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THE CHEMISTRY OF HEAVY DONOR ATOM COMPLEXES, I

COORDINATION CHEMICAL STUDY OF THE THIONALID COMPLEXES OF TRANSITION METALS

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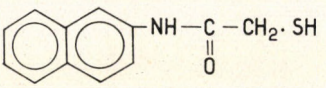
Received February 23, 1967

In our earlier studies we have demonstrated by equilibrium measurements [1, 2], IR spectrometry [3, 4] and MÖSSBAUER spectra [5] the effect of back-coordination in the case of various transition metal dioxime chelates. In these complexes electron transfer takes place from the non-σ-bonding d orbitals of the central atom to the p_π orbitals of the ligand. Investigation of a system in which the π acceptor orbitals of the ligand are d_π orbitals promised therefore to be of particular interest. In ligands with sulphur donor atom, the d_π orbitals of the sulphur may serve as acceptors for the electrons donated by the central atom. This induced us to subject to a coordination chemical examination complexes with sulphur donor atoms. Work with such systems may, however, involve experimental difficulties owing to the proneness of the ligands to readily undergo oxidation which may give rise to undesirable side reactions. We have therefore chosen thionalid as the substance to be investigated, which is relatively stable towards oxidation. Thionalid (mercaptoacetic acid β-aminonaphthalide) is a reagent well known in analytical chemistry:



The complex forming properties of thionalid were recognized as far back as the 1930's and the compound was recommended as a qualitative analytical reagent and for the determination of several heavy metals in the presence of one another [6—10]. The reagent is still in use for the gravimetric, nephelometric and colorimetric determinations of arsenic, cadmium, mercury, copper, silver, bismuth, ruthenium, rhodium and antimony [11, 12]. There are no data in the literature on the stability of thionalid complexes, only the composition of some complexes prepared in the solid state have been reported. From the complexes of the $3d^5$—$3d^{10}$ transition metals only the composition of the solid copper(II) complex is known.

We wish to report in the following on our coordination chemical investigation of the complexes of thionalid with bivalent ions of $3d^5$—$3d^{10}$ transition

metals. The acid dissociation constant of the ligand, the equilibrium constants of the complex formation, the compositions of the complexes, their magnetic susceptibility, and the MÖSSBAUER spectrum of the iron(II) complex have been studied.

I. Experimental

Reagents

Dioxan Commercial analytical grade dioxan was purified by distillation from stannous chloride and again from potassium hydroxide. Freshly distilled dioxan was used in all measurements.

$HClO_4$ 0.1 *M* and 0.001 *M* standard solutions were prepared from analytical grade concentrated $HClO_4$ by dilution; the solutions were standardized against $KHCO_3$.

NaOH 0.1 M, 0.01 M and 0.005 M standard solutions. Analytical grade sodium hydroxide pellets were used for the preparation of a 50% solution; the carbonate-free solution was diluted with boiled distilled water and standardized with perchloric acid solution.

Thionalid Thionalid *(Merck)*, analytical grade, showed in dioxan solution by spectrophotometric measurements considerable decomposition within a few days; therefore a fresh solution had to be prepared for each measurement.

Metal salts The solutions of metal salts were prepared from analytical grade reagents and checked by complexometric titration.

Instruments

A *Radelkisz OP 205* pH-meter with an *OP 802/A* combined glass electrode was applied for the potentiometric measurements.

A *Labor* ultrathermostat was used in the experiments.

The spectrophotometric measurements were carried out with a *Unicam SP 700* recording spectrophotometer.

A *Zeiss UR 10* IR spectrophotometer was used for the infrared spectrometric measurements.

Measurement of the MÖSSBAUER effect was carried out with an apparatus constructed in the *Department of Nuclear Physics of the L. Eötvös University*. Cobalt-57 diffused in the surface of a palladium plate served as the source. The isomeric shift of $K[Fe(CN)_6]$. 3 H_2O compared to this source was 0.12 $\pm$ 0.02 mm/sec at 195°C.

The magnetic measurements were made by means of a GOUY balance constructed in the *Central Physical Research Institute of the Hungarian Academy of Sciences*. The authors' thanks are due to Dr. T. TARNÓCZY for his valuable help in these measurements.

Potentiometric equilibrium measurements

The pH-metric equilibrium measurements were carried out at 20.00 $\pm$ 0.05°C in a total volume of 50.0 ml, in 75% dioxan solution, in order to keep the metal complexes in solution.* The ionic strength was adjusted with $NaClO_4$ to I = 0.1. Dissociation of the ligand was repressed with $HClO_4$. For the titrations with sodium hydroxide a microburette was used; the solution containing the metal ion and the blank were titrated in succession without changing the setting of the pH-meter.

The compositions of the solutions to be titrated were the following:

(1) 5.0 ml of 10^{-2} *M* thionalid in dioxan + 5.0 ml of 10^{-3} *M* metal salt in water + 5.0 ml of 1 *M* $NaClO_4$ + 2.0 ml of 10^{-2} *M* $HClO_4$ + 32.5 ml of dioxan; made up with water to 50.0 ml.

(1a) 1.25 ml of 10^{-2} *M* thionalid in dioxan + 1.25 ml of 10^{-3} *M* metal salt in water + 5.0 ml of 1 *M* $NaClO_4$ + 2.0 ml 10^{-3} *M* $HClO_4$ + 36.25 ml of dioxan, made up with water to 50.0 ml.

* Even at these high concentrations dioxan does not interfere with the pH-metric equilibrium measurements [13].

(2) (blank) 5.0 ml of 10^{-2} *M* thionalid in dioxan + 5.0 ml of 1 *M* $NaClO_4$ + 2.0 ml of 10^{-2} *M* $HClO_4$ + 32.5 ml of dioxan; made up with water to 50.0 ml.
(2a) (blank) 1.25 ml of 10^{-2} *M* thionalid in dioxan + 5.0 ml of 1 *M* $NaClO_4$ + 2.0 ml of 10^{-3} *M* $HClO_4$ + 36.25 ml of dioxan; made up with water to 50.0 ml.

Solutions (1) and (2) were titrated with 10^{-2} *M* NaOH; solutions (1a) and (2a) with $5 \cdot 10^{-3}$ *M* NaOH.

During titration the solutions were stirred by a stream of hydrogen bubbles.

Owing to the low solubility of the complexes it was impossible to examine them over a wider concentration range.

The following solutions were used for the determination of the acid dissociation constant of thionalid:

(1) 5.0 ml of 10^{-2} *M* $HClO_4$ + 5.0 ml of 1 *M* $NaClO_4$ + 10.0 ml of 10^{-2} *M* thionalid in dioxan + 27.5 ml of dioxan; made up with water to 50.0 ml.
(2) (blank) 5.0 ml of 10^{-2} *M* $HClO_4$ + 5.0 ml of 1 *M* $NaClO_4$ + 37.5 ml of dioxan; made up with water to 50.0 ml.

Both solutions were titrated with 0.1 *N* NaOH.

Spectrophotometric measurements

The compositions of the complexes were determined in 75% dioxan solution by JOB's method. The required isomolar solutions were prepared from a 10^{-4} mole per litre solution of thionalid in 75% dioxan, and from a 75% dioxan solution containing the metal salts in the same concentration. The pH's of the solutions were adjusted with 0.01 *N* NaOH to a value at which, according to the equilibrium measurements, the formation of the complex is quantitative. The measurements were performed in 4-cm quartz cells; 75% dioxan was used as the reference solution. Absorption spectra were measured in the wavelength range between 36,000 and 16,000 cm^{-1}. In each series of measurements the spectra of the solutions containing thionalid only or metal ion only were also registered.

Preparation of the complexes

The solid complexes necessary for the magnetic and MÖSSBAUER measurements were prepared by the reaction of thionalid dissolved in dioxan with the aqueous metal salt solutions. The latter solutions were added in small portions, under constant stirring (with hydrogen bubbles), to the dioxan solution containing excess thionalid, followed by the addition of 0.1 *M* NaOH standard solution till the appearance of a precipitate. The precipitate was removed by centrifuging, washed with dioxan and water, and dried at room temperature in a vaccum desiccator. The amount of alkali required for the formation of the precipitate was determined pH-metrically (this shows the number of protons split off during the formation of the complex molecule precipitating from the solution). The compositions of the solid complexes were checked by elemental analyses (determination of the C, H, N, O, and metal contents).

Results

Determination of the acid dissociation constant of thionalid

It is shown by the pH-metric equilibrium measurements that up to pH 11 thionalid dissociates one proton, *i.e.* it behaves as a monovalent acid. IR spectrometric measurements have shown that the proton produced in the dissociation comes from the sulphur of the ligand, as the S — H stretching vibration at 2560 cm^{-1} is absent in the IR spectrum of the sodium salt of the ligand, indicating the cleavage of the S — H bond.

The BJERRUM's formation curve [14] calculated from pH-metric titration curves was evaluated by the DYRSSEN—SILLÉN curve-fitting method [15, 16] (Fig. 1). The $Y(\lg v)$ curve was used as normalized curve where $Y = \frac{v}{1+v}$.

According to the measurements, the logarithm of the acid dissociation constant of thionalid in 75% dioxan is -10.20 ± 0.05 at 20.0°C.

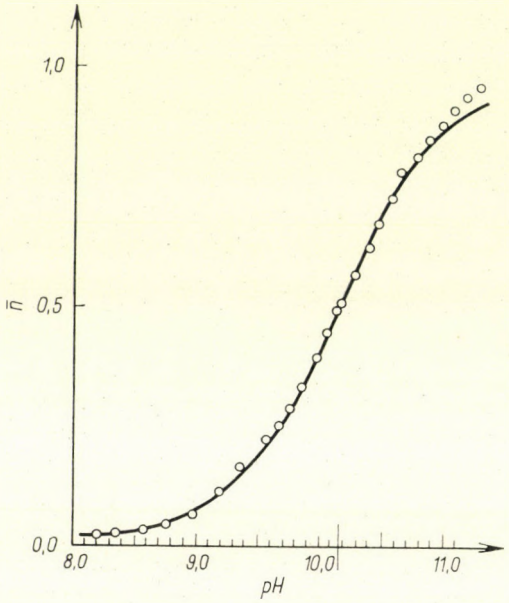


Fig. *1.* BJERRUM's formation curve used in the determination of the acid dissociation constant of thionalid. The circles stand for the points calculated from the experimental data. The full line is the normalized curve

Composition of the solid thionalid complexes

It appeares from the potentiometric titration curves obtained up to the precipitation of the complex that the formation of one complex molecule is accompanied by the liberation of two protons. In view of the fact that in accordance with our previous experiments the ligand is a monovalent acid, it seems reasonable to assume a composition of $MeTd_2$ for the solid complexes. This composition has been verified by the elementary analyses of the precipitates.

Succesive stability constant and the composition of the complexes in solution

Equilibrium measurements by pH-metry in 75% dioxan at concentrations and under conditions to keep the complexes formed in solution have indicated that three protons are split off during the formation of one complex molecule. Accordingly, the composition of the complexes (metal to ligand ratio) would be 1 : 3 in solution, and 1 : 2 in the solid state. Spectrophotometric measurements were carried out in order to decide whether the third proton

is liberated owing to coordination of the third ligand, or as a result of hydrolysis in alkaline medium.

Results of the spectrophotometric measurements

The compositions of the complexes in solution were determined by JOB's method [17]. In the region below 28,000 cm^{-1}, a 75% dioxan solution of the ligand has no absorption, while with the exception of zinc thionalid the complexes absorb light also at these wavelengths. Spectrophotometric measurements have confirmed the 1 : 3 composition for iron(II),cobalt (II), manganese(II) and copper(II) thionalids, while the composition of nickel thionalid has been shown to correspond to a ratio of 1 : 2. The composition of the zinc complex in solution could not be determined with this method.

Results of potentiometric measurements

The BJERRUM formation function [14] was calculated from the titration curves in order to determine the successive stability constants. The formation curve was evaluated by the DYRSSEN—SILLÉN curve-fitting method [15, 16], by using the $Y(\lg v)_p$ family of curves plotted from the function

$$Y = \frac{v + 2pv^2}{1 + v + pv^2}$$

as normalized curve. The values of $\lg K_3$ and $\lg \beta_3$ were determined from the half-value points, and the results were checked by back-calculating this section of the formation curve. A satisfactory agreement between the formation curves was obtained for equilibrium measurements made with two metal concentrations. This proves that in the concentration range investigated the complexes are mononuclear. The BJERRUM's formation curves are summed up in Fig. 2, the stability data in Table I.

Table I

Stability constants of the thionalid complexes of transition metals
(In 75% dioxan, at 0.1 M ionic strength and 20.0°C)

	$\lg K_1$	$\lg K_2$	$\lg K_3$	$\lg \beta_2$	$\lg \beta_3$
Mn(II)	4.4 ± 0.3	4.4 ± 0.3	—	8.8 ± 0.1	—
Fe(II)	7.0 ± 0.2	6.7 ± 0.2	5.5 ± 0.3	13.7 ± 0.1	19.2 ± 0.3
Co(II)	7.3 ± 0.1	6.8 ± 0.1	6.0 ± 0.3	14.1 ± 0.1	20.1 ± 0.3
Ni(II)	6.9 ± 0.3	6.5 ± 0.3	—	13.4 ± 0.1	—
Cu(II)	10.3 ± 0.2	9.7 ± 0.2	8.4 ± 0.3	20.0 ± 0.1	28.4 ± 0.3
Zn(II)	7.8 ± 0.1	7.1 ± 0.1	—	14.9 ± 0.1	—

Magnetic and Mössbauer measurements

Magnetic measurements for the solid nickel(II)-, cobalt(II)-, and iron(II) thionalids gave the following susceptibility values:

$CoTd_2$	$\chi = 1.79 \cdot 10^{-6}$	(at 283°K)
$NiTd_2$	$\chi = 0$	(at 283°K)
$Fe(II)Td_2$	$\chi = 20.28 \cdot 10^{-6}$	(at 283°K)

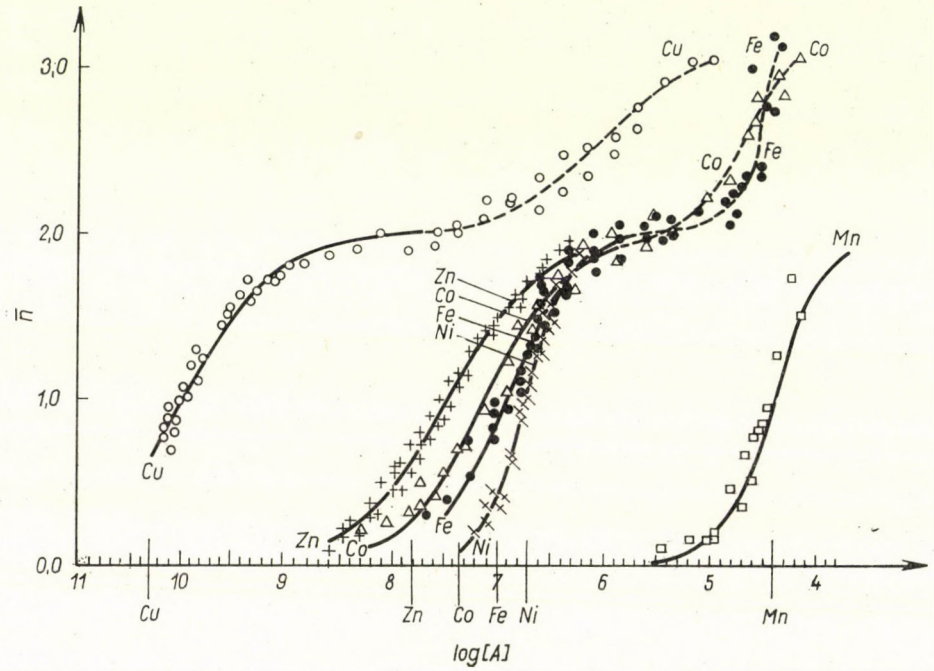


Fig. 2. BJERRUM's formation curves of the thionalid complexes of $3d^5$—$3d^{10}$ transition metals. The points stand for the values calculated from the experimental data, the fully drawn curves are the best fitting normalized curves

Molar susceptibilities were calculated from the magnetic susceptibility values and the magnetic moments were then obtained by introducing a diamagnetic correction. The following values were obtained for the magnetic moments:

$CoTd_2$	$\mu_{eff} = 1.22$	B.M.
$NiTd_2$	$\mu_{eff} = 0.0$	B.M.
$Fe(II)Td_2$	$\mu_{eff} = 4.53$	B.M.

It appears from the MÖSSBAUER spectrum of iron(II) thionalid (Fig. 3) that the value of the isomeric shift is 0.2 mm/sec. and that of quadrupole splitting is 0.6 mm/sec.

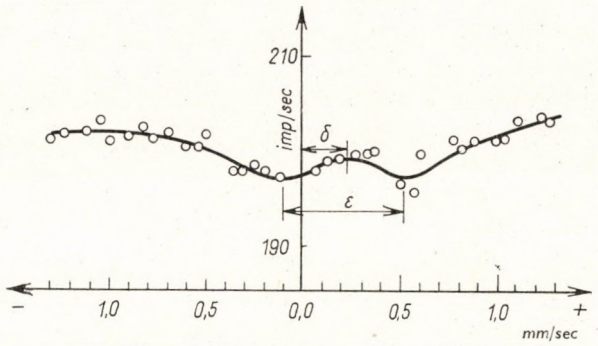


Fig. 3. MÖSSBAUER spectrum of iron(II) thionalid

Discussion

The stability constants show the overall effect of all factors which have an influence on stability. To separate the various effects, the values of ligand-field stabilization have been determined (Table II); these show two maxima for the iron and copper complexes. Nickel thionalid has a remarkably low ligandfield stabilization.

Table II

The values of ligand-field stabilization

	$\lg K_1$	$\lg K_2$	$\lg \beta_2$
Fe(II)	1.9	1.8	3.8
Co(II)	1.5	1.3	2.7
Ni(II)	0.4	0.5	0.9
Cu(II)	3.3	3.1	6.3

The results of the equilibrium measurements suggest that the high ligand-field stabilization of the iron(II) complex is caused by back-coordination. Of all the metals investigated, iron has the lowest third ionization potential, indicating the greatest possibility of back-coordination i. e. metal → ligand electron-transfer in the iron(II) complex.

The existence of back-coordination has been verified by the MÖSSBAUER measurement of the iron(II) complex. Owing to the asymmetry of the $t_{2g}^4 e_g^2$ electronic structure, a line with high quadrupole splitting appears in the MÖSSBAUER spectra of the iron(II) compounds of high spin number, while in the MÖSSBAUER spectrum of iron(II) thionalid (Fig. 3) the value of quadrupole splitting is not more than $\varepsilon = 0.6$ mm/sec, corresponding to the ε value of iron(III) complexes of high spin numbers. At the same time, the magnetic moment (4.53 B.M.) of the complex indicates the presence of four unpaired electrons providing unequivocal evidence for the presence of an iron(II)

compound. The low quadrupole splitting in the MÖSSBAUER spectrum is produced by back-coordination reducing the *d*-electron density in the non-σ-binding t_{2g} orbitals of the central atom, thereby creating an electron structure of nearly spherical symmetry similar to the d^5 state of iron(III).

Consequently, the MÖSSBAUER spectrum and the magnetic moment together point to back-coordination whose stabilizing effect is reflected in the ligand-field stabilization.

The magnetic moments of the cobalt(II) and nickel(II) complexes gave evidence for the low spin number of these complexes. According to the measurements, the iron(II) complex is of a high spin number.

The high ligand-field stabilization found for the copper complex and the extremely high stability of this complex are probably due to the fact that out of the six metal ions investigated copper has the smallest covalent ionic radius which provides favourable conditions for the stable coordination of the ligands.

The experiments carried out so far offer yet no explanation for the particular stability conditions of the nickel(II) complex.

SUMMARY

The value of $10^{-10.20}$ has been found for the acid dissociation constant of thionalid by pH-metric equilibrium measurements. Potentiometric and spectrophotometric methods have been used to determine the compositions and stability constants of the thionalid complexes of $3d^5$—$3d^{10}$ transition metals (Table I). The magnetic susceptibilities of nickel(II)-, cobalt(II)- and iron(II) complexes showed that nickel(II) and cobalt(II) ions form low spin complexes with thionalid, while the iron(II) complex is of high spin number. The MÖSSBAUER spectrum of the iron(II) complex revealed the effect of back-coordination.

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ON THE ROLE OF WATER IN ELECTRON TRANSFER REACTIONS, V*

RATE LAW FOR REACTIONS PROCEEDING WITH POSITIVE ENTROPY OF ACTIVATION

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In a previous paper [1] the positive change in the entropy of activation has been interpreted on the basis of the "band model" [2, 3], making use of the collision probability of the reactant particles.

It has been shown that the entropy of activation is, in general:

$$\Delta S^* = \Delta S_t^* + \Delta S_i^* + \Delta S_e^* - \mathbf{R} \tag{1}$$

where ΔS_t^* is the change in the entropy due to the change in the degree of freedom of the translational movement of the reactant species forming the activated complex. ΔS_t^* is connected with the collision probability, *i.e.* with the average distance between the reactant species in solution. This latter quantity can be expressed by the so-called "normalized concentration", c_*, for which we have:

$$c_* = (d^3 N_A \cdot 10^{-3})^{-1} \tag{2}$$

where d is the distance between the reactants in the activated complex and N_A is the AVOGADRO's number. The collision probability is unity when the average distance of the reactants in solution is equal to the distance required by the configuration of the activated complex. In this particular case for the concentration of the reactants, $[A]$ and $[B]$, the following equation should be valid:

$$c_*^2 = [A]\,[B] \tag{3}$$

The correct normalization of the rate should be given with respect to this c_* concentration, and not to the conventional 1 mole/litre. The relation between ΔS_t^* and c_* is:

$$\Delta S_t^* = -2\,\mathbf{R} \ln c_* . \tag{4}$$

* Part IV: Acta Chim. Acad. Sci. Hung., **52**, 251 (1967).

In Eq. (1), ΔS_e^* is connected with the transition probability of the electron in question, while ΔS_i^* represents all other parts of the activation entropy, such as changes in the degrees of freedom of rotation, vibration, *etc.*

The basis of the band model is the assumption of indirect electron transfer mediated by the formation of H_3O or OH radical. The reaction is an *electron* transfer indeed, if the reaction takes place *via* the formation of H_3O, it is, however, a hole transfer, if an OH radical is formed intermediately.

Thus, in the case of transfer above the potential barrier,* the transition probability for the electron or hole is unity as long as the reactants are inside the effectivity space of the H_3O or OH radical, respectively. The BOHR's radii of these radicals have been estimated to be about 40 Å in water. This means:

$$d \simeq 80 \text{ Å} \tag{5}$$

Thus

$$\Delta S_e^* = 0, \tag{6}$$

and, if the reactants may be considered to have spherical symmetry, also:

$$\Delta S_i^* = 0. \tag{7}$$

Taking the highest d into account, it can be written:

$$\Delta S^* = 21 \text{ e.u.} \tag{8}$$

This approximate value is in good agreement with the experimental results as it formerly has been shown [1]. Thus it can be stated that the positive entropy of activation arises from the high collision probability of the reactant particles in the case of electron transfer above the barrier ("classical transfer").

This entropy change, however, is not quite a real one. This follows from the fact that the intrinsic normalized condition for this type of electron transfer reactions is not the criterion:

$$[A]\,[B] = c_*^2 = 1, \text{ mole}^2/\text{litre}^2, \tag{9}$$

but — from Eqs. (2) and (5):

$$c_*^2 \cong 9 \cdot 10^{-6}. \tag{10}$$

This result is a good example to show that any change of the degree of freedom of translation, *i.e.* the collision probability, can be very important in the interpretation of the entropy of activation.

* Transfer by tunnelling is not considered in this paper.

Namely, electron transfer reactions are usually very fast; their kinetic investigation requires suitable techniques and, in most cases, low reactant concentrations such as 10^{-5}—10^{-4} mole/litre for both reactants. In the calculation of the rate constant essentially the rate observed at a low concentration is "extrapolated" for 1 mole/litre concentration of both reactants. Considering the physical meaning of the processes, the normalization to the conventional 1 mole/litre is formal, and so it leads to formal thermodynamic parameters. Let the rate measurements be made e.g. at 10^{-5}, 10^{-4}, 10^{-3}, . . ., 1 mole/litre concentrations of both reactants. Since the rate law is usually of second order, up to 10^{-3} mole/litre the rate law is, indeed:

$$R = k[A]\,[B]. \tag{11}$$

(A is for instance the oxidizing and B the reducing agent.) At higher concentrations, however, no further increase in rate will be observed, because in these cases the particles are closer to one another than the minimum required distance: above $3 \cdot 10^{-3}$ mole/litre, the reactant species are inside the effectivity space of an H_3O or OH radical and it is entirely unimportant at what distance they actually are.

Thus the value in Eq. 8 has been derived incorrectly when the rate *vs.* concentration curve, showing a "knee" at $3 \cdot 10^{-3}$, was linearly extrapolated to 1 mole/litre.

The rate law of electron transfer reactions of this type can be formulated as follows:

$$R = \begin{cases} k_* \,[A]\,[B], & \text{if } [A]\,[B] \leqslant c_*^2 \\ k_*, & \text{if } [A]\,[B] \geqslant c_*^2 \end{cases} \tag{12}$$

where k_* is the correctly calculated rate constant taking c_* into account.

Unfortunately, no such reactions can be found in the literature which proceed with positive entropy of activation and at the same time, which have been, or could be, measured in the critical concentration range. The only case is the cerous-ceric exchange reaction [4, 5], but it has been proved that this process takes place *via* two parallel paths: one of them with positive, the other with negative activation entropy. The latter has been explained [2, 3] as an electron transfer by tunnelling, while the former hole transfer is just the case under discussion. Thus the expected concentration dependence of the rate has the shape shown in Fig. 1. The rate below the critical concentration is:

$$R_1 = k_1\,[\mathrm{Ce(III)}]\,[\mathrm{Ce(IV)}] + k_*\,[\mathrm{Ce(III)}]\,[\mathrm{Ce(IV)}] \tag{13}$$

and above that we have:

$$R_2 = k_1\,[\mathrm{Ce(III)}]\,[\mathrm{Ce(IV)}] + k_*. \tag{14}$$

Since the concentration range investigated is rather broad, it would be useful to plot the log-log function; so Eq. 13 gives:

$$\lg R_1 = \lg \frac{[\mathrm{Ce\,(III)}]\,[\mathrm{Ce\,(IV)}]}{c_*^2} + \lg (k_1 + k_*) + \lg c_*^2 \qquad (15)$$

Actually the intercept of the line corresponding to Eq. (14) is small, thus it can be neglected at higher reactant concentrations, *i.e.:*

$$\lg R_2 = \lg \frac{[\mathrm{Ce\,(III)}]\,[\mathrm{Ce\,(IV)}]}{c_*^2} + \lg k_1 + \lg\ c_*^2 \qquad (16)$$

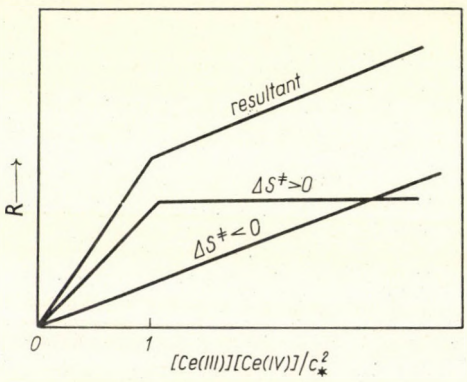

Fig. 1

In this way two parallel straight lines corresponding to these equations are predicted by the starting assumptions of the band model. Their slopes are expected to be unity, and the intercept determined by Eq. (15) is higher than that given by Eq. (16).

Exactly this has been observed experimentally [5], as it is demonstrated in Fig. 2.

It must be noted, however, that one straight line can also be drawn across the experimental points within the error which would mean that the overall order of the reaction is smaller than two. This was explained [4, 5] by assuming a reaction path of zero order with respect to ceric ion. Such a rate law would be unique among electron transfer reactions, thus this assumption is improbable, though cannot be excluded.

On the other hand, the interpretation [4] of a supposed first order path is rather formal. Namely, in electron transfer reactions every excitation involves the FRANCK—CONDON restriction which can be regarded simply as a "collision" of the metal ion with the solvent molecules. The reactant

ions are never in direct collision with one another, not even when inner sphere mechanism is in operation. Therefore the first order path does not seem to be interpretable if it exists at all, since the errors of the measurements permit both explanations.

The concentration dependence predicted by Eq. (12) is expected to be valid for reactions in which the oxidizing reactant is a very strong one, such as Ce(IV), Co(III), Mn(III), *etc.*, since the potential barrier of the reaction is

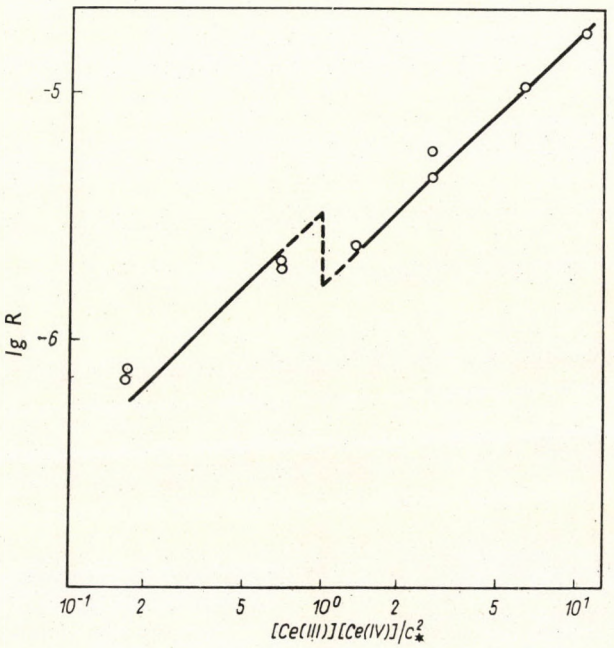

Fig. 2

determined by the oxidation-reduction potential [2, 3]: the stronger the oxidizing agent, the lower the barrier, and the more easily the top of the barrier can be reached by the hole.*

Such a very strong oxidizing agent is the periodate ion, too. Perhaps the observed concentration dependence of the periodate-ethylene glycol reaction that has a similar "knee" in the rate *vs.* concentration curve [6] is also caused by hole transfer above the barrier.

* Similar electron transfer reactions cannot be observed, since they would require a reducing agent with a normal oxidation-reduction potential of about 1.7 v.

SUMMARY

On the basis of the "band model", a rate equation has been deduced for electron transfer reactions proceeding *via* charge transfer above the potential barrier, *i.e.* with positive activation entropy. The concentration dependence of the rate of the cerous-ceric exchange reaction is interpreted by the theoretical results.

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FERMI STATISTICAL TREATMENT OF ACID-BASE PROCESSES, I

A NEW DEFINITION OF pH

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1. Introduction

In the theoretical treatment of electron transfer reactions in solution, FERMI statistics proved to be a useful tool [1]. The identification of the oxidation-reduction potential with the FERMI level of the system resulted in an equation more general than the NERNST—PETERS formula, the latter, under certain conditions of approximation, being a limiting case of the general expression.

FERMI statistics is known in general as a theory describing the behaviour of elementary particles in the "gaseous state". However, its basic assumptions do not contain any criterions which actually limit the applicability of this theory to the description of only these or approximately such systems, stipulating only that FERMI statistics deal with equilibrium processes of particles of non integer spin which are in completely free energy exchange with one another.

Further on, the importance and applicability of FERMI statistics in solid state physics is well known. With the aid of the FERMI level certain phenomena, such as the contact potential or the junction appearing between two semiconductors of different impurities, *etc.*, can be interpreted and calculated. Therefore, it is to be expected that statistical mechanics will also yield important information on potentials of this character (oxidation-reduction potential, hydrogen electrode), playing an important role in the case of solutions. All the more, as there is a close analogy between the electrical properties of electronic semiconductors and protonic solvents, namely, the latter systems may actually be considered to be protonic semiconductors. This analogy is most obvious in the mechanism of conduction: *n*-type conduction corresponds to the conduction due to H_3O^+ ions of great mobility, and *p*-type conduction to a charge transport by OH^- ions of similar mobility. The first case represents an excess in electrons or protons, respectively, the second their lack.

The application of statistical mechanics requires the knowledge of the energy levels and number of the given particles. Thus, in the mentioned case, the relationship describing the oxidation-reduction potential can be obtained under consideration of the possible energy levels and the number of the

electrons. Similarly, for acid-base processes of protonic solvents, the energy and number of protons must be taken into account. Each energy level belongs to some definite state of the protons. FERMI statistics yields information also on the occupation of the given levels, say, on the number (and, thus, on the concentration) of the various proton states, which, besides the energy states, is also an important factor.

Owing to the relative simplicity of the mathematical treatment involved, it is to be hoped that this method will lead to a more profound interpretation of some physical parameters such as those determining the activity coefficient, the solvation of protons, and the properties of non-aqueous solvents or solvent mixtures.

Our present work deals with this problem. The first part of the series discusses a mathematical model and its application to relatively simple cases.

2. The model

The FERMI level of a system is determined by the following expression:

$$N = \sum_i \varrho(E_i) \tag{1}$$

where N is the total number of the particles in the system whose statistical distribution is being investigated, thus in the present case the total number of protons: E_i is the energy of the ith level; and $\varrho(E_i)$ denotes the probability of the occupation of the ith energy level, *i.e.* the following function:

$$\varrho(E_i) = \frac{1}{1 + \exp \dfrac{E_i - E_F}{kT}} \tag{2}$$

where E_F is the FERMI level of the system. In Eq. (1), $i = 1, 2, 3, \ldots, i_t$, where i_t is the number of all levels.

Thus, for a calculation of the FERMI level, the number of protons in the solution and the energies of the individual levels, that is the given proton states have to be determined.

Let us consider a solution containing an n_a number of acid molecules HA, an n_b number of base molecules B, and n_0^0 water molecules. In this case, H_3O^+ ions, OH^- ions, undissociated acid molecules HA, acid anions A^-, BH^+ ions, B molecules and H_2O will certainly be present in the solution. Therefore, there will be an n_0 number of generally unoccupied energy levels, belonging to the ion H_3O^+. If this level is unoccupied that means a water molecule, when occupied, it is an H_3O^+ ion. If the solution is sufficiently diluted so that very few H_3O^+ ions will be formed,

$$n_0 \approx n_0^0, \tag{3}$$

since there exists a level suitable for the acceptance of one proton on each water molecule. If many H_3O^+ ions are present in the solution (concentrated solutions of strong acids), n_0 will gradually decrease, since the excess proton of H_3O^+, owing to its electrostatic repulsion, will modify the energy level of the water molecules in the neighbourhood. Thus, the number of water molecules which are the easiest to occupy will decrease; on the other hand, unoccupied levels will occur, the occupation of which results in particles such as $(H_3O \cdot H_2O \cdot H_3O)^{2+}$ or $(H_3O \cdot H_3O)^{2+}$. Evidently the levels of these particles will be of higher energy.

Let the energy of the initially unocuppied level of the base B be E_b. Occupied, this gives the particle BH^+. Similarly, the initially occupied level of HA of an energy of E_a results (after dissociation) unoccupied state due to the ion A^-.

The data of the possible levels are summarized in Table I. If the discussion is limited to dilute solutions, the interactions between hydronium ions can be neglected. However, it must be pointed out that the interaction of all protons (including the protons in the water molecules) cannot be neglected. This results in an energy band of a level density of n_0^0 in the case of both H_2O- and H_3O^+-protons. Within this bands, the distance in energy between the single levels is very small. Since they depend according to the occupation numbers [Eq. (2)] exponentially on the energy, when $E_i > E_F$, it is sufficient to consider only the corresponding flank of the band in the calculations.

Table I

Number	Symbol of the energy of the levels	Value (e.v.) ($T = 298°K$) of the energy of the levels	Occupied state	Unoccupied state
n_0	E_{0^+}	0.106	H_3O^+	H_2O
n_b	E_b	variable	HB^+	B
n_a	E_a	variable	HA	A^-
n_0	E_0	−0.943	H_2O	OH^-

The expression of the FERMI level according to Eq. (1) can be written therefore as follows:

$$n_0^0 + n_a = n_0^0\, \varrho(E_0) + n_0^0\, \varrho(E_{0+}) + n_a\, \varrho(E_a) + n_b\, \varrho(E_b) \qquad (4)$$

It follows from the expression of ϱ according to Eq. (2) that Eq. (4) is implicit with regard to E_F. Thus, E_F cannot be calculated by algebraic methods, however it can be obtained without any difficulty numerically with the aid of a computer.

Moreover, certain approximate assumptions permit to reduce Eq. (4), so that E_F can be expressed explicitly as well. A few of these cases will be presented below.

3. Expression of the Fermi level in simplified cases

(i) *The case of pure water.* For this system

$$n_a = n_b = 0, \tag{5}$$

and Eq. (3) certainly holds. Hence, Eq. (4) can be reduced to the form

$$\varrho(E_0) + \varrho(E_{0+}) = 1. \tag{6}$$

A simple transformation gives:

$$E_F = \frac{E_{0+} + E_0}{2}. \tag{7}$$

From this, the relationship between the concept of pH and E_F can already be seen, since the relation for the self-dissociation constant of water is:

$$\mathrm{pH} = -\frac{1}{2} \lg K_w \tag{8}$$

where K_w is the ion product of water. At the same time, the following equation is valid:

$$\frac{K_w}{[\mathrm{H_2O}]^2} = \exp\left(-\frac{E_{0+} - E_0}{kT}\right). \tag{9}$$

A proportionality between the pH value and the FERMI level is to be expected already on the basis of these relationships.

(ii) *The case of a strong dilute acid.* The consideration of a dilute solution of a strong acid furnishes an exact correlation between the two values. Eq. (3) is still valid, but here only

$$n_b = 0. \tag{10}$$

Thus, Eq. (4) can be reduced as follows:

$$n_a = n_0^0 \varrho(E_{0+}), \tag{11}$$

as

$$E_a > E_F, \tag{12}$$

and

$$E_0 < E_F, \tag{13}$$

and hence

$$n_a \varrho(E_a) \approx 0 \tag{14}$$

and

$$n_0^0 \approx n_0^0 \varrho(E_0) \tag{15}$$

In consideration of the fact that, according to Eq. (2), the occupation numbers depend exponentially on the corresponding energy, Eqs. (14) and (15) will give a good approximation even when E_a and E_0 differ but moderately from E_F, according to Eqs. (12) and (13). On the basis of Eq. (11), and since $n_0^0/n_a \gg 1$:

$$E_F = E_{0+} - kT \ln n_0^0 + kT \ln n_a. \tag{16}$$

On the other hand, the pH of a dilute solution of a strong acid is expressed by the relation:

$$\mathrm{pH} = -\lg c_a. \tag{17}$$

It may be seen that Eq. (16) becomes equal to Eq. (17), when mole numbers are used, further when

$$E_{0+} = kT \ln n_0^0 \tag{18}$$

and

$$\mathrm{pH} = -\frac{\lg e}{kT} E_F. \tag{19}$$

Eq. (18) fixes the zero point of the energy scale with respect to the conventional pH scale. Since the definition of pH is referred to litre as the unit volume, the mole number of the solvent molecules contained in 1 litre, that is in case of water 55.5 moles must be substituted for n_0^0.

Considering the fact that the potential of an electrode measuring the pH is the difference between the FERMI energies of the protons of the electrode and of the solution, the result expressed by Eq. (19) is not suprising, since the pH is proportional to the electrode potential.*

(iii) *The pH of strong bases* in dilute solution can be obtained in an entirely identical way as above. In this case

$$n_a = 0, \tag{20}$$

and

* As it is well known, a given constant number of protons are present both in glass and platinum electrodes (the dissolution of hydrogen by platinum metals gives hydrogen in the "metallic" state, that is free electrons and protons), so that also the FERMI energy of the protons of the electrode will be constant.

$$E_b < E_F, \tag{21}$$

$$E_{0+} > E_F, \tag{22}$$

and owing to Eq. (3)

$$n_0^0 = n_0^0 \varrho(E_0) + n_b \varrho(E_b). \tag{23}$$

From this, considering Eqs. (9) and (18), we have:

$$E_F = kT \ln K_w - kT \ln n_b, \tag{24}$$

and, with regard to the definition in Eq. (19), the known equation is obtaine d

$$\mathrm{pH} = -\lg K_w + \lg c_b. \tag{25}$$

(iv) The approximate equation for *the pH of a weak acid* can also be obtained, since in this case, too, Eq. (15) represents a good approximation, thus:

$$n_a = n_a \varrho(E_a) + n_0^0 \varrho(E_{0+}). \tag{26}$$

Elementary transformations yield

$$n_a \exp \frac{E_a - E_F}{kT} + n_a \exp \frac{E_a + E_{0+} - 2E_F}{kT} = n_0^0 + n_0^0 \exp \frac{E_a - E_F}{kT}. \tag{27}$$

As long as

$$\exp \frac{E_a - E_F}{kT} \ll 1 \tag{28}$$

(which means that the solution is more acidic than the pH of the buffer of the composition $[HA] = [A^-]$), it can be written:

$$n_0^0 + n_0^0 \exp \frac{E_a - E_F}{kT} \approx n_0^0, \tag{29}$$

and under consideration of the fact that, owing to $n_a \ll n_0^0$, the first term on the left hand side of Eq. (27) can be neglected too, the FERMI energy takes the following form:

$$E_F = -\frac{1}{2}\left(E_{0+} + E_a - kT \ln \frac{n_a}{n_0^0} \right). \tag{30}$$

On the other hand, according to the definition

$$E_a = -kT \ln K_d, \tag{31}$$

hence:

$$pH = \frac{1}{2}(pK_d - \lg c)\,. \tag{32}$$

The approximate relationships giving the pH of weak bases as well as hydrolyzing salts, can be derived in a similar way.

4. Results of the numerical solutions of the exact relation for dilute solutions

Eq. (4) was solved also by the iteration method, using an *Ural 2* computer, for various values of the parameters (E_a, E_b, n_a and n_b).

Fig. 1 shows the dependence of the pH of weak acids on the concentration. The numbers written on the curves indicate the negative values of the logarithm of the acid dissociation constants. It may be seen that within the striated area the exact equation and the approximate Eq. (32) give identical

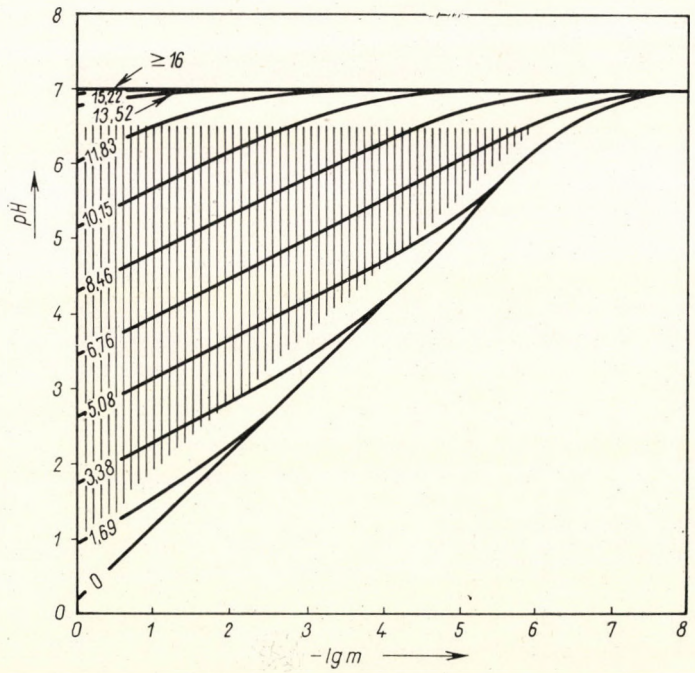

Fig. 1. Calculated pH values of solutions of acids of different strength as the function of the concentration. (The pK_a values are shown on the curves.)

results, namely, parallel straight lines of a slope 1/2 have been obtained. However, at very low concentrations or in case of very weak or medium weak acids, a deviation appears towards the pH value of 7, or toward values determined by Eq. (17), respectively.

Thus, Eq. (4) gives exact results also in those cases, when no approximate relationship is available. A typical example is the hydrolysis of salts formed by weak acids with weak bases. Figs 2—4 illustrate a few of these

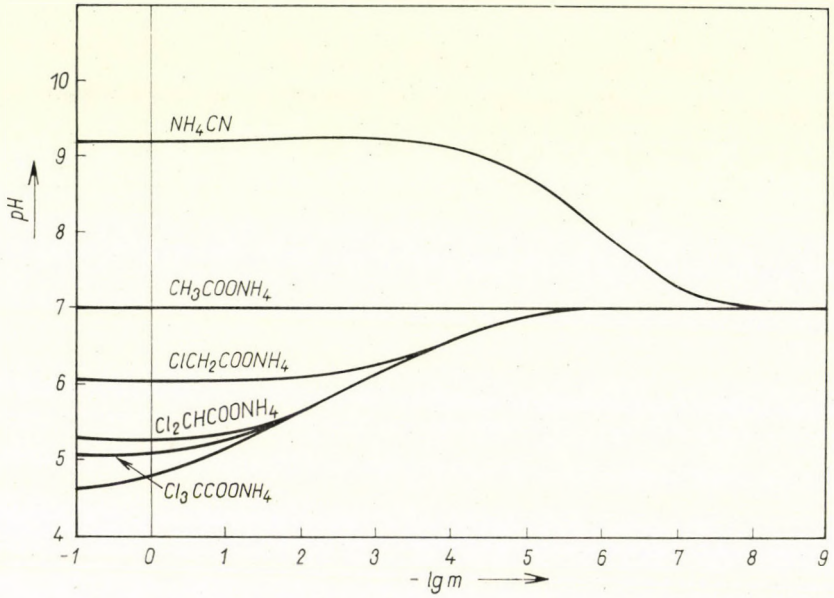

Fig. 2. Calculated pH values of ammonium salt solutions *versus* the concentration

cases. The exact solution proves the correctness of the approximate graphical method of FLOOD [2], insofar as in a given concentration range and at an appropriate strength of the acid and the base, the pH is independent of the concentration. The corresponding curves are resultants of the pH values adjusted separately by the acid and base components.

On the basis of these findings, the definition of the pH in Eq. (19), as a quantity proportional to the FERMI level of the protons in the solution, appears to be generally correct, and Eq. (4) seems suitable for the calculation of pH in the whole range.

The actual calculations discussed so far concerned only aqueous solutions. However, it may be seen that this definition of the pH can theoretically be applied without any restrictions to acid-base equilibria in non-aqueous protonic solvents. In this case, n_0^0 will have a different numerical value, and,

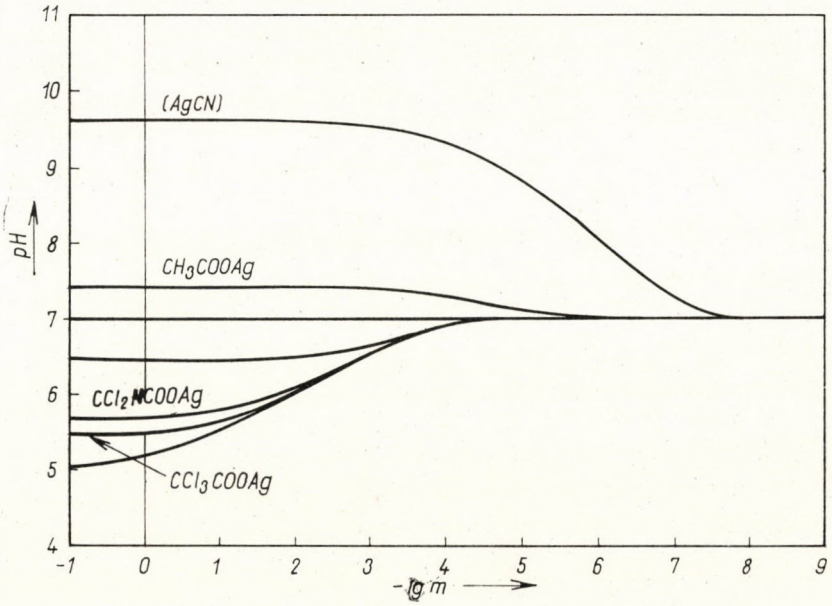

Fig. 3. Calculated pH values of silver salt solutions *versus* the concentration. (Owing to complex formation, the curve for AgCN is fictive)

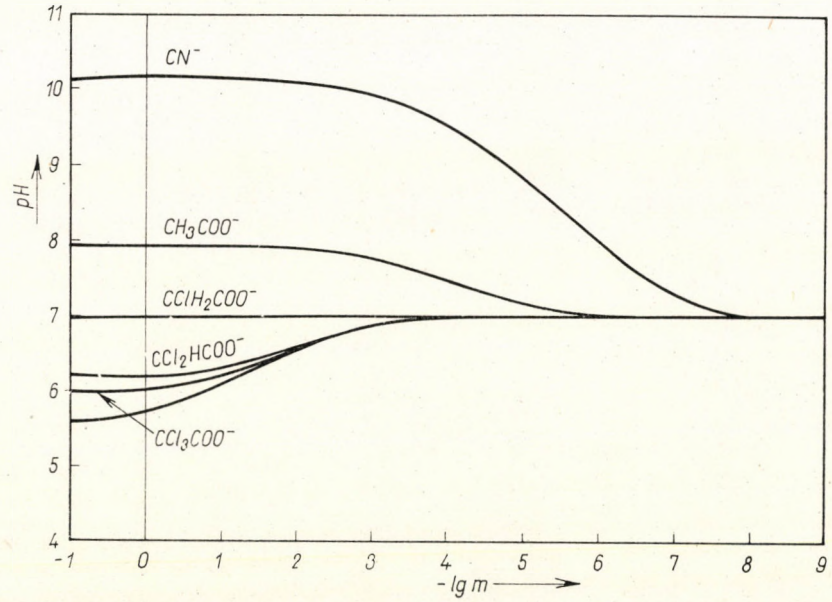

Fig. 4. Calculated pH values of diethylamine salt solutions *versus* the concentration

owing to the energy scale which has been referred to water, the expression of E_{0+} will be expanded by an energy term ε:

$$E_{0+,\,i} = kT \ln n^0_{0,\,i} + \varepsilon . \tag{33}$$

Actually, ε expresses the shift between the acid scales of the two solvents.

SUMMARY

The following concept is suggested for the definition of the pH of protonic solvents: the pH is identical with the FERMI energy of the protons of the solution, when the energy is measured in $-kT$ ln 10 units. The relations between approximate equations for the calculation of the pH and the expression describing the FERMI level of the solution are demonstrated. Numerical solution has proved the suitability of the latter expression for the calculation of pH of solutions for which the usual approximate equations do not hold.

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CYANOMETRISCHE BESTIMMUNG SUBSTITUIERTER ISOCHINOLIN-DERIVATE IN NICHTWÄßRIGER LÖSUNG

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Eingegangen am 20. Januar 1967

Es wurde schon über die cyanometrische Bestimmung von heterocyclischen quaternären Ammoniumsalzen in nichtwäßriger Lösung berichtet [1]. Im Laufe jener Arbeit wurde schon an die Möglichkeit gedacht, die Methode zur Bestimmung solcher heterocyclischen Verbindungen anzuwenden, die mit Hilfe von Alkylhalogeniden in quaternäre Ammoniumsalze übergeführt werden können. Läßt man z. B. 6,7-Dimethoxy-3,4-dihydro-isochinolin (**I**) mit Methyljodid reagieren, so erhält man ein quaternäres Ammoniumsalz (**II**), das mit Kaliumcyanidmaßlösung zu titrieren ist. Die einzelnen Vorgänge sind in Abb. 1 dargestellt.

Um die best geeigneten Umstände zur Überführung in quaternäre Ammoniumsalze zu bestimmen, wurden Versuche in verschiedenen Lösungsmitteln mit unterschiedlichen Methyljodidmengen bei 25 und 50°C unternommen und es wurde gefunden, daß Aceton das entsprechendste Lösungsmittel ist. In Aceton scheidet sich das entstehende quaternäre Ammoniumsalz aus, es wird zur Titration in Chloroform aufgenommen.

10 ml der acetonischen 6,7-Dimethoxy-3,4-dihydroisochinolinlösung (1 g/100 ml) wurden in doppelwändige Titriergefäße gebracht und der Reihe nach im Molverhältnis 1 : 1, 1 : 2, 1 : 3, 1 : 10, 1 : 15, 1 : 20 mit Methyljodid versetzt. Dann ließ man die Reaktionsgemische 10, 30 bzw. 60 Minuten stehen, wonach 10 ml Chloroform zugefügt wurden. Nachdem die chloroformische Lösung mit 40 ml Isopropylalkohol verdünnt worden war, titrierte man mit 0,1 *n* Kaliumcyanidmaßlösung in Isopropylalkohol zwischen Kalomel- und Glaselektroden potentiometrisch.

Die Ergebnisse der bei 25° durchgeführten Titrationen sind in Abb. 2 zusammengefaßt. Wie man sieht, ist die Menge des entstehenden quaternären Ammoniumsalzes vom Methyljodidüberschuß und der Reaktionszeit abhängig. In 10 Minuten verlief die Umwandlung nur in Gegenwart eines zwanzigfachen Methyljodidüberschusses quantitativ, in Anwesenheit von weniger Methyljodid stellte sich ein Gleichgewicht ein, die Reaktion war auch nach 60 Minuten Wartezeit noch nicht vollständig abgelaufen.

