac{\nu_\sigma}{\nu_{st}} \exp - \left(\frac{E_\phi^\sigma - E_\phi^{st}}{RT} \right) \exp \left(\frac{\Delta E}{RT} \right) \quad (8)$$

where $\Delta E = E_{st} - E_\sigma$.

Employing Eq. (5) for substituting the E_ϕ values in the exponent of Eq. (8), the following relation is obtained:

$$\ln \frac{k_\sigma^H}{k_{st}^H} = \ln \frac{RH}{R'H} \cdot \frac{\nu_\sigma}{\nu_{st}} + \left[\Delta E_\Sigma - \frac{M_\sigma}{M_{st}} \cdot \left(\frac{\nu_\sigma}{\nu_{st}} \right) \cdot E_\phi^{st} \right] \frac{1}{RT} \quad (9)$$

where $\Delta E_\Sigma = \Delta E + E_\phi^{st}$

According to Eq. (9) the pre-exponential factor is a function of ν_σ/ν_{st} whereas the energy factor is a function of the square of the same quantity. This relation of functions gives always a straight line when represented as shown in Fig. 3. At the same time, the ratio of the rate constants of the two parallel reactions depends on the composition of the mixture. This concentration dependence is of general validity; in every case when two different substances react with the same reactant in a system, and the process of activation is a function of the energy of vibration holding together the molecules in the condensed phase, the ratio of the rate constants of the two parallel reactions is a function of the composition.

From Eqs (8) and (5) a linear relation may be derived between the pre-exponent and the energy exponent, which is suitable for calculation. First the following simplifications are introduced:

$$\begin{aligned} M_\sigma &\sim M_{st} \\ [RH] &\sim [R'H] \\ q_c &\approx q_c^{st} \end{aligned}$$

and

$$v_{\sigma} = v_{st}(1 + \alpha)$$

where

$$\alpha \ll 1, \text{ and } \ln(1 + \alpha) \sim \alpha.$$

$$\text{Then: } \frac{k_{\sigma}^H}{k_{\sigma st}^H} = (1 + \alpha) \exp(\Delta E(RT) \exp \left[-\frac{2v_{st}^2 \mathcal{J}(1 + \alpha)2}{RT} \right]) \quad (10)$$

When the substitution $\Delta E'_x = \Delta E - 2v_{st}^2 \alpha \eta \mathcal{J}$ is made, the following function is obtained:

$$RT \ln \frac{A_{\sigma}^H}{A_{\sigma st}^H} = RT \ln \frac{k_{\sigma}^H}{k_{\sigma st}^H} + \frac{1}{2v_{st}^2 \mathcal{J}} (\Delta E'_x - \Delta E) \quad (11)$$

Employing the data $v = 1.1 \cdot 10^{12} \text{ sec}^{-1}$ and $q = 0.5 \text{ \AA}$ of WARING and BECHER [28] obtained for *n*-heptane, the slope of Eq. (11) gives $\frac{1}{RT 2v_{st}^2 \mathcal{J}} = 0.54 \cdot 10^{-3} \text{ mole/cal}$ at the average temperature of the experiments (75°C), whereas the value calculated from the slope of the straight line of the saturated hydrocarbons shown in Fig. 3 is $0.57 \cdot 10^{-3}$. It is seen that Eq. (11) deduced for ideal conditions and with rough approximations gives an unexpectedly good agreement with the experimental results.

According to Eq. (11), a linear correlation between the activation energy and enthalpy can only be obtained if $\Delta E = \text{const}$. The effective activation energies, on the other hand, may be calculated from the kinetic data of these reactions measured in the gaseous phase, when for the absolute values of the activation energies 8.0–8.3 kcal/mole is obtained in case of saturated hydrocarbons [35]. Consequently, the activation energy and entropy functions of the examined reactions must be represented by straight lines in the case of saturated hydrocarbons, and the apparent activation energy differences observed by us are to be interpreted in terms of phase structural instead of molecular structural reasons.

SUMMARY

By employing the isotope-kinetical method, the relative reactivities of hydrocarbon^s have been measured in an elementary free-radical reaction of the type $\text{RH} + \text{CH}_3 \cdot \longrightarrow \text{CH}_4$ in the liquid phase. The rate constant of each process was related to the rate constant of the same reaction of a tritium-labelled "standard" compound, and the ratio of the two rate constants was employed to characterize the reactivity. The two processes took place parallel in the same system.

Aliphatic and alicyclic hydrocarbon molecules were chosen for models containing primary, secondary and tertiary carbon atoms, furthermore isolated and conjugated C=C bonds. On the basis of the obtained kinetic results connexions have been found between the reactivity of the breaking C—H bond and the molecular structure.

It is shown that the ratio of the rate constants calculated from the rate equations of the parallel reactions depends linearly on the composition of the system. This special concentration dependence can be well interpreted partly with the close packing of the molecules of the liquid mixture, partly with its quasi-crystalline structure.

The activation energy and entropy differences calculated from the temperature dependence of the relative rate constants show a definite compensation effect. This effect can be accounted for by the quasi-crystalline structure of the liquid mixture, if the process of activation is attributed to an elementary cell as to a vibrational system.

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100-летие периодической системы Менделеева

В. К. Григорович: *Периодический закон Менделеева и электронное строение металлов.*, Изд. «Наука», Москва, 1966.