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Wir dachten, durch Temperaturerhöhung den Wirkungsgrad der Reaktion zu verbessern, weshalb ähnliche Versuche bei 50°C durchgeführt wurden. Die Ergebnisse dieser Versuchsserie sind in Abb. 3 dargestellt. Wie zu sehen

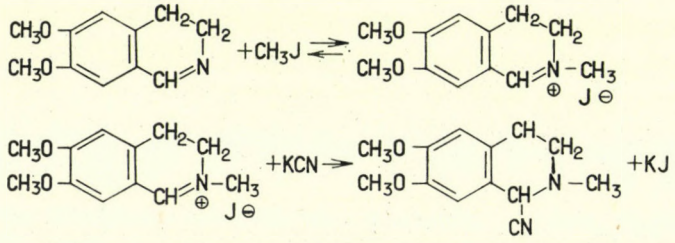

Fig. 1

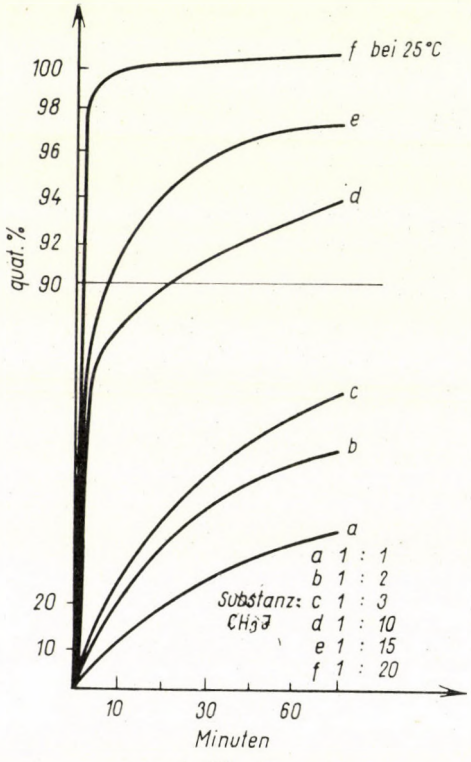

Fig. 2

ist, gelingt eine quantitative Umwandlung auch bei 50° nur in Anwesenheit eines 20fachen Methyljodidüberschusses. Mit weniger Methyljodid sind 60 Minuten Wartezeit noch ungenügend. Auf Grund der Versuche wird folgende Methode zur cyanometrischen Bestimmung von Isochinolinderivaten empfohlen:

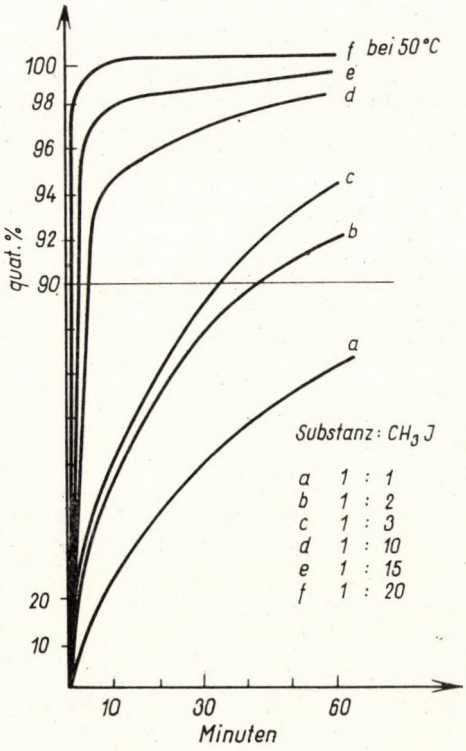

Fig. 3

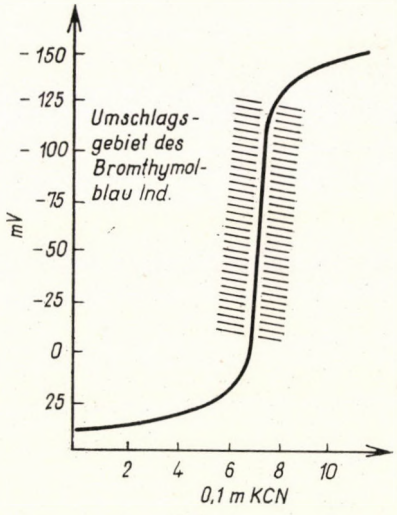

Fig. 4

Lösungen und Geräte:

6,7-Dimethoxy-3,4-dihydro-isochinolin, aus Petroläther zweimal umkristallisiert. (Das so erzeugte Produkt ist ölig, beim Stehen wird es kristallin.)

Methyljodid, pa., D.: 2,28.

Aceton, Chloroform, Isopropylalkohol, alle analyserein.

0,1 *n* isopranolische Kaliumcyanidmaßlösung: 6,5 g KCN werden in 100 ml Wasser gelöst und mit Isopropylalkohol auf 1000 ml ergänzt. Die Maßlösung ist gegen den Kohlendioxydgehalt der Luft zu schützen. Der Faktor der Lösung wird gegen 0,1 *n* Silbernitratlösung folgendermaßen eingestellt: 20 ml Kaliumcyanidlösung werden in einen 250-ml-Erlenmeyerkolben pipettiert, mit 50 ml Wasser, 2 ml 6 *n* Ammoniumhydroxydlösung und ungefähr 0,5 g Kaliumjodid versetzt, dann solange mit der 0,1 m Silbernitratlösung titriert, bis eine bleibende Trübung in der Lösung entsteht.

Bromthymolblau-Indikator: 0,1%ige Lösung in 20%igem Alkohol. 3—4 Tropfen werden für 20 ml Titriervolumen benötigt.

pH-Meßgerät, Glas- und Kalomelelektrode. (Wir gebrauchten ein Radelkisz-Gerät Type OP 203 und Metrohm kombinierte Glas- und Kalomelelektrode.)

Bestimmung:

Ungefähr 100 mg der zu bestimmenden Substanz werden in einen Kolben eingewogen, der bei konstanter Temperatur gehalten werden kann. Man stellt die Temperatur auf 25° ein und löst die Substanz unter Umrühren in 10 ml Aceton. Dann versetzt man mit 0,7 ml Methyljodid, rührt 10 Minuten mit einem Magnetrührer und gibt 10 ml Chloroform und bald danach 40 ml Isopropylalkohol hinzu. Dann titriert man zwischen Glas- und Kalomelelektroden mit 0,1 *n* isopropanolischer Kaliumcyanidmaßlösung. Während der Titration soll Stickstoffgas durch die Lösung geleitet werden. Den Endpunkt kann man auch visuell bestimmen; wie die potentiometrische Titrationskurve (Abb. 4) erkennen läßt, liegt der Potentialsprung im Umschlagsgebiet des Bromthymolblaus. Zu einer Titration sind 3—4 Tropfen des Indikators zu gebrauchen.

Unsere Ergebnisse sind in Tab. I dargestellt. Die Standard-Deviation war auf Grund der Parallelen ±0,105%.

Tabelle I

Bestimmung von 6,7-Dimethoxy-3,4-dihydroisochinolin

Einwaage mg	0,1 n KCN Verbrauch ml	Gefunden mg	Abweichung %
114,21	6,63	113,20	−0,8
114,21	6,63	113,20	−0,8
114,21	6,70	114,30	+0,0
114,21	6,63	113,20	−0,8
114,21	6,65	113,60	−0,7
114,21	6,63	113,20	−0,8

Wir danken Herrn Prof. L. ERDEY für seine Ratschläge bei unserer Arbeit.

ZUSAMMENFASSUNG

Substituierte Derivate des Isochinolins lassen sich bestimmen, indem sie mit Methyljodid in quaternäre Ammoniumsalze übergeführt und als solche mit isopropanolischer Kaliumcyanidlösung titriert werden. Die Methode wurde beim 4,7-Dimethoxy-3,4-dihydroisochinolin erprobt; sie ist geeignet für alle Derivate, die mit Alkylhalogenid quantitativ das Ammoniumsalz liefern. Die Abweichung von der Einwaage betrug bei den Bestimmungen −0,9%, die Standard-Deviation ±0,105%.

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Acta Chimica Academiae Scientiarum Hungaricae Tomus 55 (1), pp. 29—32 (1968)

INVESTIGATION OF THE POLAROGRAPHIC ADSORPTION OF 4,4-BIS (TRIAZINYLAMINO)-STILBENE-2,2-DISULFONIC ACID DERIVATIVES WITH TRIANGLE VOLTAGE POLARIZATION IMPULSE TECHNIQUE*

(SHORT COMMUNICATION)

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Received March 27, 1966

In the course of systematic investigations [1—6] of the polarographic adsorption of 4,4'-bis(triazinylamino)stilbene-2,2'-disulfonic acid derivatives, it has been established that the main polarographic adsorption characteristics of these compounds agree with one another. Using 1 *M* KOH solution as supporting electrolyte, the compounds are adsorbed from the positive end of the polarogram. Desorption occurs between —1.40 and 1.45 V (SCE) if the aromatic character of the triazine rings has not been disturbed by substitution [4]. In the case of some compounds, within certain limits of the adsorption potential range, an increase in the thickness of the adsorption layer is observed which can probably be explained by the formation of a polylayer [6].

The previous investigations had been performed by means of the electrocapillary curves, by d.c., a.c. and a.c. oscillopolarographic techniques. In the first case the polarization voltage can be regarded as constant; in the case of the d.c. technique the speed of the potential change is ~0.01 V/sec. This value is similar in the a.c. technique, with the difference that here a small (5 mV), indicating alternating potential, is also superposed on the polarizing potential (this essentially does not affect the electrode processes); in a.c. oscillopolarography the speed of the voltage change is 200 V/sec. Since in the polarographic techniques used in the former investigations the speed of the potential change had been rather different, it seemed reasonable to investigate the compounds with a technique employing medium speed of potential change, such as about 1 V/sec, to find out whether the speed of the change of the polarizing potential affects essentially the adsorption process.

The triangle voltage impulse technique [8—14] appeared suitable to realize this aim. It is known [7] that the current (i), flowing through an elec-

* A part of the author's C. Sc. Thesis.

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trode polarized by a linear current impulse sweep, is directly proportional to the differential capacity (C_d):

$$i = A \cdot v \cdot C_d$$

where A — is the surface area of the electrode and
v — is the speed of the potential change.

Thus adsorption effects can be investigated advantageously by this method as both at the adsorption and desorption potentials a change appears in the differential capacity resulting in a capacity wave in the polarogram.

Experimental

The usual experimental technique and the instrument described in detail by VALENTA [8] was used.

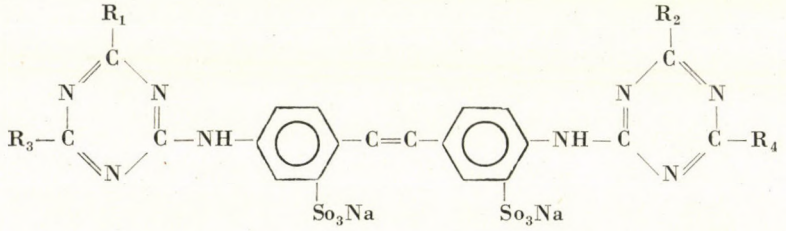
The drop time of the capillary used was about 7 sec. Before switching on the polarizing impulse, the mercury drop was polarized for 4.3 sec with −0.2 V (SCE) potential. The slope of the voltage pulse was 0.46 V/sec.

1 *M* potassium hydroxide solution was used as the supporting electrolyte, and a mercury pool as the references electrode.

The compounds investigated were laboratory products, the purity of which had been checked by paper chromatography [15].

Results and discussion

Ten variously substituted derivatives of 4,4'-bis(triazinyl-amino)stilbene-2,2'-disulfonic acid have been studied. The compounds contained methoxy, phenoxy, (2-hydroxyethyl)amino, di-(2-hydroxyethyl)amino and anilino substituents.



The following variations have been investigated: $R_1 = R_2 = R_3 = R_4$, $R_1 = R_2 = R_3 \neq R_4$, $R_1 = R_2 \neq R_3 = R_4$, $R_1 = R_3 \neq R_2 = R_4$, $R_1 = R_3 \neq \neq R_2 \neq R_4$ and $R_1 = R_2 \neq R_3 \neq R_4$.

In the polarograms, both in the case of curves corresponding to increasing and decreasing voltage, a capacitive wave appears, the peak potential (average value of 10 measurements) of the former being -1.41 ± 0.03 V (SCE), and that of the latter -1.28 ± 0.02 V (SCE). (The deviation from the average is given in terms of standard deviation.) As the polarograms agree with one another in their main features, only one polarogram is presented here as example (Fig. 1), which shows the curve of the compound where $R_1 = R_2 =$ = methoxy and $R_3 = R_4 =$ phenoxy groups.

The results obtained by the triangle impulse method show good agreement with previous measurements made by other techniques. The potential difference between the peaks registered with increasing and decreasing voltage, and the direction and extent of this difference are in agreement with the similar

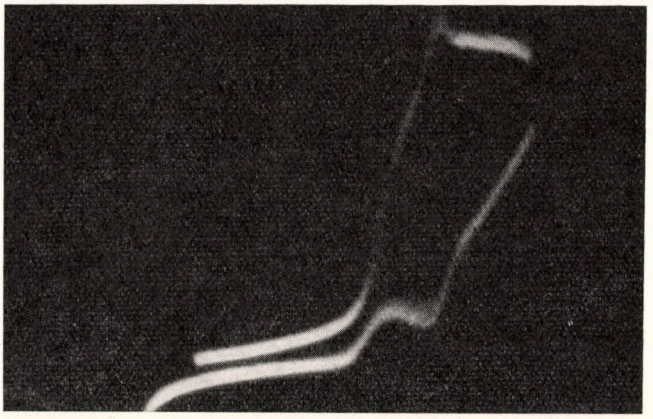


Fig. 1. Impulse polarogram of the compound $R_1 = R_2 =$ methoxy; $R_3 = R_4 =$ phenoxy

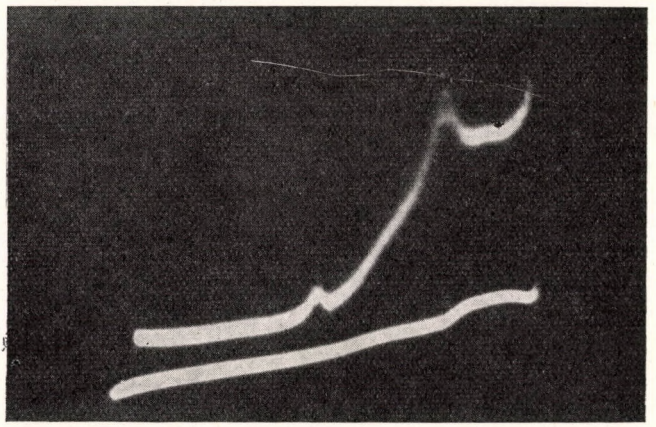


Fig. 2. Impulse polarogram of the compound $R_1 = R_2 =$ (2-hydroxyethyl)amino $R_3 =$ = methoxy; $R_4 =$ ethoxy

deviations obtained with the oscillopolarographic method [1]. This observation shows that the quantitative conditions of the adsorption process are affected by the potential change even in the present method notwithstanding that the potential is changed at an essentially lower rate.

In the polarogram on one of the compounds ($R_1 = R_2 =$ (2-hydroxyethyl)amino $R_3 =$ methoxy; $R_4 =$ ethoxy) (Fig. 2), showing the recently reviewed [6] boat-like depression in the a.c. polarogram, a small wave can

be observed at the potential corresponding to the inflexion point of the decreasing branch of the boat-like depression. However, this wave does not afford further information about the nature of the process causing the boat-like depression.

The author is indebted to Dr. P. VALENTA for his valuable help and advice and to the J. HEYROVSKY *Polarographic Institute of the Czechoslovak Academy of Sciences* (Praha) for making possible to perform the measurements.

SUMMARY

Ten variously substituted derivatives of 4,4'-bis-(triazinylamino)stilbene-2,2'-disulfonic acid have been investigated by means of the triangle impulse polarographic method. The results are in good agreement with the observations made with other techniques.

When polarizing the electrode by increasing and decreasing voltage, the compounds give rise to waves having the peak potential of 1.41 ± 0.03 V (SCE) and 1.28 ± 0.02 V (SCE), respectively.

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Gyula PÁLYI; Veszprém, Schönherz Z. u. 10

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BESTIMMUNG DES AMINOSTICKSTOFFGEHALTS VON γ-GLUTAMYLPEPTIDEN MIT HILFE EINES MODIFIZIERTEN VAN SLYKESCHEN VERFAHRENS

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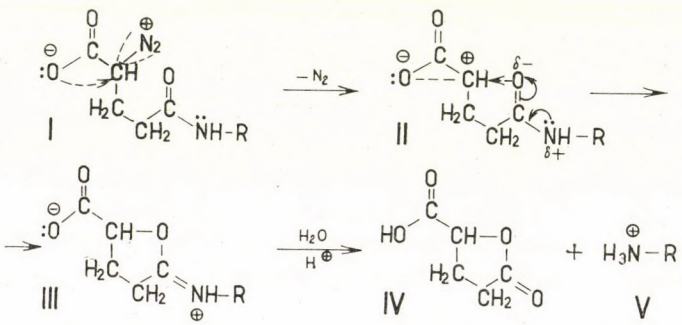
Die quantitative Bestimmung des Aminostickstoffgehalts von Aminocarbonsäuren und Peptiden läßt sich am einfachsten nach der Methode von VAN SLYKE [1] durchführen. Aus dem Aminostickstoffwert kann man oft auch das Molekulargewicht berechnen, und eben dies stellt eines der einfachsten Verfahren zur Ermittlung des durchschnittlichen Molekulargewichtes von Polyaminosäuren dar [2].

Nach dem ursprünglichen Verfahren von VAN SLYKE [1] wird die Desaminierung in wäßriger Essigsäure mit Natriumnitrit bzw. mit der aus ihrem Salz freigesetzten salpetrigen Säure bewirkt. Unter solchen Bedingungen kann es jedoch bei einigen Aminosäuren und Peptiden, ferner bei einer Reihe von anderen Aminoverbindungen zu unerwünschten Nebenreaktionen kommen, wodurch eine größere Menge Stickstoff freigesetzt wird, als der Aminogruppe entspräche. Mehrere Forscher studierten derartige unerwünschten Nebenreaktionen und schlugen zwecks ihrer Unterdrückung verschiedene Modifizierungen des ursprünglichen VAN SLYKEschen Verfahrens vor. Besonders eingehende Untersuchungen in dieser Beziehung hat KAINZ [3] durchgeführt und nach systematischem Überblick und gründlicher Analyse der Nebenreaktionen verschiedener Typen die Versuchsbedingungen auf verschiedene Art geändert. Es gelang ihm dadurch zur Bestimmung des Aminostickstoffgehalts von vielerlei Aminoverbindungen zuverlässige Methoden auszuarbeiten. Als besonders brauchbar erwies sich die Abänderung, laut welcher die Desaminierung in Eisessig durch Nitrosylbromid bewirkt wird [4]. Das hierzu nötige Reagens wird durch Zusatz von Natriumnitrit zu einer Lösung von Brom in Eisessig hergestellt. Das Reagens enthält — eben zur Unterdrückung gewisser Nebenreaktionen — überschüssiges Brom [4]. Die Durchführung dieser Bestimmung nach KAINZ ist bedeutend einfacher als das ursprüngliche manometrische Verfahren von VAN SLYKE.

SACHS und BRAND [5] haben als erste darauf hingewiesen, daß Peptide mit N-terminaler γ-Glutamylgruppe im Laufe der VAN SLYKEschen Bestimmung nicht bloß eine Desaminierung der N-terminalen Aminogruppe erleiden, sondern daß zugleich die zum nächsten Aminosäureglied gehörige (ursprünglich

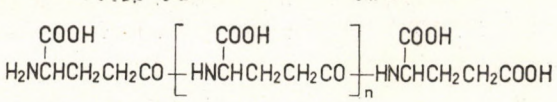
in die Peptidbindung eingebaute) Aminogruppe freigesetzt wird, und nachher mit salpetriger Säure sofort reagiert. Dementsprechend liefert die Bestimmung z. B. im Falle des γ-Glutamyl-glycins und der γ-Glutamyl-glutaminsäure zwei freien Aminogruppen entsprechende Werte, und im Falle der γ-Glutamyl-γ-glutamyl-glutaminsäure werden sogar drei Mole Stickstoff pro Mol Substanz freigesetzt. Dieses sonderbare Verhalten von γ-Glutamylpeptiden, das KAINZ[4] in seine Untersuchungen nicht einbezogen hat, haben SACHS und BRAND [6] auch zu deuten versucht. Dabei stützten sie sich auf Analogiefälle und auch auf die Ergebnisse einiger Sonderversuche, ein strenger Beweis der Richtigkeit des von ihnen vorgeschlagenen Mechanismus steht jedoch noch aus. Laut ihrer Vermutung wird die aus der Aminogruppe des N-terminalen γ-Glutamylrestes gebildete Diazoniumgruppe unter Mitwirkung der benachbarten α-Carboxylgruppe (bzw. des Carboxylat-Anions), dem Grunde nach im Sinne eines SN1 Mechanismus [7] abgespalten (**I** → **II**); das so entstandene Carboniumion (**II**) ist von seiner Rückseite von dem Carboxylat geschützt, so daß ein nucleophiler Angriff nur von derselben Seite erfolgen kann, an welcher sich ursprünglich die Diazonium- bzw. Aminogruppe befand. Dieser nucleophile Angriff erfolgt durch das stark negativ polarisierte Sauerstoffatom der γ-Peptidbindung, wodurch ein γ-Lactonimin(**III**) entsteht, das dann im wäßrigen Medium gleich zum entsprechenden γ-Lacton(**IV**) hydrolysiert, unter gleichzeitiger Freisetzung der Aminogruppe der ursprünglich zweiten Aminosäure(**V**); diese neugebildete Aminogruppe wird selbstredend von der salpetrigen Säure desaminiert, wobei abermals ein Mol Stickstoff freigesetzt wird. Die geschilderten Reaktionsschritte sind nachstehend formuliert:



Dieser spezielle Abbau, den γ-Glutamylpeptide in wäßrigem Medium durch Einwirkung von salpetriger Säure erleiden, hatte eine nachteilige Auswirkung auf Untersuchungen, die die Synthese von stereoisomeren γ-Polyglutaminsäuren anstrebten, da die Bestimmung des durchschnittlichen Molekulargewichtes des synthetischen Produktes durch Ermittlung des Amino-

stickstoffgehalts nach VAN SLYKE nicht möglich war [8]. Im Sinne des von SACHS und BRAND vermuteten Mechanismus sollte eine γ-Polyglutaminsäure im Laufe der VAN SLYKEschen Reaktion einen dem Gesamtstickstoffwert gleichen Aminostickstoffwert liefern, vorausgesetzt, daß genügend salpetrige Säure angewandt und die Reaktionsdauer genügend lang gehalten wurde. Hingegen hat die Erfahrung gezeigt, daß zwar die Menge des freigesetzten Stickstoffs mit der Verlängerung der Reaktionsdauer ansteigt, jedoch die dem Gesamtstickstoff entsprechende Menge bei weitem nicht erreicht wird. Die unter den üblichen, standarden Bedingungen durchgeführte Bestimmung nach VAN SLYKE lieferte in der Regel ungefähr den sechsfachen Wert des tatsächlichen Aminostickstoffgehalts. Dies konnte aus dem nach VAN SLYKE ermittelten Aminostickstoffwert einer Anthrax-Polyglutaminsäure (d. h. γ-Poly-D-glutaminsäure) festgestellt werden, deren Molekulargewicht mit Hilfe der Lichtbeugungsmethode bestimmt wurde [8].

Nach dem von SACHS und BRAND vorgeschlagenen, früher bereits erörterten Mechanismus erscheint die neue Aminogruppe infolge der spontanen Hydrolyse des aus dem γ-Glutamylpeptide intermediär gebildeten Lactonimins(**III**). Da diese Reaktion in wasserfreiem Medium nicht stattfinden kann, versuchten wir die von KAINZ [4] ausgearbeitete Desaminierungsmethode, die als Reagens in Eisessig gelöstes Nitrosylbromid und Brom verwendet, auf γ-Glutamylpeptide zu übertragen. Als Modellverbindungen wurde eine Reihe von Glutaminsäure-γ-oligopeptiden herangezogen, und zwar von der γ-Glutamyl-glutaminsäure beginnend bis zur γ-Heptaglutaminsäure (**VI**; $n = 0-5$):*



VI

Unsere Versuchsergebnisse sind in Tabelle I zusammengefaßt. Wie ersichtlich, stimmen die mit Hilfe des von KAINZ modifizierten Verfahrens bestimmten Aminostickstoffwerte mit den berechneten genügend überein. Die Fehlergrenze beträgt rund $\pm 0{,}3\%$, d. h. sie zeigt einen bei Mikroanalysen allgemein zulässigen Wert. Etwas größere Abweichungen in einigen Fällen sind nicht der Ungenauigkeit der Methode zuzuschreiben, sondern damit zu deuten, daß einige Oligopeptide dieser Reihe nicht in wasserfreien Zustand gebracht werden können, und das gebundene Wasser nicht direkt bestimmt werden kann.

* Über die Synthese dieser Oligopeptide, deren Konfigurationsbezeichnungen hier der Einfachkeit wegen fortgelassen wurden, wird an anderer Stelle [9] berichtet.

Tabelle I

Versuchsergebnisse der Stickstoffanalyse von Glutaminsäure-γ-oligopeptiden

Substanz	Berechnet		Gefunden		
				Amino-N%	
	Gesamt-N%	Amino-N%	Gesamt-N% (DUMAS)	VAN SLYKEsches Verfahren	KAINZsches Verfahren
Dipeptid	10,14	5,07	9,89	9,37	5.00 5,13
Tripeptid	10,38	3,47	10,21	10,22	3,38 3,50
Tetrapeptid	10,48	2,63	9,65	8,38 8,49	2,48 2,50
Pentapeptid	10,55	2,12	9,86	7,56 7,60	1,94 2,19
Hexapeptid	10,60	1,77	10,45	7,05	1,68 1,74
Heptapeptid	10,64	1,52	10,12	7,62	1,45 1,54

Zum Vergleich enthält die Tabelle auch »Aminostickstoffwerte«, die mit Hilfe des ursprünglichen VAN SLYKEschen Verfahrens ermittelt worden sind. Man sieht, daß die so gewonnenen Werte ganz falsch sind und ferner, daß nur im Falle des Di- und Tripeptids ein vollständiger Abbau stattgefunden hat, während die höheren Oligomere weniger Stickstoff abgeben als dem Gesamtstickstoffgehalt entspräche.

Die an Hand der aufgezählten Oligopeptide erprobte Bestimmungsmethode erwies sich auch zur Bestimmung der Aminostickstoffwerte von γ-Polyglutaminsäuren als geeignet. Die aus den so ermittelten Werten berechneten Molekulargewichte zeigten eine befriedigende Übereinstimmung mit den auf anderen Wegen bestimmten Molekulargewichten [10]. Somit kann also die Methode von KAINZ [4] auch zur Bestimmung des Aminostickstoffgehalts von γ-Polyglutaminsäuren herangezogen werden, und dies ermöglicht die Bestimmung ihres durchschnittlichen Molekulargewichtes auf recht einfache Art.

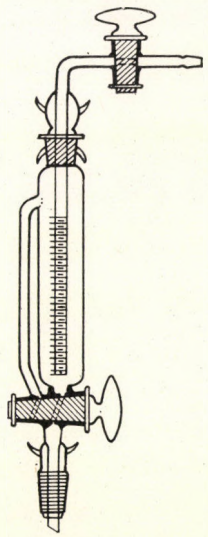
Nun haben wir versucht zu entscheiden, ob der Abbau von γ-Glutamylpeptiden unter den von uns nach der Angabe von KAINZ angewandten Versuchsbedingungen in der Tat nur deshalb nicht erfolgt, weil das zum Einsetzen der Teilreaktion **III** → **IV** + **V** nötige Wasser fehlt. Zur Entscheidung dieser Frage haben wir eine Probe von γ-Glutamyl-glutaminsäure (**VI**; $n = 0$) in Eisessig mit Hilfe von Nitrosylbromid desaminiert und nach Ablauf der

Reaktion (wobei pro Mol Substanz ein Mol Stickstoff entwickelt worden war) das Reaktionsgemisch — unter Luftausschluß — mit dem gleichen Volumen Wasser versetzt. Unter diesen Bedingungen sollte das **III** Lacton-imin hydrolysieren, somit die Aminogruppe der C-terminalen Glutaminsäure freigesetzt werden und sofort mit der durch Hydrolyse des überschüssigen Nitrosylbromids gebildeten salpetrigen Säure reagieren. Entgegen dieser Erwartung wurde jedoch nach dem Wasserzusatz keine erneute Stickstoffentwicklung beobachtet. Es ist somit sehr wahrscheinlich, daß die N-terminale γ-Glutamylgruppe vom Nitrosylbromid im Sinne der gut bekannten Reaktion der α-Aminosäuren [11] zur α-Bromglutarylgruppe umgewandelt wird, daß also das intermediäre Carboniumion (**II**) mit dem aus dem Nitrosylbromid gebildeten Bromidion reagiert, und somit die Bildung des **III** Lactonimins nicht mehr möglich ist.

Experimentelles

Die Analysen wurden (von geringfügigen Abänderungen abgesehen) in dem von KAINZ [4] beschriebenen Apparate nach seiner Vorschrift durchgeführt. Im Falle von γ-Polyglutaminsäuren, die allgemein nur 0,1—0,5% Aminostickstoff enthielten, betrug die Einwage 30—40 mg anstatt der sonst üblichen 2—3 mg; bei solchen größeren Einwagen wurden 4 ml anstatt der vorgeschriebenen 2 ml des Reagens eingeführt, da dieses zugleich als Lösungsmittel dient. Deshalb wurde auch der Apparat entsprechend vergrößert, und zwar der Reaktionskolben von 7 ml auf 15 ml, das Reagensgefäß von 15 ml auf 30 ml. Auch wurde eine zweckmäßige Änderung am Reagensgefäß durchgeführt; sie ist aus Abb. 1 ersichtlich. Die Durchführung einer Bestimmung dauert samt Vorbereitung 40—45 Minuten. Es lassen sich etwa 8 Analysen nacheinander ohne Austausch und erneute Auslüftung des Reagensgefäßes durchführen. Die Maße der Apparatur wurden schon zwecks Ermöglichung von Serienanalysen vergrößert.

Im Laufe von Peptidsynthesen kann das Fortschreiten einer Kupplungsreaktion durch zeitweise Bestimmung des Aminostickstoffgehalts des Reaktionsgemisches verfolgt werden



Fgi. 1

Es wurde deswegen untersucht, ob die Methode von KAINZ auch dann anwendbar wäre, wenn der Bestimmung nicht isolierte Substanzen, sondern ihre Lösungen unterworfen werden; dabei kommen selbstredend nur solche wasserfreie Lösungsmittel in Betracht, die bei den erwähnten Kupplungsreaktionen angewendet werden können. Unsere diesbezüglichen Versuche ergaben befriedigende Resultate; erprobt wurden Dimethylformamid, Pyridin, Acetonitril, Dioxan und Tetrahydrofuran. Es wurden jeweils 1—2 ml der Substanzlösung angesetzt (d. h. ungefähr 10 μMol der gelösten Aminoverbindung) und dazu 2—5 ml (ungefähr das zweifache Volumen) der Reagenslösung verwendet. In diesen Fällen muß jedoch für jedes Lösungsmittel vorerst ein Blindwert bestimmt werden, der dann bei der Berechnung der Analyse in Betracht zu ziehen ist.

Herrn Prof. V. BRUCKNER sei für die Anregung dieser Arbeit und für seine wertvollen Ratschläge auch an dieser Stelle gedankt.

ZUSAMMENFASSUNG

Der Aminostickstoffgehalt von γ-Glutamylpeptiden läßt sich mit Hilfe der ursprünglichen VAN SLYKEschen Methode nicht bestimmen, da solche Peptide im Laufe dieser Bestimmung nebst Desaminierung eine allmähliche Spaltung der γ-Peptidbindung erleiden, wodurch auch die Aminogruppe des nächsten Aminosäureglieds freigesetzt wird. Hingegen wurde jetzt an Hand einer Reihe von Glutaminsäure-γ-oligopeptiden bewiesen, daß die von KAINZ modifizierte Bestimmungsmethode die richtigen Aminostickstoffwerte liefert. Diese Methode ist auch zur Bestimmung der Aminostickstoffwerte von γ-Polyglutaminsäuren und somit zur Ermittlung ihrer durchschnittlichen Molekulargewichte geeignet.

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INVESTIGATION OF MECHANICALLY ACTIVATED CATALYSTS, VI*

CATALYTIC HYDROGENATION OF PHENOL AND HIGHER ALCOHOLS WITH MECHANICALLY ACTIVATED COMMERCIAL NICKEL POWDER

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Introduction

Recently, it has been reported that the reactivity of solids may be considerably enhanced by means of mechanical treatment, such as scratching, pulverizing, rolling or grinding in a ball mill [1—5]. The first studies in this field were mainly of theoretical interest, and the methods of mechanical activation have only achieved practical importance after the development and introduction of vibration mills of continuous operation.

We have shown in previous researches [6—9] that the disarrangement of a crystal lattice, as produced by the vibration grinding of solids, has a decisive effect on chemical reactivity.

Mechanical activation is of prominent importance also in the field of catalysis. The effect of rolling and grinding on catalytic activity has been proved by ECKEL [10] and RIENÄCKER [11, 12], while that of pressure by HEINLE and KROGMANN [13]. The effect of mechanical treatment (scratching by materials of adequate hardness) on the activity of metal plates has been studied by HEINICKE and LISCHKE [14]. PAUDERT [15] investigated the changes in activity of vanadium pentoxide applied as catalyst in the oxidation of sulphur dioxide. KIPERMAN, BALANDIN and DAVYDOVA [16] established the effect of super-pulverization by vibration grinding on the activity of catalysts of nickel skeleton. In our earlier investigations we have shown that it is possible to prepare active catalysts by subjecting a catalytically inactive metal powder to vibration grinding [17]. Studies on the degree of activity of various catalysts prepared from commercial powders of cobalt and nickel and from those subjected to reduction, showed that mechanical treatment of these powders in a vibration mill markedly raised the catalytic activity in the hydrogenation of benzene. The rise of activity was found to be correlated with the length of the activation period. It was verified by surface area measurements, X-ray diagrams, and by magnetic and kinetic investigations that the formation of a so-called "active lattice" is actually responsible for the activity of these

* Part V: SCHRADER, R., JACOB, G.: Chem. Techn. (In the press.)

catalysts [18—20]. In order to confirm these results, it appeared desirable to apply the same types of mechanically activated commercial nickel powders also in hydrogenation reactions other than the hydrogenation of benzene.

Experimental

Hydrogenation of phenol under atmospheric pressure

A fluidized bed apparatus (Fig. 1) was applied in the experimental hydrogenations of phenol under atmospheric pressure. A uniform dispersion in phenol of the nickel catalyst was prepared in the reaction zone of the apparatus by passing an ascending current of hydrogen through this zone. The temperature of the hydrogenation apparatus was kept constant by means of contact thermometers. The mass ratio phenol : catalyst was chosen to be equal to unity; the flow rate of hydrogen ranged 100 litres/hr. Phenol was hydrogenated under these conditions in the presence of nickel catalysts prepared by mechanical activation for various

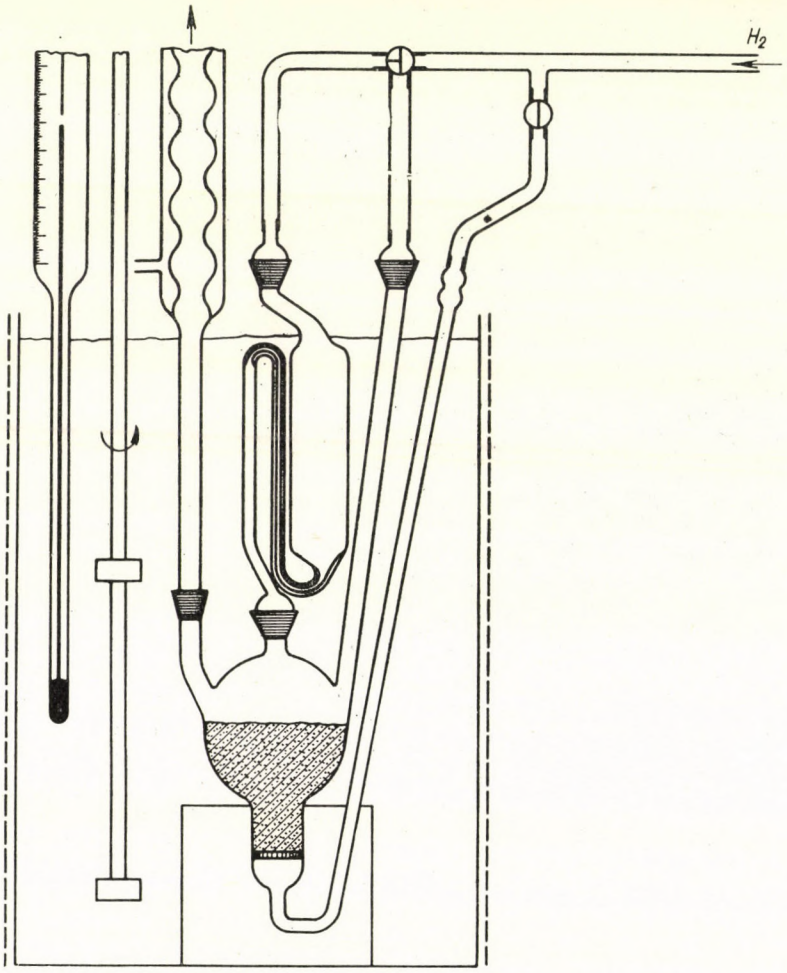

Fig. 1. Fluidized bed apparatus for hydrogenation

periods. The conversion rates of phenol were determined by means of a refractometer, comparing the values with a standard curve (phenol : cyclohexanol). Repeated runs proved that the experimental values were reproducible.

The conversion rates of phenol plotted against the reaction times, obtained in experiments at 150° in the presence of nickel catalysts prepared by mechanical activation for various

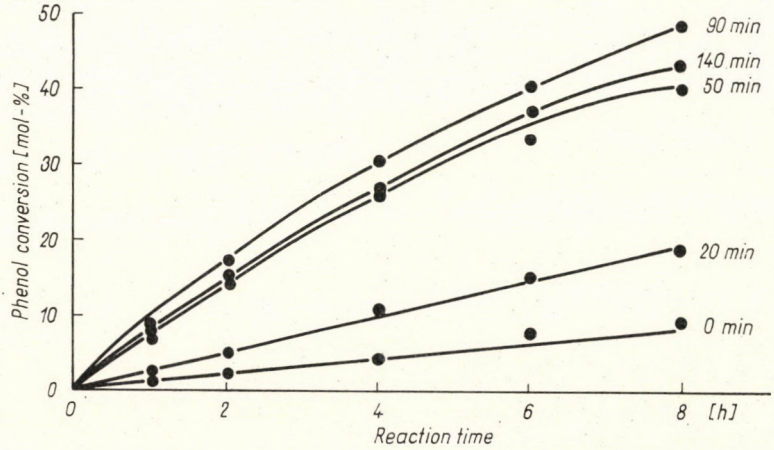

Fig. 2. Conversion rates of phanol plotted against the reaction time (fluidized bed hydrogenation) Parameter: Activation period of nickel catalyst, minutes

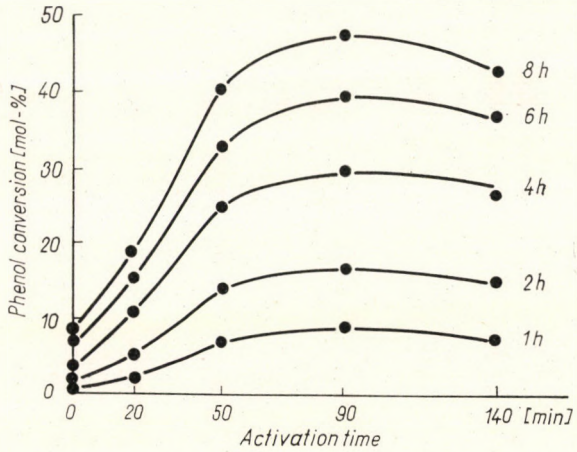

Fig. 3. Conversion rates of phenol plotted against the activation periods of the nickel catalyst (fluidized bed hydrogenation). Parameter: Time of reaction, hrs.

periods, are shown in Fig. 2. Only very slight conversion of phenol was obtained with untreated nickel powder, while in the case of mechanically activated catalysts the conversion rates disclosed an almost linear rise with the activation periods, up to eight hours. The reaction rate of the hydrogenation of phenol was found to be a function of the length of the activation period of the nickel catalyst.

In an experiment carried out at 150° with a catalyst prepared by activation for 90 minutes, after a prolonged reaction period a limit value was attained; above this value the conversion rates did not rise linearly any more. An equilibrium was observed at a phenol conversion of about 70 mole-%.

Conversion rates of phenol plotted against the periods of activation of the applied catalysts, taking into account also the reaction times, are presented in Fig. 3. It can be seen that, up to an activation treatment of about 50 minutes, conversion rates steeply rise with the length of the activation periods. On further increasing the length of treatment, the conversion rates of phenol rise but slightly, while on applying a nickel catalyst, previously subjected to excessively long periods of activation, some decrease of the catalytic activity is observed.

On examining the dependence on temperature of the hydrogenation of phenol at atmospheric pressure in the range between 120 and 170°, the maximum rates of conversion were found at 150°. Above that temperature, the catalytic activity began to decrease.

Possible errors in establishing the rates of conversion of phenol may be due to losses caused by discharge of the product into the cooling system, to formation of cyclohexanone as by-product in the hydrogenation of phenol, to absorption of water by the final product and to improper sampling. However, since these errors are rather small and as they have partly increasing and partly reducing effect on the obtained values of conversion, they compensate one another, and they do not exceed the order of accuracy of reading the refractometer.

Hydrogenation of phenol under high pressures

In the high-pressure experiments of phenol hydrogenation a shaking autoclave was employed. A thermal control system equipped with a platinum resistance thermometer was used to maintain the prescribed temperature. A hydrogen pressure of 120 atm. was applied for 10 hrs., and the hydrogenation experiments were carried out at various temperatures in the presence of nickel catalysts prepared by activation treatment for different periods. When

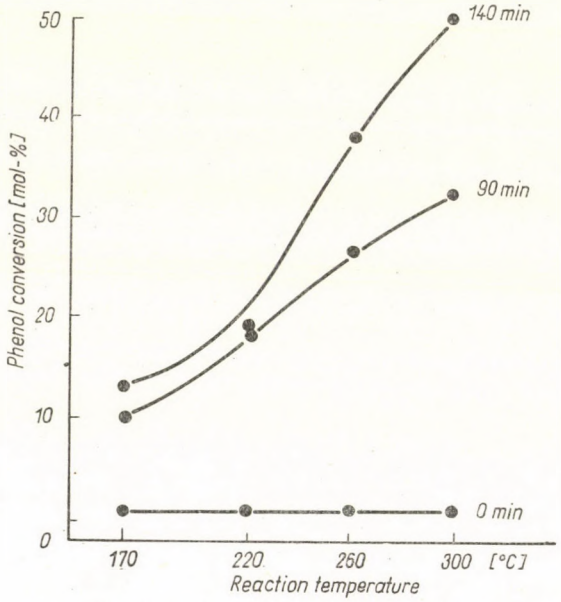

Fig. 4. Conversion rates plotted against the reaction temperature (hydrogenation in an autoclave). Parameter: Activation periods of nickel catalyst, minutes

hydrogenation had been completed, the conversion rates of phenol were established by means of refractometer readings, and the diagrams temperature *versus* time, and pressure *versus* time were plotted. The respective diagrams are presented in Fig. 4.

It can be clearly seen that practically no conversion of phenol took place throughout the entire temperature range when untreated nickel powder was applied, proving that the hydrogenation of phenol is impossible without a previous mechanical activation of the nickel

catalyst. On employing a nickel catalyst activated for 80 minutes, the conversion rates of phenol ranged from 10 to 30%, depending on the temperature applied. With nickel catalysts activated for 140 minutes, still higher rates of conversion were obtained which could be even further increased by raising the reaction temperature. *E.g.*, at a reaction temperature of 300°, exclusively cyclohexane was formed with no cyclohexanol at all.

The formation of cyclohexanone and cyclohexane as by-products of the hydrogenation of phenol in the liquid phase under high pressure and particularly at high temperatures had also been described by IPATIEV [21].

Hydrogenation of higher alcohols

In order to understand more thoroughly the behaviour of mechanically activated nickel powders as catalysts, higher alcohols were also subjected to hydrogenation tests. The commercial product *Ocenol 70* was chosen as a model substance. In the hydrogenation experiments of *Ocenol 70* the apparatus used was the same as that employed in the hydrogenation of phenol. Throughout the experiments, a mixture of 45 g of *Ocenol 70* and 8 g of nickel catalyst was subjected to hydrogenation at 200° and 240° at a flow rate of 125 litres of hydrogen per hour. Nickel catalysts previously activated for different periods were employed. The conversion rates were established by the semi-micro determination of the iodine number of the product according to Kaufmann.

Changes in the iodine number of the hydrogenation product plotted against the reaction times at 200° are presented in Fig. 5. The results distinctly show the increase of the rate of hydrogenation of Ocenol 70 with the length of the activation period of the catalyst. This increase is particularly marked in the case of short reaction times.

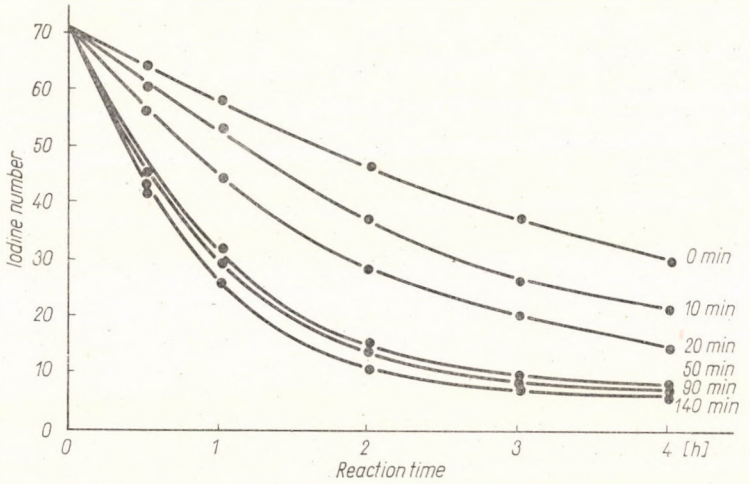

Fig. 5. Hydrogenation of ocenol (as determined from the iodine numbers) plotted against the reaction time. Parameter: Activation period of nickel catalyst, minutes

Untreated nickel powder had only a slight catalytic action. However, when a nickel powder previously activated for at least 50 minutes was applied as the catalyst, a final product of iodine number 7 was obtained after a reaction time of about 3 hrs. Fig. 6 shows the progress of the hydrogenation of *Ocenol 70* at 200° plotted against the length of the activation periods of the nickel catalyst applied. It appears clearly from these data that, up to an activation period of 50 minutes, the iodine numbers of the hydrogenation products show a rise parallel to the length of the activation periods. Above this limit value, no essential effect of prolonged periods of activation can be observed. It also follows from the results presented in Fig. 6 that a hydrogenation period of 3 hrs. in the presence of a nickel catalyst activated by a 50-minute treatment had optimum effect. On carrying out the hydrogenation at 240° instead of 200°, the curves showing the iodine number of product *versus* the reaction time are less

divergent, they are lower and approach the curves obtained with untreated nickel powder. This effect is ascribed to the deterioration of the catalyst at elevated temperatures. In the hydrogenation of benzene, a similar loss of activity of the nickel catalyst activated under identical conditions has been reported by GRUND [22].

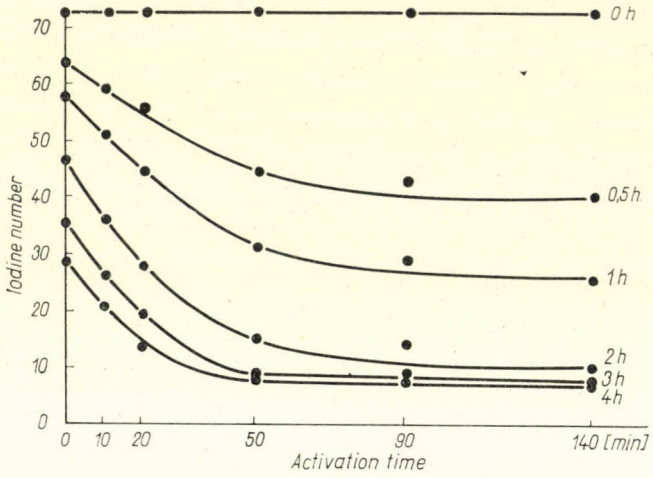

Fig. 6. Hydrogenation of ocenol (as determined from the iodine numbers) plotted against the activation periods of nickel catalysts

Discussion of the experimental results

In order to obtain evidence about the basic principles playing part in the increase of the catalytic activity of nickel powder catalysts activated mechanically in a vibration mill, the phenol conversion (under atmospheric pressure) and the surface, lattice distortion and lattice defects of the catalyst have been plotted in a combined form in Fig. 7 against the lengths of the activation periods.

The activity of the solid particles of the catalyst samples was determined by a method evolved earlier [22], and based on a standard preparation of nickel catalyst. Comparing the curve of the percentage phenol conversion with that representing the increase of the catalyst surface, it is found that both functions increase with the length of the activation period, up to the time of 50 minutes. Above this value, the curve of the percentage phenol conversion still shows a rising tendency, while the value of catalyst surface (determined by the micro-BET method with an error of $\pm 5\%$) decreases. Consequently, the increase of activity of the nickel powder cannot be explained by the larger values of free surface area alone. In contrast to the values of free surface, the functions representing lattice deformations [23] and lattice defects [24] are in good agreement with the curve of phenol conversion. These observations indicate that the lattice distortions and lattice defects created in the nickel catalyst

by vibration milling are of decisive importance from the aspect of catalytic activity. In other words, instead of the free surface area, rather the state of disarrangement appears to be responsible for the enhanced activity of mechanically activated nickel catalysts.

The experimental data of the hydrogenation of phenol in an autoclave under high pressure cannot be interpreted either by the increase of the free surface area or by the disarrangement of the lattice of the catalyst. Owing to

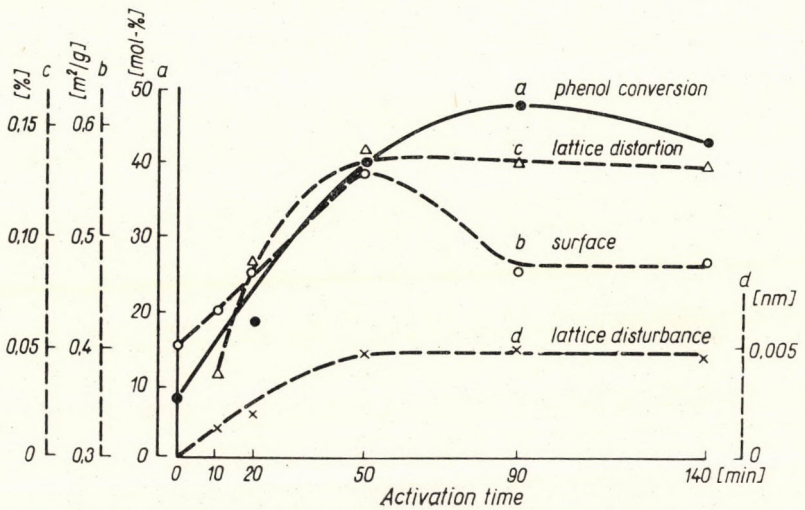

Fig. 7. Phenol conversion, surface area, lattice distortion, and lattice defects plotted against the activation periods of the nickel catalysts

the extreme experimental conditions (high pressure and temperature), a confirmity of the experimental data of this nature has not been expected either.

The data of the hydrogenation of *Ocenol 70*, in turn, enabled us to draw conclusions very similar to those obtained in the case of phenol hydrogenation under atmospheric pressure. The data of catalyst surface area, lattice deformation and lattice defects plotted against the lengths of the activation periods of the nickel catalyst are shown in Fig. 8.

It follows from these data that changes in the catalyst surface area alone are again unsatisfactory to explain the increase of catalytic activity in the hydrogenation of *Ocenol 70*. Though the catalyst surface area decreased after activation periods of about 50 minutes, the rate of hydrogenation of *Ocenol 70* was still rising, thus indicating that the free surface alone had no decisive effect on the activity of the nickel catalyst. The experimental results obtained in the hydrogenation of *Ocenol 70* can be well interpreted, however, by the state of disarrangement (lattice distortions or lattice defects) of the nickel catalyst. Namely, the increases in the percentage conversion well agree

with the actually established changes in lattice deformations and lattice defects. The fast progress of the hydrogenation of *Ocenol 70* corresponds to the marked increase in the number of lattice deformations and lattice defects produced by activation, depending on its length. When the catalyst was subjected to prolonged periods of grinding, the conversions were found to be constant, in accordance with the fact that the disarrangement of the lattice of the catalyst attained a constant state of maximum disorder. When this

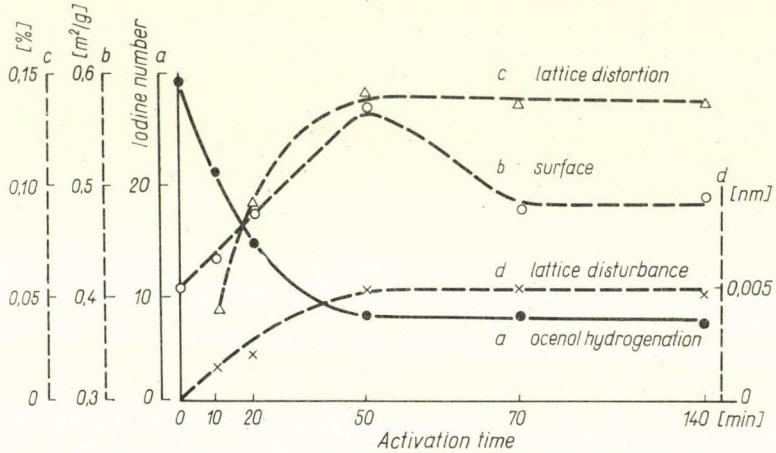

Fig. 8. Hydrogenation of ocenol (as determined from the iodine numbers), surface area lattice distortion, and lattice defects plotted against the activation periods of nickel catalysts

optimum order has been attained, and the number of lattice distortions and lattice defects cannot be increased anymore, further prolongation of the period of activation in a vibration mill is obviously inefficient, since it cannot create further change in the state of disorder of the lattice of catalyst.

The present investigations have led to the conclusion that the catalytic effect of mechanically activated catalysts depends primarily on the degree of disorder of the crystallites, *i.e.* on the "active lattice", and only to a lesser extent on the area of catalyst surface.

SUMMARY

It has been proved by a series of investigations that solids can be converted into catalysts by mechanical activation. As a model substance, nickel powder of commercial grade was subjected to batchwise treatments in a *Vibratom* laboratory pendulum mill for various periods. The products were characterized by their surface area determined by the BET method, and by X-ray investigations (dimension of elementary particles, number of lattice deformations and lattice defects). The catalytic activity of the various nickel catalysts was studied in the hydrogenation of phenol under atmospheric and high pressure, and in the hydrogenation of *Ocenol 70*. Nickel catalysts previously subjected to mechanical treatment in the vibration mill showed in all experiments appreciably higher activity. It has been shown that the observed increase of catalytic activity in the hydrogenation of phenol under atmospheric pressure and

in the hydrogenation of *Ocenol 70* is not a function of the catalyst surface, but it runs parallel with the actual lattice deformations and lattice defects. Consequently, the degree of disorder of the crystallites, *i.e.* the so-called "active lattice" is presumably responsible for the activity of mechanically activated catalysts; the increase of the free surface area is of secondary importance only. In the hydrogenation of phenol in an autoclave under high pressure rather different results were obtained, which may be ascribed to the extreme experimental conditions (high pressure and temperature) applied.

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CHEMICAL TRANSFORMATIONS OF DIOLS AND CYCLIC ETHERS, XXII*

STUDY OF THE TRANSFORMATION OF TRIMETHYLENE OXIDE IN THE PRESENCE OF PLATINUM CATALYSTS IN THE VAPOUR PHASE BY THE MICROREACTOR TECHNIQUE

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There are only few publications in literature concerning the contact catalytic transformations of trimethylene oxide. YUR'EV and LEVI studied the reaction of trimethylene oxide over aluminium oxide catalyst at 250° [1], when through an isomerization process propionaldehyde and allyl alcohol were formed. The main process was accompanied by secondary ones, giving rise to acrolein and propyl alcohol. Similar results were obtained by PONOMAREV et al. [2]. HAMADA and co-workers reported slight isomerization of trimethylene oxide in the presence of cobalthydrocarbonyl catalyst to propionaldehyde [3]. NIENBURG and ELSCHNIG [4] obtained γ-butyrolactone in 55—60% yield by the reaction of trimethylene oxide and carbon monoxide in the presence of cobaltoctacarbonyl catalyst at 200° and 200—250 atm.

In the course of the recent investigations the transformations of trimethylene oxide in the presence of platinum catalysts deposited on thermolite and activated charcoal were studied. As method the more simple "impulse" input variant of microreactor technique was applied. The microreactor was directly attached to a *Willy Giede GCHF 18/2* gas chromatograph.** Prior to the experiments with Pt/thermolite catalyst, the effect of the carrier itself was determined at various temperatures.

Transformation of trimethylene oxide on thermolite

The transformation of trimethylene oxide on thermolite was examined at 250—500°.

Fig. 1 shows a graphic representation of the amount of trimethylene oxide converted as a function of temperature.

* Part XXI: Acta Phys. et Chem. Szeged **13**, 67 (1967).

** The method of examination of contact catalytic transformations of exetanes (microreactor technique, analysis of the products) have been described in detail in parts XV [5], XVI [13] and XIX [6] of the series.

As it can be seen from the figure, the decomposition proceeds with considerable rate only above 375°, and becomes complete above 500°. The chromatogram of the products of decomposition at 400° is shown in Fig. 2.

It can be seen from these experiments that the carrier does not catalyze the decomposition of trimethylene oxide below 350°. Thus all transformations proceeding in the presence of platinum-thermolite catalyst at about 300° may be attributed to the effect of platinum (no synergetic effect is expected between

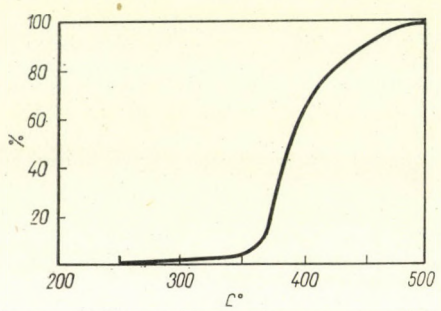


Fig. 1. Transformation of trimethylene oxide in the presence of thermolite as a function of temperature

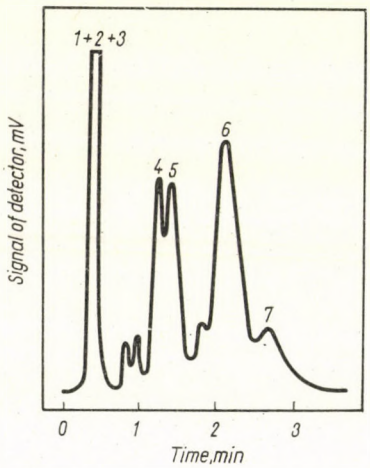


Fig. 2. Chromatogram of the transformation products of trimethylene oxide over thermolite 1* 1.1 T, 400; 2 1TCP; 3 140; 4 50 He; 5 140; 6 1/2; 7 0.01. Marking of the peaks: 1 + 2 + 3: CO + ethane + ethylene; 3 propionaldehyde; 5 acrolein; 6 trimethylene oxyde; 7 allyl alcohol

* *Notations:* 1 the amount (ml) and temperature (°C) of the microreactor charge of 0.2—0.4 mm diameter. Q — quartz, T — thermolite, C — activated charcoal;

2 length (m) of the chromatograph column of 5 mm internal diameter and its packing (20% distributor on thermolite of 0.2—0.4 mm diameter, or aluminium oxide);

3 temperature (°C) of the chromatograph thermostat;

4 rate of flow (ml/min) of helium (He) or hydrogen (H_2) carrier gas;

5 detector current (mA);

6 sensitivity of the *Willy Giede GCHF 18/2* gas chromatograph (1: maximum deviation of compensograph 2 mV; 1/2: max. deviation of compensograph 4 mV; 1/4— . . . *etc);*

7 quantity (ml) of sample introduced to the microreactor. TCP: tricresylphosphate.

thermolite of relatively low specific surface and the platinum deposited thereon). The processes taking place on this catalyst will be discussed in the following part of this paper.

Transformation of trimethylene oxide over platinum/thermolite catalyst (Pt/T)

Fig. 3 shows the degree of transformation of trimethylene oxide over Pt/T catalyst as the function of temperature and *vs.* the rate of flow of the helium carrier gas.

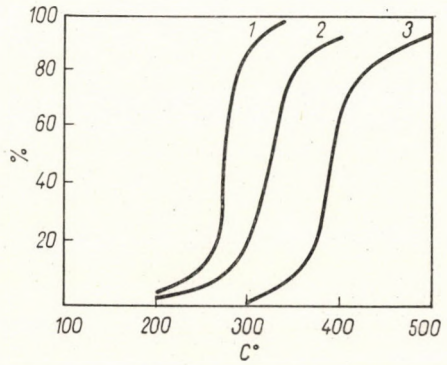


Fig. 3. Transformation of trimethylene oxide over platinum/thermolite catalyst
1. 1.1 Pt/T (Pt 10%); 2. 1TCP; 3. 140; 4. 50; 100 He; 5. 140; 6. 1/4; 7. 0.01
1 Pt/T, 50 ml/min. He; 2 Pt/T, 100 ml/min. He; 3 T, 50 ml/min. He

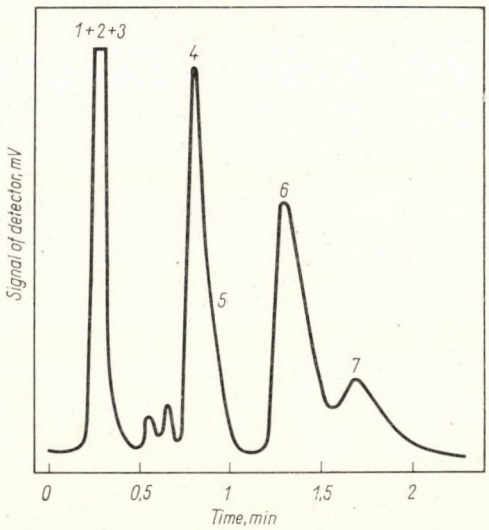


Fig. 4. Chromatogram of the transformation products of trimethylene oxide over Pt/T catalyst
1. 1.1 Pt/T, 350; 2. 1 TCP; 3. 140; 4. 100 He; 5. 140; 6. 1/4; 7. 0.01

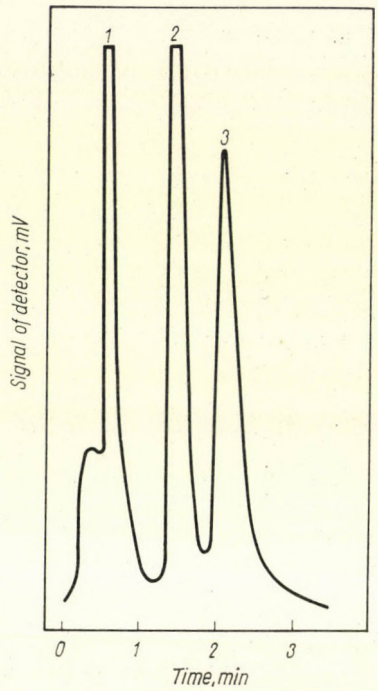
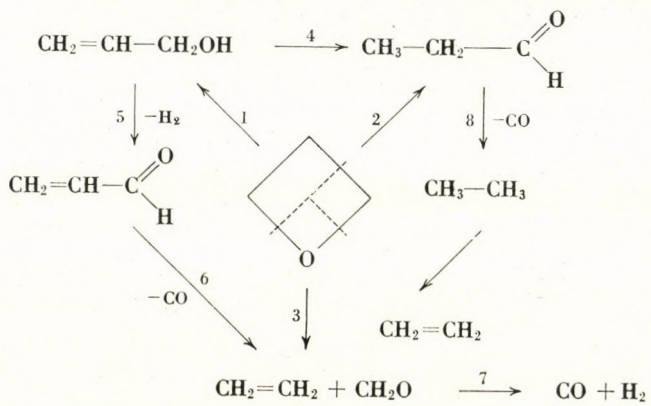


Fig. 5. Chromatogram of the transformation products of trimethylene oxide over Pt/T catalyst

1. 1.1 Pt/T, 350; 2. 1 Al_2O_3; 3. 80; 4. 50 He; 5. 140; 6. 1; 7. 0.01

A characteristic chromatogram of the products of decomposition at 350° and 100 ml/min rate of flow of helium is shown in Fig. 4. This chromatogram reflects well the quality and quantity of the products of higher boiling point. Fig. 5 shows the composition of the gaseous products of a similar experiment.

On considering the products it can be seen that the transformation in the presence of Pt/T catalyst is a rather complex process. The primary decomposition reactions are accompanied by secondary ones. The formation of the various reaction products can be summarized as follows:



Demonstration of the reality of the chemical reactions (1—8), shown in the scheme, implies a hard task. It is obviously more difficult to obtain evidence for the primary transformation (1, 2, 3) than for the secondary ones (4, 5, 6, 7, 8). Of the three primary reactions illustrated, two are isomerizations and one is decomposition.

The formation of the end-products of decomposition (ethylene, carbon monoxide and hydrogen), though it may also be pictured leading through allyl alcohol and involving several secondary processes, is actually explainable by splitting of the molecule into two parts. This process has been preparatively

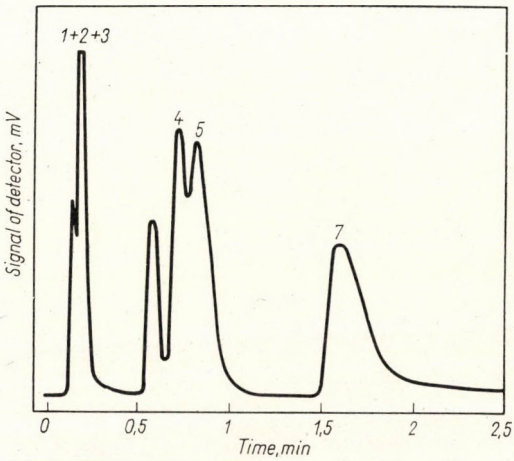


Fig. 6. Chromatogram of the transformation product of allyl alcohol over Pt/T catalyst. (For the experimental conditions see *Fig. 4)*

proved in a study of the thermal decomposition of oxetanes [7]. Namely, in that case formaldehyde does not suffer decarbonylation, but it remains in the reaction vessel as paraformaldehyde.

The direct formation of allyl alcohol is possible from trimethylene oxide only, thus the primary character of this process is obvious.

No such unequivocal decision can be made concerning the formation of propionaldehyde. Namely, the isomerization process allyl alcohol → propionaldehyde has been experimentally proved. Not only the results of FREIDLIN *et al.* [8] may be quoted here, but this isomerization takes place also in the presence of Pt/T catalyst under the experimental conditions of the transformation of ethylene oxide (Fig. 6).

On the basis of these experimental results, a higher probability might be attributed to processes 1 + 4 than to a direct transformation of trimethylene oxide to propionaldehyde. Since, however, the contact catalytic isomerization reactions of 3-, 5- and 6-membered cyclic ethers to carbonyl compounds seem to be acknowledged in literature [9—11], and the formation of propional-

dehyde from trimethylene oxide may be explained similarly to the case of allyl alcohol involving the same intermediate, the isomerization of trimethylene oxide to propionaldehyde may also be regarded as a primary process. From a macroscopic point of view, a 1,3-migration of "hydrogen" is involved in both cases.

The secondary processes shown in the above scheme were examined under identical conditions, and thus the reality of all the five (4, 5, 6, 7, 8) of them could be experimentally proved. Fig. 6 shows the chromatogram of the transformation of allyl alcohol. Under the conditions applied acrolein reacts further very fast. With a flow rate of 50 ml/min. of helium carrier gas, this compound could not be detected at all above 270°. At a flow velocity of 100 ml/min., however, acrolein was observed even at 350°. In the decomposition of propionaldehyde, at 340°, considerable formation of ethylene was found (of the ethane formed in the reaction 25% contained ethylene). Thus in the decomposition process of trimethylene oxide there are three possible sources of ethylene formation, ethane may originate from propionaldehyde only.

A quantitative evaluation of the overall process shows that the transformation of trimethylene oxide over Pt/T gives, depending on the activity of catalyst and on temperature, propionaldehyde in about 70%, and ethylene, carbon monoxide and hydrogen in about 30% yields, by isomerization and decomposition, respectively. The use of higher temperatures and contact times may increase the rate of secondary processes so much that the presence of primary products can no longer be detected in the end-product.

Transformations of trimethylene oxide in the presence of platinum catalyst deposited on active charcoal (Pt/C)

The transformation of trimethylene oxide was studied in the presence of Pt/C catalyst containing 20% platinum, in 0.3 ml catalyst volume,* by the microreactor technique at 260—310°.

On the basis of the results obtained the following conclusion may be drawn. The Pt/C catalyst proved to be more selective than Pt/T. The transformation of trimethylene oxide proceeded at relatively lower temperatures. No acrolein formation could be detected, and the amount of ethylene formed was also lower. The activity of Pt/C, like that of the Pt/T catalyst, decreased with the time of use. Deactivation of the catalyst manifested itself in a decrease of the rate of transformation and in an increase of the relative amount of ethylene as compared to that of ethane. This can be seen well in Figs 7 and 8.

* In case of higher catalyst volumes the evaluation of the reaction proved difficult because of the slow desorption of the products.

Accordingly, the experimental results prove that the primary main process in the presence of Pt/C catalyst is isomerization to propionaldehyde, which is then followed by decarbonylation of the aldehyde to ethane as a secondary reaction. At the same time it has also been supported experimentally that olefins can be hydrogenized with formaldehyde over the highly active Pt/C catalyst at 300—340°. Thus this process may also have some role in the formation of higher amounts of ethane.



Fig. 7

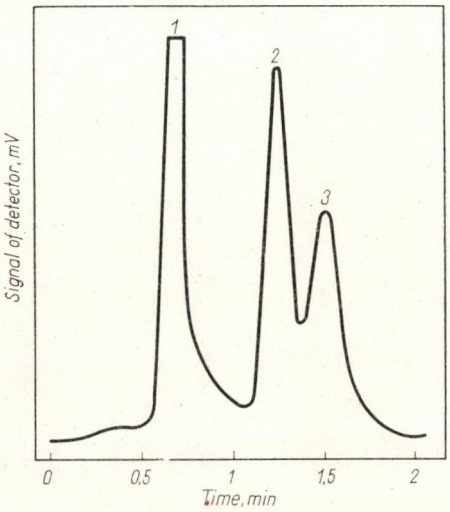


Fig. 8

Fig. 7—8. Chromatograms of the transformation product of trimethylene oxide over Pt/C catalysts of different activity. 1. 0.3 Pt/C, 320; 2. 1 Al_2O_3; 3. 80; 4. 50 He; 5. 140; 5. 1; 6. 0.005

Transformation of trimethylene oxide on platinum/thermolite and platinum/active charcoal catalysts in hydrogen stream

The transformations of trimethylene oxide over a Pt/T catalyst containing 10% platinum, and a Pt/C catalyst containing 20% platinum, were studied with 1.1 and 0.3 ml catalyst volumes, respectively, by the microreactor technique at 200—350°, in the presence of hydrogen carrier gas. Apart from the carrier gas, the experimental conditions were identical with those described at the experiments with helium. The purpose of these experiments was to reveal the effect of hydrogen upon the rate and direction of the reaction.

With Pt/T catalyst no significant change was observed in the direction of the reaction, as compared to similar experiments in helium. On the other hand, the rate of transformation increased to a certain extent. Two charac-

teristic chromatograms of the transformation over Pt/T catalyst at 320° in hydrogen stream are shown in Figs 9 and 10.

With Pt/C catalyst significant differences were experienced both in the rate and direction of the transformation. The rate of reaction of trimethylene

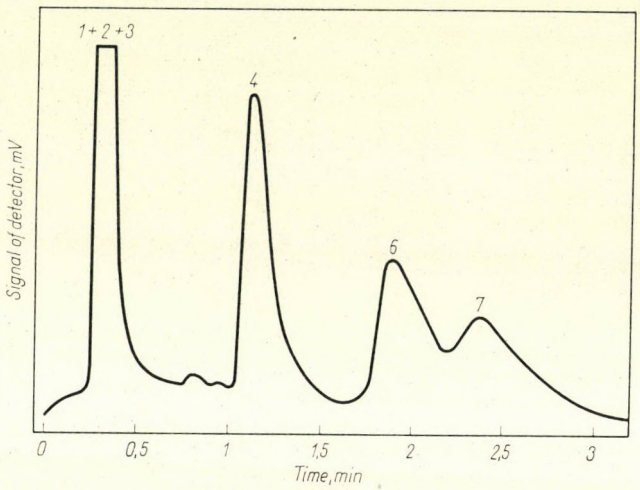


Fig. 9

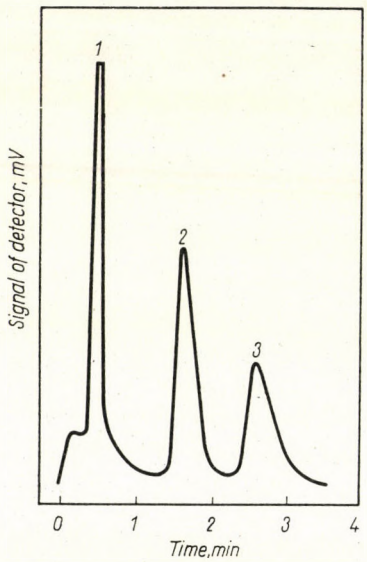


Fig. 10

Fig. 9–10. Chromatograms of the transformation products of trimethylene oxide over Pt/T catalyst in hydrogen stream

Fig. 9. 1. 1.1 Pt/T, 320; 2. TCP; 3. 140; 4. 50 H_2; 5. 140; 6. 1/4; 7. 0.01 *Fig. 10.* 1. 1.1 Pt/T, 320; 2. 1 Al_2O_3; 3. 80; 4. 50 H_2; 5. 140; 6. 1/2; 7. 0.01 (Marking of the peaks is identical with that in Fig. 2)

oxide was considerably higher in the presence of hydrogen than in helium gas. As regards the direction of the reaction, the main difference lies in the absence of olefinic compounds in the reaction product.

These results indicate that in case of Pt/C catalyst the hydrogen carrier gas takes part in the reaction, which is a consequence of the enhanced activity of the catalyst. The difference in activity of the two catalysts is well seen in Fig. 13.

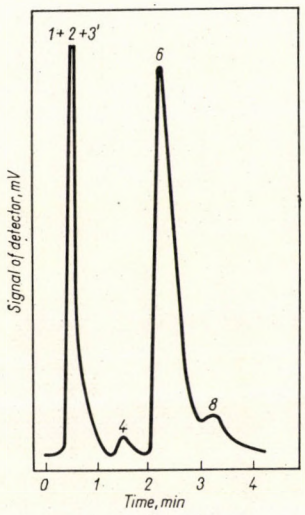


Fig. 11

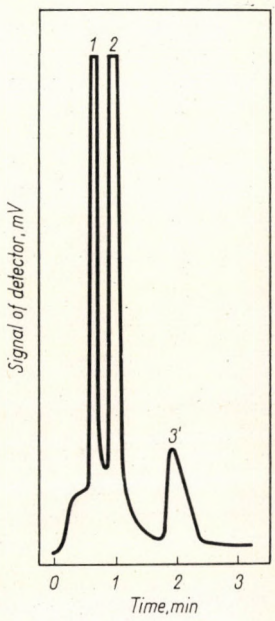


Fig. 12

Fig. 11—12. Chromatograms of the transformation products of trimethylene oxide over Pt/C catalyst in hydrogen stream. 1. 0.3 Pt/C, 250 and 320°, respectively; 2. 1 TCP and 1 Al_2O_3, resp.; 3. 140 and 120°, resp.; 4. 50 H_2; 5. 140; 6. 1/2; 7. 0.01 and 0.005, resp. (Marking of the peaks are the same as in Fig. 2, and 3': propane, 8: propanol)

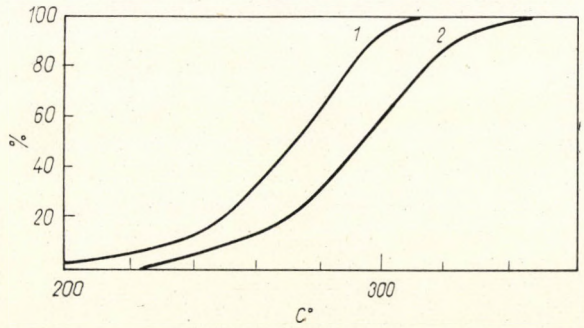
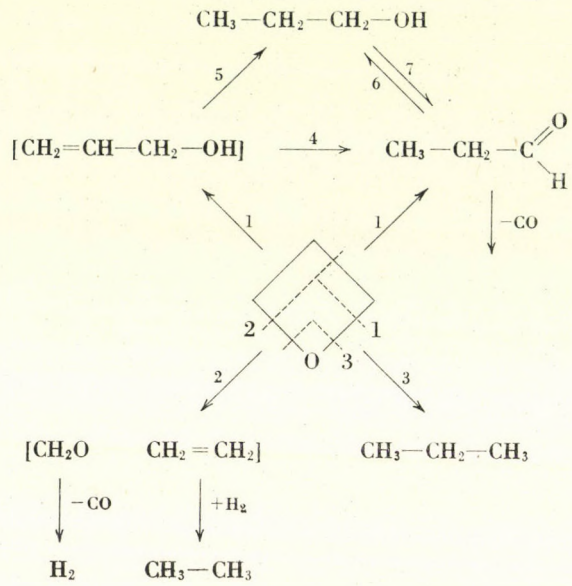


Fig. 13. Dependence of the transformation of trimethylene oxide over platinum catalysts in hydrogen stream upon the temperature and the carrier of the catalyst 1 Pt/C, 2 Pt/T

At the present stage of our experiments, no unambiguous decision can be made concerning the mechanism of formation of the products. The transformations of trimethylene oxide taking place over Pt/C catalyst in the presence of hydrogen can be summarized as follows:



The formation of ethane may follow two main reaction paths: isomerization to propionaldehyde followed by decarbonylation, and decomposition followed by hydrogenation. The occurrence of both secondary processes could be proved experimentally. Of the primary processes the formation of propionaldehyde can be demonstrated at lower temperatures only, as this compound suffers rapid decarbonylation over a Pt/C catalyst in the presence of hydrogen. Detection of the primary products possibly formed in process 2 (ethylene and formaldehyde) is impossible, because under the conditions applied they rapidly undergo further reactions. On the other hand, the essentially higher probability of process 1 is unequivocally proved besides the detection of propionaldehyde by the results obtained with helium carrier gas, and by the considerably higher thermal requirement of process 2. The reason why some possibility is attributed to process 2, is that the formation of ethylene could be detected in helium carrier gas under identical experimental conditions. The experimental confirmation may be carried out according to the method of BALANDIN and co-workers [12].

The occurrence of the secondary processes 4, 5, 6 and 7 can be proved under identical conditions as described for the reaction of trimethylene oxide (Figs 14, 15 and 16).



Fig. 14

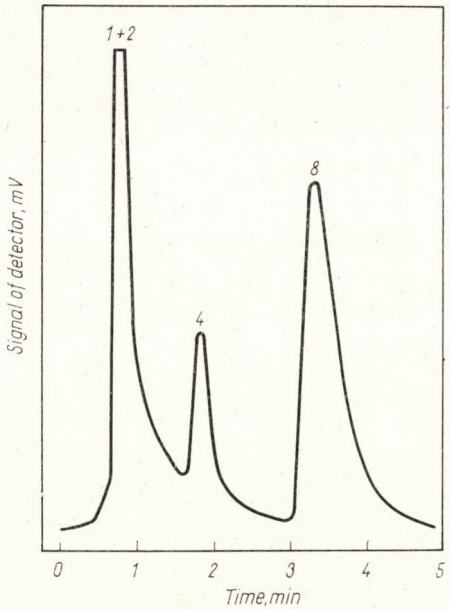


Fig. 15



Fig. 16

Fig. 14—16. Chromatograms of the transformation products of allyl alcohol, propionaldehyde and propyl alcohol over Pt/C catalyst in hydrogen stream
1. 0.3 Pt/C, 230; 2. 1 TCP; 3. 140; 4. 50 H_2; 5. 140; 6. 1/2; 7. 0.01

Under the conditions applied the formation of propane, too, can be observed, as a result of hydrogenolysis of trimethylene oxide (Fig. 12, Peak 3′). The quantity of propane may increase to as high as 20%, based on the trimethylene oxide introduced, depending on the reaction parameters.

Summarizing the results it can be stated that the transformation of trimethylene oxide at about 300° in the presence of Pt/C catalyst, and hydrogen yields, depending upon the conditions of the reaction, 80—90% of ethane and 10—20% of propane. The formation of ethane can be explained mainly by isomerization to propionaldehyde, while that of propane by hydrogenolysis of the ring.

SUMMARY

The transformations of trimethylene oxide have been studied in the presence of thermolite platinum/thermolite or platinum/activated charcoal catalyst and helium or hydrogen carrier gas by the microreactor technique. Dependence of the degree and different courses of the reaction upon the experimental conditions — microreactor charge, carrier gas, temperature — have been examined. Under the conditions applied, the transformation of trimethylene oxide is a complex reaction, consisting of several primary and secondary processes. The mechanism of formation of the various products has also been investigated. The main path of the reaction is isomerization to propionaldehyde. This reaction can be regarded as a 1,3-rearrangement.

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CHEMICAL TRANSFORMATION OF DIOLS AND CYCLIC ETHERS, XXIII*

STUDY OF THE TRANSFORMATION OF 3-MONOALKYLOXETANES IN THE PRESENCE OF PLATINUM CATALYSTS BY THE MICROREACTOR TECHNIQUE

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Received October 27, 1966

In connection with a study of the chemistry of cyclic ethers, their transformations in the presence of contact catalysts have been investigated. The purpose of these investigations was to examine the isomerization of various-membered cyclic ethers to oxo compounds, to draw general conclusions about the isomerization activity of the catalysts used, and to find relationships between the directions and extents (rates) of the processes occurring parallel with isomerization and the structures of the starting materials. The present communication reports our results in the contact catalytic transformations of 3-monoalkyloxetanes. To the authors' knowledge, there is no reference in literature concerning this field.

The reactions of 3-methyl-, 3-ethyl-, 3-*n*-propyl-, 3-*i*-propyl-, 3-*n*-butyl- and 3-cyclohexyl-oxetanes were examined in the presence of platinum-thermolite (Pt/T) or platinum-activated charcoal (Pt/C) catalyst and helium or hydrogen carrier gas at 220—320°, under conditions identical with those described for trimethylene oxide [1]. As method, the more simple "impulse" input variant of microreactor techniques was applied. The microreactor was directly attached to a *Willy Giede GCHF 18/2* gas chromatograph.**

In an earlier communication [1] the effect of carriers and platinum catalysts upon the decomposition of trimethylene oxide was dealt with in detail. In the knowledge of these experimental data, the transformation of 3-monoalkyl-substituted oxetanes was studied in the presence of Pt/T catalyst. In some cases the processes taking place over Pt/C catalyst were also examined, knowing that due to the higher activity of this catalyst the processes proceed at lower temperatures and more selectively.

* Part XXII: previous paper in this number.

** The method of examination of contact catalytic transformations of oxetanes (microreactor technique, analysis of the products) have been described in detail in Parts XV [2], XVI [3] and XIX [4] of the series.

Transformation of 3-monoalkyloxetanes in the presence of Pt/T catalyst

Data of the transformation of 3-methyl-, 3-ethyl-, 3-propyl-, and 3-*n*-butyloxetanes over Pt/T catalyst in the presence of hydrogen and helium carrier gas, as expressed in per cent *vs.* temperature, are shown in Figs 1 and 2, respectively.

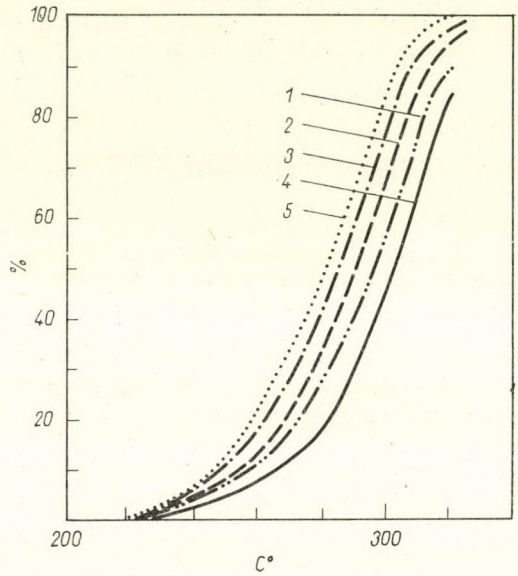


Fig. 1

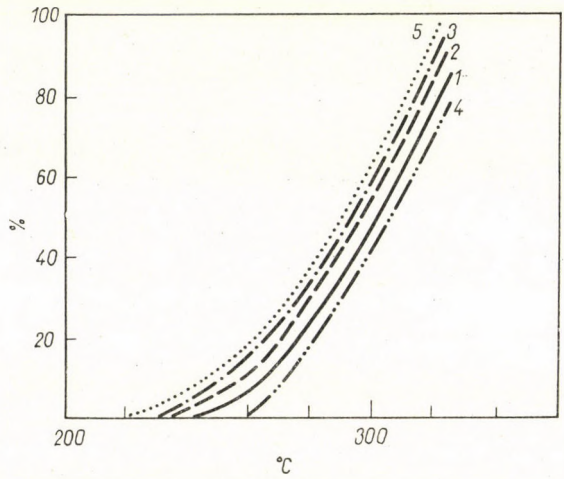


Fig. 2

Fig. 1—2. Extent of the transformation of 3-monoalkyloxetanes over Pt/T catalyst in the presence of hydrogen and helium gas, respectively, as the function of temperature
1. 3-methyl-, 2. 3-ethyl-, 3. 3-propyl-, 4. 3-*i*-propyl-, 5. 3-*n*-butyl-oxetane

The figures show that the presence of hydrogen facilitates the decomposition of 3-monoalkyloxetanes, similarly as it has been observed with trimethylene oxide. Since, however, it has no significant influence upon the directions of the processes, the above fact may be explained by a continuous

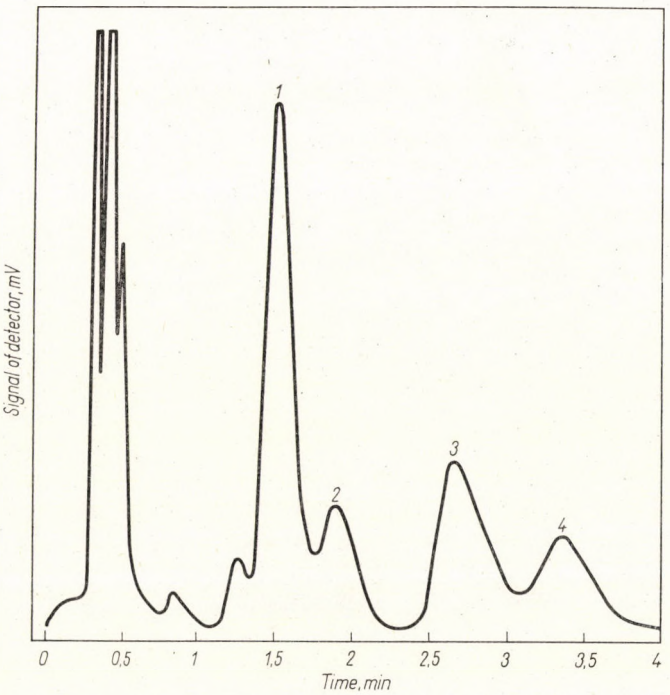


Fig. 3. Chromatogram of the transformation products of 3-methyloxetane over Pt/T catalyst

1.* 1.1 Pt/T, 320; 2. 1 TCP; 3. 140; 4. 50 He; 5. 140; 6. 1/2; 7. 0.01**

**Notations:* 1. the quantity (ml) and temperature (°C) of the microreactor charge of 0.2—0.4 mm diameter; Q — quartz; T — thermolite; C — activated charcoal;

2. length (meter) of the chromatographic column of 5 mm internal diameter and its packing [20% distribution fluid on thermolite or aluminium oxide (Al_2O_3) of 0.2—0.4 mm diameter];

3. temperature (°C) of the chromatographic thermostat;

4. rate of flow (ml/min) of helium (He) or hydrogen (H_2) carrier gas;

5. detector current (mA);

6. sensitivity of the *Willy Giede GCHF 18/2* gas chromatograph (1: maximum deviation of the compensograph 2mV; 1/2: max. deviation of compensograph 4 MV,1/4 — ... *etc.)*;

7. sample introduced to the microreactor (ml)

TCP: tricresylphosphate; ODP: β,β'-oxydipropionitril ether; AG: apiezon grease "L".

** The maxima marked with numbers in the Figures correspond to the following substances: 1. aldehyde isomeric with the oxetane homologue;

2. α,β-unsaturated aldehyde of identical carbon number with the oxetane homologue;

3. starting material (the corresponding oxetane);

4. α,β-unsaturated alcohol of identical carbon number with the oxetane homologue.

The first peaks correspond to carbon monoxide and the corresponding saturated and unsaturated hydrocarbons resulting from decarbonylation, respectively.

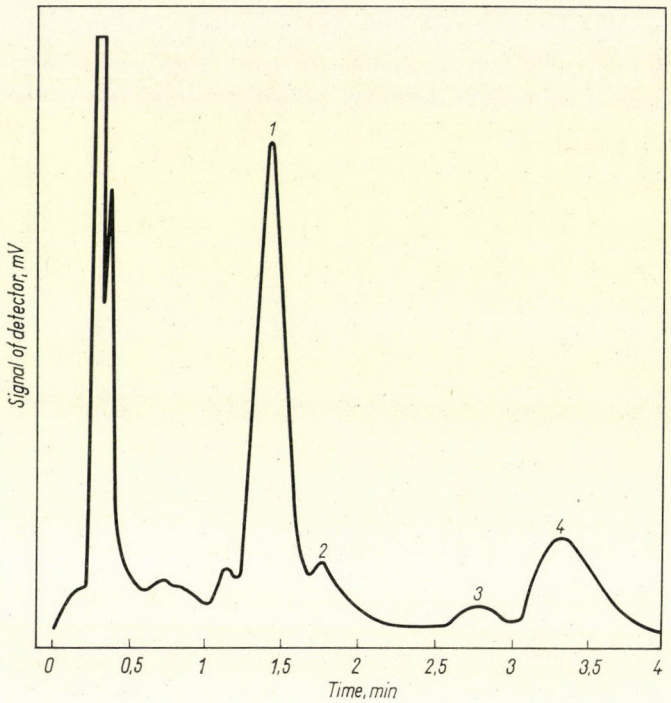


Fig. 4. Chromatogram of the transformation products of 3-methyloxetane over Pt/T catalyst

1. 1.1 Pt/T, 320; 2. 1 TCP; 3. 140; 4. 50 H_2; 5. 140; 6. 1/2, 7. 0.01

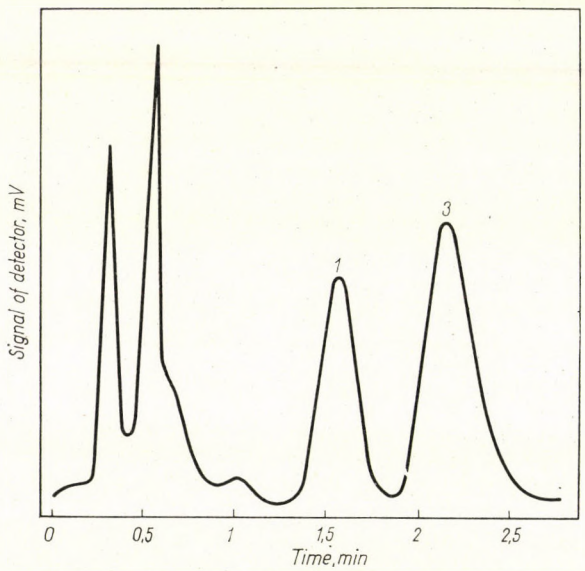


Fig. 5. Chromatogram of the transformation products of 3-isopropyloxetane over Pt/T catalyst

1. 1.1 Pt/T, 320; 2. AG; 3. 180; 4. 50 He; 5. 140; 6. 1/4; 7. 0.01

activation of the platinum catalyst during the reaction *i.e.* the catalyst did not become deactivated in the presence of hydrogen. The figure also indicates that an increase in the +I effect of the substituent enhances the rate of transformation. The only exception is found with isopropyloxetane, which is the slowest to react. This fact, which is explainable with the place of the isopropyl group in the BAKER—NATHAN series, is in accord also with the observations



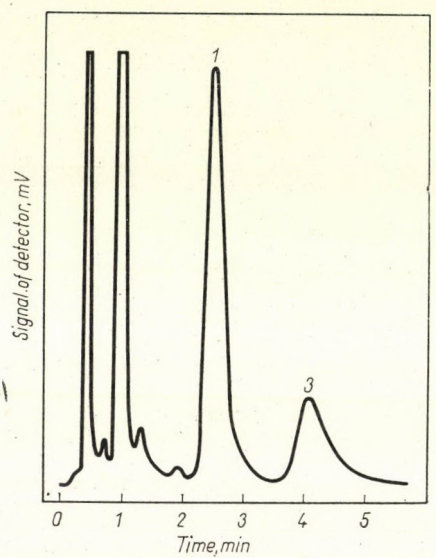
Fig. 6. Chromatogram of the transformation products of 3-isopropyloxethane over Pt/T catalyst. 1. 1.1 Pt/T, 320; 2. 1 AG; 3. 180; 4. 50 H_2; 5. 140; 6. 1/2; 7. 0.01

concerning the activity of the catalysts, namely, this compound decreases the activity of the catalyst extremely fast. Thus, between two successive experiments the catalyst was activated in hydrogen stream for twenty minutes. Similar results were obtained in a study of the thermal decomposition of isopropyloxetane derivatives [4, 5].

The directions of the transformations could be determined by evaluating the chromatograms. Figs 3—8 show some characteristic chromatograms of the transformation products of 3-methyl-, 3-isopropyl- and 3-*n*-butyloxetanes.

The first peaks correspond to carbon monoxide and the corresponding saturated and unsaturated hydrocarbons resulting from decarbonylation, respectively.

The chromatograms indicate the effect of carrier gas upon the degree of transformation, moreover the difference in reactivity in case of the isopropyl



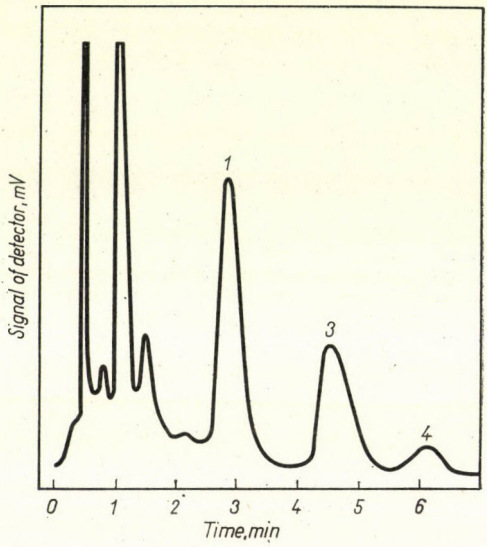
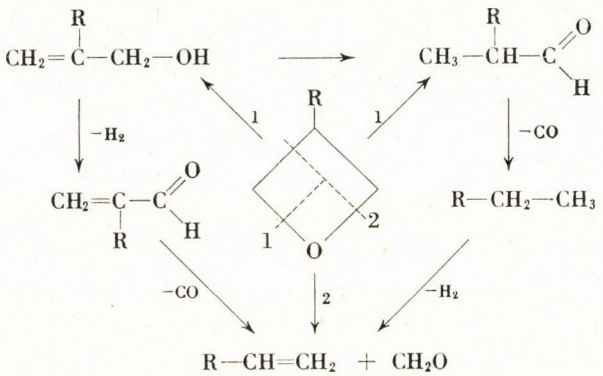


Fig. 7—8. Chromatograms of the transformation products of 3-*n*-butyloxetane over Pt/T catalyst

Fig. 7. 1. 1.1 Pt/T, 320; 2. 1 AG; 3. 180; 4. 50 He; 5. 140; 6. 1/4; 7. 0.01

Fig. 8. 1. 1.1 Pt/T, 285; 2. 1 AG; 3. 180; 4. 50 H_2; 5. 140; 6. 1/2; 7. 0.01

substituent. On basis of the experimental results, the following scheme can be given for the reaction of 3-monosubstituted exetanes in the presence of Pt/T catalyst:



$$R{-}CH{=}CH_2 + CH_2O$$

where R = methyl, ethyl, *n*-propyl, i-propil, *n*-butyl, cyclohexyl.

The processes shown in the scheme are not discussed here in detail, since the statements made and the problems raised in connection with the similar transformation of trimethylene oxide [1] are valid for this type of oxetanes as well.

According to the scheme, the two main processes are isomerization to the corresponding aldehyde (1), and decomposition giving rise to olefins and formaldehyde (2). At the same time, the experiments also prove the complex nature of the reactions, as the primary processes are accompanied by secondary ones. The chromatograms (3—8) unequivocally prove the formation of oxygen-containing products in the primary processes. Besides the aldehydes, the corresponding unsaturated alcohols (peaks marked 4) can also be found in low concentrations. The formation of an unsaturated aldehyde could be observed only in the case of 3-methyloxetane (peak marked 2).

An evaluation of the primary and secondary processes giving rise to hydrocarbons is hindered by the fact that the hydrocarbons primarily formed can undergo isomerization in the presence of the platinum catalyst both with a change in their carbon skeleton and with the migration of the double bond. It can be stated, however, that the transformation of 3-alkyloxetanes over Pt/T catalyst is accompanied by considerable olefin formation. The olefin formation is facilitated by an increase in the temperature of the catalyst space, namely. The Pt/T catalyst also increases the rate of thermal decomposition leading to the formation of formaldehyde and olefin.

The figures clearly show that at 340° the amount of olefin exceeds that of the saturated hydrocarbons. Otherwise, no quantitative evaluation of the dependence of the two main processes (isomerization and thermal decomposition) upon the temperature and the nature of the substituent was attempted.

A few experiments concerning the transformation of 3-cyclohexyloxetane over Pt/T catalyst in the presence of hydrogen carrier gas have also been carried out. It was found that the above processes take place with this compound as well. However, at elevated temperatures (above 340°) the dehydrogenation of the cyclohexane skeleton also occurs, giving rise to ethylbenzene, styrene, *etc.*

To sum up the experimental results in brief, it can be stated that the direction of the transformation of 3-monosubstituted oxetanes over Pt/T catalyst highly depends on the activity of the catalyst and on the temperature. The two main processes are isomerization and splitting of the molecule, giving rise to aldehydes, and to olefins and formaldehyde, respectively. The primary processes are accompanied by secondary decarbonylation and dehydrogenation reactions. On the basis of the chromatograms, at about 300—320° the quantity of aldehydes is 30—40% based on the starting oxetane. At the same temperature, however, another part of the aldehydes formed reacts further, and thermal decomposition also occurs. These latter processes increase the amount

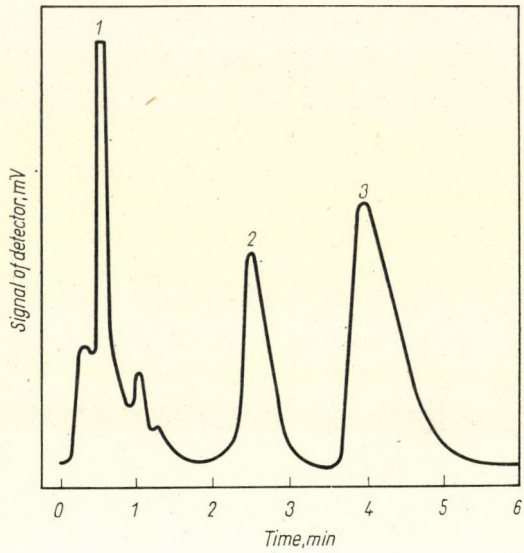


Fig. 9

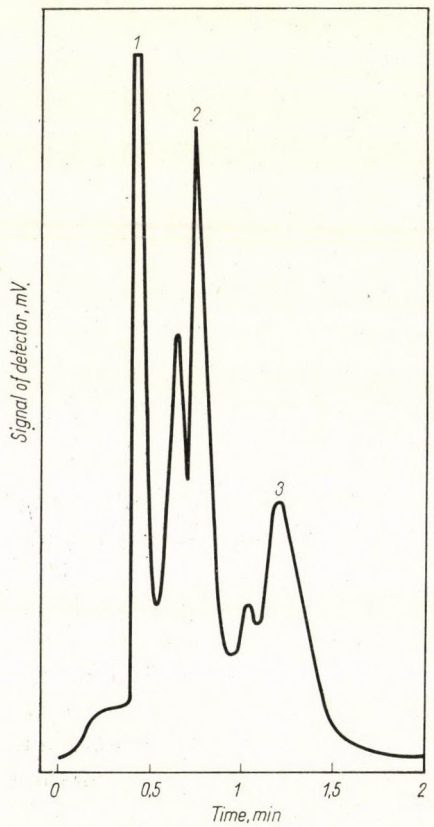


Fig. 10

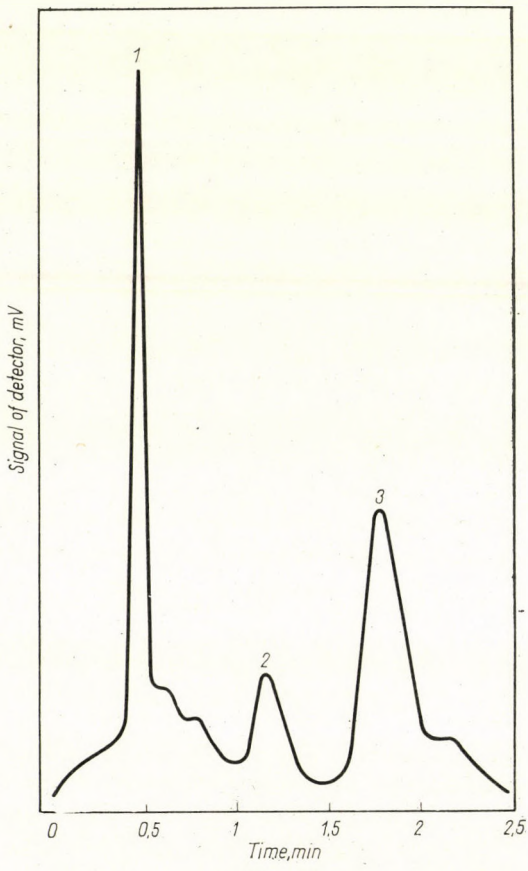


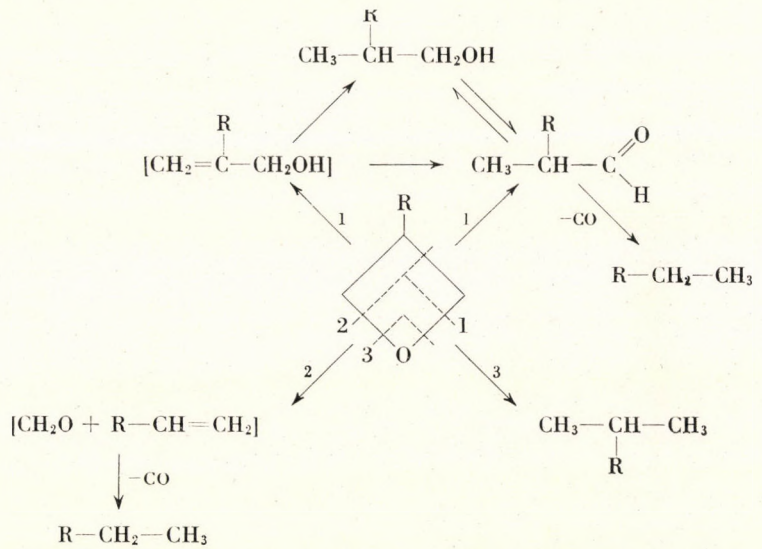
Fig. 11

of olefins, which at higher temperatures *(e.g.*, 340—350°), through dehydrogenation reactions, considerably exceeds the quantity of the corresponding saturated hydrocarbons. As the net result of these reactions the transformation leads to isomerization in 60—70% (aldehyde and saturated hydrocarbon) and to thermal decomposition in 30—40%. A more exact quantitative evaluation is possible, besides kinetical examination of the transformation of oxetanes, by studying the individual reactions of the intermediary products under identical conditions.

Transformation of 3-monoalkyloxetanes over Pt/C catalyst

In the following the differences observed in the catalytic transformations of 3-monosubstituted oxetanes over Pt/C catalyst in the presence of hydrogen, as compared to that over Pt/T catalyst, will be briefly considered.

The processes observed in the presence of Pt/C catalyst and hydrogen may be summarized as follows:



where R = methyl, ethyl, *n*-propyl, isopropyl, *n*-butyl, cyclohexyl.

Fig. 9—11. Chromatograms of the hydrocarbons resulting from the transformation of 3-methyl-, 3-isopropyl- and 3-*n*-butyloxetanes over Pt/T catalyst

1. 1.1 Pt/T, 340; 2. 1 Al_2O_3, ODP, ODP; 3. 120, 30, 30; 4. 50 H_2; 5. 140; 6. 1, 1, 1/2; 7. 0.01*

* Marking of the peaks: 1. CO; 2. saturated hydrocarbons resulting from Reaction 1; 3. olefins formed in the process and containing one carbon atom less than the starting oxetane.