Как классические произведения музыки и литературы в руках современного интерпретатора открывают свои новые стороны, потому что содержание их неисчерпаемо, так и дух великих научных творений и самых классиков являются неисчерпаемыми. Периодическая система Менделеева является бесспорно таким классическим произведением в области химии. В. К. Григорович в своей работе, изданном московским издательством «Наука» в честь 100-летнего юбилея открытия периодической системы, трактует периодическую систему с наивысшей взыскательностью современного интерпретатора. Трудно перечислить всё то большое количество работ, вышедших в свет в нашем столетии, предметом которых является периодическая система. Но Григорович сумел сказать что-то новое, и это является в основном следствием того, что автор, обратившись к подлинникам Менделеева, понял самобытные замыслы и стремления великого ученого со знанием и научной подготовкой современного ума. Для этого, разумеется, не достаточно пассивная позиция историка науки, а необходима, как упомянуто во вступлении, активная интерпретация великих замыслов, движущая науку вперед в современном духе.

Каковы важнейшие черты работы Григоровича? В первую очередь, пожалуй, следует упомянуть то, что автор рассматривает многообразие элементов с точки зрения представлений современной квантовой химии теории металлов. Неоспоримым является тот факт, что хотя большая часть элементов представляет собой металлы, однако, как в принципах неорганической химии, так и при разборе периодической системы обычно доминируют металлоидные элементы. Григорович с большой последовательностью исчерпывает возможности, скрытые в построении электронной структуры атомов. Так принцип из подлинных работ Менделеева о смещении элементов внутри столбца, раскрывающийся между аналогами, автор развил дальше, а именно дальнейшие оттенки в построении электронной структуры выражаются, как меньшие смещения внутри столбца. В результате этого элементы второго периода, так называемые «легкие элементы», не попадают безо всего в один столбец с их «тяжелыми» родственниками. Это смещение является особенно ценным и полностью соответствует химическим наблюдениям, согласно которым известно, что ошибочными являются те укоренившиеся прежние представления о характеристичности таких элементов, как, например, бор, углерод, азот и кислород для всего столбца, которые, даже наименование столбцов ведут от них. В этом отношении интересно отметить, что на такое различие уже указал и Менделеев.

Последовательно следуя представлениям Менделеева, Григорович вступает в противоречие с практикой отдельного помещения лантанидов и актинидов: автор помещает их в периодическую систему как третью подгруппу. Построение таким образом таблицы, несомненно, является более konsekventным и позволяет лучшее объяснение целого ряда — в особенности физических — экспериментальных фактов. Автор имеет в этом вопросе наиболее многосторонние, убеждающие аргументы, хотя и в этих представлениях имеются свои слабые стороны.

Современный читатель, возможно, будет поражаться, читая тот факт, являющийся интересным с точки зрения истории науки, что в работах Менделеева, изданных в 1869—1871 годах — как это показывает Григорович на основе подлинников Менделеева — находятся не только всегда приписываемая ему, так называемая, «короткая» форма, но и две другие основные — «удлиненная» и «пирамидальная» формы системы. С этой точки зрения было бы интересно провести более обширный обзор иностранного влияния и взаимодействия, возникших в этом вопросе, так как это дополнило бы новыми сторонами научно-историческую роль Менделеева.

Даже в телеграфном стиле нельзя описать то многообразие областей, в которых автор приводит практическую проверку общих принципов. Является достаточным, пожалуй, обратить внимание на то, что характерные особенности электронной структуры, справедливость периодических закономерностей иллюстрируются в областях аналитической химии, термодинамики, электрохимических потенциалов, гидратации и т. д. Смещения внутри столбцов подтверждаются анализом атомных радиусов, а также металлохимическими и геохимическими наблюдениями. Является очень наглядным и интересным включение некоторых, совершенно новых, глав современной химии в эту картину. Так, например, автор на новой квантово-химической основе обсуждает направленные связи внутри металлических систем, влияние высокого давления на фазовые диаграммы металлов, электрические свойства и т. д. Хорошо согласуются с этими представлениями и новейшие результаты химии благородных газов. 126 рисунков и 43 таблицы, помещенные в работе, делают ее наглядной и легкой для обозрения. Работа Григоровича по содержанию, трактовке представлений и выполнению является достойной выбранного предмета.

Т. Секеи

H. L. SCHLÄFER und G. GLIEMANN: *Einführung in die Ligandenfeldtheorie*. Akademische Verlagsgesellschaft, Frankfurt am Main, 1967. XIV + 535 S.

Es ist eine besondere Freude für den Rezensenten, über ein Werk berichten zu können, wie es die »Einführung in die Ligandenfeldtheorie« von H. L. SCHLÄFER und G. GLIEMANN ist. Seit dem Erscheinen der grundlegenden Arbeit von F. E. ILSE waren wir Zeugen einer mächtigen Entwicklung in der mathematischen Behandlung der Ligandenfeldtheorie, sowie deren praktischen Anwendung auf die Lösung konkreter physikalischer und chemischer Probleme. Inzwischen sind zahlreiche Handbücher und Monographien erschienen, die die Grundlagen und verschiedene Anwendungen dieser Theorie zum Gegenstand haben. Meiner Ansicht nach ist das Buch von Schläfer und Gliemann als aus dieser großen Zahl weit hervorragend zu beurteilen.