The chromatograms clearly indicate that, as compared to the results obtained with Pt/T catalyst, 3-monosubstituted oxetanes react fast over Pt/C catalyst to yield, through decarbonylation of the aldehydes formed *via* isomerization, the corresponding saturated hydrocarbons (Peak 2). At the same

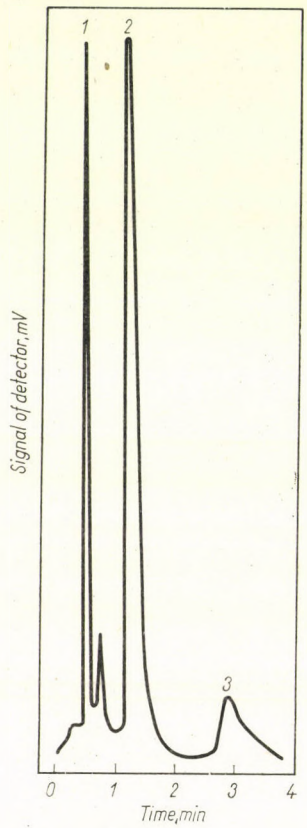


Fig. 12

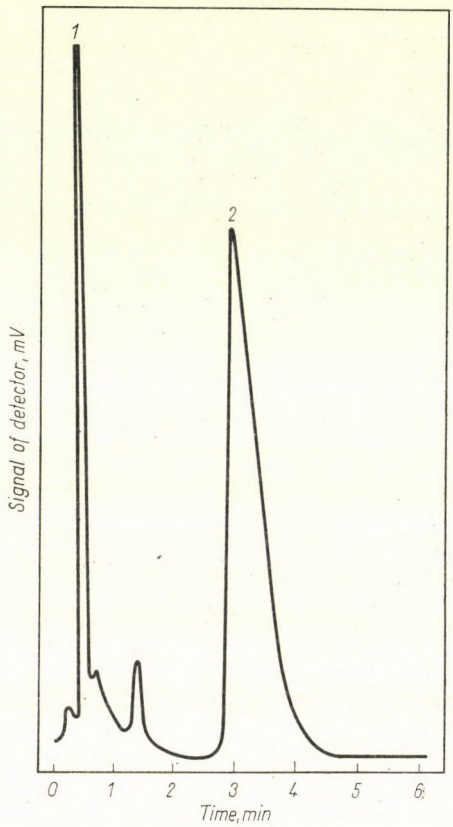


Fig. 13

Fig. 12—13. Chromatograms of the transformation products of 3-methyl- and 3-ethyloxetanes over Pt/C catalyst

1. 0.3 Pt/C, 330; 2. 1 Al_2O_3; 3. 140; 4. 50 H_2; 5. 140; 6. 1/2, 1; 7. 0.01*

* Marking of the peaks: 1. CO; 2. saturated hydrocarbons of one carbon atom less than the starting oxetane; 3. saturated hydrocarbon of identical carbon number as the starting oxetane.

time, in accord with the experiences gained with trimethylene oxide, the formation of saturated hydrocarbons through hydrogenation of olefins formed by thermal decomposition may be excluded, either. The simultaneous hydrogenolysis of both C—O bonds of the cyclic ether results in the formation of a saturated hydrocarbon of identical carbon number with the starting oxetane molecule (Peaks 3).

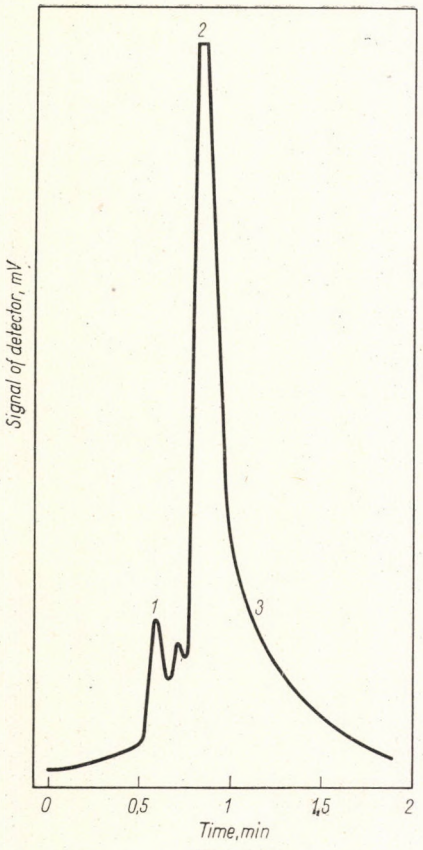


Fig. 14

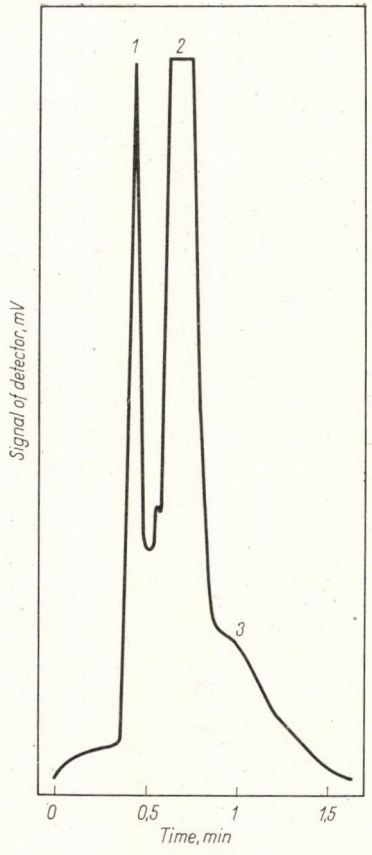


Fig. 15

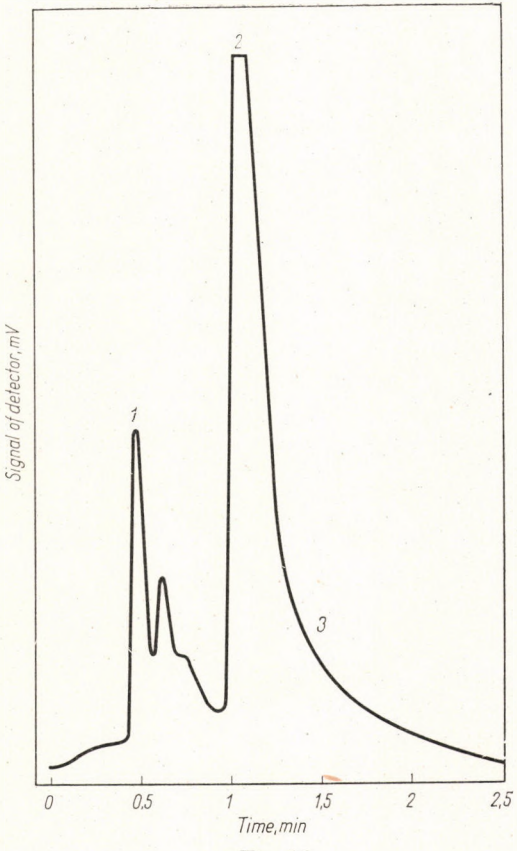


Fig. 16

Fig. 14—16. Chromatograms of the transformation products of 3-*n*-propyl-, isopropyl- and *n*-butyloxetanes over Pt/C catalyst
1. 0.3 Pt/C, 320; 2. 1 ODP; 3. 40, 30, 40; 4. 50 H_2; 5. 140; 6. 1; 7. 0.005*

* Marking of the peaks: 1. CO; 2. saturated hydrocarbons of one carbon atom less than the starting oxetane; 3. saturated hydrocarbon of identical carbon number as the starting oxetane.

SUMMARY

The transformations of 3-monoalkyloxetanes (methyl, ethyl, *n*-propyl, isopropyl, *n*-butyl, cyclohexyl) have been studied on thermolite- and charcoal-supported platinum catalysts in the presence of helium and hydrogen at 220—320°, using the microreactor technique. Under the conditions applied, the main direction of the transformations are isomerization to aldehydes and decomposition to olefins and formaldehyde. The primary reactions are accompanied by secondary ones. Conclusions have been drawn concerning the degree of transformation of oxetanes and the direction of the processes depending on the various parameters, such as the catalyst, temperature, carrier gas, and the structure of the oxetane used.

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CHEMISTRY OF FREE RADICALS, V

ESR INVESTIGATION OF THE TRIPHENYLMETHYL RADICAL

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Received March 15, 1967

The triphenylmethyl radical (TPM), whose free radical character was discovered by GOMBERG in 1900, is of basic importance in both ESR spectroscopy and quantum chemistry. Owing to the extremely high symmetry of the molecule, to the lack of heteroatoms, *etc.*, this radical lends itself particularly well to check the efficiency of different approximate methods in quantum chemistry. By means of ESR investigations the spin density values are measurable and comparable with the results of quantum chemical calculations. The electron structure of the radical is only partly known. In the present paper we report about our investigations concerning the experimental determination of the π-electron distribution of the TPM free radical.

There are two possibilities for the determination of spin densities with the aid of the ESR method:

(1) Having determined the coupling constants (a^H) of the H atoms assigned to C atoms of sp^2 hibridization, the spin density (ϱ^π) of the C atom can be calculated by means of the well-known MCCONNELL equation:

$$a^H = Q \cdot \varrho^\pi . \tag{1}$$

Thus, the spin densities (ϱ^π) of all C atoms of the radical to which a hydrogen atom is attached can be calculated.

Earlier ESR investigations with the TPM free radical [1, 2, 3, 4, 5] did not yield such high resolution spectra from which the proton coupling constants could have been determined with satisfactory accuracy. Later, D. B. CHESNUT and G. J. SLOAN [6] further P. B. AYSCOUGH and collaborators [7] determined the coupling constants of the ortho meta and para protons of a high resolution ESR spectrum, with an accuracy of 1%.

The theoretical spin density distribution of the TPM radical was calculated by approximate quantum chemical methods by several investigators [8, 9, 10, 11, 12]. The spin density values obtained are shown in Table I.

When comparing the coupling constants and spin densities, several problems are encountered. The Q value resulting as the ratio of the experi-

mentally determined a^H and the theoretical spin densities depends on the method applied for calculating ϱ^π on the one hand, and on the position of the C atom on the other. Furthermore, the fact that the value of Q is smaller than 23—25 Oe repeatedly has been proved experimentally and accepted for aromatic systems.

(2) Another method is also at our disposal: for determining spin densities between the spin densities, ϱ_i^π and the coupling constant, $a^{13}C$, of the ^{13}C nucleus the equation KARPLUS—FRAENKEL [13] holds:

$$a^{13C} = \left[S^C + \sum_{i=1}^{3} Q_{CX^i}^C \right] \varrho^\pi + \sum_{i=1}^{3} Q_{X^iC}^C \varrho_i^\pi \qquad (2)$$

Table I

Theoretical spin densities of the triphenylmethyl radical

Calculation method	ϱ_α^π	ϱ_1^π	ϱ_2^π	ϱ_3^π	ϱ_4^ψ
LCAO—MO, HÜCKEL[8]	0.308	0.000	0.077	0.000	0.077
LCAO—MO—SCF [12]	0.413	—0.045	0.114	—0.044	0.101
Valence-bond [11]	0.564	—0.230	0.200	—0.104	0.182

Knowing the $a^{13}C$ coupling constant values in all different positions of the radical, we may obtain from Eq. (2) the spin density values for all C atoms.

The preparation of derivatives labelled with ^{13}C isotope is an extremely difficult task. In this respect the derivative labelled in α position makes the only exception. The latter has been synthesized by S. I. WEISSMAN *et al.* with 53% enrichment [14], and according to their measurements $a_\alpha{}^{13}C = 26$ Oe. The investigations of P. B. AYSCOUGH *et al.* [7], carried out with a radical of 10% enrichment, gave $a_\alpha{}^{13}C = 26 \pm 3$ Oe.

To avoid the complicated synthesis, we examined the artificially non-labelled radical, part of which is inherently labelled with the ^{13}C isotope occurring in 1.1% natural abundance.

Experimental

TPM free radical was prepared from triphenylchloromethane by treatment with zinc dust. Oxygen was removed from a toluene solution of triphenylchloromethane by boiling, then it was mixed with a suspension of zinc dust in toluene from which oxygen had also been removed by boiling. (The last traces of oxygen not removed by boiling react with the formed TPM radical and thus the radical solution is absolutely free from oxygen.) The best radical concentration can be adjusted by approximate measuring. The splitting of ESR spectra and the amplitude of isotope lines is greatly influenced by the radical concentration of the sample. In case of a too high radical concentration a remarkable dipole-dipole broadening is observed, which leads to considerable overlapping of the spectrum lines. On the other hand, too low radical concentrations render impossible the detection of lines originating from the ^{13}C isotope.

In the determination of the ESR spectrum of the TPM radical at different temperatures, it must be taken into account that with a decrease of temperature the concentration of triphenylmethyl radical decreases owing to dimerization to hexaphenylethane. If the concentration of the sample was found too high for measuring, the excess of TPM radicals were reacted with cyanopropyl radicals; as a result of this reaction a stable recombination product is formed, unable to dissociate. Cyanopropyl radicals were produced by the thermal decomposition of azobisisobutyronitrile (AIBN) at 50—60°. AIBN was added to the solution in advance. By controlling the reaction time at constant temperature the radical concentration could be adjusted with adequate accuracy, that is, the radical concentration could be calculated from the AIBN dissociation rate. This procedure may be regarded as a special case of the inhibition method, well known in radical chemistry [16]. It is to be noted that in practice the procedure is extremely simple and expeditious, and therefore more advantageous than the usual methods *(e.g.*, it does not require a high-vacuum instrument, nor the performance of different procedures in closed vessel).

Our investigations were carried out with a *JES—P—10* type spectrometer. To examine the isotropic hyperfine splitting of ^{13}C nuclei occurring in natural abundance, only a spectrometer of high resolution, high sensitivity and good stability can be used, as it has been proved by J. R. BOLTON [15].

To obtain the resolving power needed, the homogeneity of the electromagnet was increased by diamagnetic shielding. By selecting the parameters of the lock-in detector, a further increase in the resolving power was obtained. This goes with a certain distortion of the line. By adjusting thus the lock-in detector, lines of low intensity can be detected extremely well in the immediate environment of high-intensity lines.

The simultaneous detection of lines of low intensity originating from the ^{13}C nucleus, and of lines of considerably higher intensity originating from protons, necessitate a high signal to noise ratio. In the spectrometer employed by us, the small degree of hysteresis distortion of the ESR spectrum goes inevitably with the slow recording; the distortion was reduced to the minimum, but could not be eliminated entirely.

In order to increase the signal to noise ratio — which is especially necessary in case of lines of low intensity emerging on the flanks of the spectrum — we employed the filtering allowed by the recording rate (approx. 2 Oe/min). A further signal to noise ratio increase could be obtained by employing the so-called "time averaging" (or accumulation) method [17, 18, 19, 20]. Accumulation was performed with a Spectrum Accumulator Type *JRA—1*. For further decrease of the noise, a 10-fold "smoothing" was effected, also with the aid of the Spectrum Accumulator.

The ESR spectrum of the tetracene positive ion was used for the relative measuring of the magnetic field [21]. From the measured values of coupling constants a confidence interval was determined, overlapping the real value with 95% reliability.

Results

1) For the determination of the coupling constants of naturally abundant ^{13}C nuclei, the knowledge of the proton coupling constants and the positions of the lines originating from protons is absolutely indispensable. Therefore, we dealt first with the determination of these.

The origin and theoretical intensities of the lines derived from protons, as well as their distance measured from the centre of the spectrum are shown in Table II. 184 of the lines present in the spectrum of the TPM radical were identified as being due to interaction with protons.

The 95% confidence intervals determined for the values of proton coupling constants, measured at different temperatures, are presented in Table III. The temperature dependence of the coupling constants are shown in Fig. 1.

Table II

Theoretical intensities of the lines produced by the protons of the triphenylmethyl radical and the distances from the middle of the spectrum

No.	Origin of the line	Oersted	Intensity
1	$3/2\,a_p + 3\,a_0 + 3\,a_m =$	15.342	1
2	$3/2\,a_p + 3\,a_0 + 2\,a_m =$	14.209	6
3	$3/2\,a_p + 3\,a_0 + 1\,a_m =$	13.076	15
4	$3/2\,a_p + 2\,a_0 + 3\,a_m =$	12.770	6
5	$1/2\,a_p + 3\,a_0 + 3\,a_m =$	12.524	3
6	$3/2\,a_p + 3\,a_0 =$	11.943	20
7	$3/2\,a_p + 2\,a_0 + 2\,a_m =$	11.637	36
8	$1/2\,a_p + 3\,a_0 + 2\,a_m =$	11.391	18
9	$3/2\,a_p + 3\,a_0 - 1\,a_m =$	10.810	15
10	$3/2\,a_p + 2\,a_0 + 1\,a_m =$	10.504	90
11	$1/2\,a_p + 3\,a_0 + 1\,a_m =$	10.258	45
12	$3/2\,a_p + 1\,a_0 + 3\,a_m =$	10.198	15
13	$1/2\,a_p + 2\,a_0 + 3\,a_m =$	9.952	18
14*	$-1/2\,a_p + 3\,a_0 + 3\,a_m =$	9.706	3
15	$3/2\,a_p + 3\,a_0 - 2\,a_m =$	9.677	6
16	$3/2\,a_p + 2\,a_0 =$	9.371	120
17	$1/2\,a_p + 3\,a_0 =$	9.125	60
18	$3/2\,a_p + 1\,a_0 + 2\,a_m =$	9.065	90
19	$1/2\,a_p + 2\,a_0 + 2\,a_m =$	8.819	108
20	$-1/2\,a_p + 3\,a_0 + 2\,a_m =$	8.573	18
21*	$3/2\,a_p + 3\,a_0 - 3\,a_m =$	8.544	1
22	$3/2\,a_p + 2\,a_0 - 1\,a_m =$	8.238	90
23	$1/2\,a_p + 3\,a_0 - 1\,a_m =$	7.992	45
24	$3/2\,a_p + 1\,a_0 + 1\,a_m =$	7.932	225
25	$1/2\,a_p + 2\,a_0 + 1\,a_m =$	7.686	270
26	$3/2\,a_p + 3\,a_m =$	7.626	20
27	$-1/2\,a_p + 3\,a_0 + 1\,a_m =$	7.440	45
28	$1/2\,a_p + 1\,a_0 + 3\,a_m =$	7.380	45
29	$-1/2\,a_p + 2\,a_0 + 3\,a_m =$	7.134	18
30	$3/2\,a_p + 2\,a_0 - 2\,a_m =$	7.105	36
31*	$-3/2\,a_p + 3\,a_0 + 3\,a_m =$	6.888	1
32	$1/2\,a_p + 3\,a_0 - 2\,a_m =$	6.859	18
33	$3/2\,a_p + 1\,a_0 =$	6.799	300
34	$1/2\,a_p + 2\,a_0 =$	6.555	360
35	$3/2\,a_p + 2\,a_m =$	6.493	120
36	$-1/2\,a_p + 3\,a_0 =$	6.307	60

Table II. (continued)

No.	Origin of the line	Oersted	Intensity
37	$1/2\,a_p + 1\,a_0 + 2\,a_m =$	6.247	270
38	$-1/2\,a_p + 2\,a_0 + 2\,a_m =$	6.001	108
39	$3/2\,a_p + 2\,a_0 - 3\,a_m =$	5.972	6
40	$-3/2\,a_p + 3\,a_0 + 2\,a_m =$	5.755	6
41*	$1/2\,a_p + 3\,a_0 - 3\,a_m =$	5.726	3
42	$3/2\,a_p + 1\,a_0 - 1\,a_m =$	5.666	225
43	$1/2\,a_p + 2\,a_0 - 1\,a_m =$	5.420	270
44	$3/2\,a_p + 1\,a_m =$	5.360	300
45	$-1/2\,a_p + 3\,a_0 - 1\,a_m =$	5.174	45
46	$1/2\,a_p + 1\,a_0 + 1\,a_m =$	5.114	675
47	$3/2\,a_p - 1\,a_0 + 3\,a_m =$	5.054	15
48	$-1/2\,a_p + 2\,a_0 + 1\,a_m =$	4.868	270
49	$1/2\,a_p + 3\,a_m =$	4.808	60
50	$-3/2\,a_p + 3\,a_0 + 1\,a_m =$	4.622	15
51	$-1/2\,a_p + 1\,a_0 + 3\,a_m =$	4.562	45
52	$3/2\,a_p + 1\,a_0 - 2\,a_m =$	4.533	90
53	$-3/2\,a_p + 2\,a_0 + 3\,a_m =$	4.316	6
54	$1/2\,a_p + 2\,a_0 - 2\,a_m =$	4.287	108
55	$3/2\,a_p =$	4.227	400
56	$-1/2\,a_p + 3\,a_0 - 2\,a_m =$	4.041	18
57	$1/2\,a_p + 1\,a_0 =$	3.981	900
58	$3/2\,a_p - 1\,a_0 + 2\,a_m =$	3.921	90
59	$-1/2\,a_p + 2\,a_0 =$	3.735	360
60	$1/2\,a_p + 2\,a_m =$	3.675	360
61	$-3/2\,a_p + 3\,a_0 =$	3.489	20
62	$-1/2\,a_p + 1\,a_0 + 2\,a_m =$	3.429	270
63	$3/2\,a_p + 1\,a_0 - 3\,a_m =$	3.400	15
64	$-3/2\,a_p + 2\,a_0 + 2\,a_m =$	3.183	36
65	$1/2\,a_p + 2\,a_0 - 3\,a_m =$	3.154	18
66	$3/2\,a_p - 1\,a_m =$	3.094	300
67*	$-1/2\,a_p + 3\,a_0 - 3\,a_m =$	2.908	3
68	$1/2\,a_p + 1\,a_0 - 1\,a_m =$	2.848	675
69	$3/2\,a_p - 1\,a_0 + 1\,a_m =$	2.788	225
70	$-1/2\,a_p + 2\,a_0 - 1\,a_m =$	2.602	270
71	$1/2\,a_p + 1\,a_m =$	2.542	900
72	$3/2\,a_p - 2\,a_0 + 3\,a_m =$	2.482	6
73	$-3/2\,a_p + 3\,a_0 - 1\,a_m =$	2.356	15
74	$-1/2\,a_p + 1\,a_0 + 1\,a_m =$	2.296	675

Table II (continued)

No.	Origin of the line	Oersted	Intensity
75	$1/2\,a_p - 1\,a_0 + 3\,a_m =$	2.236	45
76	$-3/2\,a_p + 2\,a_0 + 1\,a_m =$	2.050	90
77	$-1/2\,a_p + 3\,a_m =$	1.990	60
78	$3/2\,a_p - 2\,a_m =$	1.961	120
79	$-3/2\,a_p + 1\,a_0 + 3\,a_m =$	1.744	15
80	$1/2\,a_p + 1\,a_0 - 2\,a_m =$	1.715	270
81	$3/2\,a_p - 1\,a_0 =$	1.655	300
82	$-1/2\,a_p + 2\,a_0 - 2\,a_m =$	1.469	108
83	$1/2\,a_p =$	1.409	1200
84	$3/2\,a_p - 2\,a_0 + 2\,a_m =$	1.349	36
85	$-3/2\,a_p + 3\,a_0 - 2\,a_m =$	1.223	6
86	$-1/2\,a_p + 1\,a_0 =$	1.163	900
87	$1/2\,a_p - 1\,a_0 + 2\,a_m =$	1.103	270
88	$-3/2\,a_p + 2\,a_0 =$	0.917	120
89	$-1/2\,a_p + 2\,a_m =$	0.857	360
90	$3/2\,a_p - 3\,a_m =$	0.828	20
91	$-3/2\,a_p + 1\,a_0 + 2\,a_m =$	0.611	90
92	$1/2\,a_p + 1\,a_0 - 3\,a_m =$	0.582	45
93	$3/2\,a_p - 1\,a_0 - 1\,a_m =$	0.522	225
94	$-1/2\,a_p + 2\,a_0 - 3\,a_m =$	0.336	18
95	$1/2\,a_p - 1\,a_m =$	0.276	900
96	$3/2\,a_p - 2\,a_0 + 1\,a_m =$	0.216	90
97*	$-3/2\,a_p + 3\,a_0 - 3\,a_m =$	0.090	1
98	$-1/2\,a_p + 1\,a_0 - 1\,a_m =$	0.030	675

Lines unrecognizable in the spectrum are marked with *

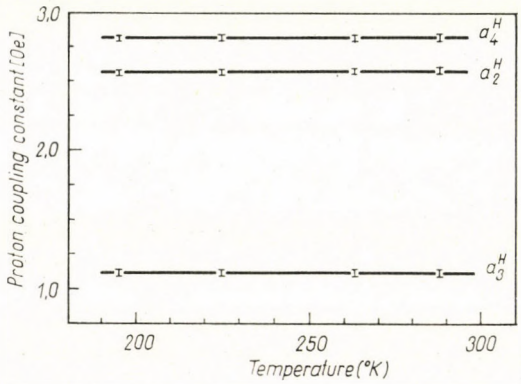

Fig. 1. Temperature dependence of the proton coupling constants

The ^{13}C lines were not needed for the determination of the proton coupling constants. Therefore conditions resulting in minimum hysteresis distortion could be realized.

Employing the proton coupling constants given above, we simulated with the aid of our Spectrum Accumulator the ESR spectrum originating exclusively from protons (Fig. 2). By comparing the simulated and measured spectra, the lines produced by the isotropic hyperfine interaction of ^{13}C nuclei were selected.

Knowing the position of the adsorption lines originating from the proton (Table II), the lines originating from the ^{13}C nuclei of identical position could

Table III

Proton coupling constants of the triphenylmethyl radical at different temperatures

Temperature, °K	a^H_2	a^H_3	a^H_4
	Oersted		
195	[1.11; 1.13]	[2.54; 2.57]	[2.79; 2.82]
225	[1.12; 1.14]	[2.56; 2.59]	[2.80; 2.84]
263	[1.12; 1.15]	[2.55; 2.59]	[2.80; 2.84]
295	[1.13; 1.15]	[2.56; 2.60]	[2.80; 2.84]

be determined. Three groups emerged in the middle part of the spectrum and two on the flanks. The latter could only be detected in the spectrum recorded at 220°K after 9-fold accumulation (Fig. 3).

The determination of the origin of the five different groups of lines was carried out by intensity estimation. For the distinction of groups of lines originating from ^{13}C nuclei in ortho and meta positions, the width of lines determined by different spin densities of the positions in question were employed [22]. In this procedure, spin densities obtained with the aid of the proton coupling constants have been considered. However, distinction of groups of lines originating from ^{13}C nuclei in para- and "1" position cannot be achieved by this method.

Of the lines originating from ^{13}C nuclei of the same position one has to choose possibly that of the highest intensity. Measuring the distance of the choosen line from the nearest line originating from a proton, the coupling constant of the ^{13}C nucleus in question was obtained. Employing this procedure on both flanks of the spectrum and averaging the results obtained, the inaccuracy owing to hysteresis distortion is considerably decreased. It is to be noted that the coupling constant of the radical labelled in α-position and appearing with lowest intensity can be determined by this method with least certainty.

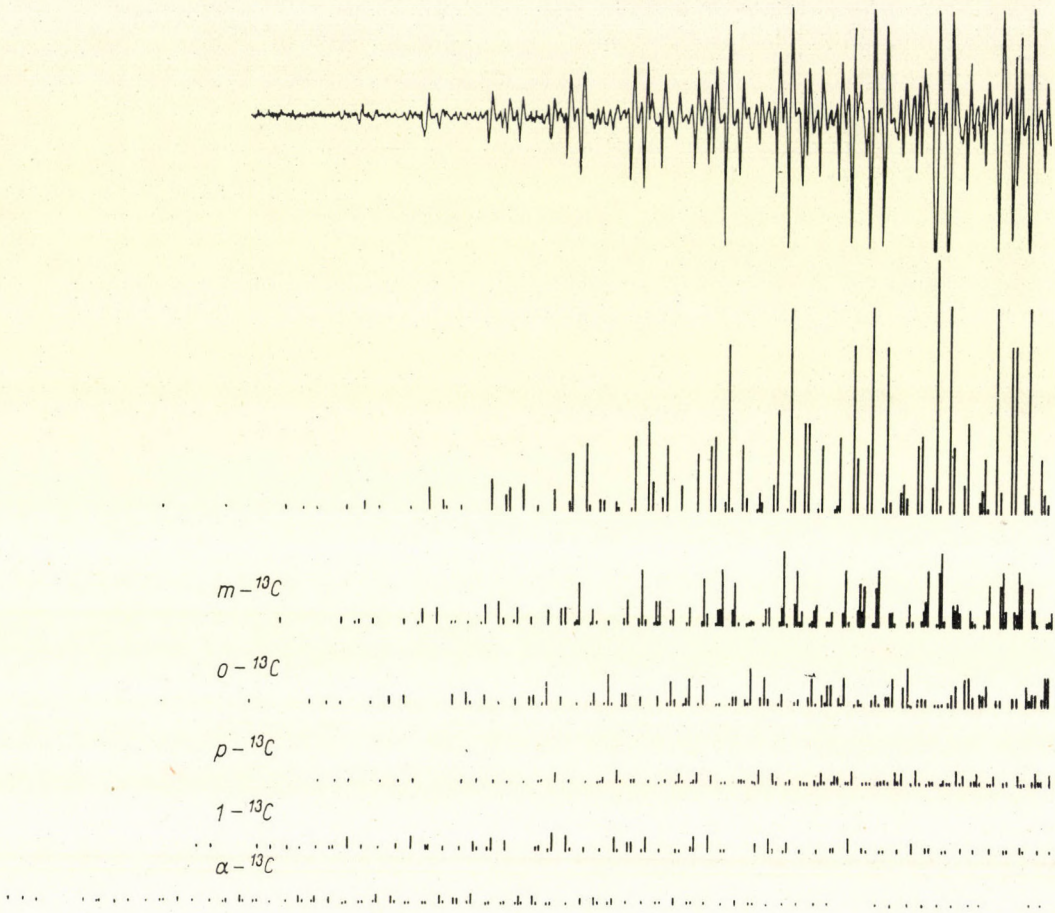

Fig. 2. ESR spectrum of the triphenylmethyl radical and its stick diagrams

Table IV contains the coupling constants of ^{13}C nuclei ($a_i{}^{13}C$) in different positions.

In Fig. 2, one half of the "stick" diagrams of the ESR spectrum of the TPM radical, that of the 15 protons, and of the spectrum produced by ^{13}C nuclei are shown. In Fig. 3, the ESR spectrum recorded after 9-fold accumulation and 10-fold smoothing of the parts of low intensity of Fig. 2, further the respective parts of the "stick" diagrams are presented. It is to be mentioned, that for the sake of good comprehension, the spectra of non-labelled radicals are shown with considerably smaller intensity. The intensities of the spectra of labelled radicals are represented in approximate ratio.

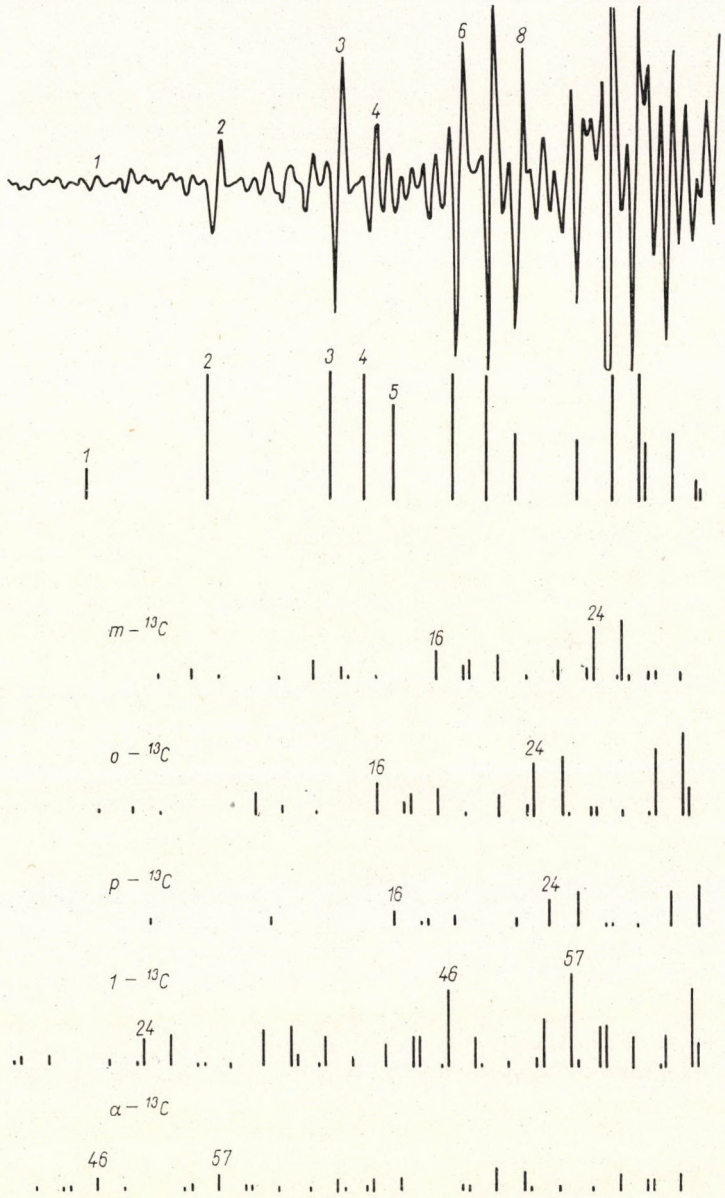

Fig. 3. Extreme low-intensity lines of the ESR spectrum of the triphenylmethyl radical

Table IV

Coupling constants of the ^{13}C isotope of the triphenylmethyl radical

Position	α	1	2	3	4
a^{13C}	+20.1 Oe	−13.6 Oe	+6.4 Oe	−5.3 Oe	+6.1 Oe

Discussion

On the basis of our results we have come to the following conclusions:

(1) The suitable selection of the radical concentration is of decisive importance for a successful investigation of the spectrum of the TPM free radical. Our method developed for this purpose can be applied — with more or less change — to the cases of other free radicals as well.

(2) The coupling constants of protons of the TPM radical do not depend on temperature. An eventual temperature dependence — as may be observed, *e.g.*, in the case of different disubstituted nitrogen oxide radicals (results of our own investigations in this matter will be reported in forthcoming publications) may be explained by supposing the torsion of the temperature-dependent amplitude of the TPM phenyl rings. The independence from the temperature of the coupling constants leads to the conclusion that the structure of the TPM radical is rigid, and that the torsion of the phenyl rings can be of very small amplitude only. The rigid structure is a consequence of the strong resonance energy of the TPM radical. Namely, a twisting of the phenyl rings along the $C_1 - C_\alpha$ bond resonance energy would decrease rapidly.

(3) After having determined the absolute values of the ^{13}C coupling constants in different positions, two problems remain unsolved:

a) Which are the signs of the $a^{13}C$ coupling constants?

b) The assignments of the corresponding coupling constants to positions "1" and "4".

From the measured values of $a^{13}C$ the ϱ_i^π values can be calculated in all positions of the TPM radical with the aid of the KARPLUS—FRAENKEL equation. Accepting the fact of the sign alteration of the coupling constants, the two spin density values can be calculated for each position; one from the combination

$$+ a_\alpha^{13C} - a_1^{13C} + a_2^{13C} - a_3^{13C} + a_4^{13C} \tag{3}$$

and the other from the combination with opposite signs. As the values 13.6 Oe and 6.1 Oe both can be assigned to position 1 and 4, in both combinations two more possibilities are given. Nevertheless, the spin density values have to satisfy the equation

$$\varrho_\alpha^\pi + 3\varrho_1^\pi + 6(\varrho_2^\pi + \varrho_3^\pi) + 3\varrho_4^\pi = 1 \tag{4}$$

as well.

Owing to this criterion, it is possible to choose among the different spin density series. The spin density series which satisfies Equation (4) most correctly has to be considered as the real one. In case of the coupling constants, that sign combination is used which results in the best spin density values.

For the determination of the ϱ_i^π values, $S^C = -12.7$ Oe; $Q_{CH}^C = +19.5$ Oe; $Q_{CC}^C = +14.4$ Oe; and $Q_{C'C}^C = -13.9$ Oe were considered [13]. Spin densities

calculated with sign combination (3) and values $a_4^{^{12}C} = 6.1$ Oe, $a_1^{^{13}C} = 13.6$ Oe, are shown in Table V.

Substituting the data of Table V in Equation (4), $+0.931$ is obtained as the sum of spin densities, which may be considered a good approximation of the theoretical value.

Comparing the data of Tables V and I it may be concluded that none of the quantum chemical methods employed gives such results which would agree satisfactorily with the experimental spin density values in all positions

Table V

Experimental spin density values of the triphenylmethyl radical

α	1	2	3	4
+0.505	−0.112	+0.115	−0.054	+0.130

of the radical. The discrepancies may have — beyond the theoretical errors of the different approximate methods — also a structural reason. At present the angle of twist of the phenyl rings from the plane of coplanarity is not yet known.

(4) Knowing the coupling constants a_i^H and $a_i^{^{13}C}$, the absolute value of Q in the McCONNELL equation can be determined with the aid of the KARPLUS—FRAENKEL relation, making use of the expressions

$$|Q_3| = \frac{35.6\,|a_3^H| - 13.9\,(|a_2^H| + |a_4^H|)}{|a_3^{^{13}C}|} \tag{5}$$

and

$$|Q_4| = \frac{35.6\,|a_4^H| - 27.8\,|a_3^H|}{|a_4^{^{13}C}|}. \tag{6}$$

From expressions (5) and (6) the following results are obtained:

$$|Q_3| = 21.70 \text{ Oe}$$

$$|Q_4| = 21.55 \text{ Oe}$$

Employing the ϱ_i^π values determined from Eq. (2), we have:

$$|Q_2| = 22.68 \text{ Oe}$$

and the mean value:

$$|\bar{Q}| = 21.98 \text{ Oe}.$$

The Q values resulting as the ratio of the proton coupling constants and spin densities shown in Table V are the following:

$$|Q_2| = 22.22 \text{ Oe}$$

$$|Q_3| = 20.92 \text{ Oe}$$

$$|Q_4| = 21.59 \text{ Oe}$$

and the mean value of these data is:

$$|\overline{Q}| = 21.58 \text{ Oe}.$$

The agreement of the $|Q|$ values and mean values, calculated in two ways, may be considered satisfactory. The Q values in different positions agree within a few per cent; this fact supports the correctness of the assumption of a constant value of Q in an aromatic system.

(5) The value of $a_\alpha^{^{13}C}$ given by us differs considerably from the results of S. I. WEISSMAN [14] and P. B. AYSCOUGH [7]. As already mentioned, the value of $a_\alpha^{^{13}C}$ can be determined from the spectra with least certainty, but it may be stated that the value $a_\alpha^{^{13}C} = 26$ Oe is not consistent with the experimental spectrum. The different resolutions of the spectra employed may be considered as the probable cause of the discrepancy.

(6) Summing up what has been said above, we may state the following:

(a) the KARPLUS—FRAENKEL equation is regarded as the correct description of the real conditions of the TPM radical;

(b) MCCONNELL's Q value is by 10% lower, than in the case of other aromatic systems;

(c) the cause of discrepancies between the a^H coupling constants and theoretical spin densities is to be sought most probably in the roughness of the methods used for the calculation of the spin densities.

We wish to thank Miss M. VÁRI and Mr. K. JÓKAY, for their assistance in the experimental work.

SUMMARY

The ESR spectrum of the triphenylmethyl radical has been investigated in the temperature range 190°K—290°K in toluene solution. The values of the proton coupling constants [a_4^H(para) = 2.81 Oe; a_3^H(meta) = 1.13 Oe; a_2^H(ortho) = 2.57 Oe] do not depend on the temperature. The isotropic hyperfine splitting values of the ^{13}C nuclei occurring in natural abundance have been measured:

$$a_\alpha^{^{13}C} = +20.1 \text{ Oe}; \quad a_1^{^{13}C} = -13.6 \text{ Oe}; \quad a_2^{^{13}C} = +6.4 \text{ Oe};$$

$$a_3^{^{13}C} = -5.3 \text{ Oe}; \quad a_4^{^{13}C} = +6.1 \text{ Oe}.$$

The ϱ^π spin densities and MCCONNELL's absolute Q value are reported.

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THE STRUCTURE OF AMIDAZOPHEN–BARBITURATE MOLECULAR COMPOUNDS

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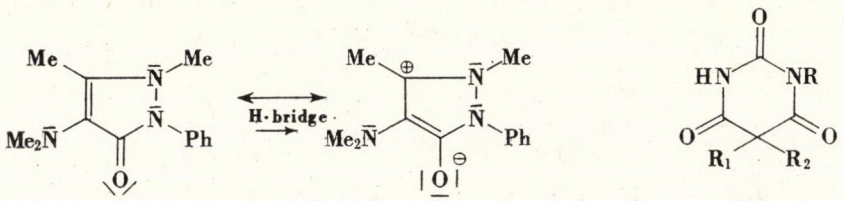
Introduction

Molecular compounds of amidazophen (**I**) with various barbiturates (**II**) *(e.g. Cibalgin, Veramon, Veralgit)* have been in general medical use for decades Namely, from a therapeutical point of view, the application in form of molecular compounds has several advantages.



I Ia II

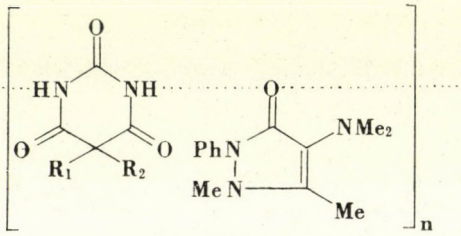
STARKENSTEIN and KLIMESCH [1, 2] found that in case of rectal application the molecular compound exerts its analgetic effect four times faster than a mechanical mixture of the same two medicaments. According to the clinical observations of KÄER and LOEWE [3] and OHATA [4] the sedative effect is enhanced on the simultaneous application of the two substances. Their concentration in the blood raises more slowly, whereby the effect is extended. The toxicity of the molecular compound is smaller than that of the components.

The favourable pharmaceutical effect of the molecular compound was attributed by STARKENSTEIN and KLIMESCH [1, 2] to its better dissolving and adsorption properties as compared to those of the components. According to ANSELMI and DAVID [5], moreover CAGNOLI [6], the molecular compound exists in aqueous medium, hence in plasm, too, therefore it can directly bind to cellular proteins.

The molecular compound is prepared by crystallization from some polar solution of the two components. Thus it can be expected that the associate may be formed in living organisms.

Since the difference in effectiveness may also be related to the structure of the molecular compound, structural elucidation is of equal interest both from the pharmacological aspect and pharmaceutical-chemical point of view.

PFEIFFER [7] was the first to point out that amidazophen and 5,5-diethyl barbituric acid were present in a ratio of 1 : 1 in the molecular compound. On the contrary, some other authors [5, 8] found the ratio to be 2 : 1. This again has been disproved by other authors [6, 9, 10, 11] confirming PFEIFFER's results. The first formula relating to the structure of the molecular compound originates from HERTEL [10]. Accordingly, the two components are linked together in the ratio of 1 : 1 by means of hydrogen bonds, as shown by structure **III**. This structure was derived theoretically. No suggestion was given concerning the dimension of the association chain.



III

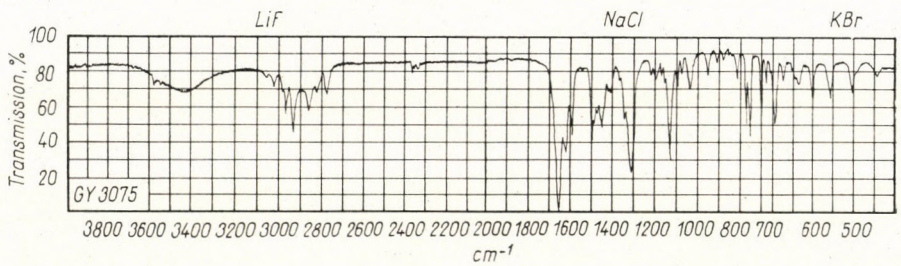
In explaining the characteristic pharmacological properties, BÜSSEMAKER [12] assumed the formation of a complex, whose structure was, however, not detailed.

KASHIMA, WATARI and MIKUBO [13] concluded from the Raman spectrum of the amidazophen — 5,5-diethyl barbituric acid molecular compound that the structure (**III**) of HERTEL was correct. However, the region between 3600 and 2800 cm^{-1}, the most important range for hydrogen bonds and of OH and NH stretching frequencies, was not examined.

Accordingly, the structure of the amidazophen — barbiturate molecular compound has not been, so far, unambiguously elucidated. It was the purpose of the present work to solve this problem.

Discussion

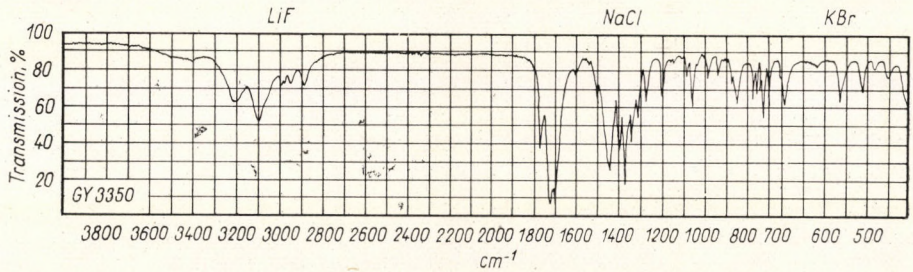
The spectra of amidazophen (Spectrum No. 1) and of the following barbiturates and their reaction products were taken:



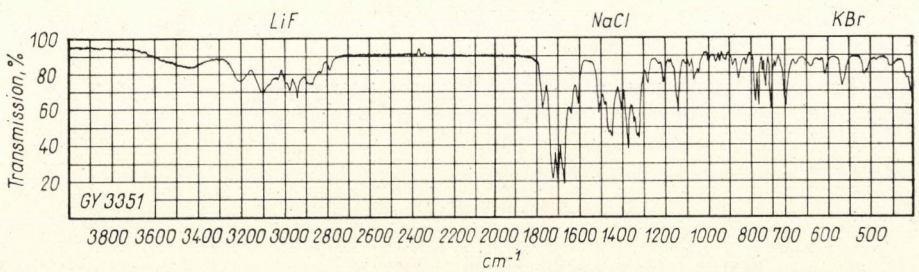
Spectrum No. 1 Amidazophen

5-ethyl-5-phenyl barbituric acid	(**II**, R=H, R_1=Et, R_2=Ph)
5,5-diethyl barbituric acid	(**II**, R=H, R_1=R_2=Et)
5-ethyl-5-butyl barbituric acid	(**II**, R=H, R_1=Et, R_2=*n*-butyl)
N-methyl-5-ethyl-5-phenyl barbituric acid	(**II**, R=Me, R_1=Et, R_2=Ph)
N-methyl-5-methyl-5-cyclohexenyl barbituric acid	(**II**, R=R_1=Me, R_2= )
N-methyl-5-isopropyl-5-(2-bromo)allyl barbituric acid	(**II**, R=Me, R_1=*i*-propyl, R_2=2-bromoallyl).

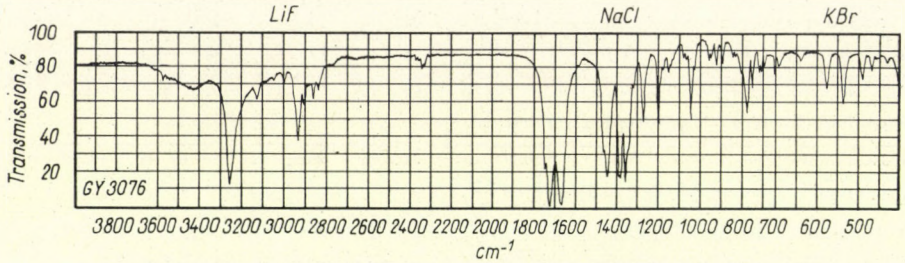
It was found that the last three of these compounds did not react with amidazophen, *i.e.* simple mechanical mixtures of the components were obtained. Accordingly, the spectra were superpositions of those of amidazophen and the barbiturates. To evidence this statement the spectra of N-methyl-5-ethyl-5-phenyl barbituric acid, N-methyl-5-methyl-5-cyclohexenyl barbituric acid, N-methyl-5-isopropyl-5-(2-bromo)allyl barbituric acid (Spectra No. 2, 4 and 6) and of the corresponding amidazophen — barbiturate mixtures (spectra No. 3, 5 and 7) are presented. The relative band intensities are identical with those observed in the spectra of the pure components and as compared to one another correspond to a mixture of molar ratio 1 : 1.



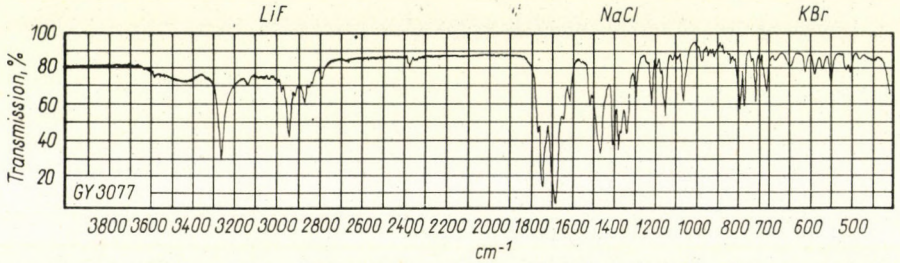
Spectrum No. 2 N-methyl-5-ethyl-5-phenyl barbituric acid



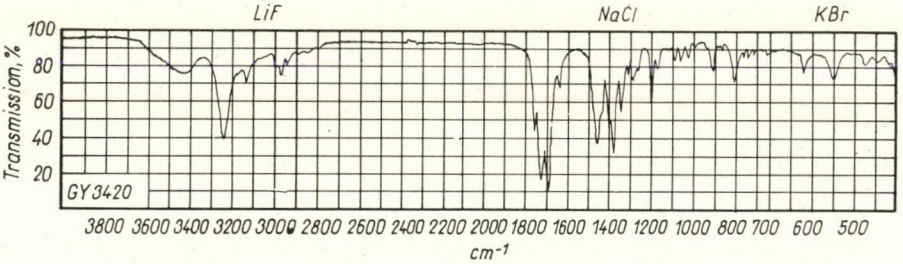
Spectrum No. 3 Mixture of amidazophen and N-methyl-5-ethyl-5-phenyl barbituric acid



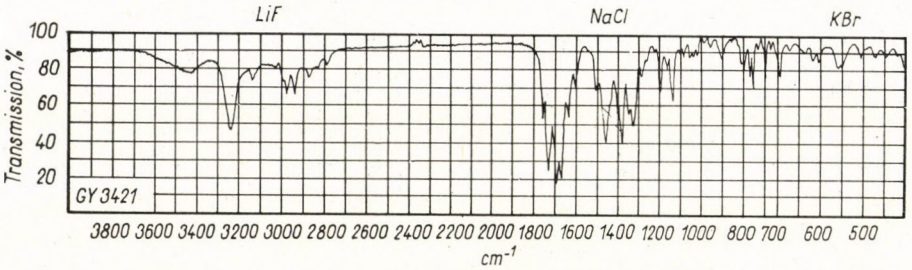
Spectrum No. 4 N-methyl-5-methyl-5-cyclohexenyl barbituric acid



Spectrum No. 5 Mixture of amidazophen and N-methyl-5-methyl-5-cyclohexenyl barbituric acid

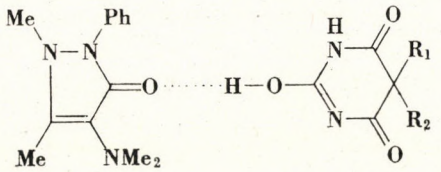


Spectrum No. 6 N-methyl-5-isopropyl-5-(2-bromo)allyl barbituric acid

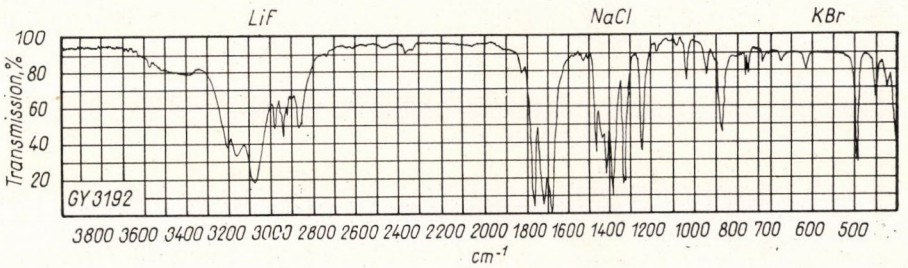


Spectrum No. 7 Mixture of amidazophen and N-methyl-5-isopropyl-5-(2-bromo)-allyl barbituric acid

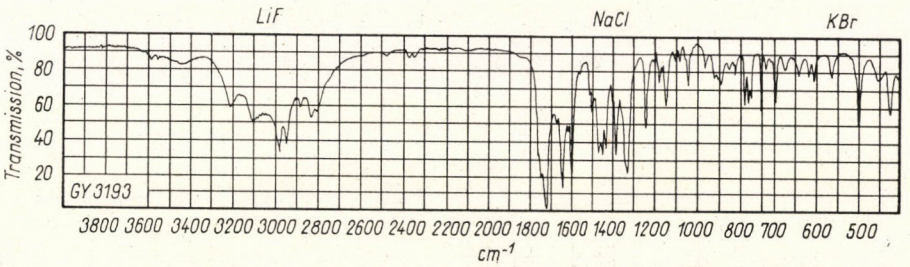
On the contrary, the other three barbiturates react with amidazophen, which is proved by the spectra of the corresponding molecular compounds. Naturally, the spectrum here is no longer a simple superposition of the spectra of the pure components, but fundamentally different curves are obtained, which show, however, far-extending analogy with one another, making sure that the structure of the molecular compounds is the same, irrespective of the nature of groups R_1 and R_2 in **II**. Comparison of the spectra of the components and their molecular compounds supports the conclusion that the latter correspond rather to structure **IV** than **III**, where intermolecular hydrogen bonds are formed between the hydroxyl group of the hemi-iminohydrin (lactim) tautomer of barbiturates and the amidazophen carbonyl group.



IV



Spectrum No. 8 5,5-diethyl barbituric acid

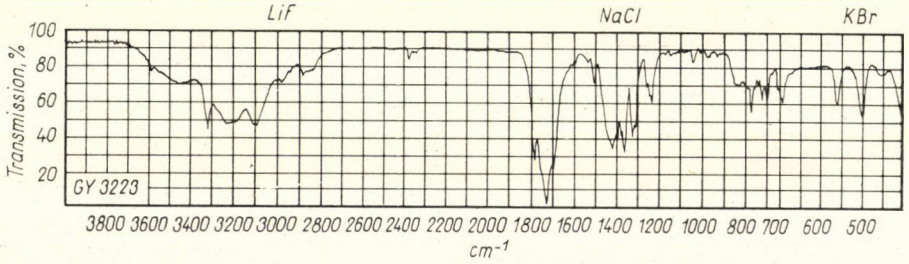


Spectrum No. 9 Molecular compound of amidazophen and 5,5-diethyl barbituric acid

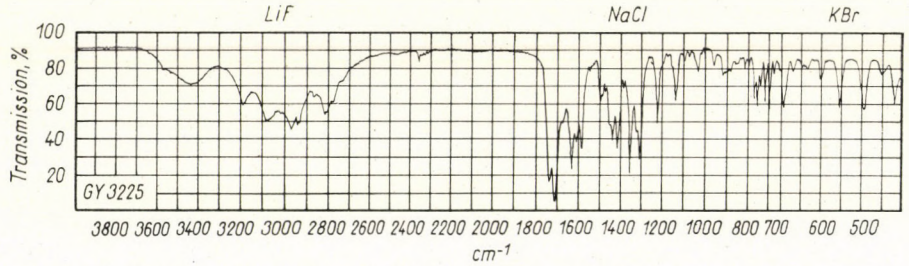
In support of this, the spectra of amidazophen (Spectrum No. 1), 5,5-diethyl barbituric acid (Spectrum No. 8), and of the molecular compound of the two (Spectrum No. 9) have been determined. The spectra of the other two barbiturates and their molecular compounds are quite analogous. For com-

parison purposes the spectra of 5-ethyl-5-phenyl barbituric acid, 5-ethyl-5--butyl barbituric acid and their molecular compounds are also presented (Spectra No. 10, 12, 11, 13).

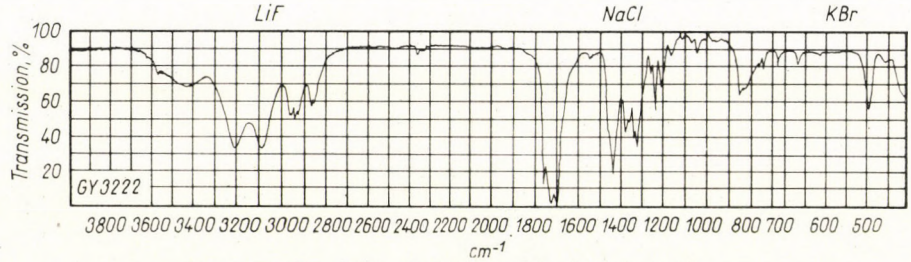
In Spectrum No. 8 of 5,5-diethyl barbituric acid the stretching vibrations of the two NH groups appear at 3300—3000 cm^{-1} with triple maximum at about 3215, 3170 and 3080 cm^{-1}, probably corresponding to the two different types of associated molecules. Namely, a chain of *cis* association (**V**, $R_1 = R_2 = Et$) formed with the participation of one of the NH groups and the C—2 carbonyl is feasible, as well as a probably cyclic, dimeric structure with hydrogen bonds again, in which both NH groups take part (**VIa**, **VIb**, $R_1 = R_2 = Et$). The coupled stretching vibrations of the three carbonyl groups absorb at 1775, 1730 and 1690 cm^{-1}, respectively. From a point of view of structure elucidation of the molecular compound the region above 1500 cm^{-1} is the decisive, and besides



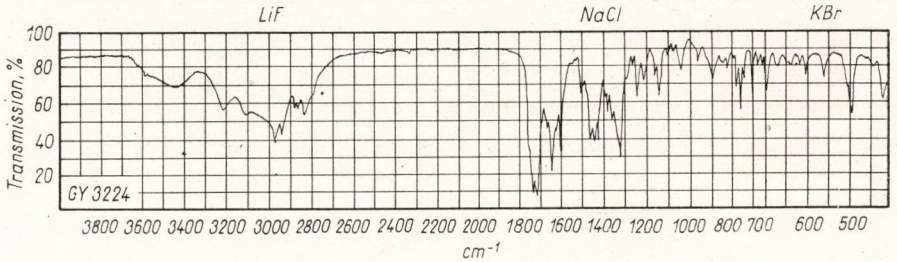
Spectrum No. 10 5-ethyl-5-phenyl barbituric acid



Spectrum No. 11 Molecular compound of amidazophen and 5-ethyl-5-phenyl barbituric acid



Spectrum No. 12 5-ethyl-5-butyl barbituric acid

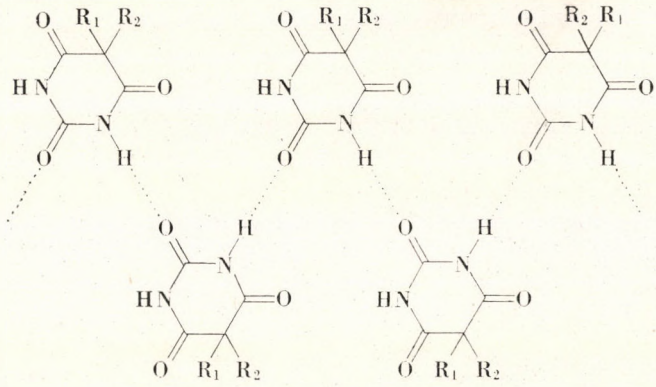


Spectrum No. 13 Molecular compound of amidazophen and 5-ethyl-5-butyl barbituric acid

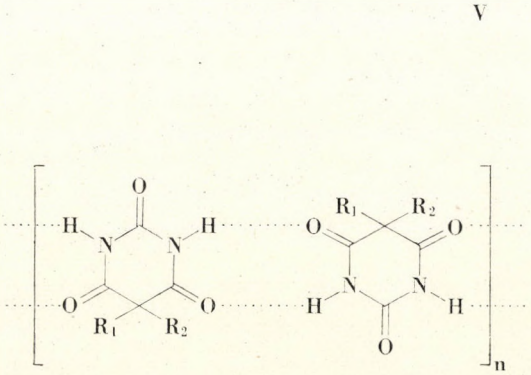
the above mentioned ones only the aliphatic CH stretching vibration bands of medium intensity appear in this region, between 3000 and 2800 cm^{-1}.

In the spectrum of amidazophen (Spectrum No. 1) the CH stretching vibrations of medium intensity appear between 3050 and 2750 cm^{-1}. The amide-I band occurs at 1665 cm^{-1}, the stretching vibration of the C=C double bond of the heterocyclic ring at 1640 cm^{-1}, while the two aromatic skeletal vibrations of medium intensity at 1600 and 1500 cm^{-1}.

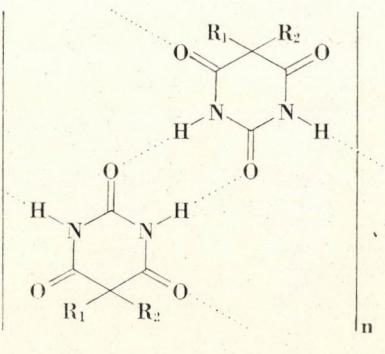
In the spectrum of the molecular compound (Spectrum No. 9) the amidazophen amide-I band is shifted from 1665 to 1640 cm^{-1}, while the stretching frequency of the heterocyclic C=C double bond increases by



V



VIa



VIb

15 cm^{-1}, up to 1665 cm^{-1}, thus the two bands appear as if they changed places, which unequivocally follows from the intensity ratios. All these are explainable by a shift in the **I** ↔ **Ia** mesomeric system towards **Ia**, caused by the strong hydrogen bonds, from which really a decrease in frequency of the amide-I band (a result of decrease in bond order of amide carbonyl) and an opposite change in the C=C stretching vibration (increasing electron attracting effect of the carbonyl group) may be expected.

The other bands of amidazophen presumably do not change significantly, and actually all the intensive ones may be found (obviously with proportionally decreased intensities) in the spectrum of the molecular compound; see the bands at 1330, 1130, 1050, 780, 765, 700, 605 and 560 cm^{-1}.

Naturally, the spectrum of 5,5-diethyl barbituric acid is more essentially altered, because of tautomerism.

The stretching vibration bands of the hydroxyl and secondary amine groups appear together with the maxima of aromatic and aliphatic CH stretching vibrations in the 3300—2600 cm^{-1} region. The broad, diffuse absorption proves the presence of strong hydrogen bonds and indicates that besides C=O . . . H—O linkages, resulting in the formation of the molecular compound itself (according to structure **IV**), the amide groups of the barbiturate moiety also associate to a chain polymer or cyclic dimer.

In accord with the disappearance of one of the carbonyl groups, the three maxima do not appear between 1800 and 1650 cm^{-1}; instead a doublet may be expected at low frequencies, which can actually be observed in the spectra of the 5-ethyl-5-phenyl barbituric acid- and 5-ethyl-5-butyl barbituric acid—amidazophen molecular compounds (at 1740 and 1720, and 1730 and 1710 cm^{-1}, respectively in Spectra No. 12, and No. 13), while in Spectrum No. 9 these appear together as a maximum at 1720 cm^{-1}, the only sign of splitting being a shoulder at about 1740 cm^{-1}. The stretching vibration of the C=N double bond of the hemiiminohydrin tautomer is found at 1590 cm^{-1} (the weak band at 1605 cm^{-1} belongs to the aromatic skeletal vibration of the amidazophen moiety). The substantial decrease in intensity of the NH out-of-plane deformation vibration (found at 880 cm^{-1} in Spectrum No. 8) in the spectrum of the molecular compound (Spectrum No. 9) is further evidence for structure **IV**. Owing to the tautomerism, a number of other bands, too, shift as compared to Spectrum No. 8, and even new ones appear; *e.g.*, the bands at 1420, 1390, 1250, 950, 455, and 395 cm^{-1} are shifted, and new maxima are found at 750 and 425 cm^{-1}.

Further evidence for structure **IV** was obtained by comparing the spectra of the components and the molecular compounds in dilute dichloromethane solution, when the molecular compounds decomposed, and the spectra consisted of simple superpositions of the components, similarly to the spectra of N-methylbarbiturates taken in the solid state. For illustration

the NH and C=O stretching vibrations in the spectra of the components and the decomposed molecular compounds of 5,5-diethyl barbituric acid and 5--ethyl-5-pehnyl barbituric acid in dichloromethane solution are shown in Fig. 1. This result is quite obvious, since the molecular compound of structure **IV** is formed by means of intermolecular hydrogen bonds, and these are known to split in polar solvents at high dilution [14]. As the association ceases, the labile hemi-iminohydrin tautomer of the barbiturate component immediately

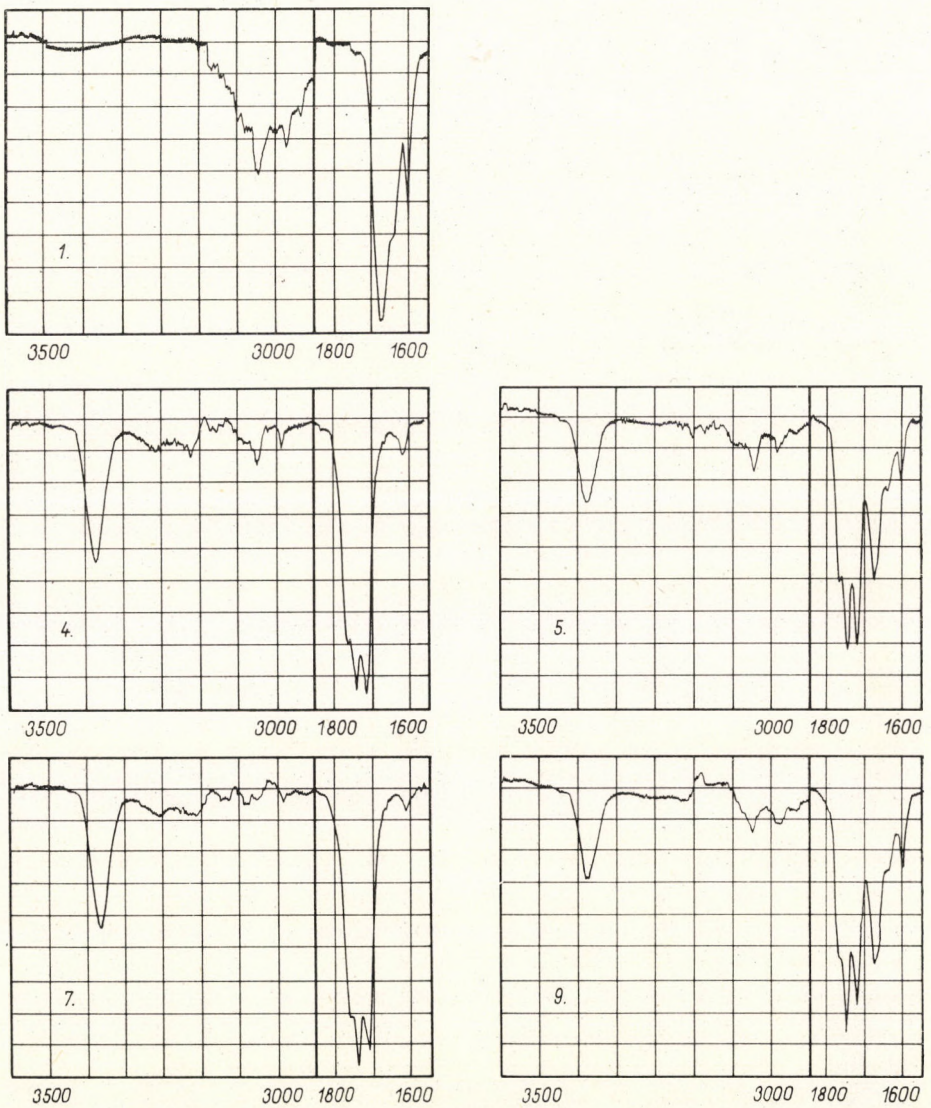
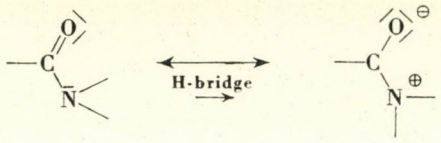


Fig. 1. Spectra of amidazophen (10), 5,5-diethyl barbituric acid (8) and 5-ethyl-5-phenyl barbituric acid (10), moreover the molecular compounds of the latter two with amidazophen (9 and 11) in dilute (cca 10^{-1} mole/l.) CH_2Cl_2 solution, in the regions 3600—2800 and 1850—1550 cm^{-1}.

transforms back to the amide form, hence really the pure components are existing in the solution only. This fact evidences that the assumption of the authors [1, 2] referred to in the introduction, namely, that the advantageous pharmacological properties of the molecular compound are connected with its better solubility and absorption, has been wrong.

Structure **IV** makes also clear why N-substituted barbiturates do not form molecular compounds.

Namely, it is known that the lactam-lactim (amide-iminohydrin) tautomeric equilibrium is generally shifted towards the amide form, because it is stabilized [15] by the considerable mesomeric energy of the mesomeric system possible with amides and illustrated by structures **VII** and **VIII**.



VII VIII

Under the effect of cyclic dimeric association, general with lactams [16—22] and occurring here simultaneously with the formation of the polymers *(cf., e.g.,* structures **VIa** and **VIb**), the equilibrium otherwise strongly shifted towards **VII** changes in favour of **VIII**, and since the two limit structures contribute thus to about the same degree, the mesomeric energy increases. This is so even with pyridones [23], where, however, the appearance of the lactim tautomer is accompanied by the formation of an aromatic π-electron sextet. In case of barbiturate derivatives bearing no substituent on the nitrogen atoms, cyclic dimeric association remains possible at the other amide group of the hemi--iminohydrin from thus further allowing the favourable shift of the mesomeric equilibrium. Therefore there is no hindrance for tautomerization and with that for the formation of a molecular compound of structure **IV**. The cyclic dimeric association would be no more possible in the lactim tautomer of N-substituted derivatives (the hydroxyl group would associate with the partner for molecular compound formation, and instead of the other NH group an N-methyl group is to be found in the molecule). Hence here the mesomeric system would shift almost completed to **VII**, and the mesomeric energy would diminish. This is why the state in which the amide group associates to cyclic dimers is more stable than that in which the hydroxyl group of the iminohydrin tautomer forms hydrogen bonds with other (amidazophen) molecules. That is the reason why N-substituted barbiturates do not form molecular compounds with amidazophen. The phenomenon is similar to that observed in the acylation of phthalic hydrazide, when in the first step the O-monoacylates of the hemi--iminohydrin tautomer are formed, while the second acyl group attacks always the nitrogen atom, to yield N,O-diacyl compounds [16].

Experimental

The formation of molecular compounds of amidazophen with six barbituric acid derivatives of different structures was attempted. The barbituric acid derivatives and the amidazophen used were *Merck AG.* (Darmstadt) A. R. substances, except N-methyl-5-iso-propyl-5-(2-bromo)allyl barbituric acid, which was a *Riedel—de Haän G. m. b. H.* (Seelze) A. R. product.

Description of the preparation

$8 \cdot 10^{-2}$ molar solutions were prepared in abs. ethyl alcohol at room temperature from both components. The corresponding solutions were combined in molar equivalent amounts, and the solvent was removed in vacuum at 25°. The crystals were collected and dried in vacuum at 30° for 1 hr. The products were examined soon after their preparation.

The spectra were taken by a *Zeiss* (Jena) UR—10 double-beam infrared spectrometer using KBr pellets.

The spectra of solutions were taken in NaCl cuvettes of 1 mm thickness, in dichloromethane solution at about 10^{-1} mole/litre concentration.

SUMMARY

Amidazophen forms molecular compounds with various barbiturates in the molar ratio of 1 : 1, which decompose in dilute solutions. With N-substituted barbiturate derivates such molecular compounds cannot be prepared. It has been shown by means of infrared spectroscopic analysis that in the analogous molecular compounds of various barbiturates hydrogen bonds are formed between the amidazophen carbonyl group and the hydroxyl group of the hemi-iminohydrin tautomer of the barbiturates. The reason why N-substituted barbiturates do not form molecular compounds is that their lactim tautomer is less stable than the lactam form, the latter being stabilized by mesomeric energy increased by cyclic dimeric association.

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TRANSFORMATION OF STEROIDS BY ABSIDIA ORCHIDIS, I

HYDROXYLATION OF ANDROST-4-ENE-3,17-DIONE

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The industrial value of the fungus *Absidia orchidis* is given by its capability of producing hydrocortisone from pregn-4-ene-17α, 21-diol-3,20-dione (from the Reichstein-S compound) by introducing a 11β hydroxyl group. During this microbiological process, besides hydrocortisone, an appreciable amount of pregn-4-ene-11α, 17α, 21-triol-3,20-dione is also produced [1]. In addition, the formation of small amounts of pregn-4-ene-1β, 17α, 21-triol-3,20-dione [2] and pregn-4-ene-17α, 21-diol-3,11,20-trione (cortisone) has been observed as well. In the fermentation of cardiac aglycones by Absidia orchidis, hydroxylation at the positions 1β, 5β and 7β was found by Japanese authors [3]. It is apparent from these data that the investigated fungus is capable of forming a hydroxyl group at various carbon atoms of the sterane skeleton, and it may be presumed that the site of hydroxylation depends on the structure of the steroid. In order to confirm this presumption, we have investigated the products formed in the fermentation of androst-4-ene-3,17--dione, a compound containing no side chain and having a structure different from those mentioned above.

When androst-4-ene-3,17-dione (**I**) is subjected to fermentation by a suitable culture of our strain of *Absidia orchidis*, it is converted into steroids which are, according to investigations by paper chromatography, of more polar character. The products of microbiological oxidation obtainable from the fermentation liquor by extraction can be separated by partition column chromatography. We have detected by paper chromatography, in the fractions of the ciolumn chromatography, the presence of four conversion products having smilar polarities (denoted as **II**, **III**, **IV** and **V**, in the order of the polarities), and these products have been isolated from the corresponding fractions.

On basis of the elemental analyses, UV and IR spectroscopical data, and the mobilities observed by paper chromatography, it can be stated that all four conversion products have a monohydroxyandrost-4-ene-3,17-dione structure. In the spectra of the conversion products, in addition to the bands of the five-membered cyclic ketone, conjugated six-membered cyclic ketone

and carbon-carbon double bond, characteristic of the infrared spectrum of androst-4-ene-3,17-dione, also a hydroxyl is found. The ultraviolet spectra of the conversion products show an absorption characteristic of ketones conjugated with a double bond, while in the spectra of the corresponding thiosemicarbazones a maximum is found at 302 nm, a very characteristic feature of Δ 4—3-thiosemicarbazone structure.

The hydroxyl group of product **II** can be acylated with acetic anhydride at room temperature, and with chromium trioxide it is oxidized to a carbonyl group. These observations indicate that the hydroxyl group in compound **II** is secondary. According to spectroscopic evidence, the new carbonyl group of the oxidation product (**VII**) obtained with chromium trioxide is in conjugation with the Δ 4—3-keto structure. The ultraviolet absorption maximum of compound **VII** appears at 251 nm, while that of the thiosemicarbazone of **VII** at 348 nm. The observed bathochromic effect can readily be interpreted by presuming conjugation. Conjugation is also indicated by the fact that in the infrared spectrum of compound **VII**, the merging of the two carbonyl bands can be observed. As expected, the physical constants of **VII** are identical with those of androst-4-ene-3,6,17-trione [4]. The hydroxyl group of **II** can be split off by treatment with mesyl chloride in pyridine. The elimination product (**VIII**) obtained in this way has been identified as androsta-4,6-diene-3,17-dione. This fact proves that the hydroxyl group of **II** is really located at C_6. The physical constants of **II** and its acetate (**VI**) are identical with those of 6β-hydroxy- and 6β-acetoxy-androst-4-ene-3,17-dione [4], and differ considerably from the constants of the corresponding 6α-epimers [5], confirming in this way that compound **II** is actually androst-4-ene-6β-ol-3,17-dione.

Compound **III** has been found resistant to both acetylation by acetic anhydride in pyridine, and to oxidation by chromium trioxide. These facts indicate the tertiary nature of the hydroxyl group in **III**. According to the data of literature [6], a hydroxyl group introduced by microbiological oxidation substitutes the hydrogen atom of identical steric position. Thus, only three possible locations of the hydroxyl group are in accordance with our experimental results, namely the positions 8β, 9α and 14α. The physical constants of **III** are the same as those of 14α-hydroxyandrost-4-ene-3,17-dione [7], but they differ from those of 8β-hydroxy- [8] and 9α-hydroxyandrost-4-ene-3,17-dione [9]. Consequently, compound **III** should be considered as androst-4-ene-14α-ol-3,17-dione.

The hydroxyl group of compound **IV** can be acetylated under mild conditions, and it is oxidized to carbonyl by chromium trioxide. In the infrared spectrum of the oxidation product (**X**), the new carbonyl band is found at 1708 cm^{-1}, indicating that the C=O group is attached to a six-membered ring, and it is isolated from the double bonds. Since the carbonyl at C_1 is correlated, owing to enolization, with the Δ 4—3-keto structure [3], the investi-

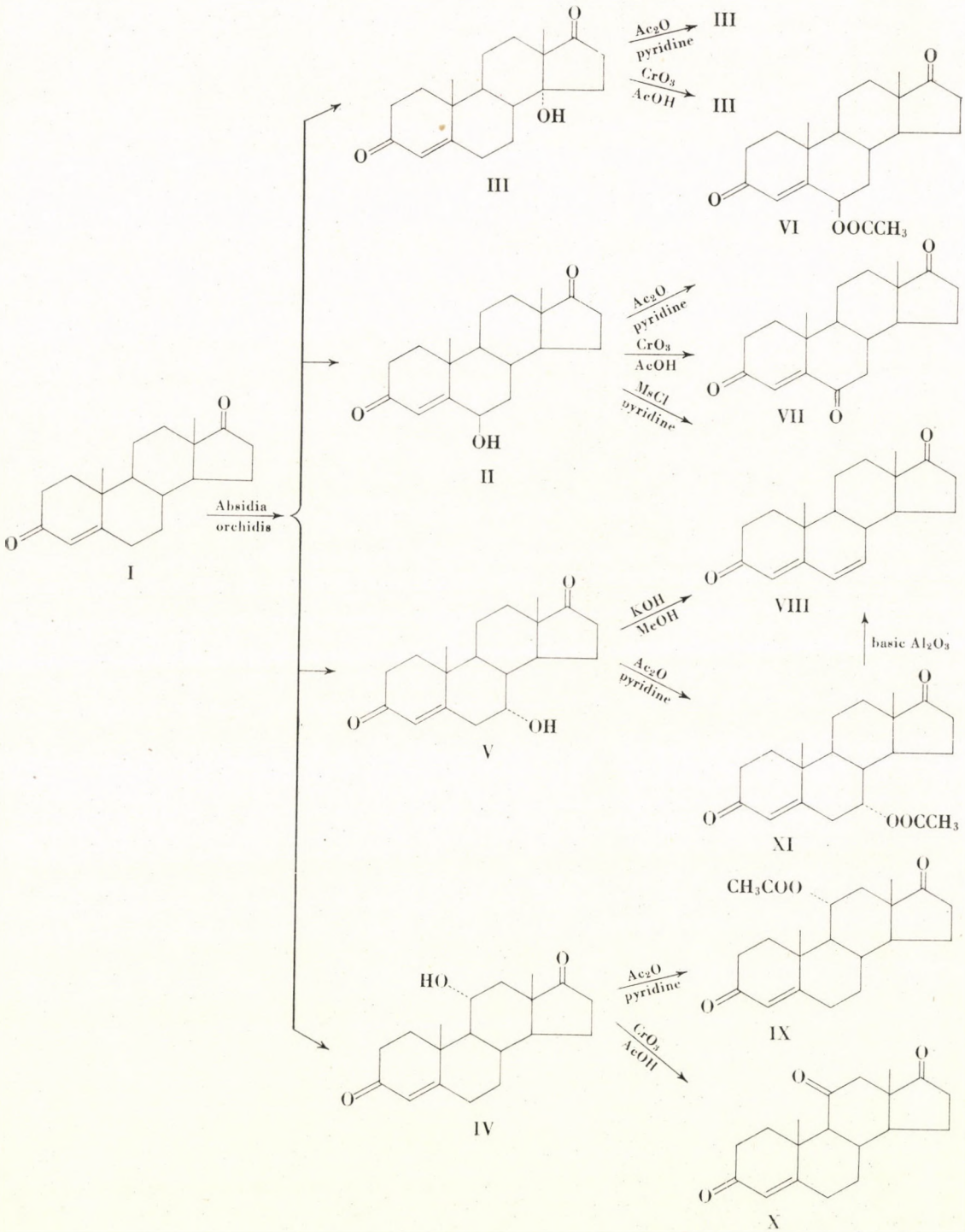

Fig. 1. Structures of the products from the microbiological oxidation of androst-4-ene-3,17-dione

gated carbonyl group of **X** cannot be in ring A. Consequently, acaording to the spectrospecial evidence this carbonyl may be only in ring B or C, at the positions C_7, C_{11} or C_{12}. SCHUBERT has shown [10] that the hydroxyl group at C_7 in steroids of Δ 4—3-keto structure cannot be directly oxidized to carbonyl with chromium trioxide. The choice between the remaining two possibilities was easy, because the physical constants of **X** are in accordance with those of androst-4-ene-3,11,17-trione [11], while they differ from those of androst-4-ene-3,12,17-trione [12]. Since a 11β-hydroxyl group would not undergo acetylation under the mild reaction conditions applied for the acetylation of **IV**, owing to the shielding effect of the C_{18} and C_{19} methyl group which are in *cis* (1,3-diaxial) position with it, the hydroxyl group of **IV** must be in 11α-position. Indeed, as expected, the physical constants of **IV** are identical with those of androst-4-ene-11α-ol-3,17-dione [13].

The hydroxyl group of **V** can be acetylated in pyridine with acetic anhydride. When treated with alkali, the hydroxyl group of **V** and the acetate group of **XI** (obtained from **V**) are equally split off, yielding androsta-4,6-diene-3,17-dione as the elimination product. Oxidation of the hydroxyl group of **V** by chromic acid did not afford the ketone. The obtained data unequivocally indicated the presence of a C_7 hydroxyl group. The physical constants of **V** and **XI** are in agreement with those of 7α-hydroxy- and 7α-acetoxy-androst-4-ene-3,17-dione [14], respectively, therefore **V** is androst-4-ene-7α-ol-3,17-dione.

Thus, the structural investigations have shown that in the course of the fermentation process, hydroxyl groups are introduced into positions 6β, 7α, 11α and 14α of androst-4-ene-3,17-dione. This result is in accordance with the assumption that the positions of the hydroxyl groups introduced by the fungus markedly depend on the structure of the steroid used.

Experimental

The fermentation process

10 g of androst-4-ene-3,17-dione in 1000 ml of ethanol was added to 50 litres of a submerged culture of *Absidia orchidis* prepared as reported earlier [1]. The culture was subjected to fermentation for 16 hrs at 25°. The course of the fermentation process was followed by paper chromatography using the solvent system ethylene glycol-methanol (3 : 7) as the stationary phase (ZAFFARONI type), and toluene-methylcyclohexane (1 : 1) as the developing solvent.

Recovery and separation of the products of fermentation

The fermentation liquor was extracted three times, in each case with 1/3 volume of ethyl acetate, and the combined extracts were evaporated in vacuum. The residue (18.5 g) was dissolved in dichloroethane, the solution transferred to a silica gel column and subjected to fractionation. The column was prepared from 1.2 kg of silica gel (200 to 400 mesh) previously deactivated with ethanol. Elution was effected with portions of dichloroethane containing

increasing quantities of ethanol. The fractions obtained from the column were analyzed by paper chromatography. The fractions eluted with dichloroethane containing 0.25% ethanol (fraction A, combined and evaporated) contained unchanged **I.** Increase of the ethanol content of the eluting agent up to 1.25% did not result in the elution of any new steroid. Dichloroethane containing 1.5% ethanol eluted the conversion products in the order of their polarities. Combining the fractions which contained the single products in pure state and evaporation afforded fractions B, C, D and E. A further increase of the ethanol content of the eluting agent did not give any other steroid-containing fraction.

Isolation of androst-4-ene-3,17-dione (I)

Fraction A (365 mg) was crystallized from a mixture of ether and hexane. The product, on recrystallization from acetone, afforded 34 mg of **I.**

Isolation of androst-4-ene-6β-ol-3,17-dione (II)

Recrystallization of fraction B (1750 mg) from a mixture of acetone and ether gave 505 mg of a crude product which was recrystallized from methanol, to yield 408 mg of **II**, m.p. 191—193°; $[\alpha]_D = +108°$ ($c = 1$, in chloroform).

$C_{19}H_{26}O_3$ (302.40). Calcd. C 75.46; H 8.67. Found C 75.57; H 8.75%.

λ_{max} (in ethanol) 236 nm (log ε : 4.13).

Infrared spectrum: ν OH 3470 cm^{-1}; ν C=O 1740 cm^{-1} (ketone 17); 1666 cm^{-1} (ketone 3); ν C=C 1611 cm^{-1}.

Isolation of androst-4-ene-14α-ol-3,17-dione (III)

Repeated recrystallizations of fraction C (410 mg) from acetone gave 89 mg of **III**, m.p. 259—262°; $[\alpha]_D = +173°$ ($c = 0.5$, in chloroform).

$C_{19}H_{26}O_3$ (302.40). Calcd. C 75.46; H 8.67. Found C 75.76; H 8.87%.

λ_{max} (in ethanol) 240 nm (log ε : 4.20).

Infrared spectrum: ν OH 3525, 3432 cm^{-1}; ν C=O 1735 cm^{-1} (ketone 17); 1665 cm^{-1} (ketone 3); ν C=C 1612 cm^{-1}.

Isolation of androst-4-ene-11α-ol-3,17-dione (IV)

Fraction D (980 mg), obtained by crystallization from a mixture of acetone and ether, was repeatedly recrystallized from ethyl acetate to yield 360 mg of **IV**, m.p. 224—227°; $[\alpha]_D = +161°$ ($c = 0.8$, in chloroform).

$C_{19}H_{26}O_3$ (302.40). Calcd. C 75.46; H 8.67. Found C 75.62; H 8.74%.

λ_{max} (in ethanol); 241 nm (log ε : 4.18).

Infrared spectrum: ν OH 3430 cm^{-1}; ν C=O 1739 cm^{-1} (ketone 17); 1648 cm^{-1} (ketone 3); ν C=C 1610 cm^{-1}.

Isolation of androst-4-ene-7α-ol-3,17-dione (V)

Fraction E (1830 mg) was crystallized from a mixture of acetone and ether. Recrystallization of the product from methanol gave 432 mg of **V**, m.p. 254—256°; $[\alpha]_D = +164°$ ($c = 0.5$, in chloroform).

$C_{19}H_{26}O_3$ (302.40). Calcd. C 75.46; H 8.67. Found C 75.14; H 8.37%.

λ_{max} (in ethanol): 241 nm (log ε : 4.20).

Infrared spectrum: ν OH 3435 cm^{-1}; ν C=O 1742 cm^{-1} (ketone 17); 1664 cm^{-1} (ketone 3); ν C=C 1619 cm^{-1}.

Androst-4-ene-6β-ol-3,17-dione-6β-acetate (VI)

90 mg of **II** in 1 ml of pyridine was acetylated with 0.25 ml of acetic anhydride at room temperature. Recrystallization of the crude product from methanol gave 64 mg of **VI**, m.p. 200—202°; $[\alpha]_D = +112°$ ($c = 1$, in chloroform).

$C_{21}H_{28}O_4$ (344.43). Calcd. C 73.23; H 8.19. Found C 73.05; H 8.36%.
λ_{max} (in ethanol): 235.5 nm (log ε : 4.12).
Infrared spectrum: ν C=O 1740 cm^{-1} (acetate and ketone 17); 1678 cm^{-1} (ketone 3); ν C=C 1625 cm^{-1}; ν C—O—C 1019 cm^{-1}, 1250 cm^{-1} (acetate).

Androst-4-ene-3,6,17-trione (VII)

120 mg of **II** in 4 ml of glacial acetic acid was oxidized for 1.5 hr. at room temperature with a solution of 150 mg of chromium trioxide in 2 ml of water. Recrystallization of the crude product from a mixture of acetone and ether afforded 62 mg of **VII**, m.p. 221—224°; $[\alpha]_D$ = = +44° (c = 0.8, in acetone).
$C_{19}H_{24}O_3$ (300.38). Calcd. C 75.97; H 8.05. Found C 76.14; H 8.09%.
λ_{max}: 251 nm (log ε : 4.03).
Infrared spectrum: ν C=O 1740 cm^{-1} (ketone 17); 1690 cm^{-1}, 1675 cm^{-1} (ketones 3 and 6, coupled); ν C=C 1604 cm^{-1}.

Androsta-4,6-diene-3,17-dione (VIII) from II

92 mg of mesyl chloride was added by drops to a solution of 120 mg of **II** in 1 ml of pyridine. The reaction mixture was allowed to stand 18 hrs at room temperature. Repeated recrystallizations of the crude product from a mixture of acetone and petroleum ether yielded 36 mg of **VIII**, m.p. 171—173°; $[\alpha]_D$ = 134° (c = 1, in chloroform).
$C_{19}H_{24}O_2$ (248.38). Calcd. C 80.24; H 8.51. Found C 80.61; H 8.71%.
λ_{max} (in ethanol): 283 nm (log ε : 4.47).
Infrared spectrum: ν C=O 1743 cm^{-1} (ketone 17); 1662 cm^{-1} (ketone 3); ν C=C 1618 cm^{-1}, 1582 cm^{-1}.

Androst-4-ene-11α-ol-3,17-dione-11α-acetate (IX)

90 mg of **IV** was acetylated as described for compound **VI**. 103 mg of **IX** was obtained as an oil.
$C_{21}H_{28}O_4$ (344.43). Calcd. C 73.23; H 8.19. Found C 73.05; H 8.28%.
λ_{max} (in ethanol): 239 nm (log ε : 4.19).
Infrared spectrum: ν C=O 1745 cm^{-1} (ester and ketone 17); 1680 cm^{-1} (ketone 3); ν C=C 1620 cm^{-1}; ν C—O—C 1248, 1028 cm^{-1} (ester).

Androst-4-ene-3,11,17-trione (X) from IV

120 mg of **IV** was oxidized as described in connection with compound **VII**. Crystallization of the crude product from a mixture of acetone and hexane gave 78 mg of **X**, m.p. 224—226°; $[\alpha]_D$ = +279° (c = 0.5, in chloroform).
$C_{19}H_{24}O_3$ (300.38). Calcd. C 75.97; H 8.05. Found C 75.82; H 8.13%.
λ_{max} (in ethanol): 239 nm (log ε : 4.17).
Infrared spectrum: ν C=O 1745 cm^{-1} (ketone 17); 1708 cm^{-1} (ketone 11); 1672 cm^{-1} (ketone 3); ν C=C 1610 cm^{-1}.

Androst-4-ene-7α-ol-3,17-dione 7α-acetate (XI)

90 mg of **V** was acetylated for 48 hrs. as described for compound **II**. Repeated recrystallizations of the crude product from a mixture of acetone and hexane yielded 62 mg of **XI**, m.p. 178—180°; $[\alpha]_D$ = +78° (c = 1, in chloroform).
$C_{21}H_{28}O_4$ (344.43). Calcd. C 73.23; H 8.19. Found C 73.24; H 8.21%.
λ_{max} (in ethanol): 238 nm (log ε : 4.19).
Infrared spectrum: ν C=O 1735 cm^{-1} (ester and ketone 17); 1678 cm^{-1} (ketone 3); ν C=C 1622 cm^{-1}; ν C—O—C 1250 cm^{-1}; 1026 cm^{-1} (ester).

Androsta-4,6-diene-3,17-dione (VIII) from V

120 mg of **V** was refluxed 1 hr. with 5 ml of a 2% solution of potassium hydroxide in methanol. The reaction mixture was then diluted with water, neutralized, and extracted with chloroform. The residue obtained by evaporating the extract was crystallized from a mixture of acetone and petroleum ether; yield: 42 mg of **VIII**, m.p. 168—170°; λ_{max}: 283 nm.

Androsta-4,6-diene-3,17-dione (VIII) from XI

An ethereal solution of 25 mg of **XI** was poured on a chromatographic column of 10 g of basic aluminium hydroxide. The column was eluted with 100 ml of ether containing 20% of benzene. Crystallization from ether of the residue obtained by evaporating the eluate gave 9 mg of **VIII**, m.p. 169—172°.

λ_{max} (in ethanol): 283 nm.

Recording of the ultraviolet spectra of the thiosemicarbazones of the conversion products and their derivatives

10 ml of an ethanolic solution of the investigated steroid, containing 10 μg of steroid per ml, was allowed to react for 2 hrs at 40° (in a thermostat) with 2 ml of a 0.5 *M* solution of thiosemicarbazide in hydrochloric acid. Subsequently, the spectrum of the reaction mixture was obtained in the conventional way.

The absorption maxima of compounds **I**, **II**, **III**, **IV**, **V** and **X** appeared at 302 nm, that of **VII** at 348.5 nm, and that of **VIII** at 329 nm.

Thanks are expressed to Dr. L. VARGHA, member of the *Hungarian Academy of Sciences*, director of the institute, for the possibility to carry out this research. Thanks are due to Prof. O. CLAUDER for his valuable advice, and to Dr. P. SOHÁR for the infrared spectra.

SUMMARY

It has been found that *Absidia orchidis* is capable of converting androst-4-ene-3,17-dione into 6β-, 7α-, 11α- and 14α-hydroxyandrost-4-ene-3,17-diones.

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HOMOGENKATALYTISCHE HYDRIERUNG VON ALDEHYDEN MIT RHODIUMCARBONYL-KATALYSATOREN, II*

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Wie schon früher berichtet [1], können Aldehyde mit Kohlenoxyd-Wasserstoff Gemischen in Gegenwart von rhodiumhaltigen Katalysatoren zu Alkoholen hydriert werden. Vorversuche deuteten darauf, daß kohlenoxydhaltige, im Reaktionsgemisch gelöste Rhodiumkomplexe als eigentliche Katalysatoren der Hydrierung zu betrachten sind. Im weiteren sollte versucht werden, den Mechanismus dieser homogen-katalytischen Hydrierung zu klären.

Dieses Ziel wurde auf zwei, prinzipiell verschiedene Wege angestrebt. Einerseits wurde die Kinetik der Reaktion ermittelt, andererseits wurden mit Hilfe von IR-spektroskopischen Untersuchungen die unter den angewandten Reaktionsbedingungen in Lösung existenzfähigen Rhodiumcarbonyl-Komplexe identifiziert.

Kinetische Messungen

Die Ergebnisse unserer kinetischen Untersuchungen sind in den Tabellen I—IV zusammengefasst. Abbildung 1 dient zur Ermittlung der Reaktionsordnung bezüglich der Aldehydkonzentration, während die Reaktionsgeschwindigkeit-Konstanten als Funktion der untersuchten Parameter in den Abbildungen 2—4 dargestellt sind.

Den Ergebnissen gemäß kann die Geschwindigkeit der Hydrierung von Aldehyden zu Alkoholen in Gegenwart von Rhodium Katalysatoren mit Hilfe folgender kinetischen Gleichung beschrieben werden:

$$\frac{d\,(\text{Alkohol})}{dt} = k\,[\text{Aldehyd}]\,[\text{Rh}]^{1/6}\,(p_{H_2})^{0,5}\,(p_{CO})^{-0,3} \qquad \text{(a)}$$

* Teil I: HEIL, B., MARKÓ, L.: Chem. Ber. **99**, 1086 (1966).

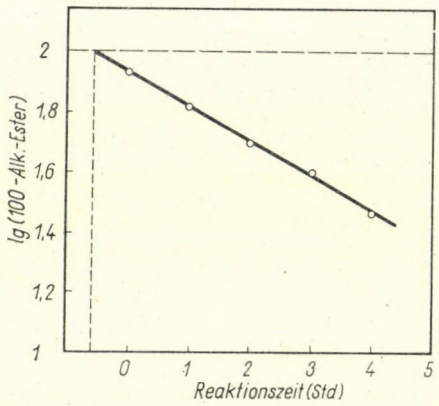


Abb. 1 Aldehydkonversion als Funktion der Reaktionszeit. Reaktionsbedingungen s. Tab. I.

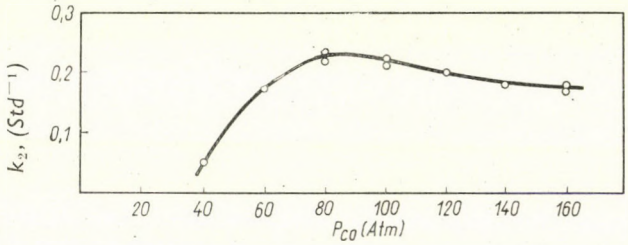


Abb. 2 Einfluß des Kohlenoxyd-Partialdruckes auf die Reaktionsgeschwindigkeit. Reaktionsbedingungen s. Tab. II.

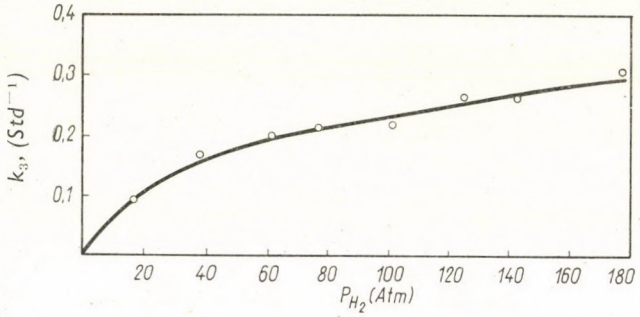


Abb. 3 Einfluß des Wasserstoff-Partialdruckes auf die Reaktionsgeschwindigkeit. Reaktionsbedingungen s. Tab. III.

Diese Gleichung ist gültig unter den folgenden Bedingungen:
Temperatur 160°C
Kohlenoxyd-Partialdruck mindestens 80 Atm
Aldehydkonversion höchstens 70%

Die Beschränkung hinsichtlich des Kohlenoxyd-Partialdruckes ist auf die Tatsache zurückzuführen, daß die Hydrierungsgeschwindigkeit als Funktion

des Kohlenoxyd-Druckes ein ausgeprägtes Maximum aufweist (Abb. 2). Diese Erscheinung kann wahrscheinlich dadurch erklärt werden, daß — ähnlich den Verhältnissen mit Kobaltcarbonyl-Katalysatoren [3] — das Rhodium bei niedrigeren Kohlenoxyd-Partialdrucken nur teilweise in Carbonyle übergeführt wird, so daß die Katalysator-Konzentration nicht konstant ist. Der aufsteigende Abschnitt der Kurve wird also eigentlich durch die Erhöhung der Rhodiumcarbonyl-Konzentration im Reaktionsgemisch verursacht.

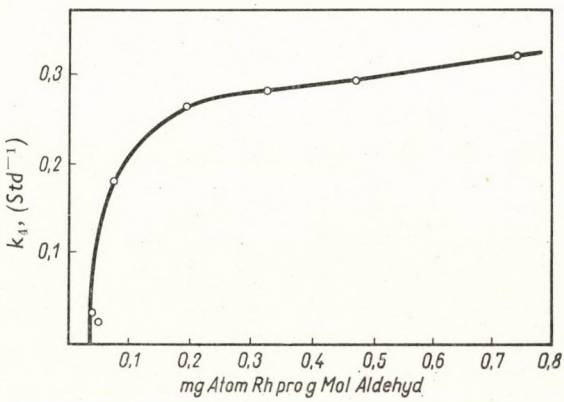


Abb. 4 Einfluß der Rhodium-Konzentration auf die Reaktionsgeschwindigkeit. Reaktionsbedingungen s. Tab. IV.

Tabelle I

Aldehydkonversion als Funktion der Reaktionszeit

Aldehyd: 25% *n*-Butyraldehyd, gelöst in Hexan
Katalysator: 3,2 mg Atom Rh/gMol Aldehyd, in Form von $RhCl_3 \cdot 3\ H_2O$
Temperatur: 160°C
Kohlenoxyd-Partialdruck: 120 Atm
Wasserstoff-Partialdruck: 160 Atm

Reaktionszeit, Stunden	Aldehyd, umgesetzt zu Alkohol, %	Reaktionsgeschwindigkeit-Konstante der Alkoholbildung, k_1, Std^{-1}	
		Ohne Korrektion der Reaktionszeit	mit Korrektion der Reaktionszeit*
0	11,6	—	0,208
1	32,6	0,400	0,250
2	48,3	0,343	0,263
3	57,2	0,292	0,245
4	68,5	0,298	0,259

* Wie aus Abb. 1 ersichtlich, kann die Aldehydreduktion bezüglich der Aldehydkonzentration bis zu 70%iger Konversion als Reaktion erster Ordnung behandelt werden, falls die während des Aufheizens des Autoklaven stattfindende Hydrierung in Form einer Zeitkorrektion von 0,6 Stunden in Betracht genommen wird.

Tabelle II

Einfluß des Kohlenoxyd-Partialdruckes auf die Reaktionsgeschwindigkeit

Aldehyd: 25% *n*-Butyraldehyd, gelöst in Hexan
Katalysator: 3,2 mg Atom Rh/gMol Aldehyd, in Form von $RhCl_3 \cdot 3\ H_2O$
Temperatur: 160°C
Wasserstoff-Partialdruck: 115 Atm
Korrigierte Reaktionszeit: 3,6 Stunden

Kohlenoxyd-Partialdruck, Atm	Aldehyd, umgesetzt zu Alkohol, %	Reaktionsgeschwindigkeit-Konstante der Alkoholbildung, k_2, Std^{-1}	$k_2 \cdot (p_{CO})^{0,3}$
40	16,5	0,050	0,152
60	45,6	0,173	0,592
80	54,1	0,223	0,830
80	56,1	0,236	0,879
100	53,3	0,216	0,860
100	53,0	0,223	0,888
120	50,7	0,202	0,580
140	47,3	0,183	0,808
160	46,3	0,182	0,834
160	44,9	0,170	0,779

Tabelle III

Einfluß des Wasserstoff-Partialdruckes auf die Reaktionsgeschwindigkeit

Aldehyd: 25% *n*-Butyraldehyd, gelöst in Hexan
Katalysator: 3,2 mg Atom Rh/gMol Aldehyd, in Form von $RhCl_3 \cdot 3\ H_2O$
Temperatur: 160°C
Kohlenoxyd-Partialdruck: 120 Atm
Korrigierte Reaktionszeit: 3,6 Stunden

Wasserstoff-Partialdruck, Atm	Aldehyd, umgesetzt zu Alkohol, %	Reaktionsgeschwindigkeit-Konstante der Alkoholbildung, k_2, Std^{-1}	$k_2 \cdot (p_{H_2})^{-0,5}$
17	29,0	0,096	0,0233
38	44,6	0,168	0,0273
61	50,5	0,200	0,0256
77	53,0	0,213	0,0243
101	53,4	0,218	0,0217
125	61,0	0,266	0,0238
143	59,4	0,261	0,0218
177	65,4	0,309	0,0232

Tabelle IV

Einfluß der Rhodium-Konzentration auf die Reaktionsgeschwindigkeit

Aldehyd: 25% *n*-Butyraldehyd, gelöst in Hexan
Katalysator: $Rh_4(CO)_{12}$
Temperatur: 160°C
Kohlenoxyd-Partialdruck: 110 Atm
Wasserstoff-Partialdruck: 140 Atm
Korrigierte Reaktionszeit: 3,6 Stunden

Katalysator-Konzentration, mg Atom Rh pro gMol Aldehyd	Aldehyd, umgesetzt zu Alkohol, %	Reaktionsgeschwindigkeit-Konstante der Alkoholbildung k_4, Std^{-1}	$\frac{k_4}{([Rh] - 0{,}04)^{1/6}}$*
0	0	0	—
0,041	11,4	0,036	0,101
0,052	8,5	0,025	0,052
0,076	46,7	0,182	0,316
0,195	60,8	0,265	0,362
0,325	63,0	0,281	0,347
0,468	64,3	0,293	0,338
0,740	67,9	0,321	0,341

* Wie aus Abb. 4 ersichtlich, können die Versuchsergebnisse nur in dem Falle mit einer einfachen Kurve dargestellt werden, wenn 0,04 mg Atom Rh/gMol Aldehyd als katalytisch inaktiv betrachtet werden. Diese Tatsache läßt sich dadurch erklären, daß diese äußerst geringe Katalysatormenge durch unvermeidliche Verunreinigungen (z. B. Spuren von Schwefelverbindungen) vergiftet wird [2].

Verhalten der Rhodiumcarbonyle unter den Reaktionsbedingungen der Aldehydhydrierung

Bevor wir auf die ausführliche Deutung der kinetischen Gleichung eingehen, sollen die Ergebnisse unserer IR-spektroskopischen Untersuchungen erörtert werden.

Von den, in der Literatur bisher beschriebenen Rhodiumcarbonylen waren unter unseren Reaktionsbedingungen die folgenden zu erwarten:

$Rh_2(CO)_8$ [4]
$Rh_4(CO)_{12}$ [4]
$Rh_6(CO)_{16}$ [4, 5]
$HRh(CO)_4$ [4]
$[Rh(CO)_2Cl]_2$ [4] (im Falle von $RhCl_3 \cdot 3\,H_2O$ als Katalysator)

IR-spektroskopische Daten sind bisher nur von $Rh_4(CO)_{12}$ [6], $Rh_6(CO)_{16}$ [6] und $[Rh(CO)_2Cl]_2$ [7] bekannt. Gestützt auf die zu erwartende Analogie zwischen den IR-Spektren von $Co_2(CO)_8$ und $HCo(CO)_4$ [8] einerseits sowie

von $Rh_2(CO)_8$ und $HRh(CO)_4$ anderseits sollte aber versucht werden, mit Hilfe von eventuell auftretenden unbekannten Absorptionsbanden die zwei genannten Rhodiumcarbonyle zu identifizieren.