Das Werk gliedert sich in drei Hauptteile. In Teil A behandeln die Verfasser — nach einem Überblick der Versuchsergebnisse an einigen ausgewählten Beispielen — das klassische elektrostatische und das kovalente Modell, die Grundkonzeption der Ligandenfeldtheorie, die Annäherungsmethode des schwachen und starken Feldes, die Termdiagramme, die Dq -Werte, das RACAH-Parameter B, die spektroskopischen und nephelauxetischen Serien, Intensitätsverhältnisse, Spin-Bahn-Kopplung, die Anwendung der MO-Methode und die Charge-Transfer-Spektren. Dann werden die Probleme der magnetischen Eigenschaften, der Ionenstabilität, der JAHN—TELLER-Theorie, der kinetischen Stabilität von Übergangsmetallkomplexen und schließlich die Frage der Bindungsverhältnisse behandelt.

In Teil B sind die Theorie der freien Atome und Ionen, gruppentheoretischen Methoden, die Anwendung der Ligandenfeldtheorie im Falle konkreter Elektronenzahlen, weitere Entwicklungsmöglichkeiten der Theorie, die Spin-Bahn-Kopplung und die magnetischen Eigenschaften in einer außerordentlich klar und logisch aufgebauten theoretischen Behandlung zu finden. Dieser 257 Seiten umfassende Teil kann als der wertvollste des Buches betrachtet werden.

In Teil C — die als organische Ergänzung von Teil B anzusehen ist — geben die Verfasser die zur Behandlung der Theorie nötigen mathematischen Formeln, Charakterentafeln, die wichtigsten Molekülsymmetrien, die Hybridisierung von Zentralionenfunktionen in der Theorie der Valenzstrukturen und die Auswahlregeln.

Der — wie schon aus diesem kurzen Überblick hervorgeht — sehr umfassende Stoff wird von den Verfassern in einem äußerst klaren, allgemeinverständlichen und — was dem Buche einen besonderen Wert verleiht — sehr lesbaren Stil vorgetragen. Die glücklich gewählten Beispiele — vor allem aus eigenen Untersuchungen der Verfasser — sowie die 147 Figuren und 73 Tabellen tragen zur maximalen Verständlichkeit des Stoffes bei.

Die weitere Bearbeitung der behandelten Probleme wird durch die zitierten mehreren Hundert Literaturhinweise sowie den am Schlusse des Buches befindlichen — mit kurzen Bewertungen versehenen — systematischen Literaturnachweis erleichtert.

Ich möchte jedoch auf zwei Problemenkreise hinweisen, die bei einem Teil der Leser eventuell ein Mangelgefühl hinterlassen könnten. Es wäre nicht uninteressant gewesen, auch auf die Komplexe der Elemente der zweiten und dritten Übergangsreihe sowie auf das f-Elek-

tronenproblem einzugehen, selbstverständlich mit Rücksicht auf die hier — unbedingt stärker als bei dem 3d-Problem — auftretenden Schwierigkeiten. Die auf die Komplexe dieser beiden Gruppen bezüglichen Untersuchungen nehmen an Intensität ständig zu, und die Bearbeiter dieses Gebietes hätten eine kurze Behandlung dieser Fragen Gruppe sicher mit Freude begrüßt.

Diese Bemerkung ändert aber keineswegs an dem hervorragenden Werte des Werkes. Die äußerst gefällige Ausstattung und die drucktechnisch vollkommene Arbeit — wofür der Akademischen Verlagsgesellschaft, Frankfurt am Main, jedes Lob gebührt — tragen dazu bei, daß man das Buch gern in die Hand nimmt und benützt. Ich bin überzeugt davon, daß das Werk im Kreise der Komplexchemiker ungeteilten Beifall ernten und für alle auf diesem Gebiete Tätigen eine wertvolle und unentbehrliche Hilfe bedeuten wird.

J. CSÁSZÁR

E. PUNGOR: *Flame Photometry Theory*. Akadémiai Kiadó, Budapest, 1967 (in English).

The great interest that followed the publication in 1962 of the Hungarian version of this book prompted Akadémiai Kiadó to publish it in a foreign language, too.

The book treats the theoretical background of the physics of flames used in flame photometry, and the chemical processes taking place in flames during combustion excitation. The book contains 200 pages, divided into 6 chapters, with 47 tables and 112 figures. The general theoretical problems of flames are dealt with in so much detail and with such a scientific thoroughness that the book is very useful not only for the chemist working in the field of flame photometry, but also for those dealing with the technological application of flames.

Chapter 1 deals with the theory and methods of measurement of flame velocity and with the theory of flame propagation. Some important characteristics of flames, such as wall effect, extinction diameter, extinction distance, the dependence of the latter on the pressure and temperature, striking back, lifting of flame and ignition temperature are also discussed.

Chapter 2 describes methods for the determination of the concentration of H and OH radicals, and also radical equilibria in the flame.

In Chapter 3 the methods of measuring the flame temperature are dealt with.

In chapter 4 some types of flames used in flame photometry are treated, and their composition and properties are discussed.

In chapter 5 the theory of atomization and spray coagulation is given, this begins one of the fields of research of the author.