Es konnte trotz zahlreicher Versuche, die unter stark verschiedenen Bedingungen (20—220°C, 0—150 Atm p_{H_2}, 15—460 Atm p_{CO}), ohne oder mit Lösungsmittel (Hexan) durchgeführt wurden, und bei denen Rhodium in Form von feinverteiltem Metall auf Kieselgel, $RhCl_3$, $RhCl_3 \cdot 3\,H_2O$, $Rh_4(CO)_{12}$ oder $Rh_6(CO)_{16}$ angewendet wurde, in keinem Falle die Bildung von $HRh(CO)_4$ und $Rh_2(CO)_8$ IR-spektroskopisch beobachtet werden. Die Hexan Lösungen der so erhaltenen Reaktionsprodukte zeigten immer nur die Banden charakteristisch für $Rh_4(CO)_{12}$, $Rh_6(CO)_{16}$ oder $[Rh(CO)_2Cl]_2$. Dieser Befund schließt natürlich die Anwesenheit von kleinen, IR-spektroskopisch nicht nachweisbaren Mengen von $HRh(CO)_4$ und $Rh_2(CO)_8$ in den Reaktionsgemischen der Aldehydhydrierung nicht aus. Alle unsere Ergebnisse deuten aber eindeutig darauf hin, daß es sich bei diesen zwei Komplexen — im Gegensatz zu den entsprechenden Kobaltverbindungen — um äußerst labile und präparative nur unter den extremsten Bedingungen zugängliche Substanzen handeln muß.

Die Versuche zeigten ferner, daß unter den Bedingungen der Aldehydhydrierung das $Rh_6(CO)_{16}$ die thermodynamisch stabile Rhodiumverbindung ist. Sowohl die Reaktionsprodukte der kinetischen Versuche als auch die Produkte der in reinem Hexan unter Hydrierbedingungen durchgeführten Modellversuche enthielten immer nur $Rh_6(CO)_{16}$ gelöst. Die Bildung des $Rh_6(CO)_{16}$ verläuft im Falle von $RhCl_3$ und $RhCl_3 \cdot 3\,H_2O$ als Ausgangssubstanz über $[Rh(CO)_2Cl]_2$ und $Rh_4(CO)_{12}$. $[Rh(CO)_2Cl]_2$ verschwindet während des Aufheizens des Autoklaven bei 130—140°C. Bei 160°C enthält das Reaktionsgemisch anfangs gleichzeitig $Rh_4(CO)_{12}$ und $Rh_6(CO)_{16}$, die Konzentration des Dodecacarbonyls nimmt aber bei dieser Temperatur schnell ab. Wurde als Ausgangssubstanz metallisches Rhodium benützt, so blieb die Bildung des Carbonylchlorids natürlich aus, das intermediäre Auftreten von $Rh_4(CO)_{12}$ war aber auch in diesem Falle gut zu beobachten.

Theoretisch ist zwischen $Rh_4(CO)_{12}$ und $Rh_6(CO)_{16}$ ein Gleichgewicht zu erwarten, dessen Lage durch Senkung der Temperatur und Erhöhung des Kohlenoxyd-Partialdruckes nach der Seite des Dodecacarbonyls verschoben werden kann:

$$3\,Rh_4(CO)_{12} \underset{P}{\overset{T}{\rightleftharpoons}} 2\,Rh_6(CO)_{16} + 4\,CO$$

Versuche, dieses Gleichgewicht auch experimentell zu beweisen, brachten das Ergebnis, daß selbst bei der relativ niedrigen Temperatur von 80°C und bei dem relativ hohen Kohlenoxyddruck von 380 Atm nur ein sehr kleiner Teil des Rhodiums von $Rh_6(CO)_{16}$ in $Rh_4(CO)_{12}$ übergeführt werden kann.

Diese Ergebnisse zeigen den klaren quantitativen Unterschied zwischen Rhodium- und Kobaltcarbonylen: während im Falle des Kobalts unter den

erwähnten Bedingungen das kohlenoxydreichste $Co_2(CO)_8$ die stabile Verbindung ist [3], reicht im Falle des Rhodiums derselbe Kohlenoxyd-Partialdruck nur zur Sicherung einer kleineren $Rh_4(CO)_{12}$-Konzentration und die eigentlich stabile Verbindung ist das noch kohlenoxydärmere Hexadecacarbonyl. Dieses Ergebnis steht im Einklang damit, daß das kohlenoxydreiche $Rh_2(CO)_8$ unter unseren Versuchsbedingungen überhaupt nicht erhalten werden konnte.

Neben diesem thermodynamischen Unterschied zwischen Rhodium und Kobaltcarbonylen ist noch die Beobachtung zu erwähnen, daß unseren Erfahrungen gemäß die Umwandlung der verschiedenen Rhodiumcarbonyle in einander augenfällig langsamer abläuft, als die der Kobaltcarbonyle unter ähnlichen Bedingungen. Während also die Rhodiumcarbonyle thermodynamisch labiler sind, als die entsprechenden Kobaltcarbonyle, sind sie in kinetischer Hinsicht gewissermaßen stabiler. Diese kinetische Stabilität ermöglicht die Herstellung von $Rh_4(CO)_{12}$ aus $RhCl_3 \cdot 3\ H_2O$ unter Bedingungen, unter denen unseren Untersuchungen nach schon das $Rh_6(CO)_{16}$ die thermodynamisch stabile Verbindung ist: die weitere Umwandlung des intermediär auftretenden $Rh_4(CO)_{12}$ ist langsam.

Mechanismus der Aldehydhydrierung

Es kann als bewiesen betrachtet werden, daß im Reaktionsgemisch unter den Reaktionsbedingungen der Aldehydhydrierung das eingesetzte Rhodium überwiegend in Form von $Rh_6(CO)_{16}$ gelöst anwesend ist. Das Glied $[Rh]^{1/6}$ in der kinetischen Gleichung (a) kann demgemäß mit der Annahme gedeutet werden, daß ein — mit dem $Rh_6(CO)_{16}$ im Gleichgewicht stehendes — einkerniges Rhodiumcarbonyl der aktive Katalysator ist.

Das Glied $(p_{H_2})^{0,5}$ läßt darauf schließen, daß dieses einkernige Rhodiumcarbonyl ein Wasserstoffatom enthält, so daß seine Konzentration der Quadratwurzel des Wasserstoff-Partialdruckes proportional ist. Der inhibierende Einfluß des Kohlenoxyd-Partialdruckes (Exponent $= -0{,}3$) deutet auf die bei durch Metallcarbonyl katalysierten Reaktionen ganz allgemeine Erscheinung, daß der eigentliche Katalysator ein mit Kohlenoxyd nicht gesättigter Komplex sein muß [9].

Wir schlagen also folgenden Mechanismus für die homogenkatalytische Hydrierung von Aldehyden mit Rhodiumcarbonyl Katalysatoren vor:

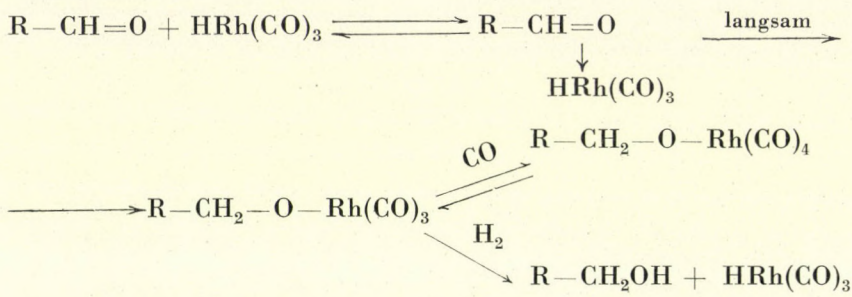
A) Bildung des Katalysators:

$$2\ Rh_6(CO)_{16} + 4\ CO \rightleftharpoons 3\ Rh_4(CO)_{12}$$

$$Rh_4(CO)_{12} + 2\ H_2 \rightleftharpoons 4\ HRh(CO)_3$$

$$HRh(CO)_3 + CO \rightleftharpoons HRh(CO)_4$$

B) Katalytische Reaktion:



Als eigentlicher Katalysator wird also — analog der Hydrierung mit Kobaltcarbonylen als Katalysatoren [9g] — das koordinativ ungesättigte $HRh(CO)_3$ betrachtet, der geschwindigkeitsbestimmende Schritt ist die Reaktion des Rhodiumtricarbonylhydrids mit dem Aldehyd unter Bildung eines Komplexes mit O—Rh σ-Bindung (I). Die Hydrogenolyse dieser Bindung unter Bildung von Alkohol und $HRh(CO)_3$ wird für schnell angenommen.

In diesem Fall kann die experimentell bestimmte kinetische Gleichung (a) durch die folgende vereinfachte Gleichung ersetzt werden:

$$\frac{d\,(\text{Alkohol})}{dt} = k\,[\text{Aldehyd}]\,[\text{Katalysator}] \qquad \text{(b)}$$

wo also

$$[\text{Katalysator}] = [\text{Rh}]^{1/6}\,(p_{H_2})^{0{,}5}(p_{CO})^{-0{,}3}$$

sein muß.

Die Glieder $[Rh]^{1/6}$ und $(p_{H_2})^{0{,}5}$ finden durch die Gleichgewichte zwischen $Rh_6(CO)_{16}$, $Rh_4(CO)_{12}$ und $HRh(CO)_3$ ihre Erklärung.

Die inhibierende Wirkung des Kohlenoxyds kommt in der Bildung des als katalytisch inaktiv betrachteten Rhodiumtetracarbonylhydrids zum Ausdruck. Abhängig von der tatsächlichen Lage des Gleichgewichtes zwischen $HRh(CO)_3$ und $HRh(CO)_4$ kann nämlich die Konzentration von $HRh(CO)_3$ mit folgenden zwei Grenzformeln ausgedrückt werden:

$$[HRh(CO)_3] = f([Rh]^{1/6}\,(p_{H_2})^{0{,}5}\,(p_{CO})^{0{,}33})$$

(Gleichgewicht ganz auf der Seite von $HRh(CO)_3$)

$$[HRh(CO)_3] = f([Rh]^{1/6}\,(p_{H_2})^{0{,}5}\,(p_{CO})^{-0{,}67})$$

(Gleichgewicht ganz auf der Seite von $HRh(CO)_4$)

Der experimentell für p_{CO} bestimmte Exponent von $-0{,}3$ deutet darauf, daß dieses Gleichgewicht in keine Richtung stark verschoben ist, daß also

beide Rhodiumcarbonylhydride in ungefähr gleicher — sehr geringer — Konzentration im Reaktionsgemisch zugegen sind. Unter ähnlichen Reaktionsbedingungen liegt das

$$HCo(CO)_3 + CO \rightleftharpoons H\,Co(CO)_4$$

Gleichgewicht vollständig auf der Seite von $HCo(CO)_4$. Dieser Unterschied ist ein weiteres Beispiel dafür, daß im Falle des Rhodiums die weniger Kohlenoxyd enthaltenden Carbonyle relative stabiler sind.

Auffallend ist die große Ähnlichkeit mit dem Mechanismus der entsprechenden kobaltkatalysierten Hydrierung [9g]. Der gleichzeitig große Unterschied zwischen den kinetischen Gleichungen dieser zwei Reaktionen ist einerseits auf die abweichenden Konzentrationsverhältnisse der einzelnen Carbonyle, andererseits auf die verschiedenen geschwindigkeitsbestimmenden Teilreaktionen zurückzuführen.

Es sei noch erwähnt, daß neben *n*-Butanol als Hauptprodukt immer untergeordnete Mengen (1—4%) von *n*-Butylformiat gebildet wurden. Diese Erscheinung ist auch bei der kobaltkatalysierten Hydrierung bekannt [10]. Bei der kinetischen Auswertung der Alkoholbildung wurde diese parallele Reaktion rechnungstechnisch berücksichtigt.

Wir danken Dr. G. Bor für wertvolle Diskussionen.

Beschreibung der Versuche

$RhCl_3$ und "$RhCl_3 \cdot 3\,H_2O$" waren Handelsware *(Fluka AG)*, das wasserhaltige Rhodiumsalz enthielt 39,0% Rh. $Rh_4(CO)_{12}$ [4] und $Rh_6(CO)_{16}$ [4] wurden mit den in der Literatur beschriebenen Methoden hergestellt. Ihre Reinheit wurde IR-spektroskopisch sowie durch Bestimmung des Rhodiumgehaltes kontrolliert.

Hydrierung von n-Butyraldehyd

Die Hydrierungen wurden in einem 600-ml-Autoklav aus 18—8—Cr—Ni-Stahl durchgeführt. 165 g, 25 Mol% *n*-Butyraldehyd enthaltendes Hexan (0,5 gMol Aldehyd) und die berechnete Menge von $RhCl_3 \cdot 3\,H_2O$ (oder $Rh_4(CO)_{12}$) wurden eingewogen, der Autoklav mit Stickstoff gespült, mit einem $CO + H_2$ Gasgemisch der gewünschten Zusammensetzung aufgepreßt und unter Druck auf 160°C erhitzt. Das durch die Hydrierung verbrauchte Gas wurde durch Nachpressen von 10% Kohlenoxyd enthaltendem Wasserstoff ergänzt. Die Temperatur wurde bei ±1°C, der Druck bei ±3 Atm konstant gehalten. Nach Ablauf der Reaktionszeit wurde der Autoklav abgekühlt, sodann entspannt. Die Zusammensetzung des Endgases wurde kontrolliert und Versuche, bei denen p_{H_2} und p_{CO} nicht auf ±4 Atm konstant waren, wurden nicht in Betracht gezogen. Die quantitative Zusammensetzung des Produktes wurde chromatographisch und mit Hilfe von Funktionsgruppen-Analysen (Säurezahl, OH-Zahl, Carbonylzahl und Verseifungszahl) bestimmt.

IR-spektroskopische Untersuchungen

Die IR-Spektren wurden mit einem Doppelstrahl-Spektrometer UR—10 der Fa. *Carl Zeiss*, Jena aufgenommen. Als Lösungsmittel wurde Hexan verwendet.

ZUSAMMENFASSUNG

Die Kinetik der Hydrierung von Aldehyden zu Alkoholen in Gegenwart von Rhodiumcarbonylen als Katalysatoren bei 160°C und $p_{CO} \geqslant 80$ Atm wird mit der Gleichung $\frac{d(\text{Alkohol})}{dt} = k[\text{Aldehyd}]\,[Rh]^{1/6}(p_{H_2})^{0,5}(p_{CO})^{-0,3}$ beschrieben. Das Reaktionsgemisch enthält das Rhodium hauptsächlich in Form von $Rh_6(CO)_{16}$, intermediär treten $Rh_4(CO)_{12}$ und $[Rh(CO)_2Cl]_2$ auf; $Rh_2(CO)_8$ und $HRh(CO)_4$ konnten nicht nachgewiesen werden. Als aktiver Katalysator wird der koordinativ ungesättigte Komplex $HRh(CO)_3$ angenommen. Verglichen mit Kobalt neigt Rhodium unter gleichen Bedingungen zur Bildung kohlenoxydärmerer Carbonyle.

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POLYMERISATION DES METHYLMETHACRYLATS BEI HOHEN UMSÄTZEN, IV

UNTERSUCHUNG DER VERZÖGERUNGSWIRKUNG VON DINITROPHENOLEN

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In unserer vorangehenden Mitteilung [1] wurde die verzögernde Wirkung von Mononitrophenolen untersucht. In der vorliegenden Arbeit sollen nur die Untersuchungen auf das Gebiet der Dinitrophenole ausgedehnt werden.

Der Anwendung von Dinitrophenolen als Verzögerer begegnet man hauptsächlich in der Patentliteratur; über ihre Verzögerungswirkung gibt es nur sehr wenige wissenschaftliche Untersuchungen. FOORD [2] untersuchte neben 2-Nitrophenol und 4-Nitrophenol auch die verzögernde Wirkung von 2,4-Dinitrophenol und 2,6-Dinitrophenol. Er führte seine Versuche in einem evakuierten Viscosimeter durch, verwendete Styrol als Monomer und verfolgte das Fortschreiten der Polymerisation durch den Viscositätsanstieg. Auf Grund seiner Ergebnisse konnte er feststellen, daß die Dinitroverbindungen wirksamere Verzögerer als die Mononitroverbindungen sind.

Eine ähnliche Versuchstechnik verwendete LANG [3] bei der Untersuchung der erwähnten Verbindungen mit dem Unterschied, daß er als Monomer 3-Chlorstyrol einsetzte, welches 2-Chlorstyrol-Verunreinigungen in geringer Menge enthielt. Er verglich die Wirksamkeit der genannten Verzögerer, wobei er feststellte, daß sie in der Reihenfolge 4-Nitrophenol $<$ 2-Nitrophenol $<$ 2,4-Dinitrophenol $<$ 2,6-Dinitrophenol ansteigt.

Neuerlich untersuchte TÜDŐS [4] die Verzögerungswirkung von 2,4- und 2,6-Dinitrophenol während der Styrolpolymerisation bei 50°C. Er bestimmte den Quotienten der Geschwindigkeitskonstanten von verzögernder Reaktion und Kettenwachstumreaktion zu 51,4 $\pm$ 3 im Falle des 2,6-Dinitrophenols und 30,1 $\pm$ 2 im Falle des 2,4-Dinitrophenols.

Experimenteller Teil

Zur Versuchsmethodik sowie bezüglich der Reinigung von Monomer und Initiator wird auf unsere früheren Mitteilungen verwiesen [5]. Zu unseren Untersuchungen dienten folgende Dinitrophenole:

2,4-Dinitrophenol. Das Handelsprodukt »reinst« wurde aus Äther umkristallisiert, F. 114,5°C.

2,5-Dinitrophenol. Wurde durch Nitrieren von 3-Nitrophenol hergestellt [6]. Der Schmelzpunkt des aus heißem Wasser umkristallisierten Produktes betrug 106°C.

2,6-Dinitrophenol. Hier wurde das Handelsprodukt »reinst« verwendet, dessen Schmelzpunkt bei 62,5°C liegt. Sämtliche Schmelzpunkte wurden nach der Mikromethode von KOFLER bestimmt.

Ergebnisse

Unsere Versuche wurden bei gleicher Initiatorkonzentration ($4{,}13 \cdot 10^{-2}$ mol l^{-1}), in Gegenwart unterschiedlicher Mengen der Verzögerer bei 50 und 60°C durchgeführt. Von den Zeit-Umsatz-Kurven wurden auf Abb. 1 die in Gegenwart von 2,4-Dinitrophenol erhaltenen angeführt. Die für 2,5-Dinitrophenol und 2,6-Dinitrophenol erhaltenen Kurven verlaufen ähnlich. Zur Bestimmung der Anfangsgeschwindigkeit der Polymerisation wurden die Werte von $\lg \frac{1}{1-x}$ als Funktion der Zeit aufgetragen. Die erhaltenen Geraden, aus deren Anstieg die Anfangsgeschwindigkeit der Polymerisation berech-

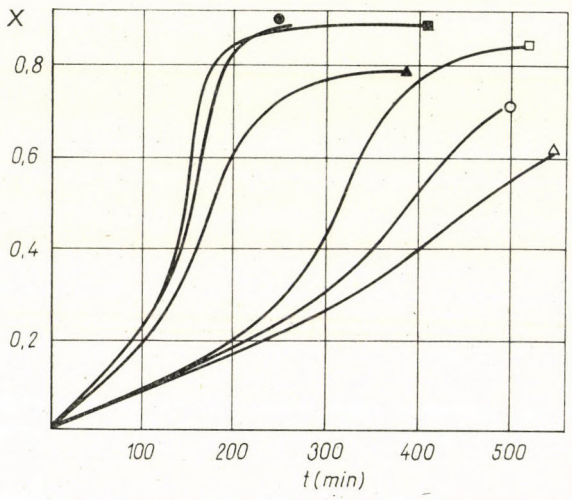

Abb. 1. Zeit-Umsatz-Kurven in Gegenwart von $4{,}13 \cdot 10^{-2}$ mol l^{-1} Benzoylperoxyd und verschiedener Mengen 2,4-Dinitrophenol. Verzögerer-Konzentrationen: Temperatur 50°C (□): $4{,}01 \cdot 10^{-4}$ mol l^{-1}; (○): $1{,}00 \cdot 10^{-3}$ mol l^{-1}; (△): $1{,}60 \cdot 10^{-3}$ mol l^{-1} Temperatur 60°C (■): $4{,}01 \cdot 10^{-4}$ mol l^{-1}; (●): $8{,}02 \cdot 10^{-4}$ mol l^{-1}; (▲): $1{,}60 \cdot 10^{-3}$ mol l^{-1}

net wurde, sind auf Abb. 2 gezeigt. Die Tabellen I, II und III enthalten die Zahlenwerte für die Anfangsgeschwindigkeit der Polymerisation.

Aus der Anfangsgeschwindigkeiten berechneten wir die von BAGDASARJAN [7] eingeführten Verzögerungsparameter, von denen die aus den in Gegenwart von 2,4-Dinitrophenol durchgeführten Messungen berechneten Werte auf Abb. 3 gezeigt sind. Ähnliche Geraden wurden auch in Gegenwart der beiden anderen Dinitrophenole erhalten. Die Anstiege der erhaltenen Geraden,

welche für die Wirksamkeit der untersuchten Verzögerer charakteristisch sind, enthält Tabelle IV. Der zur Berechnung der Verzögerungsparameter notwendige Wert der Anfangsgeschwindigkeit der Polymerisation für eine Benzoyl-

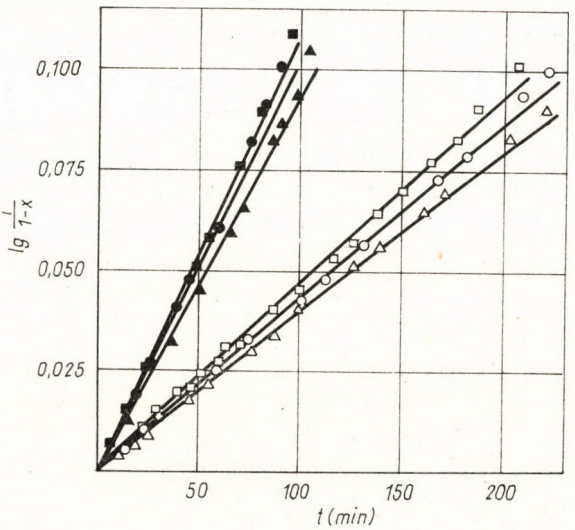

Abb. 2. Einfluß der Veränderung der Verzögererkonzentration auf die Anfangsgeschwindigkeit der Polymerisation

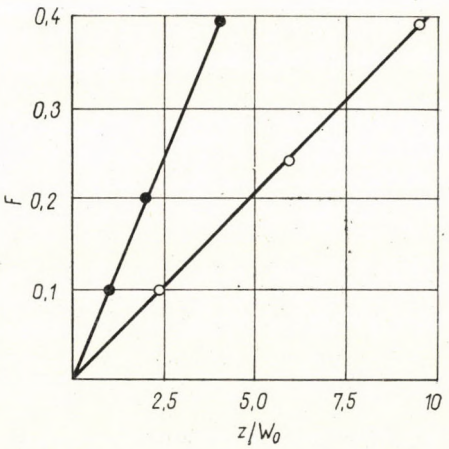

Abb. 3. Die Verzögerungsparameter als Funktionen von z/W_0 in Gegenwart von 2,4-Dinitrophenol. (○): Temperatur 50°C; (●): Temperatur 60°C

peroxyd-Konzentration von $4{,}13 \cdot 10^{-2}$ mol l^{-1} wurde aus der Mitteilung [5] übernommen.

Der Polymerisationsabschnitt nach Auftreten des Geleffektes wurde auf Grund der Gleichung von SAWADA [8] ausgewertet. Wenn gemäß der Gleichung

Tabelle I

Charakteristische Daten der Polymerisation in Gegenwart von 2,4-Dinitrophenol
Benzoylperoxyd-Konzentration: $4{,}13 \cdot 10^{-2}$ mol l^{-1}

Temperatur	z mol l^{-1}	W_{st} mol l^{-1} sec^{-1}	K_1	x_1	x_2
50°C	$4{,}01 \cdot 10^{-4}$	$1{,}607 \cdot 10^{-4}$	0,042	0,19	0,85
50°C	$1{,}00 \cdot 10^{-3}$	$1{,}496 \cdot 10^{-4}$	0,023	0,18	0,83
50°C	$1{,}60 \cdot 10^{-3}$	$1{,}386 \cdot 10^{-4}$	*	*	*
60°C	$4{,}01 \cdot 10^{-4}$	$3{,}827 \cdot 10^{-4}$	0,161	0,29	0,89
60°C	$8{,}02 \cdot 10^{-4}$	$3{,}638 \cdot 10^{-4}$	0,087	0,24	0,91
60°C	$1{,}60 \cdot 10^{-3}$	$3{,}308 \cdot 10^{-4}$	0,061	0,20	0,80

* Bei hohen Umsätzen sank die Polymerisationsgeschwindigkeit so weit ab, daß keine Daten mehr bestimmt werden konnten.

Tabelle II

Charakteristische Daten der Polymerisation in Gegenwart von 2,5-Dinitrophenol
Benzoylperoxyd-Konzentration: $4{,}13 \cdot 10^{-2}$ mol l^{-1}

Temperatur	z mol l^{-1}	W_{st} mol l^{-1} sec^{-1}	K_1	x_1	x_2
50°C	$4{,}01 \cdot 10^{-4}$	$1{,}449 \cdot 10^{-4}$	0,045	0,18	0,76
50°C	$8{,}02 \cdot 10^{-4}$	$1{,}266 \cdot 10^{-4}$	0,021	0,14	0,78
50°C	$2{,}01 \cdot 10^{-3}$	$1{,}150 \cdot 10^{-4}$	*	*	*
60°C	$4{,}01 \cdot 10^{-4}$	$3{,}733 \cdot 10^{-4}$	0,109	0,30	0,90
60°C	$8{,}02 \cdot 10^{-4}$	$3{,}465 \cdot 10^{-4}$	0,059	0,25	0,92
60°C	$1{,}60 \cdot 10^{-3}$	$3{,}016 \cdot 10^{-4}$	0,041	0,15	0,76

* Bei hohen Umsätzen sank die Polymerisationsgeschwindigkeit so weit ab, daß keine Daten mehr bestimmt werden konnten.

Tabelle III

Charakteristische Daten der Polymerisation in Gegenwart von 2,6-Dinitrophenol
Benzoylperoxyd-Konzentration: $4{,}13 \cdot 10^{-2}$ mol l^{-1}

Temperatur	z mol l^{-1}	W_{st} mol l^{-1} sec^{-1}	K_1	x_1	x_2
50°C	$4{,}01 \cdot 10^{-4}$	$1{,}583 \cdot 10^{-4}$	0,039	0,18	0,86
50°C	$8{,}02 \cdot 10^{-4}$	$1{,}496 \cdot 10^{-4}$	0,025	0,14	0,82
60°C	$4{,}01 \cdot 10^{-4}$	$3{,}796 \cdot 10^{-4}$	0,153	0,30	0,93
60°C	$8{,}02 \cdot 10^{-4}$	$3{,}591 \cdot 10^{-4}$	0,088	0,24	0,89
60°C	$1{,}20 \cdot 10^{-3}$	$3{,}418 \cdot 10^{-4}$	0,053	0,18	0,90

Tabelle IV

Verzögerungswirkung von Dinitrophenolen im Anfangsabschnitt der Polymerisation

	Temperatur	$\frac{FW_0}{z}$ 10^2
2,4-Dinitrophenol	50°C	4,10
	60°C	9,80
2,5-Dinitrophenol	50°C	12,40
	60°C	14,70
2,6-Dinitrophenol	50°C	5,14
	60°C	11,00

die Werte von $\frac{1}{x_2 - x_1} \ln \frac{x - x_1}{x_2 - x}$ als Funktion der Zeit aufgetragen werden, so erhält man Geraden, die in Abb. 4 gezeigt werden. Der Anstieg der Geraden ergibt die für den durch den Geleffekt verursachten Geschwindigkeitsanstieg charakteristischen K_1-Werte, die zusammen mit den x_1- und x_2-Werten in den Tabellen I, II und III zusammengefaßt sind. Ähnlich wie bei den Mono-

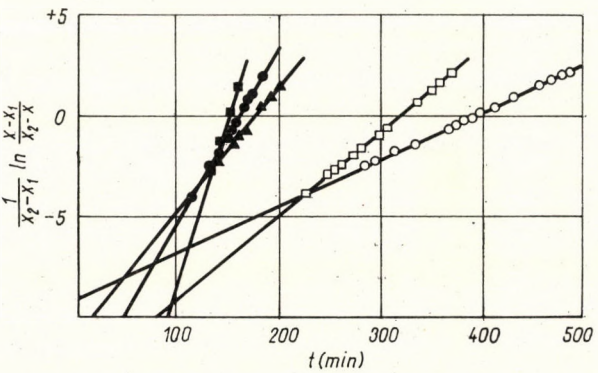

Abb. 4. Einfluß der Veränderung der 2,4-Dinitrophenol-Konzentration auf die Polymerisation bei hohen Umsätzen

nitrophenolen [1] sinkt mit dem Anwachsen der Verzögererkonzentration der Umsatzgrad x_1, bei dem der Geleffekt auftritt. Der Grenzumsatz (x_2) stellt keine eindeutige Funktion der Verzögererkonzentration dar, und sein Wert war in jedem Falle — mit Ausnahme des 2,6-Dinitrophenols — kleiner als bei gleichen Initiatormengen in Abwesenheit des Verzögerers. Die Abhängigkeit des Grenzumsatzes von der Temperatur zeigte einen ähnlichen Charakter wie die in Gegenwart von Mononitrophenolen [1].

Bei hohen Umsätzen wurden zur Charakterisierung der Wirksamkeit der untersuchten Verzögerer die Werte von $K_{1,rel}$ verwendet, welche auf Abb. 5 in Abhängigkeit von der Verzögererkonzentration gezeigt sind. Es zeigt sich, daß mit dem Anwachsen der Verzögererkonzentration die Werte von $K_{1,rel}$ in starkem Maße absinken. Beim Vergleich der relativen Polymerisationsgeschwindigkeiten mit den $K_{1,rel}$-Werten kann festgestellt werden, daß die untersuchten Verzögerer, ähnlich wie die Mononitrophenole, die Polymerisa-

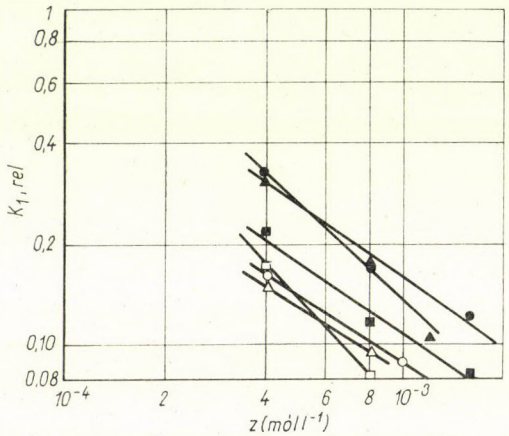

Abb. 5. Einfluß der Veränderung der Verzögererkonzentration auf die $K_{1,rel}$-Werte (○): 2,4-Dinitrophenol bei 50°C; (□): 2,5-Dinitrophenol bei 50°C; (△): 2,6-Dinitrophenol bei 50°C; (●): bei 60°C; (■): bei 60°C; (▲): bei 60°C

tionsgeschwindigkeit im Anfangsabschnitt der Reaktion in bedeutend geringerem Maße herabsetzen, als im Bereich der hohen Umsätze. Dies kann darauf zurückgeführt werden, daß die Geschwindigkeit der Reaktion zwischen den Verzögerermolekülen und den Makroradikalen eine Funktion ihrer Konzentrationen darstellt; bei hohen Umsätzen wächst aber die Konzentration der Makroradikale im hohen Maße.

Beim Vergleich der Wirksamkeit der durch uns untersuchten Verzögerer fällt auf, daß durch die Gegenwart der zweiten Nitrogruppe die verzögernde Wirkung gegenüber den Mononitrophenolen um eine Größenordnung ansteigt. Deshalb bestehen zwischen der Wirksamkeit der untersuchten Dinitrophenole weder im Anfangsabschnitt der Polymerisation, noch im Bereich hoher Umsätze keine so großen Unterschiede wie zwischen 2-Nitrophenol und den übrigen Mononitrophenolen. Unter den untersuchten Dinitrophenolen erwies sich das 2,5-Dinitrophenol als das wirksamste. Dies war hauptsächlich im Anfangsabschnitt der Polymerisation bei den bei niedrigeren Temperaturen durchgeführten Messungen zu beobachten. Die Wirksamkeit einer Temperaturänderung zeigt sich dagegen eher bei den zwei anderen Dinitrophenolen.

Die Unterschiede zwischen den untersuchten Dinitrophenolen sind bei hohen Umsätzen weniger auffallend. Es kann jedoch festgestellt werden, daß zum Erreichen identischer Werte von $K_{1,\mathrm{rel}}$ bei niedrigeren Temperaturen geringere Verzögerermengen notwendig sind.

ZUSAMMENFASSUNG

Die Blockpolymerisation von Methylmethacrylat wurde bei gleicher Initiatorkonzentration in Gegenwart unterschiedlicher Mengen von 2,4-; 2,5- und 2,6-Dinitrophenolen untersucht. Für die untersuchten Verbindungen wurden die charakteristischen Verzögerungsparameter bestimmt. Es konnte festgestellt werden, daß ähnlich dem Verhalten der Mononitrophenole, auch in diesem Falle die untersuchten Verzögerer die Polymerisationsgeschwindigkeit im Anfangsabschnitt der Reaktion weit weniger herabsetzen, als im Bereich hoher Umsätze. Die Anwesenheit der zweiten Nitrogruppe erhöht die Verzögererwirkung im Vergleich zu den Mononitrophenolen um eine Größenordnung. Unter den Dinitrophenolen erwies sich das 2,5-Dinitrophenol als das wirksamste. Die Lage der Nitrogruppen beeinflußt die verzögernde Wirkung der untersuchten Verbindungen jedoch nicht in einem solchen Maße, wie im Falle der Mononitrophenole.

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INVESTIGATION OF THE REACTIONS OF AROMATIC ALDEHYDES WITH BENZYL CYANIDE CATALYZED BY BORON FLUORIDE AND POLYPHOSPHORIC ACID

(PRELIMINARY COMMUNICATION)

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As it has been reported earlier [1], the CLAISEN—SCHMIDT condensation of benzaldehyde with acetophenone, yielding benzalacetophenone, can also be realized in a solution of anhydrous acetic acid with boron fluoride as the catalyst. When the reaction was studied with benzyl cyanide, another compound containing an active methylene group, in the presence of the stoichiometric quantity of BF_3, instead of the expected α-phenylcinnamonitrile a colourless, crystalline substance of m.p. 221—223° was obtained in a yield of 22%. This product was slightly soluble in hot alcohol, and readily soluble in hot acetic acid, bromobenzene and dimethylformamide. According to the evidence of the IR spectrum, the product contained no cyano group, while at wave numbers 1660 cm^{-1} and 3270 cm^{-1} the two bands characteristic of the C=O and N—H stretching vibrations of acid amides appeared.

Neither was the compound identical with α-phenylcinnamaldehyde, which might have been formed under the given reaction conditions. Therefore, an attempt was made to elucidate the structure of this product. Determination of the molecular weight involved difficulties. However, on carrying out the reaction with *p*-chlorobenzaldehyde and benzyl cyanide, and with benzaldehyde and *p*-chlorobenzyl cyanide, it was found, that the product contained in the second case about twice as much halogen as in the first case, indicating that its formation involved the reaction of one mole of aldehyde with two moles of cyanide. When the compound obtained from benzaldehyde and benzyl cyanide was hydrolized in glycerol with alkali, or in acetic acid in the presence of boron fluoride and the theoretical quantity of water, phenylacetamide could be isolated, while hydrolysis with aqueous mineral acids yielded phenylacetic acid. Phenylacetamide could be isolated also when the solution of the compound was reduced with nascent hydrogen (sodium in abs. ethanol). Repetition of the condensation reaction is anhydrous propionic acid yielded the same product. Though at a slower rate, the reaction proceeded also with catalytic amounts of boron fluoride. The same product was obtained also without the use of a solvent, when the aldehyd was first saturated with boron fluoride to give a solid complex, and then reacted with benzyl cyanide.

These experimental data have led to the conclusion that the compound is benzylidene-bis-(phenylacetamide), $C_6H_5CH(NHCOCH_2C_6H_5)_2$, prepared first by GUPTA [2] from phenylacetamide and benzaldehyde, by fusing the components at 160° for 2 hours. We are of the view that under the conditions applied by us, the reaction is brought about by the direct coupling of benzaldehyde and benzyl cyanide, and the acid amide groups are formed only during processing, upon the action of water. This assumption is substantiated also by the finding that the reaction between phenylacetamide and benzaldehyde gives higher yields in anhydrous acetic acid containing boron fluoride.

Subsequently, the reaction between benzaldehyde and benzyl cyanide was investigated in the presence of polyphosphoric acid. The exothermic reaction gave a yellow, crystalline substance, which was isolated in a yield of 52%. This product again was not identical with the expected α-phenylcinnamonitrile. The IR spectrum showed the absence of a cyano group, but characteristic bands at 1665 cm^{-1}, 3180 cm^{-1} and 3050 cm^{-1} indicated acid amide group in this case also.

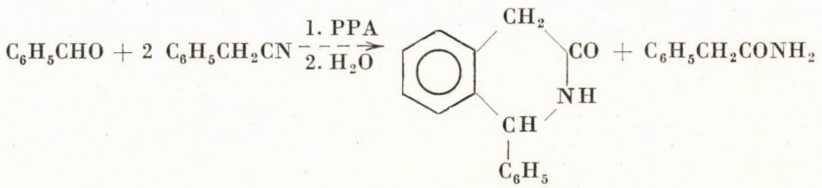
On the basis of this fact it was thought that simultaneously with the condensation also the hydration of the cyano group took place. This assumption seemed to be supported by the melting point of the product which was identical with that of α-phenylcinnamic amide, further by the finding that the product could also be prepared by reacting phenylacetamide with benzyldehyde. Inconsistent with the proposed structure was, however, the fact that contrary to data in literature, the compound was not converted to the corresponding nitrile by heating with phosphorus pentoxide in xylene. Further doubts arose concerning the structure when the reaction was carried out with *p*-nitrobenzaldehyde, and the melting point of the product differed from that reported in literature for α-phenyl-*p*-nitrocinnamic amide. Authentic α-phenylcinnamic amide, prepared as described in the literature, gave a considerable melting point depression with our product, and its IR spectrum was fundamentally different.

After having tried unsuccessfully several other methods, mass spectrometric molecular weight determination gave 223, and the molecular formula $C_{15}H_{13}NO$ was found on the basis of satisfactory analyses. In order to decide whether the active methylene group plays a part in the conversion, the reaction was carried out also with 1-phenylisobutyronitrile, which does not contain an active methyl group. On the basis of the analysis and IR spectrum, the product had the same character as that obtained from benzyl cyanide.

Further investigations showed the compound to possess slightly basic character. In anhydrous benzene the substance was converted by dry hydrogen chloride into a colourless hydrochloride salt, which suffered decomposition when exposed to air, being gradually reconverted to the yellow original compound. The substance was resistant to acids and alkalies; after prolonged

boiling with dilute or concentrated acids, or heating in a pressure tube for 8 hours at 125°, it was recovered unchanged. Heated with lithium aluminium hydride in tetrahydrofuran, or with palladium on carbon in decalin, it was not reduced or dehydrogenated. Hydrogenation in the presence of Raney nickel resulted in the saturation of one or both benzene rings, depending on the reaction conditions, as shown by the IR spectra. Reduction of the compound in abs. ethanol with sodium gave 1-phenyltetrahydroisoquinoline.

On the basis of these experimental results, the product was identified as 1-phenyl-3-(2H)-1,4-dihydroisoquinoline:



A further study of the reaction showed that phenylacetamide could be isolated as a by-product from the reaction mixture obtained with polyphosphoric acid. First, it was thought that phenylacetamide was formed from the excess of benzyl cyanide upon the action of polyphosphoric acid. However, when the applied quantity of benzyl cyanide was reduced, the yield of isoquinoline decreased. Optimum yield was obtained at a molar ratio of 1 : 2 of benzaldehyde : benzyl cyanide. This is indicative of the fact that under the given reaction conditions first an intermediate product is formed from 1 mole of aldehyde and 2 moles of nitrile, which is subsequently converted to the end-product, while phenylacetamide is splitt off. This conception was verified by the isolation of benzylidene-bis-(phenylacetamide) from the raw product of reactions conducted at lower temperatures. On the basis of our experiments it seems probable that also in polyphosphoric acid this compound is first formed, to be converted then under the cyclizing action of polyphosphoric acid, with the elimination of phenylacetamide, into the isoquinoline derivate. This view is substantied by the observation that 1-phenyl-3(2H)-1,4-dihydroisoquinoline can be prepared in even better yields when benzylidene-bis-(phenylacetamide) is used as the starting material.

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ACTA CHIMICA

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РЕЗЮМЕ

Химия комплексов, содержащих в качестве донора тяжелый атом I
Изучение комплексов переходных металлов с тионалидом

К. БУРГЕР, Л. КОРЕЦ и А. ТОТ

Были определены константы кислотной диссоциации тионалида и константы стабильности комплексов переходных металлов со структурой $3d^5$ — $3d^{10}$ с тионалидом с помощью pH-метрического измерения равновесия. Измерялась магнитная восприимчивость комплексов никеля(II), кобальта(II) и железа(II), а также снимались спектры Мёссбауэра комплекса железа(II). Согласно данным по магнитной восприимчивости комплексы ионов никеля(II) и кобальта(II) с тионалидом имеют низкое спиновое число, а комплексы железа(II) — высокое спиновое число. Спектр Мёссбауэра комплекса железа (II) указывает на эффект обратной координации.

Роль воды в реакциях перехода электрона V
Уравнение скорости для реакций с положительной энтропией активации

И. РУФФ

На основе «модели полосы» выводилось уравнение скорости реакций с переходом заряда, протекающих с переходами над активационным барьером, т. е. с положительной энтропией активации. На основе теоретических расчетов объяснялась зависимость скорости реакции обмена Ce(III)-Ce(IV) от концентрации.

Обсуждение кислотно-основных процессов на основе статистики Ферми I

И. РУФФ

Предлагается следующее определение pH для протонных растворителей: pH раствора идентично энергии Ферми, если последняя измеряется в единицах — $kT\ln 10$. Демонстрируется взаимосвязь уравнений для приблизительного расчета pH с зависимостью, описывающей уровень Ферми в растворе, и с помощью численного решения доказывается применимость последней для расчетов pH в случае таких растворов, для которых обычные приблизительные уравнения не действительны.

Цианометрическое определение замещенных производных изохинолина в неводных средах

О. ГИМЕШИ и ДЪ. РАДИ

Был разработан аналитический метод определения замещенных производных изохинолина. Метод основан на взаимодействии соединений данного типа с иодистым метилом и на титровании образующейся таким образом гетероциклической четвертичной аммо-

нийной соли раствором цианистого калия. Определения были разработаны для 6,7-диметокси-3,4-дигидро-изо-хинолина. Данный метод может быть использован для тех производных изо-хинолина, которые при взаимодействии с алкил-галогенидами претерпевают количественные превращения. Из результатов титрования, приведенных в таблицах, видно, что отклонения по отношению к взятой навеске составляют —0,9%, а стандартное отклонение ± 0,105%.

Исследование полярографической адсорбции производных 4 4'-бис(триазиниламино)стильбен-2,2'-дисульфоновой кислоты с помощью треугольно-импульсной техники

ДЬ. ПАЛИ

Исследовалось 10 различно замещенных, производных 4,4'-бис(триазиниламино) стильбен-2,2'-дисульфоновой кислоты, с помощью треугольно-импульсной полярографической техники. Результаты хорошо согласуются с более ранними наблюдениями, полученными с помощью других методов. При поляризации с возрастающим напряжением, соединения вызывают ёмкостную волну, пиковой потенциал которой равен 1,41 ± 0,03 *В* (ТКЕ), а при уменьшающемся напряжении — менее высокую волну с пиковым потенциалом в —1,28 ± 0,02 *В* (ТКЕ).

Определение содержания аминного азота в γ-глутамил-пептидах с помощью модифицированного метода Ван Слайка

Ю. КАЙТАР и М. КАЙТАР

Содержание аминного азота в γ-глутамил-пептидах не определяется с помощью оригинального метода Ван Слайка, т. к. пептиды такого типа не только дезаминируются, в условиях анализа, но одновременно происходит разрыв γ-пептидной связи, а вследствие этого аминогруппа следующей аминокислотной части становится доступной. Введенный Кайнцом модифицированный метод позволяет определить содержание аминного азота и в случае этих соединений, что было установлено путем анализа ряда γ-олигопептидов глутаминовой кислоты. Данный метод пригоден и для анализа аминного азота γ-полиглутаминовых кислот, а вследствие этого и для определения их молекулярного веса.

Исследование контактов активированных механическим путем

Р. ШРАДЕР и В. ШТЕДТЕР

В нескольких работах было показано, что в результате механического воздействия некоторые твердые тела становятся катализаторами. С этой целью продажный порошкообразный никель подвергался измельчению в лабораторной вибрационной мельнице «Вибратом». Никелевый порошок, подвергнутый активированию различной продолжительности, характеризовался измерением его поверхности по методу БЭТ и рентгенографическим определением состояния решетки (величина первичных ячеек, искажения и возмущения решетки). Каталитические свойства были изучены на моделях гидрирования фенола при нормальном и повышенном давлениях, а также гидрирования оценола. Было показано во всех случаях, что активность никелевого контакта сильно возрастает вследствие механической обработки в вибрационной мельнице. Гидрирование фенола (при нормальном давлении) и оценола показывает, что увеличение активности не зависит от увеличения поверхности, а связано с искажением и возмущением решетки. Поэтому каталитическое действие механически активированных контактов обусловливается, в первую очередь, степенью возмущения кристаллита, т. е. наличием «активной решетки» и только в меньшей степени свободной поверхностью. Результаты, полученные для фенола в автоклаве, не показывают такого эффекта, что объясняется экстремальными условиями (давлением и температурой).

Изучение реакций диолов и циклических эфиров XXII Изучение превращений триметиленоксида в газовой фазе на платиновом катализаторе с помощью микрореакторной техники

М. БАРТОК и К. КОВАЧ

С помощью микрореакторной техники изучались превращения триметиленоксида на термолите, а также на платиновых катализаторах, нанесенных на термолит и углерод, в присутствии гелия и водорода. Степень превращения и различные направления реакции изучались в зависимости от экспериментальных параметров: наполнителя реактора, газа-носителя и температуры. Превращение триметиленоксида в изученных условиях сложное, складывающееся из нескольких первичных и вторичных процессов. Изучался механизм образования различных продуктов реакций. Основное направление реакции — это изомеризация, протекающая с образованием пропиональдегида. Это химическое изменение может быть отнесено к 1,3-перегруппировкам.

Изучение реакций диолов и циклических эфиров XXIII Изучение превращений 3-моноалкилоксетанов на платиновом катализаторе с помощью микрореакторной техники

М. БАРТОК и Б. КОЗМА

Изучались превращения 3-моноалкил(метил-, этил-, н-пропил-, изо-пропил, н-бутил- и циклогексил-)оксетанов на платиновых катализаторах, нанесенных на термолит и активный уголь, в присутствии гелия и водорода, протекающие в интервале температур 220—320°С, с помощью микрореакторной техники. Основные направления превращения оксетанов в изученных условиях — это изомеризация, протекающая с образованием альдегидов, и разложение с образованием олефинов и формальдегида. Первичные процессы сопровождаются несколькими вторичными процессами. В зависимости от различных параметров: катализатор, температура, газ-носитель и структура оксетана, были сделаны выводы относительно степени превращения оксетанов и основных направлений протекающих процессов.

Изучение трифенилметильного радикала методом ЭПР

Б. МОХОШ, Ф. ТЮДЁШ и Л. ЙОКАИ

Изучался спектр ЭПР трифенилметильного радикала в толуольном растворе в интервале температур 190—290° С. Константы расщепления протонов: a_4^H (пара) = 2,81 Oe; a_3^H (мета) = 1,13 Oe; a_2^H (орто) = 2,57 Oe не зависят от температуры. Были измерены величины изотропного сверхтонкого расщепления атомных ядер ^{13}C, содержащихся в естественной смеси:

$$a_\alpha{}^{13}C = +20{,}1 \text{ Oe}; \; a_1{}^{13}C = -13{,}6 \text{ Oe}; \; a_2{}^{13}C = +6{,}4 \text{ Oe};$$

$$a_3{}^{13}C = -5{,}3 \text{ Oe}; \; a_4{}^{13}C = +6{,}1 \text{ Oe}.$$

С помощью уравнения Карплус—Фрэнкеля определялись значения спиновой плотности ϱ^π и абсолютные значения Q МакКоннела.

Строение молекулярных соединений амидазофен—барбитурата

П. ШОХАР, Е. ОРБАН и Г. ТОТ

Амидазофен с различными барбитуратами образует молекулярное соединение с молярным составом 1:1, которое в разбавленных растворах распадается. Однако, CN-замещенными барбитуратами не удалось получить молекулярного соединения. На основе ик-спектроскопических исследований удалось показать, что в молекулярных соединениях с различным строением аналогов барбитурата между карбонильной группой амидазофена и гидроксильной группой таутомера полуиминогидрина барбитурата образуются водородные связи. N-замещенные барбитураты же не образуют молекулярного соединения, т. к. их лактим-таутомерная форма гораздо менее стабильна, чем лактамовая форма, которая стабилизуется за счет мезомерной энергии, возрастающей в результате ассоциации циклического димера.

Превращение стероидов с помощью Absidia orchidis I Хидроксилизация андрост-4-ен-3,17-диона

Г. АМБРУШ и Дь. ВИКС

Absidia orchidis андрост-4-ен-3,17-дион превращает в 6β-, 7α-, 11α- и 14α-хидрокси андрост-4-ен-3,17-дион.

Гомогенное каталитическое гидрирование альдегидов с карбонилами родия как катализатором, II

Б. ХЕЙЛ и Л. МАРКО

Кинетика гидрирования альдегидов в спирты в присутствии карбонилов родия как катализатора при 160°C и $p_{CO} \geqslant 80$ атм может быть представлена следующим уравнением:

$$\frac{d\,(\text{спирт})}{dt} = k\,[\text{альдегид}]\,[Rh]^{1/6}\;(p_{H_2})^{0,5}\;(p_{CO}CO)^{-0,3}$$

Реакционная смесь содержит родий принципиально в форме $Rh_6(CO)_{16}$, комплексы же $Rh_4(CO)_{12}$ и $[Rh(CO)_2Cl]_2$ образуются в качестве промежуточных продуктов, а $Rh_2(CO)_8$ и $HRh(CO)_4$ не были обнаружены. Предполагается, что ненасыщенный комплекс $HRh(CO)_3$ является активным катализатором гидрирования. При прочих равных условиях родий обычно склонен к образованию карбонилов, содержащих в молекуле меньше групп окиси углерода, чем карбонилы кобальта.

Полимеризация метилметакрилата при высоких степенях конверсии IV. Изучение замедляющего влияния динитрофенолов

И. МОНДВАИ и М. ИГЛОИ

Блочная полимеризация метилметакрилата изучалась при одинаковых концентрациях инициатора в присутствии различных количеств 2,4-, 2,5- и 2,6-динитрофенолов. Определялись параметры замедления, характерные для изученных соединений. Было установлено, что динитрофенолы, подобно мононитрофенолам, в начальной стадии полимеризации уменьшают скорость полимеризации в гораздо меньшей мере, чем в стадии, протекающей при высоких степенях конверсии. Введение второй нитрогруппы увеличивает степень замедления на целый порядок. Наиболее сильным замедлителем среди динитросоединений является 2,5-динитрофенол. Положение нитрогрупп в случае динитрофенолов, однако, не оказывает такого сильного влияния на замедляющий эффект, как в случае мононитрофенолов.

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LÁSZLÓ CHOLNOKY

(1899 — 1967)

V. BRUCKNER

Am 12. Juni 1967 verschied unerwartet in seinem 69. Lebensjahre LÁSZLÓ CHOLNOKY, korrespondierendes Mitglied der *Ungarischen Akademie der Wissenschaften*, Professor der Chemie an der *Medizinischen Universität, Pécs*. Durch seinen Tod erlitt die organisch-chemische Forschung und der Universitätsunterricht in Ungarn einen schweren Verlust.

LÁSZLÓ CHOLNOKY wurde am 29. Mai 1899 in Ozora (Komitat Tolna) geboren. Unmittelbar nach Beendigung seiner Mittelschulstudien in Veszprém wurde er während des ersten Weltkrieges zum Militärdienst einberufen und nach kurzer militärischer Ausbildung als Artillerist an der Front eingesetzt. Nach Kriegsende studierte er an der Budapester Universität Pharmazie und erwarb im Jahre 1922 das Magister-Diplom. Schon während seines Universitätsstudiums wendete sich sein Interesse vorwiegend der Chemie zu und er wurde besonders von den Vorlesungen des hervorragenden Analytikers Professor L. WINKLER beeindruckt. Seine ausgezeichneten Studienerfolge wie auch sein Geschick zur Laborarbeit machten Professor WINKLER auf ihn aufmerksam, und demzufolge ist es ihm nach Erwerbung seines Magister-Diploms möglich geworden, am Analytisch-Chemischen Institut — nunmehr als Mitarbeiter von Professor L. WINKLER — weiter zu arbeiten. Seine erste, hier durchgeführte wissenschaftliche Arbeit über die Bestimmung des Jodgehaltes organischer Verbindungen, die im Jahre 1924 erschien, bildete die Grundlage zu seiner Promovierung zum Doktor der Pharmazie. Ende 1924 nahm er eine ihm angebotene Assistentenstelle am *Chemischen Institut der Medizinischen Fakultät der Universität Pécs* an, wo zu dieser Zeit Professor L. ZECHMEISTER seine Tätigkeit als Lehrer und Forscher eben begonnen hatte. Dies war für CHOLNOKY von größter Bedeutung, da ihn Prof. ZECHMEISTER in seine wichtige Forschungsarbeit über Carotinoide gleich einbezog. Seitdem arbeitete er ununterbrochen in diesem Institut, und wurde im Jahre 1929 an der Universität Pécs zum Dr. Phil. promoviert, später zum Dozenten habilitiert. Inzwischen hatte er im Besitze von Stipendien in Jena, weiterhin im *Medizinisch-Chemischen Institut der Universität Graz* gearbeitet; hier erlernte er bei Prof. F. PREGL die Grundlagen der eben damals zum Aufschwung gekommenen

MAGYAR TUDOMÁNYOS AKADÉMIA KÖNYVTÁRA

organischen Mikroanalyse, die er dann in Pécs eingeführt hat. Im Jahre 1946 wurde er als L. ZECHMEISTERS Nachfolger zum außerordentlichen Professor und zwei Jahre später zum ordentlichen Professor ernannt. Er wirkte bis zu seinem Lebensende an der *Universität Pécs*, die kurz nach dem zweiten Weltkrieg in eine Medizinische Universität umgestaltet wurde. Ein Jahr lang fungierte er als Prorektor, dann vier Jahre hindurch (1961—1965) als Rektor seiner Universität. Seine wissenschaftliche Arbeit wurde durch Verleihung des Kossuth Preises (1959) und ein Jahr später durch die Wahl zum korrespondierenden Mitglied der *Ungarischen Akademie der Wissenschaften* anerkannt.

Die Forschungstätigkeit von L. CHOLNOKY war von 1924 bis 1940 mit der Arbeit seines hervorragenden Meisters Prof. L. ZECHMEISTER auf das engste verknüpft. Zu dieser Zeit hatten sich besonders drei Forschungsstätten die Strukturermittlung des bereits lange bekannten Carotins, Xanthophylls und einiger anderer Carotinoide, ferner die Isolierung und Untersuchung weiterer Lypochrome zum Ziel gesetzt. Außer R. KUHN (Heidelberg) und P. KARRER (Zürich) war es noch L. ZECHMEISTER, der Arbeiten auf dem Gebiet der Carotinoide in Angriff genommen hatte, und einer seiner ersten Mitarbeiter war eben L. CHOLNOKY. Zunächst gelang in Pécs die Isolierung des roten Farbstoffes der reifen Paprikaschoten, des Capsanthins, wobei zugleich eine Trennung von dem das Capsanthin begleitenden Carotin durchgeführt wurde. Die Struktur des Carotins war damals (1927) noch unbekannt, da man jedoch schon seit etwa 20 Jahren wußte, daß dieser (für einheitlich gehaltene) Farbstoff ein ständiger Begleiter des Chlorophylls ist, wurde ihm irgendeine, noch unbekannte pflanzenphysiologische Rolle zugeschrieben und seine Konstitutionsermittlung für besonders wichtig und wünschenswert gehalten. Nun lieferten ZECHMEISTER und CHOLNOKY zu den diesbezüglichen Untersuchungen einen wichtigen Beitrag, als sie im Jahre 1928 über die katalytische Hydrierung des Carotins (und dadurch zum erstenmal über die katalytische Hydrierung eines Carotinoids) berichteten. Sie konnten auf diese Art zeigen, daß das Carotin 11 Doppelbindungen enthält, deren Sättigung mit Wasserstoff zu einem Kohlenwasserstoff (Perhydrocarotin) der Bruttoformel $C_{40}H_{78}$ führt. Dadurch ließ sich auch die ursprünglich von WILLSTATTER bereits 1907 angegebene Carotinformel $C_{40}H_{56}$ sicherstellen und der Zweifel an der Verläßlichkeit der ebulioskopischen oder kryoskopischen Molekulargewichtsbestimmung dieser stark ungesättigten Substanz endgültig beseitigen. Zugleich wurde schon in dieser Arbeit auf die Möglichkeit eines genetischen Zusammenhanges zwischen Phytol und Carotin hingewiesen. In den folgenden Jahren haben ZECHMEISTER und CHOLNOKY fortlaufend über »Untersuchungen über den Paprikafarbstoff« berichtet und bereits im Jahre 1934 die chromatographische Adsorptionsanalyse in präparativem Maßstab zur Trennung der Farbstoffe herangezogen. Mit Hilfe dieser Methode ließen sich außer Capsanthin, Capsorubin und β-Carotin

auch Zeaxanthin, Kryptoxanthin und Lutein aus Paprika gewinnen. Die chromatographische Adsorptionsanalyse erwies sich alsbald als eine unentbehrliche Trennungsmethode der vergesellschaftet vorkommenden Carotinoide. Zur ganz allgemeinen und schnellen Verbreitung dieses Verfahrens hat das von L. ZECHMEISTER und L. CHOLNOKY verfaßte vorzügliche Buch »Die Chromatographische Adsorptionsmethode«, in welchem auch die eigenen Erfahrungen der Verfasser behandelt wurden, sehr viel beigetragen. Das im Jahre 1937 erschienene Buch wurde schnell vergriffen, so daß schon im nächsten Jahre eine zweite Auflage und später, in englischer Sprache, noch drei Auflagen (1943, 1948, 1957) herausgegeben wurden.

Die damals neue, präparative Trennungsmethode hat alsbald auch bei der Isolierung der Farbstoffe anderer Pflanzen gute Dienste geleistet. So konnten ZECHMEISTER und CHOLNOKY aus den reifen Beeren von *Solanum dulcamara* (Bittersüß) und von *Tamus communis* (Schmerwurz) außer Lycopin zwei diesem ähnliche, jedoch sauerstoffhaltige Farbstoffe (Lycoxanthin und Lycophyll) isolieren und später zeigen, daß der eine Farbstoff ein Monohydroxyderivat, der andere ein Dihydroxyderivat des Lycopins darstellt. Damit sind zum erstenmal offenkettige Carotinoide mit Hydroxylgruppe bekannt geworden.

Inzwischen wurden auch Untersuchungen zwecks Strukturermittlung der spezifischen Paprikafarbstoffe (Capsanthin und Capsorubin) in Angriff genommen; es wurde gefunden, daß Capsanthin ($C_{40}H_{58}O_3$) und Capsorubin ($C_{40}H_{60}O_4$) zwei acylierbare Hydroxylgruppen und eine bzw. zwei dem chromophoren System angehörende, dem aus 10 bzw. 9 Doppelbindungen bestehenden konjugierten System unmittelbar angeschlossene Carbonylgruppen enthalten. Diese Feststellung hat sich als richtig erwiesen, wenn auch die von ZECHMEISTER und CHOLNOKY abgeleitete Struktur der beiden Paprikafarbstoffe später (1960) durch KARRER eine wohlbegründete Korrektion erfahren hat. Dazu bildeten den einen Ausgangspunkt die im Jahre 1957 von CHOLNOKY erneut ermittelten Summenformeln der beiden Farbstoffe: Capsanthin $C_{40}H_{56}O_3$, Capsorubin $C_{40}H_{56}O_4$.

Die Arbeiten von ZECHMEISTER und CHOLNOKY über den Paprikafarbstoff haben noch in zwei Punkten zu interessanten Erkenntnissen geführt, die für die Entwicklung der Carotinoidchemie wichtig waren. Erstens wurde erkannt, daß die hydroxylhaltigen Polyene (wie z. B. Capsanthin und Capsorubin) in der Pflanze nicht nur frei, sondern auch als Farbstoffwachse verestert vorkommen können. Dies ließ sich ganz besonders durch den Befund beweisen, daß das aus der Bockdornsbeere isolierbare Physalien ein Dipalmitat des Zeaxanthins darstellt. Einen zweiten wichtigen Befund bedeutete die Beobachtung, daß eine benzolische Lösung, die aus chromatographisch einheitlichem Capsanthin bereitet worden war, beim wiederholten Chromatographieren zwei Zonen bildet, deren Eluat wiederum in dieselben zwei Bestandteile zerlegbar

ist. Daraus wurde bereits damals (1937) auf eine in Lösung verlaufende Gleichgewichtsisomerisierung geschlossen und dabei auch auf die Möglichkeit einer *cis-trans*-Isomerisierung hingewiesen. Kurz darauf wurden derartige Beobachtungen im Pécser Institut auch an andereren Carotinoiden gemacht; so haben z. B. ZECHMEISTER, CHOLNOKY und POLGÁR (1939) gefunden, daß auch aus einheitlichem Zeaxanthin und Physalien bereitete Lösungen beim wiederholten Chromatographieren getrennte Zonen ergeben. Schließlich konnte bewiesen werden, daß in der Tat eine *cis-trans*-Isomerisierung stattfindet, die nicht durch Einwirkung des Adsorbens hervorgerufen wird (wie dies einige Forscher vermuteten), sondern sich schon in kalter Lösung sehr langsam abspielt, jedoch durch Erwärmen, Belichtung oder Zusatz von ganz wenig Jod erheblich beschleunigt werden kann. Es ließen sich derartige Isomere sogar kristallin fassen und näher untersuchen, z. B. auf spektroskopischem Weg.

Seit 1953 hat CHOLNOKY hauptsächlich die Frage interessiert, welche pflanzenphysiologische Rolle den Carotinoiden zukommt. Er gedachte, diese Frage durch sorgfältige qualitative und quantitative Analyse der in chlorophyllhaltigen Organen (z. B. in grünen Blättern und unreifen Früchten) vorkommenden Carotinoide, weiterhin durch Ermittlung der Veränderung, die sie während des Reifens der Früchte erfahren, zu beantworten. Als Versuchsobjekte dienten zwei Paprikaarten, nämlich tomatenförmiger roter und gelber Paprika *(Capsicum annuum var. licopersiciforme rubrum* und *flavum)*. Einerseits wurden die grünen Blätter und unreifen, noch grünen Schoten, andererseits die reifen rot bzw. gelb gefärbten Schoten beider Paprikaarten sehr sorgfältig auf ihren Carotinoidgehalt untersucht. Aus den Ergebnissen dieser Untersuchungen hat CHOLNOKY darauf geschlossen, daß die Carotinoide an der photosynthetischen Betätigung der Pflanze beteiligt sind, indem sie den Sauerstofftransport besorgen. Laut seiner Hypothese synthetisiert die Pflanzenzelle primär Carotinoide mit β-Jononringen, nämlich β-Carotin und dessen 3-Mono- und 3.3'-Dihydroxyderivat, d. h. β-Kryptoxanthin und Zeaxanthin. All diese β-Carotinoide können durch Sauerstoffaufnahme in die entsprechenden 5.6-Epoxyde übergehen, aus denen dann bei der Sauerstoffabgabe entweder die ursprünglichen β-Carotinoide zurückgebildet werden, oder ihr epoxydierter Ring nebst Sauerstoffabgabe zu einem α-Jononring umgestaltet wird. Somit wären im Sauerstofftransport die folgenden drei Systeme betätigt: I. Zeaxanthin → Antheraxanthin → Lutein; II. β-Carotin → β-Carotin-5.6-epoxyd → → α-Carotin; III. β-Kryptoxanthin → β-Kryptoxanthin-5.6-epoxyd → α-Kryptoxanthin. (Letzteres α-Carotinoid wurde von CHOLNOKY und Mitarbeiter entdeckt und als 3'-Hydroxy-α-carotin erkannt.) In den chlorophyllhaltigen Organen (grüne Blätter, unreife Schoten) ist die qualitative Zusammensetzung des Farbstoffgemisches ganz gleich. Während des Reifens der Schoten verschwindet allmählich das Chlorophyll und gleichzeitig wächst die Carotinoidbildung stark an, auch ist ein Anstieg der Carotinoidepoxyde (Antheraxanthin

ACTA CHIMICA

ТОМ LV—ВЫП. 2

РЕЗЮМЕ

Некоторые данные к аналитической химии 1,2-гликолей и полиоксисоединений, VII. Определение мелибиозы через триальдегид, образующийся при перйодатном окислении

И. МОЛНАР-ПЕРЛ и Л. МАРОШ

При перйодатном окислении мелибиозы в кислом растворе (pH $\approx$ 1 ÷ 4) образуется триальдегид, образующийся стабильный альдегид-бисульфит с 3 молями сернистой кислоты. Для косвенного определения мелибиозы авторами использовался уже ранее предложенный бисульфут-цианидный иодометрический метод.

Некоторые данные к аналитической химии 1,2-гликолей и полиоксисоединений, VIII. Определение мальтозы, лактозы и целлобиозы через альдегид, образующийся при перйодатном окислении

И. МОЛНАР-ПЕРЛ и Л. МАРОШ

При окислении 1—4-восстанавливающих дисахаридов в сернокислом периоднокислом растворе (pH $\approx$ 0) образуется 3 моля альдегида (2 моля формальдегида и 1 моль глиоксильной кислоты). При окислении, начатом в сернокислом перйоднокислом растворе и продолжающемся далее в буферном уксуснокислом растворе (pH $\approx$ 4) образуется 2 моля формальдегида в качестве конечного продукта. Альдегиды измерялись с помощью предложенного ранее авторами бисульфит-цианидного иодометрического метода. Этот метод был также использован для определения 1—4-дисахаридов отдельно и в присутствии альдогексозов.

Равновесия пар-жидкость для бинарных смесей, содержащих спирт. О возможности использования модели регулярной тройной смеси типа $A\text{-}A_2\text{-}B$

Й. ЛИСИ, Ф. РАТКОВИЧ и Т. ШАЛАМОН

Изучая возможность применения модели регулярной тройной смеси типа $A\text{-}A_2\text{-}B$, было найдено, что она может быть использована для смесей этанола с 6-ью различными компонентами B. Из результатов вытекает, что расхождения расчетных и измеренных парциальных давлений во всех случаях имеют одинаковую тенденцию. Погрешность рассмотренного метода расчета не превышает погрешности расчета, проводимого на основе эмпирического уравнения, содержащего две постоянные. Преимуществом же его является то, что он содержит только одну постоянную, зависящую от качества материала компонента, находящегося в смеси с этанолом. Фигурирующая в зависимости константа равновесия

димеризации зависит лишь от температуры и может быть определена из данных газовой хроматографии чистого этанола. Постоянная ошибка расчета объясняется тем, что модель типа $A\text{-}A_2\text{-}B$ не принимает в учет существование ассоциата, содержащего более чем две молекулы этанола.

Равновесие газ-жидкость в бинарных системах, содержащих спирт, II. О применимости модели регулярной тройной смеси типа $A\text{-}A_2\text{-}B$

Й. ЛИСИ, Ф. РАТКОВИЧ и Т. ШАЛАМОН

Изучалась применимость модели регулярной тройной смеси типа $A\text{-}A_2\text{-}B$. Исходя из одной температуры, пересчитывались данные равновесия пар-жидкость для другой температуры. Было установлено, что температурная зависимость константы равновесия димеризации этанола описывается уравнением Вант-Гоффа, и что энергия перехода из одной фазы в другую не зависит от температуры. Погрешность данных давления пара, рассчитанных на основе предположений, упомянутых выше, не больше, чем методическая погрешность модели.

Теоретическая интерпретация размытой структуры ассоциированных полос валентных колебаний OH и NH (хелатных полос), расчлененных частичными максимумами

П. ШОХАР и ДЬ. ВАРШАНИ

Полосы валентных колебаний групп XH, находящихся в сильных водородных связях, часто исчезают или расчленяются размытыми частичными максимумами с необыкновенно низкими волновыми числами, наблюдающимися в равных расстояниях. Эти типы полос наблюдались в случае водородных мостиков, образующихся с участием гидроксильных групп. Согласно нашим исследованиям они появляются и в случае водородной связи N—H...X. Структура частичных максимумов полос валентных колебаний групп NH и OH особенно подобна структуре полос перпендикулярных к плоскости деформационных валентных колебаний, гидроксильных групп, совершающих внутреннее вращение. Было показано, что полоса валентных колебаний сильно ассоциированных групп OH и NH и полоса перпендикулярных к плоскости деформационных колебаний гидроксильных групп, совершающих внутреннее вращение, описываются аналогичными математическими формулами, и это является причиной подобности в структуре полос. Для этого полагалось, что протон в случае сильной водородной связи совершает самостоятельное колебательное движение между примыкающими атомами. Это движение называлось внутренним колебанием. Исходя из этого, и на основе унифицированных представлений систематизировались различные типы полос валентных колебаний групп OH и NH спектров, снятых в твердой фазе, а также было установлено, для каких видов водородных связей они являются характерными.

Общие средние квадратические амплитуды колебаний и эффект укорачивания в $CH_3C \equiv CCH_3$ и $CF_3C \equiv CCF_3$

К. ВЕНКАТЕСВАРЛУ и МАРИАММА П. МАТЬЮ

Приводится теоретическое обсуждение общих средних квадратических амплитуд колебаний молекул диметилацетилена и гексафторбутин-2. Сообщаются численные значения всех отклонений связанных и несвязанных расстояний, рассчитанные из параллельных и перпендикулярных средних квадратических амплитуд. Используя перпендикулярные средние квадратические амплитуды, определялись константы укорачивания. Все приведенные значения относятся к 300° K.

Общие средние квадратические амплитуды и коэффициенты связи Кориолиса пирамидальных молекул типа XYZ_2

К. ВЕНКАТЕСВАРЛУ, К. В. РАЯЛАКШАМИ и К. ЙОЗЕФ БАБУ

Обсуждались общие средние квадратические амплитуды и коэффициенты связи Кориолиса некоторых пирамидальных молекул типа XYZ_2. Было найдено, что величина $\langle \Delta y^2 \rangle$ является наиболее чувствительной к окружающей среде. С увеличением числа галогенных заместителей увеличивается величина $\langle \Delta z^2 \rangle$.

Изучение реакционной способности органических соединений в жидкой фазе, II. Относительная реакционная способность органических кислот в их реакциях со свободными метильными радикалами в жидкой фазе

О. ДОБИШ, И. НЕМЕШ и Р. КЕРЕПЕШ

Изотопным кинетическим методом измерены относительные реакционные способности алифатических монокарбокислот в элементарной реакции $RCOOH + CH_3 \; CH_4$ в жидкой фазе.

Установлено, что для первых шести членов гомологического ряда молекулярная способность алифатических монокарбокислот не зависит от числа $-CH_2$-групп в углеродной цепи, точнее сказать, при заданной температуре переодически меняется вблизи определенного значения.

Для меченой тритием в карбоксильной группе уксусной кислоты, растворенной в н-гептане, определена константа равновесия димеризации и энергия водородной связи.

Изучение реакционной способности органических соединений в жидкой фазе, III. Изучение ассоциации водно-спиртовой смеси

И. НЕМЕШ, Н. Н. УГАРОВА и О. ДОБИШ

Строение жидкофазной водно-спиртовой системы описывается с помощью пространственно-сеточной модели, определяющейся в первом приближении, при исключении циклических структур, множеством линейных полимерных цепей. На основе этой модели статистическим методом выделена зависимость между концентрациями свободных протонов (не образующих водородную связь) спирта и воды и общей концентрацией гидроксильных групп и воды.

В системе бутилового спирта и воды на основе полученных уравнений и химического сдвига, измеренного методом протонного резонанса, были определены константы равновесия образования ассоциатов типа спирт-спирт, вода-вода, вода-спирт и их температурная зависимость.

В этой же системе методом изотопной кинетики на основе кинетических данных определялись константы образования смешанных ассоциатов при 140°С.

Исходя из значений констант энтальпии и энтропии равновесия, образование смешанных ассоциатов является энергетически более выгодным.

Некоторые данные по химии гетероциклических псевдоосновных аминокарбинолов, XXXIII. Новый метод построения скелета бензо(а)хинолизидина

Л. ТЁКЕ, ДЬ. КАЛАУШ и Ч. САНТАИ

Был разработан новый метод получения труднодоступных 1,1,3,3-тетразамещенных бензо(а)хинолизидинов путем одновременного вступления в реакции производных 3,4-дигидро-изо-хинолина, формальдегида и соединений, содержащих активную метиленовую группу. Структура полученных продуктов доказывалась химическим и физическим путем.

und Violaxanthin) zu verzeichnen, ein Zeichen dessen, daß der Sauerstoffbedarf stark vermindert ist. Dabei ist kein Unterschied in der qualitativen Zusammensetzung in den gelben Schoten zu verzeichnen, hingegen werden in den roten Schoten im Laufe des Reifungsprozesses aus Antheraxanthin und Violaxanthin Hydroxy-keto-carotinoide, d. h. Capsanthin und Capsorubin gebildet.

Außer den sehr sorgfältig durchgeführten, mühevollen Untersuchungen über den qualitativen und quantitativen Carotinoidgehalt der erwähnten zwei Paprikaarten in verschiedenen Lebensperioden der Pflanzen, haben CHOLNOKY und Mitarbeiter neuestens in Zusammenarbeit mit B. C. L. WEEDON *(Queen Mary College, London)* und E. S. WAIGHT *(Imperial College of Science and Technology, London)* die Struktur des Foliaxanthins und Foliachroms ermittelt und in beiden u. a. eine sich dem konjugierten System anschließende Allenbindung nachgewiesen. (Ein derartiges Bindungssystem war bisher in Carotinoiden höherer Pflanzen nicht bekannt.) Später wurde in Gemeinschaft mit englischen und amerikanischen Forschern die Identität des ursprünglich von CHOLNOKY aus Paprika isolierten Foliaxanthins mit dem schon früher von H. H. STRAIN aus Haferblättern isolierten Neoxanthin bewiesen. Schließlich haben CHOLNOKY und J. SZABOLCS in Gemeinschaft mit B. C. L. WEEDON (London), weiterhin J. BALDAS und Q. N. PORTER *(University of Melbourne, Australia)* über die massenspektroskopische Untersuchung zahlreicher Carotinoid-5.6-epoxyde und Carotinoid-6.8-furanoidoxyde berichtet. In der letzten Arbeit, die CHOLNOKY und Mitarbeiter veröffentlicht haben, wird über die Reduktion von Carotinoidoxyden (Epoxyden und furanoiden 5.6-Oxyden) mit Lithiumaluminiumhydrid unter speziellen Bedingungen (IR-Bestrahlung oder 80—90° Gefäßwandtemperatur) berichtet, wobei die Oxyde nicht unter Alkoholbildung gespalten, sondern zu den Stammcarotinoiden desoxydiert werden. Die interessante Methode konnte u. a. zur Strukturerforschung des Foliaxanthins bzw. Neoxanthins und Fucoxanthins mit Erfolg eingesetzt werden. Die Verwirklichung der weiteren Pläne CHOLNOKYS, das Gebiet der Carotinoidchemie nunmehr im Rahmen einer internationalen Zusammenarbeit mit dem modernsten Rüstzeug der organisch-chemischen Forschung weiter zu bearbeiten, hat sein plötzlicher Tod vereitelt.

Nicht nur als Forscher, sondern auch als Lehrer hat L. CHOLNOKY Vorzügliches geleistet und eine Reihe von jungen Chemikern in die Forschungsarbeit eingeführt. Überdies hatte er sich viel bemüht, den Medizinern einen solchen Chemieunterricht zu geben, der sie in ihren eigentlichen Fachstudien auf das beste unterstützt. Seine geistreichen Vorlesungen, sein stets heiteres Gemüt und seine ständige Hilfsbereitschaft haben ihn bei den Studenten sehr beliebt gemacht.

Viel und sehr verantwortungsvolle Arbeit lastete auf, ihn als er vier Jahre hindurch als Rektor der Medizinischen Universität fungierte, umsomehr, da

eben zu dieser Zeit das moderne Gebäude der Universitätskliniken errichtet wurde. Sein selbstloses Tun und Wirken im Dienste der Universität ist ganz besonders anerkennenswert und wird sein Andenken ebenso dauernd bewahren wie seine wissenschaftlichen Erfolge.

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BEITRÄGE ZUR ANALYTIK DER 1,2-GLYKOLE UND POLYOXYVERBINDUNGEN, VII

BESTIMMUNG VON MELIBIOSE ÜBER DEN BEI DER OXYDATION MIT PERJODAT GEBILDETEN TRIALDEHYD

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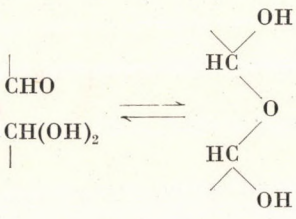
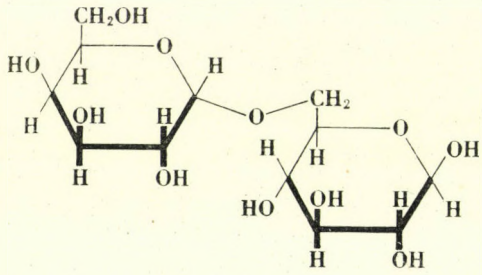
Bei der Oxydation der Disaccharide mit Perjodat bilden sich vorübergehend Polyaldehyde [1]. Nach allgemeiner Erfahrung kann die charakteristische Carbonylbande in den Infrarotspektren dieser Aldehyde nicht nachgewiesen werden, und auch ihre Reaktion mit Oxoreagenzien ist vermindert. Diese Tatsache erklären die Autoren mit der Bildung einer »Hemialdalbindung« zwischen den räumlich günstig stehenden Aldehydgruppen.



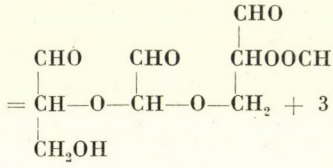
(1)

Die Oxydation der Melibiose mit Perjodat haben zahlreiche Autoren untersucht. Diese Untersuchungen dienten aber nur zur Klärung des Mechanismus der qualitativen Oxydation, zur Charakterisierung der Zwischen- und Endprodukte. Erfahrungsgemäß bildet sich in saurer Lösung auch während 1—2tägiger Oxydation kein Formaldehyd [2, 3], was die Melibiose mit ihrer 1 → 6 Glykosidbindung von den aus Aldohexosen aufgebauten Disacchariden mit 1 → 4 Glykosidbindung scharf unterscheidet. Die Oxydation der Disaccharide mit Perjodat wurde von GUERNET und Mitarbeitern [4, 5, 6, 7] eingehend untersucht. Bei der Melibiose stellten sie fest, daß mit der modifizierten BOUGALTschen Oxydationsmethode [8] nur eine Aldehydgruppe des während der Oxydation gebildeten und isolierbaren Trialdehyds bestimmt werden kann. Nach Ansicht der genannten Autoren liegen zwei Aldehydgruppen des Trialdehyds in Hemialdalbindung, die dritte in hydratisierter Form vor.

In Kenntnis der Regeln der Oxydation von Polyhydroxyverbindungen mit Perjodat kann die Oxydation der Melibiose mit nachstehender Gleichung beschrieben werden:



$+ 5\,IO_4^- =$



$+ 3\,HCOOH + 5\,IO_3^- + 2\,H_2O$ (2)

Zur weiteren Oxydation des so gebildeten Trialdehyds mit Perjodat kann es unter den üblichen Versuchsbedingungen nur dann kommen, wenn die Formylester-Bindung und die Acetalbindungen durch Hydrolyse gespalten werden. Die während der eventuellen Hydrolyse entstandenen 2 Moleküle Glycerinaldehyd und 1 Molekül Glyoxal reagieren mit weiteren 5 Molekülen Perjodat und es bilden sich 2 Moleküle Formaldehyd.

Im Laufe der orientierenden Untersuchungen wurde die Melibiose bei Zimmertemperatur in Lösungen von $p_H \approx 1$, $p_H \approx 4$ und $p_H \approx 8$ oxydiert. Das Molverhältnis von Perjodat zu Melibiose war in allen untersuchten Fällen 12 : 1. — Die Meßergebnisse sind in den Tabellen I, II und III zusammengefaßt.

Tabelle I

Messungen in perjodsaurer Lösung ($p_H \approx 1$)

Oxydationszeit	Während der Oxydation verbrauchte	Während der Oxydation gebildete	
	Mol. Perjodat / Mol. Melibiose	Mol. Aldehyd / Mol. Melibiose	Mol. Ameisensäure / Mol. Melibiose
5 Min.	4,50	1,78	2,52
10 ,,	4,67	2,81	3,02
20 ,,	5,51	2,82	3,36
40 ,,	5,83	2,95	
60 ,,	6,03	2,96	3,97
90 ,,	6,18	2,97	4,34
120 ,,	6,18	2,95	4,42
240 ,,	6,28	2,96	4,64
24 St.	6,25	2,89	4,83

Tabelle II

Messungen in gepufferter essigsaurer Lösung ($p_H \approx 4$)

Oxydationszeit	Während der Oxydation verbrauchte Mol. Perjodat / Mol. Melibiose	Während der Oxydation gebildete Mol. Aldehyd / Mol. Melibiose
5 Min.	4,22	2,79
20 ,,	5,35	2,96
40 ,,	5,70	2,97
60 ,,	5,84	2,97
90 ,,	5,93	2,96
120 ,,	6,01	2,96
240 ,,	6,08	2,98
24 St.	6,23	2,78

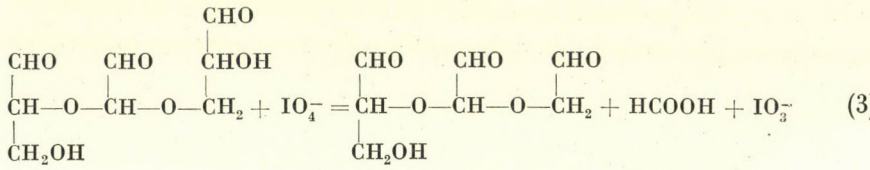
Tabelle III

Messungen in mit $NaHCO_3$ gepufferter Lösung ($p_H \approx 8$)

Oxydationszeit	Während der Oxydation verbrauchte Mol. Perjodat / Mol. Melibiose	Während der Oxydation gebildete Mol. Aldehyd / Mol. Melibiose
5 Min.	3,88	2,11
10 ,,	4,93	2,11
20 ,,	6,05	2,26
40 ,,	6,15	2,41
60 ,,	6,28	2,73
90 ,,	6,47	2,70
120 ,,	6,73	2,72
240 ,,	6,70	2,58
24 St.	7,76	2,54
48 ,,	8,95	2,16
72 ,,	9,36	1,68
96 ,,	—	1,60
144 ,,	—	1,52

Das Perjodat wurde mit dem jodometrischen Verfahren von MÜLLER und WEGELIN [9], die Ameisensäure (nach Reduktion des Perjodat-Überschusses mit Äthylenglykol) acidimetrisch und der Aldehyd mit dem von uns empfohlenen jodometrischen »Bisulfit-Cyanid« -Verfahren bestimmt [10—15].

Wie aus den Daten der Tabellen ersichtlich ist, bilden sich eindeutig 3 Aldehydgruppen schon nach verhältnismäßig kurzdauernder Oxydation, und diese Aldehyd-Menge ändert sich innerhalb der untersuchten Oxydationsdauer von 40—240 Min. nicht mehr. Durch Vergleich dieser Angaben mit der Menge der im Laufe der gleichen Zeit gebildeten Ameisensäure (Tabelle I) kann festgestellt werden, daß die Formylestergruppe des nach Gleichung (2) gebildeten Trialdehyds in saurer Lösung nicht schnell hydrolysiert. Zur Reaktion des sechsten Moleküls Perjodat kommt es nach dieser Hydrolyse:



(3)

Der so gebildete Trialdehyd kann als das stabile Endprodukt der Oxydation betrachtet werden. Hierauf kann eigentlich auch auf Grund der Untersuchungsergebnisse von GUERNET und Mitarbeitern geschlossen werden; vom analytischen Gesichtspunkte ist aber jene Erfahrung von entscheidender Bedeutung, daß der Trialdehyd mit 3 Molekülen Bisulfit ein Aldehyd-Bisulfit bildet und mit dem jodometrischen »Bisulfit-Cyanid«-Verfahren bestimmt werden kann.

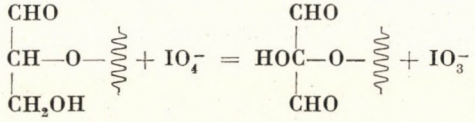
Die im Laufe der Reaktion gebildete Ameisensäure wurde im Zusammenhang mit den in perjodsauerer Lösung durchgeführten Oxydationen bestimmt. Es ist auffallend, daß die Ameisensäure-Zahl, neben der längere Zeit hindurch beobachteten konstanten Aldehyd-Zahl, monoton steigt. Auf Grund der Reaktionsgleichungen (2) und (3) kann nach dem der Hydrolyse der Formylester-Gruppe folgenden Perjodatverbrauch von 6 Molen ein Perjodat: Aldehyd: Ameisensäure Verhältnis von 6 : 3 : 5 erwartet werden. Das gemessene Verhältnis betrug aber nach 60 Min. dauernder Oxydation 6 : 3 : 4. Die genaue Erklärung des Ameisensäure-Mangels ist nicht bekannt, wir haben aber allgemein die Erfahrung gemacht, daß bei den Cyclohalbacetal-Kohlehydraten, aus denen sich während der Oxydation immer Formylester-Gruppen bilden, in jedem Fall ein bedeutender Mangel an Ameisensäure beobachtet werden kann. Aus Tabelle I ist auch ersichtlich, daß sich die Ameisensäure-Zahl nach längerer Wartezeit bedeutend erhöht, 5 Moleküle können aber auch nach 24 Stunden dauernder Oxydation nicht erreicht werden. Auf Grund des Verbrauchs an Perjodat kann eine geringgradige »Überoxydation« beobachtet werden, die Aldehyd-Zahl ändert sich jedoch nicht weiter.

Auf Grund der Ergebnisse der in essigsaurer Lösung vorgenommenen Oxydationen kann festgestellt werden, daß mit der Bisulfit-Cyanid-Methode beide Trialdehyde (auf der rechten bzw. linken Seite) der Gleichung (3) bestimmt werden können. Diese Tatsache ist vom analytischen Gesichtspunkte

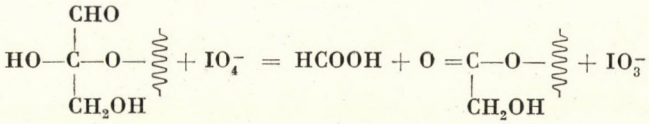
sehr günstig, die Summe der Molzahlen der beiden Aldehyde ist nämlich konstant, woraus folgt, daß die auf der Aldehydmessung beruhende Bestimmung in einem breiten Oxydationszeit-Intervall verwendet werden kann.

Nach den Ergebnissen unserer papierchromatographischen Untersuchungen ist der Trialdehyd nach 4—5 Stunden dauernder Oxydation ein einheitliches Produkt. Charakteristisch für die Stabilität der Acetalbindungen ist, daß der Trialdehyd in salzsaurer Lösung auch nach mehrstündigem Kochen weder eine qualitative (papierchromatographische Untersuchung) noch eine quantitative (Aldehydbestimmung) Änderung erfährt.

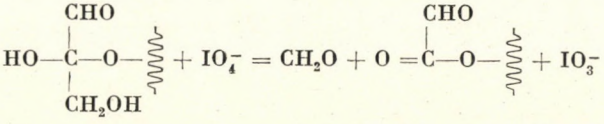
Auf Grund der in $NaHCO_3$-haltiger Lösung ($p_H \approx 8$) ausgeführten Oxydationen kann die Bildung des Trialdehyds nicht als stabiler Endzustand betrachtet werden. Mit der Verlängerung der Oxydationszeit erhöht sich auch der Perjodatverbrauch monoton und die Aldehyd-Zahl nimmt nach Erreichung des Höchstwertes von 2,7 ab. Diese Erfahrung aber kann in keinem Fall als eine Folge der Acetalhydrolyse betrachtet werden. Handelte es sich nämlich um die Acetalhydrolysen und die darauf folgenden α-Hydroxy-Oxo-Oxydationen, so betrüge die Aldehyd-Zahl im Grenzwert 2, da die so vor sich gehende »vollständige Oxydation« 2 Moleküle Formaldehyde liefern würde. Wie aus Tabelle III ersichtlich ist, sinkt die Aldehyd-Zahl nach mehrtägiger Oxydation unter 2, obwohl der Formaldehyd — wie parallele Bestimmungen ergaben — mit dem Perjodat auch während so langer Zeit nicht reagiert. Nach unserer Meinung handelt es sich hier um einen Spezialfall der sog. α-Wasserstoff-Oxydation [16], wo sich aus dem Glycerinaldehyd-Teil des Trialdehyds Glykolsäure-Ester bzw. Glykolsäure bildet, und diese Reaktion verursacht den Mangel an Formaldehyd:



(4)



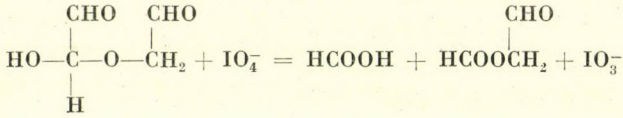
(5)



(6)

Die sich nach Gleichung (4) abspielende α-Wasserstoff-Oxydation ist ein langsamer Vorgang, dem eine rasche α-Hydroxy-Oxo- (Gleichung (5)) bzw. α-Glykol-Oxydation (Gleichung (6)) folgt. — Die Hydrolyse der gebildeten Ester ist schnell, wobei das mit dem Glykolaldehyd gebildete Halbacetal des

Glyoxals entsteht. Diese Verbindung reagiert mit dem Perjodat gleichfalls rasch.



(7)

Die Reihe der stufenweisen Oxydationen schießt die Hydrolyse des Glykolaldehyd-Formylesters und die Oxydation des Glykolaldehyds.

Nach Gleichung (6) bilden sich Glyoxylsäure und Formaldehyd. In schwach alkalischer Lösung reagiert die Glyoxylsäure mit dem Perjodat verhältnismäßig rasch (Ameisensäure und Kohlendioxyd entstehend); die Reaktion nach Gleichung (6) kann bezüglich der auf der Aldehydmessung beruhenden Bestimmung in keinem Fall als störende Nebenreaktion betrachtet werden.

Die nach Gleichung (5) entstehende Glykolsäure ist eines der stabilen Endprodukte der Oxydationen mit Perjodat; woraus folgt, daß aus dem die primäre alkoholische Hydroxylgruppe der Melibiose tragenden Kohlenstoffatom — entgegen der Erwartung — kein Formaldehyd entsteht.

Die in $NaHCO_3$-haltiger Lösung ausgeführte Oxydation der Melibiose mit Perjodat kann als quantitative Bestimmung nicht benützt werden. Die in saurer Lösung vorgenommenen Oxydationen sind aber analytisch gut verwendbar, wobei ein solcher als stabiles Endprodukt zu betrachtender Trialdehyd entsteht, der mit dem jodometrischen »Bisulfit-Cyanid«-Verfahren eindeutig bestimmt werden kann, und zur indirekten Bestimmung der Melibiose geeignet ist. Die Meßergebnisse sind in den Tabellen IV und V zusammengefaßt.

Tabelle IV

Bestimmung der Melibiose über den bei der Oxydation mit Perjodsäure gebildeten Trialdehyd

Einwaage Melibiose, $2H_2O$ g/250,00 ml	Gemessene Lösung, ml	Verbr. 0,1 *n* Jodlösung, ml		Gef. Melibiose, $2H_2O$	
		einzeln	Durchschn.	mg	%
		9,40			
	9,98	9,40	9,40	59,27	98,8
		9,40			
		4,61			
1,5022	4,98	4,62	4,63	20,20	97,6
		4,64			
		1,85			
	2,00	1,86	1,87	11,79	98,2
		1,88			

Tabelle V

Bestimmung der Melibiose über den bei der in gepufferter essigsaurer Lösung vorgenommenen Oxydation mit Perjodat gebildeten Trialdehyd

Einwaage Melibiose, $2H_2O$ g/250,00 ml	Gemessene Lösung, ml	Verbr. 0,1 *n* Jodlösung, ml		Gef. Melibiose, $2H_2O$	
		einzeln	Durchschn.	mg	%
0,4919	9,98	7,80	7,81	49,25	100,3
		7,80			
		7,82			
	4,98	3,90	3,90	24,59	100,4
		3,90			
		3,92			
	2,00	1,55	1,56	9,84	100,0
		1,55			
		1,58			

Beschreibung des Verfahrens

Reagenzien

0,1 *n* Jodlösung
5%ige Jodlösung
0,3 *m* Perjodsäurelösung
1,5 *m* Natriumsulfitlösung
20%ige NaOH-Lösung
20%ige HCl-Lösung
10%ige Essigsäurelösung
1%ige Stärkelösung als Indikator
0,1%ige alkoholische Methylrot-Lösung
Kaliumcyanid (fest)
Pentan

0,5—0,7 Melibiose — analytisch genau gewogen — werden in destilliertem Wasser gelöst. Die Lösung wird in einen 100-ml-Meßkolben gespült und bis zur Marke aufgefüllt. Aus der so vorbereiteten Stammlösung werden 10,00 ml in einen mit Glasstopfen versehenen Erlenmeyerkolben pipettiert und mit 5 ml Perjodsäurelösung versetzt. (Bei Verwendung von Na-Perjodat wird die Lösung mit 1 ml Essigsäurelösung angesäuert.) Nach ca. 1 Stunde läßt man Na-Sulfitlösung mit einer eingeteilten Pipette so lange eintropfen, bis die Farbe des anfangs ausgeschiedenen Jods verschwindet, danach wird noch 1 ml Na-Sulfitlösung zugegeben. Nachher wird in Anwesenheit von Methylrot-Indikatorlösung mit Natronlauge neutralisiert, dann mit 2 ml Essigsäurelösung angesäuert. Der verschlossene Kolben wird mehrmals geschüttelt, um auch das am Schliff haftende Perjodat zu reduzieren. Die möglicherweise erwärmte Lösung wird mit fließendem Wasser abgekühlt und die Oberfläche der Lösung mit 5 ml Pentan überschichtet.

Nach einstündiger Wartezeit wird der Sulfitüberschuß — in Anwesenheit von 10 Tropfen Stärkelösung als Indikator — mit Jodlösung oxydiert. Dies wird anfangs mit 5%iger, zum Schluß aber mit 0,1 *n* Jodlösung vorgenommen. Nach Erreichung der blauen Farbe wird die Lösung im verschlossenen Kolben energisch geschüttelt, wobei der Stopfen von Zeit zu Zeit gelockert wird, um auch das im Schliff haltende Sulfit zu reduzieren. Nötigenfalls wird die Farbe der Lösung mit 0,1 *n* Jodlösung auf beginnende Blaufärbung eingestellt.

Nach Entfernung des Sulfitüberschusses wird die Lösung mit 4 ml Natronlauge alkalisch gemacht und in den Kolben werden 0,2—0,3 g KCN gegeben. Die Lösung wird mäßig gerührt, dann aus einer eingeteilten 10-ml-Pipette mit Salzsäure neutralisiert, wonach noch 1,2—2 ml HCl-Lösung zugegeben werden. Nachher wird ohne überflüssiges Schütteln mit 0,1 *n* Jodlösung titriert. Am Anfang wird die Meßlösung in größeren Anteilen zugegeben, nach Erreichung der blauen Farbe wird im verschlossenen Kolben geschüttelt und wenn nötig, wird durch Zugabe von 1—2 Tropfen Meßlösung bis zur bleibenden blauen Farbe titriert.

Das Äquivalentgewicht der Melibiose ist in der Bestimmung: Molekulargewicht/6. 1 ml 0,1 *n* Jodlösung entspricht 6,305 mg Melibiose krist. ($C_{12}H_{22}O_{11} \cdot 2H_2O$).

ZUSAMMENFASSUNG

Bei der Oxydation der Melibiose mit Perjodat in saurer Lösung bildet sich Trialdehyd, der mit 3 Molekülen Bisulfit ein stabiles Aldehydbisulfit liefert. Zur indirekten Bestimmung der Melibiose wird das von den Verfassern schon früher empfohlene jodometrische »Bisulfit-Cyanid«-Verfahren benützt.

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BEITRÄGE ZUR ANALYTIK DER 1,2-GLYKOLE UND POLYOXYVERBINDUNGEN, VIII

BESTIMMUNG VON MALTOSE, LACTOSE UND CELLOBIOSE ÜBER DEN BEI DER OXYDATION MIT PERJODAT GEBILDETEN ALDEHYD

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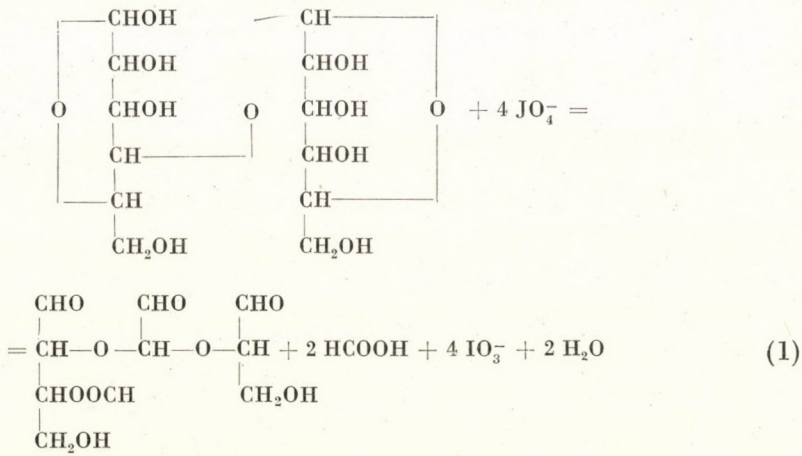
In der VII. Mitteilung dieser Serie* wurde beschrieben, daß der bei der Oxydation der Melibiose mit 1 → 6-Glykosidbindung gebildete Trialdehyd mit 3 Molekülen Bisulfit ein stabiles Aldehyd-Bisulfit bildet und so mit dem »Bisulfit-Cyanid«-Verfahren eindeutig bestimmt werden kann. Die mit Melibiose durchgeführten Untersuchungen führten zu Feststellungen, die eine eingehendere Erklärung der komplizierten Oxydation der Disaccharide mit 1 → 4-Glykosidbindung (in unserem Fall: Maltose, Lactose, Cellobiose) mit Perjodat ermöglichten.

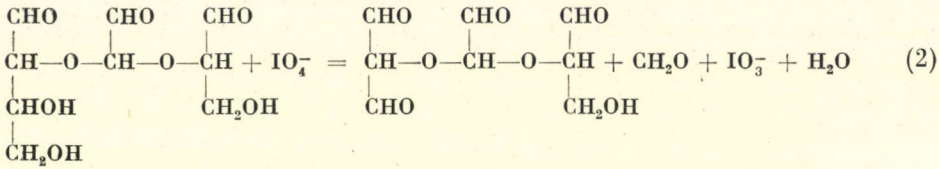
Zu Beginn der Oxydation der aus Aldohexosen aufgebauten Disaccharide mit 1 → 4-Glykosidbindung ist die Bildung eines Trialdehyds sowie von 2 Molekülen Ameisensäure zu erwarten.



$$= \begin{array}{l} CHO \\ | \\ CH-O-CH-O-CH \\ | \\ CHOOCH \\ | \\ CH_2OH \end{array} + 2\,HCOOH + 4\,IO_3^- + 2\,H_2O \qquad (1)$$

Zur Reaktion des fünften Perjodatmoleküls kommt es erst nach der Hydrolyse der am Kohlenstoffatom 3 des Tetrose-Teiles des Trialdehyds befindlichen Formylester-Gruppe.

* Vorangehende Mitteilung in diesem Heft.



(2)

Im Laufe dieser Reaktion bildet sich neben einem Tetraaldehyd 1 Molekül Formaldehyd. Der Tetraaldehyd ist ein mit Glycerinaldehyd und Tartrondialdehyd gebildetes Acetal des Glyoxals. Mit der großen Stabilität der Acetalbindungen ist es zu erklären, daß die weitere Oxydation der 1 → 4-Disaccharide mit Perjodat unter den üblichen Versuchsbedingungen (z. B. bei Zimmertemperatur, in Lösungen von $p_H \approx 1-5$) außerordentlich langsam verläuft.

Nach den Untersuchungen von AHLBORG [1] entsteht im Laufe der in ca. 10%iger schwefelsaurer Lösung bei 50°C durchgeführten Oxydationen mit Perjodat eine den 1 → 4-Disacchariden »proportionale« Jodmenge, bei den 1 → 6-Disacchariden dagegen kann diese Erscheinung nicht beobachtet werden. Nach Ansicht des genannten Autors wird die Jodbildung durch den Tartrondialdehyd hervorgerufen, diese Verbindung ist nämlich ein Isomeres des Triosereduktons nach EULER und MARTIUS [2].



(3)

Sowohl Perjodat als auch Jodat werden durch die Reduktone, als starkes Reduktionsmittel, zu Jod reduziert, die Stöchiometrie der Reaktionen ist aber unbekannt.

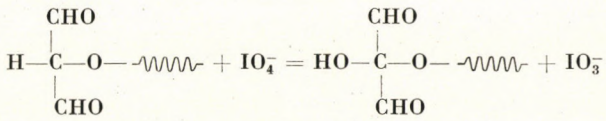
Die Oxydation der Maltose und Lactose mit Perjodat wurde von FLEURY, COURTOIS und RAMET [3, 4, 5, 6] bei Zimmertemperatur untersucht. In sauren Lösungen ($p_H = 1{,}5$ und 2,5) wurde während der 4—16 Tage dauernden Oxydationen die Entstehung von 1,3—1,5 Molekülen Kohlensäure beobachtet. (Aus der Glucose bildete sich 0,1 Molekül Kohlensäure nach 7 Tagen und 0,15 Mol nach 11 Tagen.) Der Perjodatverbrauch betrug dabei 11,2—11,8 Mol, die gebildete Ameisensäure 7,6—9 Mol und die Aldehydmenge 1,7—2,1 Mol.

Auf Grund der Untersuchsergebnisse wurde die Oxydation der 1 → 4-Disaccharide mit Perjodat von den Autoren mit der folgenden allgemeinen Gleichung beschrieben:

$$C_{12}H_{22}O_{11} + 11\ IO_4^- = 2\ CH_2O + 9\ HCOOH + CO_2 + 11\ IO_3^- \qquad (4)$$

Nach übereinstimmenden späteren Feststellungen mehrerer Autoren [7, 8, 9] ist die Kohlensäure ein typisches Produkt der Oxydation aller Saccharide, bei deren Zersetzung sich vorübergehend ein solches Tartron-Dialdehyd-

derivat bildet, in dem die am Kohlenstoffatom 2 befindliche Hydroxylgruppe in Acetalbindung vorliegt. Dieses Acetal reagiert mit dem Perjodat charakteristisch für die 1,3-Dioxoverbindungen direkt, und zwar über die sog. α-Wasserstoff-Oxydation [10].

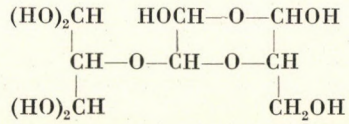


(5)

Dieser verhältnismäßig langsamen Reaktion folgen schnelle α-Hydroxy-Oxo- bzw. α-Dioxo-Oxydationen, und während der damit parallel verlaufenden Hydrolyse bilden sich 2 Moleküle Ameisensäure und 1 Molekül Kohlensäure.

Zur Bestimmung von Maltose, Lactose und Cellobiose über Kohlensäure empfehlen HOUGH und WOODS [9] eine 10—15 stündige Oxydation bei 50°C bei $p_H = 5$. Unter solchen Umständen war die Menge der bei der Oxydation von ca. 1 mg Disaccharid gebildeten Kohlensäure annähernd theoretisch. Die Autoren bedienten sich eines WARBURGschen Apparats zur Bestimmung der Kohlensäure. Der während der Oxydation gebildete Formaldehyd wurde von HOUGH und PERRY [10] mit der chromotropsauren kolorimetrischen Mikromethode bestimmt. In einer Lösung von $p_H = 8$, bei Zimmertemperatur, nach 4stündiger Oxydation, konnten 1,9, 1,85 bzw. 1,9 Mol Formaldehyd im Falle von Maltose, Lactose bzw. Cellobiose gemessen werden.

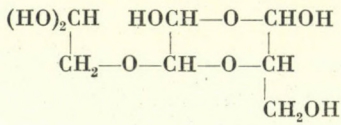
Zu Beginn der sechziger Jahre wurde der Mechanismus der Oxydation der Saccharide von GUERNET und Mitarbeitern [11—15] eingehend untersucht. Im Laufe ihrer Untersuchungen wurden — unter anderen — die bei der partiellen Oxydation gebildeten Polyaldehyde isoliert, und physikalisch (Drehungsvermögen und Schmelzpunkt) sowie chemisch (auf Grund des Hydratationsgrades und Bestimmung der Aldehyd-Zahl) gekennzeichnet. Die Aldehyde wurden mittels der modifizierten Hypojodit-Oxydationsmethode nach BOUGALT bestimmt. Mit dieser Reaktion konnte aber nur sehr wenig Aldehyd gemessen werden. Im Falle des bei der Oxydation von Lactose gebildeten Tetraaldehyds (siehe Gleichung (2)) konnten nur 1,25% der theoretischen Aldehyd-Zahl erhalten werden. Die Autoren schrieben dem bei der Oxydation der 1 → 4-Disaccharide gebildeten Tetraaldehyd die folgende Struktur zu:



(6)

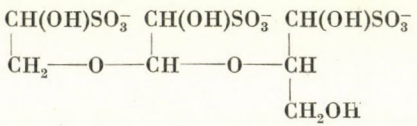
Nach dieser Formel wurde eine Hemialdalbindung zwischen den Aldehydgruppen des Glycerinaldehyds und Glyoxals weiterhin auf Grund des Hydratationsgrades (3 Moleküle Wasser) und des Infrarotspektrums eine geminale

Diol-Struktur der Aldehydgruppen des Tartrondialdehyd-Teiles angenommen· — Ein ähnlicher struktureller Aufbau wurde auch bei dem bei der Oxydation der Melibiose mit 1 → 6-Glykosidbindung entstehenden Trialdehyd festgestellt.