A separate chapter (Chapter 6) is devoted to flame emission spectroscopy and atomic absorption spectroscopy. This chapter was written by Dr. R. A. CHALMERS, an expert of the field, on the request of the author, so this chapter is an extended version of the corresponding one in the Hungarian edition.

The subject of the rather concise work is based on the literary material of the *Proceedings of the Combustion Symposium*, so most modern theories and newest results are summarized in the book.

The book is completed by an extensive literary compilation (243 original works are cited) concerning the theory of flame, and a name and subject index, which latter makes the book easy to handle. References are given in alphabetical order according to the name of author (or first author), and not in the order of occurrence in the text; this makes finding them easier.

The author said in the Preface to the Hungarian edition: "The book has a mosaic-like structure, as several separate fields are treated. This may be a drawback. Its parts are generally not — and in most cases may not be — based on the preceding ones." These sentences give a good characterization of the book.

The considerable conciseness of the book is generally not disturbing for the reader because the fundamental explanations are given, but it is sometimes necessary to consult the original work for better understanding.

It is a great merit of the book that the author treats different theories concerning the same phenomena with criticism. The section "Theory of atomization and spray coagulation" has been written on the basis of the author's research work. The very ingenious experimental solution using two connected atomizers to study spray coagulation deserves special mention.

The following remarks do not concern the essential parts of the book.

1. The data at the bottom of column 6 in Table 5.2 relating to potassium seem to indicate that under certain conditions a minimum of rate of atomization occurs at low pressures, even if an indirect atomizer is used — although this has been experienced by the author only with direct atomizers (Fig. 52).

If the data represent averages of a great number of measurements, *i.e.* the minimum is not caused by experimental errors, there must be a contradiction between these data and an earlier statement of the author, namely that "With atomizers of not concentric structure . . . no influence of pressure on the rate of atomization can be expected."

2. The spray-stabilizing effect of alcoholic solutions is characterized by "spray coalescence constants", k , derived in Section 5.3.

As proved by the author, k , *i.e.*, the stability of spray increases with increasing length of the carbon chain in alcohols. The denomination of k is not very apt, perhaps it should be called spray stabilization constant on the basis of the physical meaning. Coagulation is the opposite of stability, *i.e.* the spray can be called stable if its tendency to coalesce is small. Although the numerical value of the constant k (dimension: g^{-1}) can be interpreted correctly (the higher the value of k , the lower the degree of coagulation), the denomination "spray coalescence constant" may create misunderstanding.

Finally, a request of chemistry working with flames has to be expressed here, namely that the author should also publish a book on the practice of flame photometry.

E. KOCIS

The Production of Polymer and Plastics Intermediates from Petroleum. Editor: R. LONG. Butterworths, London, 1967, pp. 140.

The work edited by R. LONG discusses the following ten important problems of the production of polymers and plastics intermediates from petroleum:

1. Thermal cracking to olefins (pyrolysis).
2. Production of butadiene from petroleum.
3. The BASF method of acetylene production.
4. Comparison of the methods of production of acetylene and ethylene.
5. Production of acetic acid.
6. Ethylene and propylene oxides and glycols.
7. Oxo-alcohols.
8. Production of styrene.
9. Production of phenol.
10. Production of ϵ -caprolactam.

The editor is professor of the *Kingston School of Technology*. Some of the authors of the individual chapters are employees of large firms of the British chemical industry (*Imperial Chemical Industries, Ltd.*, *Shell Chemical Company, Ltd.*, etc.) while some chapters have been taken over from periodicals. The chapters are completed by references to the literature.

The mode of discussion applied in the book is of descriptive nature. It is likely that limitation in space has been responsible for the fact that the topics are not dealt with more thoroughly. The discussed subjects have not been weighted from the aspect of the economic significance of the various technologies, *e.g.* the sand-bed cracking equipment of the firm *Lurgi* is treated over as many pages as the tube-furnaces method of pyrolysis. In the technological descriptions no references are made to the requirements of power and auxiliary materials, and only the main data of yield and some initial parameters are given. The flow diagrams are of a rather schematic nature. The problem of cost as one of the parameters is entirely neglected.

Despite of these deficiencies, the book offers a good general survey of the field discussed, and it appears to be useful as a university textbook.

L. VAJTA

S. STANKOVIANSKY: *Analytická chémia kvalitatívna*. Slovenské vydavateľstvo, technickej literatúry, Bratislava, 1965, 494 Seiten.

Es handelt sich um ein Buch in slowakischer Sprache. In diesem Gebiet erschien schon ein Buch des Verfassers im Jahr 1942. Das vorliegende Buch ist natürlich der Entwicklung entsprechend neu verfaßt, umgearbeitet und erweitert worden: In erster Linie bezieht sich

das auf den theoretischen Teil, wobei aber auch der spezielle Teil erheblich modernisiert und erweitert wurde. Ein besonderer Vorteil dieses Buches gegenüber den alten ist, daß die klassischen Reaktionen, die Tüpfelreaktionen und die mikroskopischen Reaktionen von Ionen nebeneinander behandelt werden, so daß man an einem Ort beschrieben findet, wie ein gegebenes Ion nach den verschiedenen Methoden nachweisbar ist. Die Reaktionen der sog. selteneren Elemente, von denen manche in den letzten Jahrzehnten zu unerwarteter Bedeutung gelangten, sind ebenfalls angegeben, was besonders lobenswert ist.

Das Buch ist auf acht Kapitel aufgeteilt. Im ersten, in der Einleitung, ist das Zustandekommen und die Entwicklung der analytischen Chemie kurz beschrieben. Die Prinzipien der spektroskopischen, elektroanalytischen und chromatographischen Methode werden hier ebenfalls kurz beschrieben. Das zweite Kapitel bespricht die theoretischen Probleme. Es werden die Begriffe Selektivität und Empfindlichkeit, die Säuren-Basen Theorie nach ARRHENIUS und BRÖNSTED, die Fällungs- und Komplexbildungsreaktionen besprochen. Die letzten 30 Seiten des Kapitels sind der Besprechung der spezifischen Atomgruppen gewidmet.

Durch die in seiner langen analytischen Praxis erworbenen Erfahrungen war der Verfasser in der Lage, mit sehr gutem kritischen Sinn die charakteristischsten Reaktionen auszuwählen. Im dritten Kapitel werden die Reagenzien, ihre Bereitung und Prüfung kurz beschrieben. Das folgende Kapitel behandelt die sog. Klassen- oder Gruppenreaktionen. Er sucht Zusammenhänge zwischen den analytischen Klassen und den Kolonnen des periodischen Systems und faßt die Ergebnisse diesbezüglicher Untersuchungen zusammen. Sehr interessant ist das fünfte Kapitel, in welchem die Trennungsv erfahren besprochen werden, am eingehendsten die klassische Schwefelwasserstoffmethode, kürzer aber auch die neueren Verfahren, wie die von OKAČ, TANANAJEW, CHARLOT. Wertvoll sind das sechste und siebente Kapitel, wo die dilektiven Ionreaktionen erörtert werden. Schade, daß die verschiedenen Reaktionen der einzelnen Ionen nach Reagenzien nicht durch geeigneteren Druck hervorgehoben worden sind. Das letzte Kapitel befaßt sich mit den organischen Säuren.

Im Buch vereinen sich sehr glücklich Theorie und Praxis der analytischen Chemie. Die neuesten Ergebnisse der qualitativen Analyse lassen sich darin alle auffinden. Die ausführlichen Literaturhinweise sind besonders den Anfängern nützlich.

L. PÓLOS

HERRMANN J.: Lehrbuch der Vorratspflege. Haltbarmachen, Frischhalten und Lagern von Lebens- und Futtermitteln (Textbook of Preservation. The Conservation, Preservation and Storage of Foods and Feeding Stuff). VEB Deutscher Landwirtschaftsverlag, Berlin, 1963.

This very imposing volume gives much more knowledge than supposable after its title; it represents a concise summary of food chemistry and technology connected with the preservation, conservation and storage of eatable commodities and feeding stuffs. The near 1000 pages of the textbook are dealing — in two well distinguished parts — with the basic facts of food chemistry and with the special problems of preservation- and conservation-industry. Accordingly in the first part of the textbook a short introduction to biochemistry, biophysics, and microbiology can be found in connection of the composition of food and fodder, a very good account of the changes occurring during the storage of vegetable and animal products, methods for the prevention of the disadvantageous alterations, and finally the description of the fundamental methods and processes of preservation and conservation. In these chapters physical, chemical and biological methods, their theory and praxis are fully dealt with. The second part of the textbook is dedicated to the special requirements of various branches of the food- and fodder-preserving and conserving industry; among others methods of preservation for green-fodders and oil seeds, vegetables, fruits, vegetable and fruit-products, tobacco spices, are given furthermore the practice of keeping fresh eggs, milk, dairy products, animal carcasses and various kinds of meat, fishes and sea-food are shown. Although the book was written mainly for students of the agricultural sciences, the good conception and excellent treatment of the material by the experienced author succeeded to complete a textbook of great interest also for biochemists, medical experts and technicians. The exterior of the book is worthy of its content.

L. TELEGDY KOVÁTS

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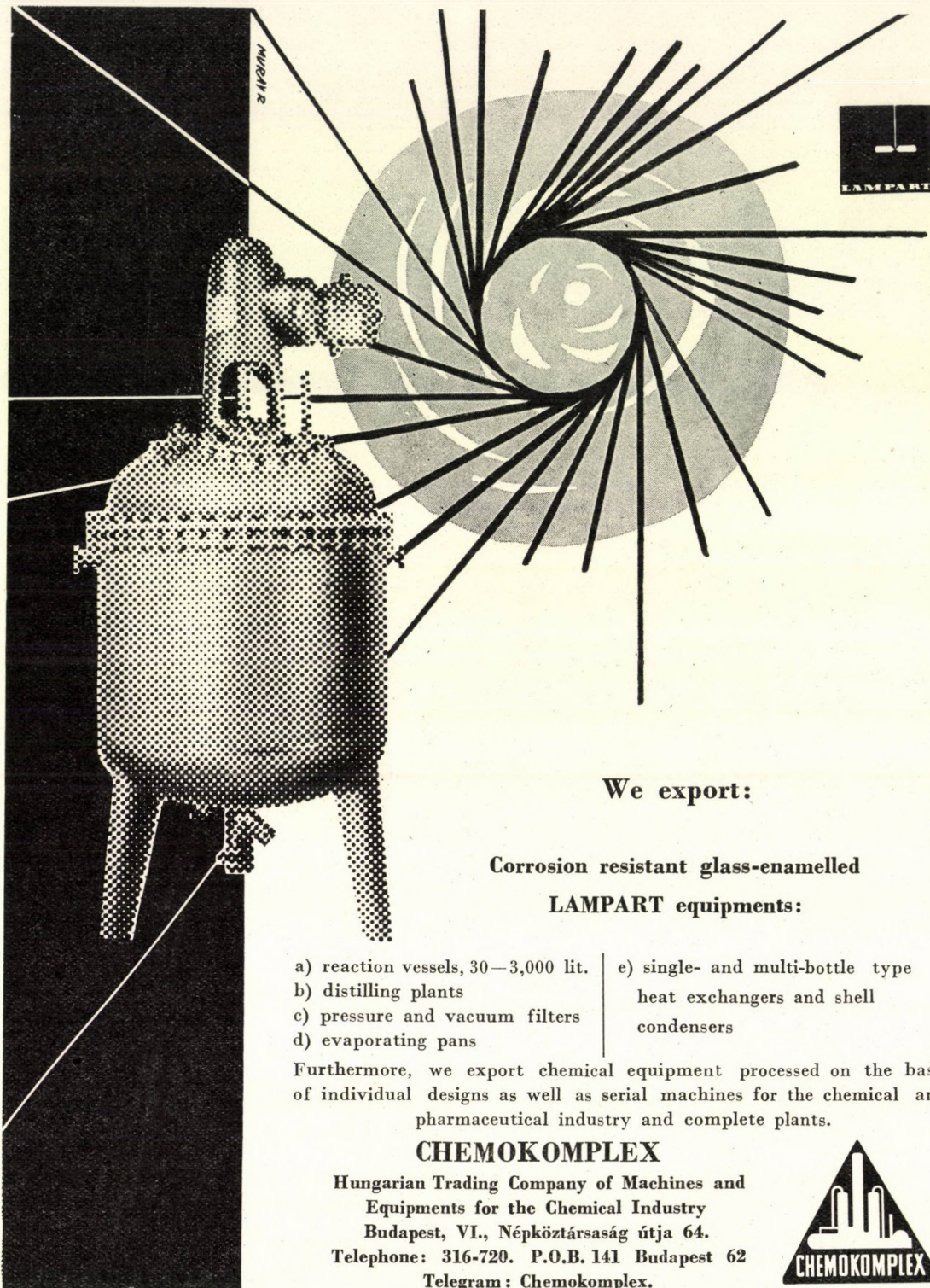
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Исследование синтетических неорганических ионо-обменников

Л. СИРТЕШ, Л. ЖИНКА, К. Б. ЗАБОРЕНКО и Б. З. ИОФА

В рамках настоящей работы был приготовлен новый член группы синтетических неорганических ионо-обменников, а именно, фосфат хрома, который при заданных отношениях PO_4/Cr описывается лучше всего формулами $\text{Cr}_2\text{O}_2(\text{HPO}_4)$ и $\text{Cr}_2\text{O}(\text{HPO}_4)_2$. Изучались некоторые свойства полученного вещества по сравнению с фосфатами циркония и титана. На основе исследований было установлено, что радикал HPO_4^{2-} является доминирующей формой в рассматриваемых соединениях, но также нужно считаться и с присутствием радикалов $\text{H}_2\text{PO}_4^{1-}$ и PO_4^{3-} . На основе значительной аналогии между кривой зависимости обменной емкости от pH и кривой диссоциации фосфорной кислоты, появление обменноспособных ионов H^+ можно представить как результат диссоциации водородно-фосфатных ионов, находящихся в ионо-обменнике. Соответственно этому, механизм процесса ионного обмена является двухступенчатым (в зависимости от величины pH). В первой ступени происходит обмен ионов водорода, образующихся в процессе $\text{H}_2\text{PO}_4^{1-} \rightarrow \text{HPO}_4^{2-}$, а на второй ступени — образующихся в процессе $\text{HPO}_4^{2-} \rightarrow \text{PO}_4^{3-}$. Было установлено, что в случае низких значений отношения $\text{PO}_4/\text{металл}$, — т. е. веществ, аморфных по строению — адсорбционные свойства также имеют большое значение. Описанные заключения, вследствие найденной высокой аналогии, могут быть одинаково приписаны всем трем изученным веществам.

Положительные результаты, относительно применимости этих веществ на практике, позволяют использовать их в радиохимии, а именно, среди многих других и для разделения продуктов различной концентрации, образующихся в параллельных ядерных реакциях, как напр., продуктов, с различной активностью, образующихся в реакции $^{59}\text{Co}(\text{n}, \gamma)$ ^{60}Co и $^{59}\text{Co}(\text{n}, \text{p})^{59}\text{Fe}$.

Активационный анализ следов примесей элементов в полупроводниках типа GaAs

Э. САБО и Х. РАУШ

Был разработан быстрый активационный аналитический метод определения меди в монокристалле GaAs. Активности примесей разделялись от активностей, образующихся в матричных элементах, с помощью экстракции, регулируемой на расстоянии. Групповой реагент дитизон позволяет наряду с медью одновременно определять дальнейшие пять примесей (Au, Hg, Cd, Zn, Co). Примеси определялись на основе их гамма-спектров и с помощью техники совпадений. Метод является более быстрым и менее трудоемким по сравнению с обычным многоступенчатым химическим разделением. Экстракция и измерение шести изученных примесей могут быть осуществлены за 4—6 часов.

Новые результаты в области исследований термического разложения полидиметил-силилена методом газовой хроматографии

Т. СЕКЕЙ, О. М. НЕФЕДОВ, Г. ГАРЗО, В. И. ШИРЯЕВ и Д. ФРИТЦ

С помощью микрореактора и газовой хроматографии изучалось термическое разложение полидиметил-силилена. Полимер подвергался продолжительной или моментальной термической обработке в микрореакторе при различных температурах и снималась хроматограмма продуктов разложения. С помощью двухканального метода детектирования ионизации в пламени водорода и ионизации в пламени метан-водорода были установлены приблизительные значения отношения чисел атомов C/Si, характерные для молекул продуктов распада. Некоторые из них на основе индексов ретенции Ковача удалось идентифицировать с простыми кремнеорганическими соединениями, полученными синтетически.

В зависимости от температуры пиролиза были обнаружены три стадии термического разложения полимера. Первая стадия характеризуется деполимеризацией с образованием небольшого количества низкомолекулярного кремнеорганического олигомера. На второй стадии разрыв связей сопровождается внутримолекулярной перегруппировкой, что приводит к образованию большого количества средне- и низкомолекулярных кремнеорганических соединений. На третьей стадии наряду с деструкцией олигомеров происходит образование, главным образом, низкомолекулярных кремнеорганических и органических веществ.

Определение длины периода ингибирования в радикальной полимеризации

Ф. ТЮДЁШ и Н. И. СМЕРНОВ

В данном сообщении мы провели точный анализ кинетики ингибирования для случая, когда ингибирование происходит в одном электронном акте. Была установлена формула для определения длины периода ингибирования на основе дилатометрических измерений. Анализировались и критически сопоставлялись также другие методы определения периода ингибирования.

Энергии связей атомов-органогенов с металлами-катализаторами

П. ТЕТЕНИ

На основе кинетических данных энергий активации различных каталитических реакций были рассчитаны энергии связей водорода, углерода и кислорода с 11 различными металлами. Показана реальность этих значений и возможность оценки с их помощью величины энергии активации для других каталитических реакций. Отмечено, что на численные значения энергий связей сравнительно мало влияет природа металла.

Колебательные спектры производных силикациклогексанов и частоты симметричных колебаний удлинения связи Si—C в силикациклоалканах с различным числом членов кольца

Г. ФОГАРАШИ, Ф. ТЁРЁК и В. М. ВДОВИН

Изучались ик-спектры и спектры комбинационного рассеивания некоторых силикациклоалканов. На основе приближенного анализа нормальных координат проводились отнесения линий скелетных колебаний молекулы силикациклогексана. Сравнивались частоты симметричных колебаний удлинения связи Si—C в производных силикациклогексана и в соответствующих силановых производных, а также изучалось изменение частот симметричных колебаний удлинения связи Si—C в шестичленном, пятичленном и четырехчленном гетероцикле. На основе этого были получены информации относительно напряжений в кольце.

Разработка различных никелевых катализаторов в процессе дегидроциклизации

З. ПАЛ и М. И. РОЗЕНГАРТ

Восстановленные катализаторы $\text{Ni}/\text{Al}_2\text{O}_3$ и металлический никель достигают их максимальной дегидроциклизирующей активности после процесса «разработки», в течение которого часть адсорбированного на поверхности водорода удаляется. Различные ходы процесса разработки наблюдались в случае двух исследованных катализаторов с разными количествами никеля. Мера и направление каталитической активности определяется решительно количеством водорода на поверхности; неполное восстановление и возможное содержание воды на катализаторе оказывают незначительное влияние на них.

Изучение каталитического гидрирования (дейтерирования) циклогексена на платиновом катализаторе, I

Д. МОГЕР, ДЬ. МИНК и Ф. НАДЬ

В связи с механизмом гидрирования циклогексена на платиновом катализаторе и с влиянием старения катализатора на механизм было установлено следующее:

1) Гидрирование протекает в двух ступенях. Первая ступень является присоединением одного атома водорода к циклогексену. Вторая ступень может протекать двояким образом: происходит либо диспропорционирование полугидрированного продукта, либо присоединение второго атома водорода.

2) Скорость реакции лимитируется адсорбцией циклогексена.

3) Влияние старения сказывается, в первую очередь, на уменьшении адсорбции циклогексена. Механизм реакции остаётся неизменным, а изменяется лишь относительный вес отдельных ступеней.

Химия свободных радикалов, VI

Исследование некоторых свободных радикалов, типа окиси азота, методом ЭПР

И. КЕНДЕ, Ф. ТЮДЁШ и Л. ШЮМЕГИ

Были синтезированы и изучены методом ЭПР стабильные свободные радикалы фенил-(2-циан-2-пропил)-окиси азота, а также 18-ти ее различных замещенных производных. Были определены константы расщепления спектров ЭПР и объяснялись на основе молекулярной структуры. Было установлено, что в случае орто-замещения эти системы не являются копланарными, вследствие чего неспаренный электрон, в основном, концентрируется на связи $\text{N}-\text{O}$. Обсуждалось влияние мета- и пара-заместителей на электронную структуру, и была установлена линейная корреляция между константой расщепления на азоте (a_N) и электрофильными константами заместителей (σ^+).

Исследование природы активных центров, инициирующих низкотемпературную полимеризацию акрилонитрила

Л. КИШ, А. Н. ПРАВЕДНИКОВ и С. С. МЕДВЕДЕВ

Была исследована радиационная полимеризация акрилонитрила под влиянием напряжения постоянного тока (12 в), в температурном интервале $+20 - 80^\circ\text{C}$. Было показано, что полимеризация инициируется анион-радикалами, причем в полимеризационной системе существует динамическое равновесие анион-радикал (дианион) $\rightleftharpoons$ би-радикал. Полимеризация при низких температурах вследствие смещения равновесия в сторону ионных продуктов протекает по ионному механизму. При повышении темпера-

туры равновесие смещается в сторону радикальных продуктов и радикальные процессы играют все большую роль. Приложение напряжения к электродам сдвигает равновесие в сторону радикальных продуктов при всех температурах, вследствие чего полимеризация при низких температурах также протекает по свободнорадикальному механизму.

Синтез и исследование свойств сульфокатионита на основе сополимера аценафтилена и дивинилбензола

ЛИ В. П.—ПАШКОВ А. Б.

Исследовалась сополимеризация аценафтилена и дивинилбензола. Было установлено, что степень превращения зависит от условий полимеризации — от присутствия инициатора, от его концентрации и от температуры реакции. Пригодный для синтеза сульфокатионита сополимер (количество растворимых — 3%) может быть получен полимеризацией в присутствии трет-бутилпербензоата в количестве 1% от веса мономеров при температуре 109°C за 14 часов.

Получились аценафтилен-дивинилбензольные сополимеры слоисто-пористой структуры. Был разработан способ быстрого определения пористости и с его помощью установили, что степень пористости зависит от соотношения инертного растворителя и степени сшивки; слоисто-пористость может быть достигнута лишь при определенном соотношении инертный растворитель — сшивающий агент. Соплимеры, обладающие достаточной пористостью и механической прочностью, могут быть получены в присутствии 40—50% инертного растворителя и 24—36% сшивки.

Было установлено, что в результате сульфирования обычных сополимеров в каждое аценафтиленовое кольцо может быть введено до 2 SO_3H^- групп.

Установили, что пористые сополимеры сульфироваться труднее обычных сополимеров. С увеличением пористости уменьшается степень сульфирования.

При исследовании свойств полученных нами катионитов было установлено, что термостойкость и химическая устойчивость, а также механическая прочность лишь в незначительной степени уступают показателям катионита КУ-2, радиационная устойчивость, напротив, в три раза превосходит радиационную устойчивость КУ-2.

О механизме структурирования эпоксисоединений

ЧИЛЛАГ Л., СТАНКАИ Г., ВАШВАР Й., КЛИНГ Ф., и АКУТИН М. С.

Исследовался процесс структурирования различных алифатических диглицидилэфиров и диандиглицидилэфира. Было установлено, что сначала самоускоряющийся процесс замедляется после превращения 60—70% эпоксидных групп. Реакционная способность алифатических диглицидилэфиров уменьшается с повышением длины цепи. Максимальная скорость реакции появляется при превращении эпоксидных групп в 25—50%, т. е. при начале образования гели. Реакционная способность диандиглицидилэфира в начальном периоде процесса является весьма высокой, однако степень его превращения меньше, чем у алифатических диэпоксидов; это вероятно объясняется стерическим препятствующим действием ароматического кольца. Общая энергия активации структурирования составляет 12—17 ккал/моль. Структурированные продукты диандиглицидилэфира являются менее упругими, но более теплостойкими, чем продукты на алифатической базе. Было обнаружено, что для полной структурированности необходимо применять дополнительное темперирование, причем структурообразование происходит после вступления в реакцию оставшихся эпоксидных групп.

Исследование реакционной способности органических соединений в радикальных реакциях в жидкой фазе

О. ДОБИШ

Методом изотопной кинетики определена относительная реакционная способность углеводородов в их элементарной радикальной реакции $RH + CH_3^{\cdot} \rightarrow CH_4$ в жидкой фазе. Для характеристики реакционной способности было использовано отношение констант скоростей изучаемой реакции и аналогичной реакции, в которой участвовало меченое тритием «стандартное соединение». Обе реакции проходили в одной и той же системе.

Для изучения реакционной способности были выбраны алифатические и алициклические углеводороды, содержащие первичные, вторичные и третичные углеводородные атомы, а также изолированные и сопряженные $C=C$ связи. На основе кинетических данных найдено отношение между реакционной способностью отрывающейся связи $C-H$ и строением молекулы.

Установлено, что вычисленные на основе уравнений скоростей параллельных реакций константы скоростей линейно зависят от состава системы. Эта своеобразная зависимость константы скоростей от концентрации хорошо объясняется, с одной стороны, плотной упаковкой молекул жидкости, а с другой стороны, квазикристаллической структурой жидкой смеси.

Вычисленные по зависимости относительной реакционной способности от температуры разницы энергии и энтропии активации показывают хорошо выраженный компенсационный эффект, который может быть объяснен квазикристаллической структурой жидкой смеси, если процесс активации отнести к элементарной ячейке, как колеблющейся системе.



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