(7)

Nach unseren Untersuchungsergebnissen kann der aus der Melibiose gebildete Trialdehyd in saurer Lösung als ein stabiles Endprodukt der Oxydation betrachtet werden, und alle drei Aldehydgruppen reagieren sehr leicht mit Bisulfit, wobei sich das entsprechende Aldehyd-Bisulfit bildet:



(8)

In $NaHCO_3$-haltiger Lösung ($p_H \approx 8$) reagiert der Trialdehyd mit Perjodat, und die Reaktionsgeschwindigkeit wird durch die Geschwindigkeit der am Kohlenstoffatom 2 des Glycerinaldehyd-Teiles eintretenden α-Wasserstoff-Oxydation bestimmt. Die nachfolgenden relativ schnellen α-Glykol-, und α-Hydroxy-Oxo-Oxydationen sowie die Esterhydrolysen führen zum Abbau des Trialdehyds wobei die Endprodukte — Formaldehyd, Ameisensäure und Glykolsäure — entstehen. Unserer Meinung nach ist die Feststellung dessen wichtig, daß die gebundenen Hydroxy- und Oxogruppen, welche auch die Richtung der weiteren Spaltungsvorgänge bei der Reaktion mit Perjodat bestimmen, nicht bei den Acetal- sondern bei den Esterhydrolysen frei werden.

Die α-Wasserstoff-Oxydation geht in Lösungen von $p_H \approx 8$ schneller vor sich als in mittelmäßig sauren Lösungen ($p_H \approx 1—4$). Diese Tatsache kann auch bei der Untersuchung der Oxydationsgeschwindigkeit der Maltose, Lactose und Cellobiose mit 1 → 4-Glykosidbindung beobachtet werden (Tabelle I, II und III).

Bei diesen Untersuchungen betrug das Molverhältnis Disaccharid : Perjodat in jedem Fall 1 : 12. Aus den Angaben der Tabellen ist sichtlich, daß der vorübergehend entstandene Tetraaldehyd in saurer Lösung auch relativ nicht als ein so stabiles Oxydationsendprodukt betrachtet werden kann als der aus der Melibiose gebildete Trialdehyd. Die nacheinander folgenden Oxydationsstufen fließen in einem solchen Maß zusammen, daß es nicht möglich zu sein scheint, eine analytische Methode auf Grund der partiellen Oxydationen auszuarbeiten. In $NaHCO_3$-haltiger Lösung sind die Oxydationsvorgänge viel schneller, und diese Tatsache wirft die Möglichkeit dessen auf, die Disaccharide mit 1 → 4-Glykosidbindung auf Grund der bei der »totalen Oxydation« gebildeten 2 Moleküle Formaldehyd mit der jodometrischen »Bi-

Tabelle I

Messungen in perjodsaurer Lösung

Oxydationsdauer	Bei der Oxydation verbrauchte Mol. Perjodsäure/Mol. Disaccharid			Bei der Oxydation gebildete Mol. Aldehyd/Mol. Disaccharid			Bei der Oxydation gebildete Mol. Säure/Mol. Disaccharid		
	Maltose	Lactose	Cellobiose	Maltose	Lactose	Cellobiose	Maltose	Lactose	Cellobiose
5 Min.	1,95	2,22	1,07	1,28	1,55	0,80	0,95	1,14	0,69
10 „	2,61	2,81	1,33	1,69	1,92	1,24	1,29	1,45	0,95
20 „	3,18	3,44	2,13	2,06	2,15	1,49	1,63	1,77	1,37
40 „	3,71	3,77	2,93	2,43	2,30	1,87	1,91	1,88	1,79
60 „	4,16	4,13	3,44	2,48	2,59	2,35	2,14	2,08	2,05
90 „	—	4,45	4,09	2,48	2,59	2,53	—	2,43	2,52
120 „	4,92	4,69	4,45	2,48	2,68	2,66	2,48	2,47	2,79
240 „	6,50	5,86	5,82	2,68	2,73	2,89	3,81	3,65	4,01
24 St.	10,10	10,28	10,03	2,10	2,26	2,08	7,28	8,40	7,73

Tabelle II

Messungen in gepufferter essigsaurer Lösung

Oxydationsdauer	Bei der Oxydation verbrauchte Mol. Perjodsäure/Mol. Disaccharid			Bei der Oxydation gebildete Mol. Aldehyd/Mol. Disaccharid		
	Maltose	Lactose	Cellobiose	Maltose	Lactose	Cellobiose
5 Min.	2,70	2,51	1,36	1,85	1,84	0,98
10 „	3,28	2,95	2,02	2,17	2,08	1,49
20 „	4,23	3,29	2,46	2,50	2,19	1,87
40 „	4,56	3,62	3,24	2,50	2,32	2,24
60 „	4,85	3,91	3,77	2,50	2,51	2,40
90 „	—	4,22	3,98	2,53	2,49	2,51
120 „	5,20	4,34	4,00	2,43	2,49	2,55
240 „	6,42	4,34	4,29	—	2,49	2,66
24 St.	6,36	4,91	4,77	2,06	2,52	2,31
48 „	6,56	—	—	2,10	—	—

sulfit-Cyanid« Methode zu bestimmen. Nach den Daten der Tabelle III weichen die Oxydationsgeschwindigkeiten — wenn auch nur in geringem Maße — von einander ab. Unsere erste Beurteilung war, daß diese, auf sterische Faktoren zurückführbare Verschiedenheit, die beim Vergleich der bei Maltose und Cellobiose erhaltenen Werte besonders gut beobachtbar ist, nur bezüglich der richtigen Wahl der zur totalen Oxydation notwendigen Zeit wichtig ist. Auf Grund

Tabelle III

Messungen in mit $NaHCO_3$ gepufferter Lösung

Oxydationsdauer	Bei der Oxydation verbrauchte Mol. Perjodsäure/Mol. Disaccharid			Bei der Oxydation gebildete Mol. Aldehyd/Mol. Disaccharid		
	Maltose	Lactose	Cellobiose	Maltose	Lactose	Cellobiose
5 Min.	4,04	3,33	2,86	1,61	1,51	1,29
10 ,,	5,25	4,35	3,91	1,97	2,13	1,91
20 ,,	6,90	5,67	5,44	1,96	2,42	2,22
40 ,,	8,35	7,72	7,80	1,96	2,37	2,35
60 ,,	9,23	8,62	8,40	2,00	2,28	2,40
90 ,,	9,72	9,45	8,82	2,00	2,21	2,43
120 ,,	9,88	10,02	9,00	2,00	2,13	2,43
240 ,,	10,00	10,50	9,37	2,00	2,08	2,38
24 St.	10,80	11,30	10,40	2,00	1,92	1,96

dieser Überlegungen wurden die Maltose, die Lactose bzw. die Cellobiose über jene Aldehydmengen bestimmt, welche während 2-, 5- bzw. 24stündiger, in $NaHCO_3$-haltiger Lösung ausgeführter Oxydation entstanden. Die Meßergebnisse sind in den Tabellen IV, V und VI zusammengestellt.

Tabelle IV

Bestimmung der Maltose in mit $NaHCO_3$ gepufferter Lösung bei der Oxydation mit Perjodat gebildeten Formaldehyd

Einwaage Maltose, g/500,00 ml	Eingemessene Lösung, ml	Verbrauchte 0,1 *n* Jodlösung, ml		Gef. Maltose	
		einzeln	Durchschn.	mg	%
2,1231	20,06	9,78 9,85 9,87 9,86	9,84	84,21	98,9
	10,00	4,86 4,87 4,89 4,84	4,87	41,68	98,1
	4,98	2,49 2,43 2,46 2,43	2,45	20,97	99,2

Tabelle V

Bestimmung der Lactose in mit $NaCHO_3$ gepufferter Lösung bei der Oxydation mit Perjodat gebildeten Formaldehyd

Einwaage Lactose, H_2O g/200,00 m	Eingemessene Lösung, ml	Verbrauchte 0,1 *n* Jodlösung, ml		Gef. Lactose, H_2O	
		einzeln	Durchschn.	mg	%
		9,75			
	20,00	9,75	9,75	87,83	97,5
		9,75			
		4,80			
0,9005	9,99	4,88	4,87	43,87	97,5
		4,86			
		2,35			
	4,98	2,40	2,38	21,44	95,6
		2,35			

Tabelle VI

Bestimmung der Cellobiose in mit $NaHCO_3$ gepufferter Lösung über den bei der Oxydation mit Perjodat gebildeten Formaldehyd

Einwaage Cellobiose g/200,00 ml	Eingemessene Lösung, ml	Verbrauchte 0,1 *n* Jodlösung, ml		Gef. Cellobiose	
		einzeln	Durchschn.	mg	%
		9,65			
	19,96	9,60	9,63	82,41	97,4
		9,63			
		4,55			
0,8475	9,98	4,50	4,55	38,94	92,1
		4,60			
		2,20			
	5,04	2,25	2,22	19,00	88,9
		2,20			

Die Ergebnisse der Maltosebestimmung sind analytisch befriedigend. Unter Berücksichtigung dessen, daß auch die Glucose über den während der Oxydation mit Perjodat gebildeten Formaldehyd eindeutig bestimmt werden kann, ergab sich eine neue Möglichkeit zur Bestimmung beider Verbindungen nebeneinander. Glucose und Maltose können nämlich mit der durch KOLT-

HOFF [16] modifizierten Methode nach WILLSTÄTTER—SCHUDEL mit befriedigender Genauigkeit bestimmt werden, und so kann man die Menge der Glucose und Maltose auf Grund der verschiedenen Äquivalentgewichte der Maltose bei den einzelnen Methoden berechnen. (Die Ergebnisse der Glucosebestimmung sind in Tabelle VII gezeigt.)

Tabelle VII

Bestimmung von Glucose in mit $NaHCO_3$ gepufferter Lösung über den bei der Oxydation mit Perjodat gebildeten Formaldehyd

Einwaage Glucose, H_2O g/100,00 ml	Eingemessene Lösung, ml	Verbrauchte 0,1 *n* Jodlösung, ml		Gef. Glucose, H_2O	
		einzeln	Durchschn.	mg	%
		9,74			
	9,98	9,75	9,73	96,40	99,8
		9,72			
		4,90			
0,9682	5,04	4,85	4,88	48,36	99,1
		4,88			
		1,91			
	2,00	1,94	1,93	19,12	98,8
		1,95			

Die Meßergebnisse bei Lactose, besonders aber bei Cellobiose sind jedoch nicht befriedigend. Bei kleineren Einwaagen, d. h. bei proportionaler Erhöhung des Perjodatüberschusses erhält man viel zu niedrige Werte.

Eine ähnliche Erscheinung konnte auch bei der in $NaHCO_3$-haltiger Lösung ausgeführten Oxydation der Melibiose beobachtet werden. Wir fanden, daß es sich hier nicht um die Oxydation des primär gebildeten Formaldehyds handelt, sondern es bildet sich während der der α-Wasserstoff-Oxydation des Glycerinaldehyd-Teils folgenden α-Hydroxy-Oxo-Oxydation Glykolsäure als stabiles Endprodukt und darauf kann der Formaldehyd-Mangel zurückgeführt werden.

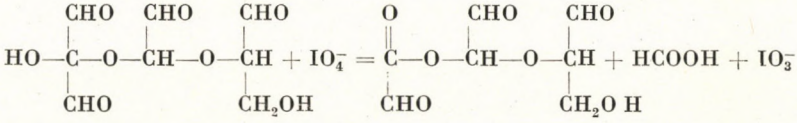
Mit dieser Oxydation kann auch der bei Cellobiose beobachtete Formaldehyd-Mangel erklärt werden. Die »totale Oxydation« von Cellobiose und Maltose ist ein langsamer Prozeß. Der aus der Melibiose gebildete Trialdehyd (Formel 7) wird jedoch erheblich langsamer oxydiert als der aus der Cellobiose gebildete Tetraaldehyd (Formel 6), und man kann dabei nach der Oxydation im ersteren Fall einen größeren Aldehyd-Mangel beobachten als im letzteren. Auf Grund der Untersuchungsergebnisse kann bezüglich des Mechanismus der

Oxydation von 1 → 4-Disacchariden mit Perjodat folgendes festgestellt werden:

1. Vom quantitativanalytischen Gesichtspunkte betrachtet ist bei der bis zum Tetraldehyd gehenden Oxydation mit keinem anomalen Prozeß zu rechnen (Gleichungen (1) und (2)).

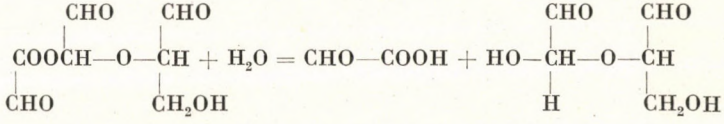
2. Die Acetalbindungen des Tetraaldehyds werden durch direkte Hydrolyse nicht gespalten.

3. Die Oxydation des Tetraaldehyds beginnt mit der α-Wasserstoff-Oxydation des Tartrondialdehyd-Teiles (Gleichung (5)). Die so gebildete Verbindung kann mit Perjodat auch unmittelbar reagieren:

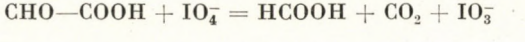


(9)

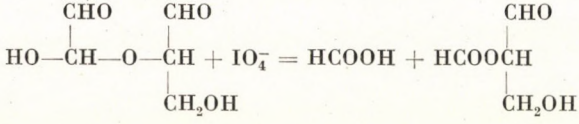
In diesem Fall ist der weitere Vorgang eine Reihe von mit Esterhydrolysen und Spaltungen der C—C-Bindungen verbundenen Oxydationen mit Perjodat.



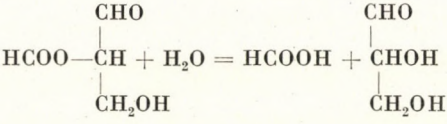
(10)



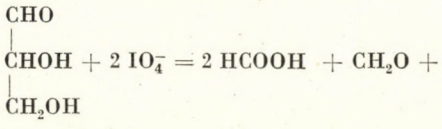
(11)



(12)



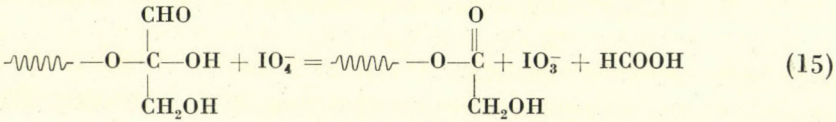
(13)



(14)

Durch Zusammenziehen der Gleichungen 1 und 2 sowie 9—14 ergibt sich die Gleichung 4, welche — wie aus den Meßergebnissen hervorgeht — von beschränkter Gültigkeit ist, vom Gesichtspunkte der Aldehydbestimmung aber den Forderungen der quantitativen Analytik am besten entspricht.

4. Nach Beendigung der Oxydation kann ein Formaldehyd-Mangel nur dann beobachtet werden, wenn die Geschwindigkeit der α-Wasserstoff-Oxydation des Glycerinaldehyd-Teiles neben den mit den Gleichungen (9—14) charakterisierten Teilvorgängen nicht vernachläßigt werden kann. In diesem Fall ist es nämlich infolge der Hydroxy-Oxo-Oxydation des gebildeten Hydroxy-Methyl-Glyoxal-Derivates möglich, daß sich Glykolsäure bildet, weshalb aus der Hydroxy-Methyl-Gruppe kein Formaldehyd entsteht.



(15)

Nach den Ergebnissen der Untersuchungen ist die α-Wasserstoff-Oxydation des Glycerinaldehyd-Teiles, im Vergleich zur ähnlichen Oxydation des Tartrondialdehyd-Teiles, ein sehr langsamer Prozeß. Die sich bei der Geschwindigkeit der Oxydation von Maltose bzw. Cellobiose zeigende Abweichung kann — wie schon erwähnt wurde — auf sterische Gründe zurückgeführt werden. Auch die Raumkonfiguration der aus diesen Verbindungen gebildeten Tetraaldehyde ist abweichend, weshalb die Bildung eventueller Hemialdalbindungen in verschiedenem Maße ermöglicht ist. Mit dem gemeinsamen Einfluß dieser Faktoren kann erklärt werden, daß die α-Wasserstoff-Oxydation des Tartrondialdehyd-Teiles des Tetraaldehyds bei der Cellobiose bedeutend langsamer ist, deshalb tritt die α-Wasserstoff-Oxydation des Glycerinaldehyd-Teiles bzw. der daraus stammende Formaldehyd-Mangel, bei größerem Perjodat-Überschuß in stärkerem Maße auf.

5. Die Ergebnisse der in sauren ($p_H \approx 1$ bzw. $p_H \approx 4$) Lösungen vorgenommenen Oxydationen weisen darauf hin, daß die Disaccharide nach 1—2-stündiger Oxydation mit etwa 5 Molekülen Perjodat reagieren. Dies bedeutet, daß sich praktisch die Vorgänge nach den Reaktionengleichungen (1) und (2) abspielen, d. h. man kann mit der Anwesenheit des Tetraaldehyds und eines Moleküls Formaldehyd rechnen. An Stelle der ca. 5 Moleküle Aldehyd konnten mit dem »Bisulfit-Cyanid«-Verfahren aber nur ca. 2,5 Moleküle Aldehyd gemessen werden was auch so bedeutend mehr ist, als die von GUERNET und Mitarbeitern, bei den mit Lactose ausgeführten Untersuchungen erhaltene Menge.

Zieht man die Ergebnisse der Aldehydbestimmung, des Perjodatverbrauches, sowie der Ameisensäurebestimmung in Betracht, so kann festgestellt werden, daß auf diesem Grad der Oxydation bei den Tetraaldehyden eine relativ stabile Hemialdalbindung bzw. eine andersartige Bindung, z. B. eine neuere Acetalbindung zustande kommt. Durch Kondensationsprozesse, zwischen Formaldehyd und den gelockerten Wasserstoffatomen des Tartrondialdehydanteils können solche dimeren Tetraaldehyde gebildet werden, die durch Methylen-

brücken verbunden sind. Dadurch wird die Menge der meßbaren Aldehyde vermindert, aber auch die Oxydation des Tetraaldehyds gehindert, da dieser Vorgang gerade durch die einfache Oxydation des gelockerten Wasserstoffs mit Perjodat eingeleitet wird. Auf Grund der orientierenden papierchromatographischen Untersuchungen kann nach einer ungefähr bis zum Tetraaldehyd geführten Oxydation ein Polyaldehydfleck von größerem Molekulargewicht unter einem langgestreckten Polyaldehydfleck von kleinerem Molekulargewicht beobachtet werden. Die Versuche zur Hydrolyse der Polyaldehyde waren erfolglos: die nach einer auf dem Wasserbad bei 100°C in 1 *n* salzsaurer Lösung vorgenommenen zweistündigen Hydrolyse gemessenen Aldehyd-Zahlen stimmten bei allen drei Disacchariden mit den ohne Hydrolyse erhaltenen Aldehyd-Zahlen überein.

Die Untersuchung der Oxydationsgeschwindigkeit zeigte, daß die Oxydation der Tetraaldehyde in einer Lösung mit $p_H \approx 4$ am langsamsten ist. Dies ist auch verständlich, wenn man bedenkt, daß die Geschwindigkeit der Esterhydrolysen hier die geringste ist. Diese Vorgänge verlaufen in gepufferter alkalischer Lösung am schnellsten, die Oxydation kann aber wegen der unter Punkt 4 beschriebenen Nebenreaktionen bei der Lactose und Cellobiose analytisch nicht genützt werden.

Neuartige und auch analytisch brauchbare Resultate wurden bei den in stark saurer ($p_H \approx 0$) Lösung ausgeführten Oxydationen erhalten. Die Ergebnisse dieser Untersuchungen sind in Tabelle VIII zusammengefaßt.

Das Perjodat wurde in diesem Fall durch Eintragen von KJ in den Kolben (nach der in saurer Lösung durchgeführten Reaktion mit Perjodat) und nachfolgender Titration des ausgeschiedenen Jods mit $Na_2S_2O_3$-Meßlösung bestimmt.

Tabelle VIII

Bestimmungen in 7%iger schwefelsaurer perjodsäurehaltiger Lösung

Oxydationszeit	Während der Oxydation verbrauchte Mol. Perjodsäure/Mol. Disaccharid			Während der Oxydation gebildete Mol. Aldehyd/Mol. Disaccharid		
	Maltose	Lactose	Cellobiose	Maltose	Lactose	Cellobiose
5 Min.	1,47	1,77	1,01	1,38	1,17	0,77
20 „	—	—	—	2,18	2,17	1,62
40 „	—	—	—	2,63	2,72	2,23
60 „	—	—	—	2,81	2,89	2,57
90 „	7,35	8,10	6,65	2,86	2,93	2,71
120 „	8,04	8,79	7,40	2,86	2,96	2,83
180 „	8,65	9,33	8,71	2,86	2,96	2,87
240 „	8,82	9,49	9,42	2,86	2,91	2,92
24 St.	9,10	10,20	10,10	—	—	—

Auf Grund der Ergebnisse geht die Oxydation in 4 Stunden praktisch zu Ende, während der 2—4 stündigen Oxydation können mit sehr guter Annäherung 3 Moleküle Aldehyd gemessen werden. Auf Grund des Perjodatverbrauches und der Aldehyd-Zahlen sind wir der Ansicht, daß die zum Perjodatverbrauch von ca. 10 Molekülen entsprechenden 3 Moleküle Aldehyd aus 2 Molekülen Formaldehyd und 1 Molekül Glyoxylsäure zusammengesetzt sind. Die in der Gleichung (11) angegebene Oxydation der Glyoxylsäure mit Perjodat geht in stark saurer Lösung — unserer Meinung nach — sehr langsam vor sich und kann, als Aldehyd, mit dem »Bisulfit-Cyanid«-Verfahren genau gemessen werden [16].

Jene Erfahrung, wonach sich die Aldehyd-Zahl im Laufe des kontinuierlichen Verbrauches der letzten 3 Moleküle Perjodat praktisch nicht mehr ändert, ist darauf zurückzuführen, daß der nach Gleichung (12) gebildete Glycerinaldehyd-2-formylester, der bei seiner Hydrolyse entstehende Glycerinaldehyd sowie der vorübergehend gebildete Glykolaldehyd mit dem »Bisulfit-Cyanid«-Verfahren gleichermaßen bestimmt werden kann. Das zweite Mol Formaldehyd bildet sich aus dem Glycerinaldehyd-2-formylester und so ist, mit Rücksicht auf die als Zwischenprodukte gebildeten Aldehyde, die Summe der Mole in der letzten Phase der Oxydation konstant. Diese Resultate stimmen mit den früheren, auf die Oxydation der Glucose mit Perjodat bezüglichen Meßergebnissen überein. Der Glycerinaldehyd-2-formylester ist auch ein Zwischenprodukt der Oxydation der Glucose.

Auch unmittelbar kann bewiesen werden, daß ein Molekül von den bei der Oxydation in stark saurer Lösung ($p_H \approx 0$) gebildeten drei Molekülen Aldehyd eigentlich freie Glyoxylsäure ist. Die Glyoxylsäure kann nämlich in essigsaurer Lösung verhältnismäßig schnell oxydiert werden (die Reaktion läuft in 1—2 Stunden vollkommen ab), gleichzeitig zeigen die Daten der Tabelle III, daß der nach Gleichung 9 gebildete Ester sehr langsam hydrolysiert wird und mit Perjodat gar nicht reagiert. Im Laufe der in sehr stark saurer Lösung begonnenen und dann in essigsaurer Lösung fortgesetzten Oxydation kann die freie Glyoxylsäure quantitative oxydiert werden, der eventuell anwesende Ester bleibt aber unverändert. Die Ergebnisse solcher Untersuchungen sind in Tabelle IX zusammengefaßt. Bei den Versuchen wurden die Disaccharide, verschieden lange Zeit, in 7%iger schwefelsaurer Lösung oxydiert, nachher wurde die Oxydation in essigsaurer Lösung von etwa $p_H = 4$ zwei Stunden lang fortgesetzt.

Wie aus den Daten der Tabelle hervorgeht, enthält die Lösung nach dreistündiger Oxydation in schwefelsaurem Medium und zweistündiger Oxydation in essigsaurem Medium keine Glyoxylsäure bzw. keinen Ester. Die Aldehyd-Zahl ist bei allen drei Disacchariden innerhalb der 3—24 Stunden dauernden Oxydation in schwefelsaurem Medium konstant. Dies bedeutet, daß sich während der unter solchen Umständen vorgenommenen Oxydationen ganz

Tabelle IX

Messungen in 7%iger schwefelsaurer perjodsaurer, nachher in gepufferter essigsaurer perjodsaurer Lösung

Oxydationszeit in schwefelsaurer Lösung, und nachher 2 St. in essigsaurer Lösung	Während der Oxydation gebildete Mol.-Aldehyd/ Mol.-Disaccharid		
	Maltose	Lactose	Cellobiose
5 Min.	2,27	2,32	2,40
20 ,,	2,22	2,47	2,37
40 ,,	2,04	2,04	2,28
60 ,,	2,00	1,94	2,19
90 ,,	1,98	1,95	2,04
120 ,,	1,98	1,94	2,00
180 ,,	1,99	1,94	1,93
240 ,,	1,94	1,94	1,94
24 St.	1,99	1,94	1,94

eindeutig 2 Moleküle Formaldehyd bilden, d. h. daß mit der störenden Nebenreaktion nach Gleichung 15 bei keinem 1 → 4-Disaccharid zu rechnen ist. Die nach der in schwefelsaurer Lösung 3 Stunden lang und in essigsaurer Lösung 2 Stunden lang geführten Oxydation ausgeführten Aldehydmessungen können zur Bestimmung von Maltose, Lactose und Cellobiose mit großer Genauigkeit verwendet werden. Die Meßergebnisse sind in den Tabellen X, XI und XII zusammengefaßt.

Nach unseren orientierenden Untersuchungen entstehen mit guter Näherung 3 Moleküle Aldehyd bei der in schwefelsaurer Lösung ($p_H \approx 0$) vor-

Tabelle X

Bestimmung von Maltose über den bei der 3stündigen schwefelsauren und nachfolgenden gepufferten essigsauren Oxydation mit Perjodat gebildeten Formaldehyd

Einwaage Maltose,H_2O g/200,0 ml	Eingemessene Lösung, ml	Verbrauchte 0,1 *n* Jodlösung, ml		Gef. Maltose, H_2O	
		einzeln	Durchschn.	mg	%
1,8006	9,98	9,96 9,96	9,96	89,52	99,8
	5,00	5,00 5,00	5,00	45,04	100,0
	2,00	2,00 2,00	2,00	18,02	100,0

Tabelle XI

Die Bestimmung von Lactose über den bei der 3stündigen schwefelsauren und nachfolgenden gepufferten essigsauren Oxydation mit Perjodat gebildeten Formaldehyd

Einwaage Lactose, H_2O g/200,00 ml	Eingemessene Lösung, ml	Verbrauchte 0,1 *n* Jodlösung, ml		Gef. Lactose, H_2O	
		einzeln	Durchschn.	mg	%
1,8001	10,00	9,95 9,95	9,95	89,63	99,6
	5,00	4,97 4,96	4,97	44,76	99,4
	2,00	2,00 2,00	2,00	18,02	100,1

Tabelle XII

Die Bestimmung von Cellobiose über den bei der 3stündigen schwefelsauren und nachfolgenden gepufferten essigsauren Oxydation mit Perjodat gebildeten Formaldehyd

Einwaage Cellobiose, g/200,0 ml	Eingemessene Lösung, ml	Verbrauchte 0,1 *n* Jodlösung, ml,		Gef. Cellobiose	
		einzeln	Durchschn.	mg	%
1,7103	10,00	9,72 9,76	9,74	83,35	97,5
	5,00	4,90 4,88	4,89	41,85	97,9
	2,00	1,96 1,95	1,96	16,77	98,1

genommenen Oxydation. Die eingehende Untersuchung der Möglichkeiten der Bestimmung über die 3 Moleküle Aldehyd ergab aber keine vollkommen befriedigenden Resultate. Auf Grund der Bestimmung des Perjodatüberschusses und der Aldehyde kann nur bei der Lactose behauptet werden, daß der mit der Bildung von 2 Molekülen Formaldehyd und 1 Molekül Glyoxylsäure vor sich gehende Oxydationsvorgang eindeutig ist (siehe Tabelle VIII)

$$C_{12}H_{22}O_{11} + 10IO_4^- = 2CH_2O + CHO - COOH + 8HCOOH + 10IO_3^-.$$

Wie aus der Tabelle XIII hervorgeht, kann die Lactose im Oxydationsintervall von 120—240 Min. auch über die 3 Moleküle Aldehyd genau bestimmt werden.

Tabelle XIII

Bestimmung von Lactose über die bei der Oxydation mit Perjodat gebildeten 2 Moleküle Formaldehyd und 1 Molekül Glyoxylsäure

Oxydationszeit	Einwaage Lactose, H_2O g/200,0 ml	Eingemessene Lösung, ml	Verbrauchte 0,1 *n* Jodlösung, ml		Gef. Lactose, H_2O	
			einzeln	Durchschn.	mg	%
2 St.		10,00	14,84 14,87	14,86	89,24	99,9
		5,00	7,42 7,35	7,39	44,38	98,6
		2,00	2,93 2,92	2,93	17,60	97,8
3 St.	1,8001	10,00	14,82 14,82	14,82	89,00	98,9
		5,00	7,46 7,45	7,46	44,74	99,4
4 St.		10,00	14,70 14,75	14,72	88,40	98,2
		5,00	7,32 7,27	7,30	43,84	97,4
		2,00	2,93 2,90	2,92	17,54	97,4

Diese Erfahrung ist analytisch gesehen von großer Bedeutung. Die Bestimmung über 3 und 2 Moleküle Aldehyd kann nämlich zur Bestimmung von Lactose neben Glucose und Galactose verwendet werden. Der Unterschied zwischen den beiden Aldehydbestimmungen ist in diesem Fall der Menge der Lactose proportional (aus den Monosacchariden bildet sich je ein Molekül Formaldehyd bei beiden Oxydationen).

In Falle von Maltose und Cellobiose ist die über die 3 Moleküle Aldehyd vorgenommene Bestimmung mit einem negativen Fehler von 2—6% verbunden. Der Fehler kann auf die die α-Wasserstoff-Oxydation des Tartrondialdehyd-Teils und auf die Bildung der Glykolsäure störende Nebenreaktion zurückgeführt werden. Unserer Meinung nach kann von einer eingehenderen Untersuchung dieser Frage wegen ihrer Kompliziertheit kein analytisch besonders wertvolles Resultat erhofft werden. Unserer Erfahrung nach tritt nämlich eine minimale Jodbildung (0,1—0,2 Äquivalente) auch bei Zimmertemperatur ein,

Tabelle XIV

Bestimmung von Maltose über die bei der Oxydation mit Perjodat gebildeten 2 Moleküle Formaldehyd und 1 Molekül Glyoxylsäure

Oxydationszeit	Einwaage Maltose, H_2O g/200,0 ml	Eingemessene Lösung, ml	Verbrauchte 0,1 *n* Jodlösung, ml		Gef. Maltose, H_2O	
			einzeln	Durchschn.	mg	%
2 St.		10,00	13,45 13,45	13,45	80,77	88,4
		5,00	6,86 6,80	6,83	41,02	89,8
		2,00	2,72 2,70	2,71	16,27	89,1
3 St.	1,8006	9,98	14,22 14,15	14,18	85,16	94,4
		4,99	7,10 7,05	7,08	42,52	94,6
		2,00	2,83 2,84	2,84	17,06	94,7
4 St.		9,98	14,04		84,38	93,9
		4,99	7,00		42,03	93,4

deren genauer Mechanismus unbekannt ist, sie deutet aber darauf hin, daß die Oxydation das sich bei der Enolisation des Tartrondialdehyds gebildeten Triosereduktons kein eindeutiger Vorgang ist.

In den Tabellen XIV und XV sind die Ergebnisse der Bestimmung von Maltose und Cellobiose über 3 Moleküle Aldehyd zusammengestellt.

Bei der Cellobiose kann die Bestimmung nach 3—4 Stunden dauernder Oxydation mit 2—3%igem negativem Fehler ausgeführt werden (siehe Tabellen XII und XV). Der Fehler der Maltosebestimmung beträgt unter ähnlichen Umständen 5—6%. Bezüglich der Maltose sei erwähnt, daß sich keine Maltose-Probe als vollkommen reines, einheitliches Produkt erwiesen hat, wie die papierchromatographischen Untersuchungen zeigten (demgegenüber waren die untersuchten Lactose- und Cellobiose-Proben chromatographisch vollkommen rein). Die Reinigung der Maltose durch Umkristallisation ergab kein günstiges Resultat, daher können die durch die Verunreinigung der Glucose und des Trisaccharids verursachten Fehler genau gar nicht festgestellt werden. Die Maltose war auf Grund der Ergebnisse der KOLTHOFFschen Oxydation mit Hypojodit 98%ig.

Tabelle XV

Bestimmung von Cellobiose über die bei der Oxydation mit Perjodat gebildeten 2 Moleküle Formaldehyd und 1 Molekül Glyoxylsäure

Oxydationszeit	Einwaage Cellobiose, g/200,0 ml	Eingemessene Lösung, ml	Verbrauchte 0,1 *n* Jodlösung, ml		Gef. Cellobiose	
			einzeln	Durchschn.	mg	%
2 St.		10,00	14,15 14,15	14,15	80,73	94,4
		5,00	6,95 6,94	6,95	39,70	92,8
		2,00	2,80 2,80	2,80	15,97	93,4
4 St.	1,7103	10,00	14,30 14,30	14,30	81,58	95,4
		5,00	7,15 7,15	7,15	40,79	95,4
		2,00	2,86 2,82	2,84	16,21	94,7

Beschreibung der Methoden

1. Die Bestimmung der 1 → 4-Disaccharide über die bei der schwefelsauren Oxydation mit Perjodat gebildeten 3 Moleküle Aldehyd

Reagenzien

0,1 *n* Jodlösung
5%ige Jodlösung
0,3 *m* Perjodsäurelösung
1,5 *m* Natriumsulfitlösung
8%-ige Natriumbicarbonatlösung
20%ige Schwefelsäure
20%ige Salzsäure
20%ige Natronlauge
1,0%ige Stärkelösung als Indikator
0,1%ige äthylalkoholische Methylrotlösung
Kaliumcyanid (fest)
Pentan

0,6—0,9 g analytisch genau gewogene kristalline Maltose, Lactose bzw. Cellobiose werden in Wasser gelöst, in einen 100-ml-Meßkolben gebracht und in diesem bis zur Marke verdünnt. Aus der so vorbereiteten Stammlösung werden 10,00 ml in einem mit Glasstopfen versehenen Erlenmeyerkolben pipettiert, der 10,00 ml Perjodsäure und 10 ml Schwefelsäure enthält. Nach 3 Stunden Wartezeit wird Na_2SO_3-Lösung so lange zur Probelösung getröpfelt, bis die Farbe des anfangs ausgeschiedenen Jods verschwindet, dann wird noch 1 ml Na_2SO_3-Lösung zugegeben. Danach wird die Lösung in Anwesenheit von 1—2 Tropfen Methylrot-Indikator mit Natronlauge neutralisiert (wird die Lösung warm, so soll sie gekühlt werden), dann mit

2 ml Essigsäure angesäuert. Der Inhalt des verschlossenen Kolbens wird mehrmals geschüttelt, um auch das am Schliff haftende Perjodat zu reduzieren. Die eventuell wieder erwärmte Lösung wird unter Wasser abgekühlt, dann wird sie mit 8—10 ml Pentan überschichtet. Nach einer Stunde wird der Sulfitüberschuß in Anwesenheit von 10 Tropfen Stärkelösung mit Jodlösung oxydiert. Anfangs wird 5%ige, zum Schluß 0,1 *n* Jodlösung verwendet. Nach Erreichung der blauen Farbe wird der verschlossene Kolben energisch geschüttelt, wobei der Stopfen von Zeit zu Zeit gelockert wird, um das am Schliff haftende Sulfit zu reduzieren und wenn nötig, wird die Farbe der Lösung mittels 0,1 *n* Jodlösung auf die bläuliche Anfangsfarbe eingestellt. Nach der Oxydation des Sulfitüberschusses wird mit 4 ml Natronlauge alkalisiert, dann werden 0,3—0,5 g KCN in den Kolben gegeben. Die Lösung wird vorsichtig gerührt, dann aus einer eingeteilten Pipette mit Salzsäure neutralisiert und nachher mit 1,5—2 ml Salzsäure angesäuert. Hierauf wird ohne lebhafteres Schütteln mit 0,1 *n* Jodlösung titriert. Am Anfang wird die Meßlösung in größeren Anteilen zugegeben; nach Erreichung der blauen Farbe wird der Kolben verschlossen, geschüttelt und wenn nötig, wird durch Zugabe weiterer 1—2 Tropfen Meßlösung bis zur bleibenden blauen Farbe titriert.

Das Äquivalentgewicht von Maltose, Lactose und Cellobiose ist bei der Bestimmung: Molekulargewicht/6.

1 ml 0,1 *n* Jodlösung entspricht: 6,000 mg kristalliner Maltose und Lactose ($C_{12}H_{22}O_{11} \cdot H_2O$) bzw. 5,705 mg Cellobiose ($C_{12}H_{22}O_{11}$).

2. Die Bestimmung der 1 → 4-Disaccharide über den bei den schwefelsauren und nachfolgenden gepufferten essigsauren Oxydationen mit Perjodat gebildeten Formaldehyd

Die Bestimmung wird bis zu der in schwefelsaurer Lösung 3 Stunden dauernden Oxydation in jeder Hinsicht nach dem in Punkt 1 beschriebenen Verfahren ausgeführt. Nach 3 Stunden wird die Lösung in Anwesenheit von 2 Tropfen Methylrot-Indikator neutralisiert (die warm gewordene Lösung wird unter fließendem Wasser gekühlt) und dann mit 2 ml Essigsäure angesäuert. Nach weiteren 2 Stunden wird Na_2SO_3-Lösung — in Anwesenheit von 1,5 ml Schwefelsäure — so lange zur Lösung getropft, bis die Farbe des Jods verschwindet, dann wird noch 1 ml Na_2SO_3-Lösung zugegeben. Im weiteren wird ebenso verfahren, wie unter Punkt 1 beschrieben wurde.

Das Äquivalentgewicht der Maltose, Lactose und Cellobiose ist bei der Bestimmung: Molekulargewicht/4.

1 ml 0,1 *n* Jodlösung entspricht: 9,008 mg kristalliner Maltose und Lactose ($C_{12}H_{22}O_{11} \cdot H_2O$) bzw. 8,558 Cellobiose ($C_{12}H_{22}O_{11}$).

3. Die Bestimmung von Maltose und Glucose über den bei der durch $NaHCO_3$ gepufferten Oxydation mit Perjodat gebildeten Formaldehyd

10,00 ml aus der nach Punkt 1 vorbereiteten Stammlösung werden in einen 10 ml Perjodsäure und 20 ml $NaHCO_3$-Lösung enthaltenden 200 ml-Erlenmeyerkolben pipettiert. Nach 60—90 Minuten wird die Probelösung in Anwesenheit von 2 ml Na_2SO_3-Lösung mit Schwefelsäure angesäuert, dann wird Na_2SO_3-Lösung bis zum Verschwinden der Farbe des Jods zugetropft, und abschließend wird noch 1 ml Na_2SO_3-Lösung zugegeben. Im weiteren wird ebenso verfahren, wie unter Punkt 1 beschrieben wurde.

Bei dieser Bestimmung ist das Äquivalentgewicht der Maltose: Molekulargewicht/4; das der Glucose: Molekulargewicht/2.

1 ml 0,1 *n* Jodlösung entspricht 9,008 mg kristalliner Maltose ($C_{12}H_{22}O_{11} \cdot H_2O$) bzw. 9,908 mg kristalliner Glucose ($C_6H_{12}O_6 \cdot H_2O$).

ZUSAMMENFASSUNG

In schwefelsaurer-perjodsaurer ($p_H \approx 0$) Lösung bilden sich bei der Oxydation der reduzierenden 1 → 4-Disaccharide 3 Moleküle Aldehyd (2 Moleküle Formaldehyd + 1 Molekül Glyoxylsäure). Bei der in schwefelsaurer-perjodsaurer Lösung beginnenden und in gepufferter essigsaurer Lösung ($p_H \approx 4$) fortgesetzten Oxydation bilden sich 2 Moleküle Formaldehyd als Endprodukt. Die Aldehyde wurden mit Hilfe des von den Verfassern früher empfohlenen jodometrischen »Bisulfit-Cyanid«-Verfahrens bestimmt, welches auch zur gesonderten sowie in Anwesenheit von Aldohexosen ausgeführten Bestimmung der 1 → 4-Disaccharide benützt wurde.

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DAMPF-FLÜSSIGKEITSGLEICHGEWICHT ALKOHOLHALTIGER BINÄRER GEMISCHE

ÜBER DIE ANWENDBARKEIT DES A-A_2-B REGULÄREN TERNÄREN MISCHUNGSMODELLS, I

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In unseren früheren Mitteilungen [1, 2] wurde bereits darüber berichtet, daß zahlreiche Eigenschaften der Alkohole mit Hilfe eines thermodynamischen Modells interpretiert werden können, wobei der reine Alkohol als ein ideales Gemisch von monomeren und dimeren Alkoholmolekülen aufgefaßt wird. In der Dampf- und Flüssigkeitsphase kann die Gleichgewichtskonstante der Assoziationsreaktion bestimmt werden, und so ergibt sich eine Möglichkeit, den Dampfdruck der monomeren und dimeren Alkohole, die Enthalpieänderung der Assoziationsreaktion usw. zu bestimmen. Das Modell eignet sich auch dazu, die Daten des Dampf-Flüssigkeitsgleichgewichtes alkoholhaltiger Gemische zu berechnen. Das Ziel unserer nachstehend beschriebenen Versuche war, die Möglichkeit der Berechnung der Dampf-Flüssigkeitsgleichgewichtsdaten außer den bereits beschriebenen Benzol-Äthanol-Gemischen auch bei anderen Systemen zu untersuchen.

1. A-A_2-B-Modell alkoholhaltiger Gemische

Die alkoholhaltigen Gemische der apolaren oder wenig polaren, aber keine Assoziate bildenden und sich auch mit dem Alkohol nicht assoziierenden Verbindungen sollen auf Grund des nachstehend zu beschreibenden Modells besprochen werden.

In erster Näherung sind reine Alkohole ideale Gemische monomerer und dimerer Alkoholmoleküle. Somit bildet ein Gemisch aus einer Komponente B und dem Alkohol eigentlich ein ternäres System, bestehend aus den Molekülen A, A_2 und B. Es ist bekannt, daß das Modell eines idealen ternären Gemisches zur Beschreibung der Dampf-Flüssigkeitsgleichgewichte von alkoholhaltigen Gemischen ungeeignet ist. Aus diesem Grunde wurde in Betracht gezogen, daß die Gemischpaare A-B und A_2-B keine idealen Gemische bilden. Es wurde vorausgesetzt, daß die letzteren Gemischpaare in erster Näherung als reguläre Gemische behandelt werden können. Nach der VAN LAARschen Theorie der regulären Gemische werden die Abweichungen vom idealen Verhalten durch die Austauschenergie gekennzeichnet.

Die zusätzliche freie Enthalpie in einem binären Gemisch ist, auf das ideale Gemisch bezogen:

$$\Delta G^E = RT[x_1 \ln \gamma_1 + x_2 \ln \gamma_2]. \tag{1}$$

Nach der Theorie der regulären ternären Gemische (3) ist

$$\mathrm{n}\ \gamma_1 = \frac{\Delta U^0}{RT} x_2^2 \text{ und } \ln \gamma_2 = \frac{\Delta U^0}{RT} x_1^2, \tag{2}$$

daher ergibt sich:

$$\Delta G^E = (x_1 x_2^2 + x_2 x_1^2)\Delta U^0 = (x_2 - x_2^2)\Delta U^0. \tag{3}$$

Im Modell-Gemisch A-A_2-B wurde vom Gemischpaar A-A_2 vorausgesetzt, daß es sich ideal verhält, d. h., daß $\Delta U^\circ_{(A\text{-}A_2)} = 0$ ist, woraus folgt, daß

$$\Delta U^0_{(A\text{-}B)} = \Delta U^0_{(A_2\text{-}B)} = \Delta U^0$$

ist.

Somit kann das System mir einer einzigen Austauschenergie gekennzeichnet werden.

Das Mengenverhältnis der monomeren Alkoholmoleküle zu den dimeren bestimmt die Gleichgewichtskonstante der Dimerisationsreaktion, die an Wert für reinen Alkohol aus gaschromatographischen Meßdaten [2] berechnet werden kann. Da monomerer und dimerer Alkohol in unserem Modell ein ideales Gemisch bilden, stimmen die Molenbrüche in reinem Alkohol mit den Aktivitäten überein.

Für die Gleichgewichtskonstante der realen Gemische gilt der folgende Zusammenhang:

$$K_a = K_x \cdot K_\gamma. \tag{4}$$

Aus den gaschromatographischen Daten (da hier nach den vorangehenden Ausführungen $K_\gamma = 1$ ist) kann der Wert von K_a unmittelbar bestimmt werden. Im Gemisch A-A_2-B ist

$$K_a = K_x K_\gamma = \frac{x_{A_2}}{x_A^2} \cdot \frac{\gamma_{A_2}}{\gamma_{A_2}}. \tag{5}$$

Die Aktivitätskoeffizienten wurden auf Grund der für die ternären Gemische angewendeten VAN LAARschen Theorie in Kenntnis der Austauschenergie bestimmt. Es ist nämlich

$$\ln \gamma_A = x_B^2 \frac{\Delta U^0}{RT} \tag{6}$$

$$\ln \gamma_{A_2} = x_B^2 \frac{\Delta U^0}{RT} \tag{7}$$

$$\ln \gamma_B = (1 - x_B)^2 \frac{\Delta U^0}{RT} . \tag{8}$$

Wie ersichtlich, ist

$$\ln \gamma_A = \ln \gamma_{A_2}, \text{ d. h. } \gamma_A = \gamma_{A_2}$$

und so ist die aus den Aktivitätskoeffizienten sich ergebende Gleichgewichtskonstante

$$K_\gamma = \frac{\gamma_{A_2}}{\gamma^2{}_A} = \frac{1}{\gamma_A} . \tag{9}$$

Die möglichen Zusammensetzungen des ternären Gemisches können auf folgende Weise berechnet Werden:

Zunächst werden die Werte von K_x bestimmt:

$$K_x = K_a \cdot \gamma_A K_a \exp\left(\frac{\Delta U^0}{RT}\right). \tag{10}$$

In Kenntnis des Wertes von K_α ergibt sich:

$$x_A = \frac{-1 \pm \sqrt{4K_x(1 - x_B) + 1}}{2K_x} . \tag{11}$$

Der Molenbruch des dimeren Alkohols im ternären Gemisch:

$$x_{A_2} = 1 - (x_A + x_B) . \tag{12}$$

In Kenntnis der Dampfdrücke, Molenbrüche und Aktivitätskoeffizienten der reinen Komponenten können die Partialdrücke auf Grund des modifizierten RAOULTschen Gesetzes berechnet werden.

Die Gleichgewichtsdampfdrücke der reinen monomeren bzw. dimeren Alkohole lassen sich aus gaschromatographischen Daten bestimmen [2], doch begeht man keinen großen Fehler, wenn — bei Vernachlässigung des Dampfdruckes des Dimeren — der Dampfdruck des reinen Monomeren auf Grund der Formel

$$P_A^\circ = \frac{P_e^\circ}{x_A} \tag{13}$$

berechnet wird.

Zu den Berechnungen bedarf es der Kenntnis der Austauschenergie ΔU°. Der Wert dieser Energie kann aus experimentellen Daten bestimmt werden.

Da auf Grund von (1)

$$\lim_{x_B \to 0} \lg \gamma_B = \frac{\Delta U^0}{2{,}3\,RT} = q \tag{14}$$

und

$$\lim_{x_B \to 0} \lg \gamma_B = \lim_{x_b \to 0} \lg \gamma_b \tag{15}$$

ist, kann die Austauschenergie des ternären Gemisches aus den Daten des binären Gemisches bestimmt werden.

Die Umrechnung des Molenbruches der Komponente B vom ternären Gemisch auf das binäre Gemisch kann mit Hilfe des Zusammenhanges:

$$x_b = \frac{x_B}{1 + x_{A_2}} \tag{16}$$

erfolgen.

2. Untersuchung der Anwendbarkeit des Modells

Zur Untersuchung der Anwendbarkeit des Modells wurden Gemische gewählt, in denen außer Äthanol verschiedene Verbindungen, mit abweichenden physikalisch-chemischen Eigenschaften, als Komponente B enthalten waren. Die als Komponente B gewählten Verbindungen sind in Tabelle I zusammengefaßt.

Tabelle I

Nr.	Name der Komponenten	Charakteristische Verbindungsgruppe	Bemerkung	Siedepunkt °C	Literatur	Meß-Temp.
1	Heptan	Normalparaffin	apolar	98,4	4	30
2	Methylcyclohexan	Cycloparaffin	apolar	100,9	5	35
3	Toluol	subst. arom. Verb.	polarisierbar	110,6	6	35
4	Chloroform	halogenierter Kohlenwasserstoff	polar	61,3	7	35
5	Bromoform	halogenierter Kohlenwasserstoff	polar	150,5	8	35

Nachfolgend sollen nun die unter Anwendung des Modells berechneten Partialdrücke in Abhängigkeit von der Zusammensetzung angeführt werden. In den Abbildungen sind die experimentell bestimmten Daten mit 0, die auf Grund des Modells berechneten Dampfdrücke mit x bezeichnet. Als experimentelle Daten sind die isothermen Meßergebnisse verschiedener Autoren angeführt [4, 5, 6, 7, 8].

Auswertung

Die berechneten und gemessenen Dampf-Flüssigkeitsgleichgewichtsdaten der 5 binären Gemischpaare (die Partialdrücke) weisen darauf hin, daß das oben beschriebene Modell für zahlreiche äthanolhaltige Gemische mit Erfolg angewendet werden kann (Tabellen II—VI).

Tabelle II

Äthanol-Heptan, $t = 30°C$

Literaturangaben [4]

x_0	y_0	p_e	p_h	$\lg \gamma_0$	$\lg \gamma_h$
0,0000	0,0000	0,00	53,20 (?)	—	—
0,0400	0,2820	22,00	56,00	0,8472	0,0008
0,0684	0,4556	47,20	56,40	0,9458	0,0017
0,1236	0,4986	56,09	56,41	0,7636	0,0437
0,2803	0,5344	62,90	54,80	0,4425	0,1165
0,3342	0,5381	63,50	54,50	0,3856	0,1479
0,5151	0,5496	65,90	54,00	0,2137	0,2817
0,5934	0,5679	68,09	51,81	0,1664	0,3195
0,7174	0,5828	69,70	49,90	0,0941	0,4814
0,7687	0,5971	70,99	47,91	0,0723	0,5520
0,8154	0,6282	73,50	43,50	0,0618	0,6064
0,8550	0,6454	73,90	40,60	0,0433	0,6822
0,8902	0,7116	79,20	32,10	0,0561	0,7001
0,9173	0,8269	87,90	18,40	0,0881	0,5899
0,9545	0,8958	86,98	10,12	0,0664	0,5822
0,9913	0,9430	77,80	4,70	0,0154	0,9676
1,0000	1,0000	78,20	0,00	0,—	—

Berechnete Daten ($q = 0{,}85$, $K_a = 500$).

Die angeführten Beispiele wurden so gewählt, daß die neben dem Äthanol vorliegende Komponente B bezüglich der Polarität, der Molekülstruktur, des Molvolumens usw. wesentlich abweichend sein soll.

Ein Vergleich der Abbildungen, die die Ergebnisse der Messungen und Berechnungen anführen, läßt deutlich erkennen, daß die berechneten Daten — nahezu unabhängig von der stofflichen Beschaffenheit der Komponente B — die experimentellen Daten ziemlich gut annähern. Der Charakter der Abweichungen ist bei den untersuchten 6 Gemischpaaren der gleiche. Mit der Zunahme

Tabelle III

Äthanol-Methylcyclohexan, $t = 35°C$

Literaturangaben [5]

x_e	y_e	P_e	p_m	$\lg \gamma_e$	$\lg \gamma_m$
0,0000	0,0000	0,00	73,62	—	—
0,0526	0,4645	62,76	72,64	1,0634	0,0120
0,1446	0,5118	75,02	71,95	0,7016	0,0934
0,2878	0,5362	80,89	70,38	0,4354	0,1206
0,4052	0,5471	83,12	69,24	0,2987	0,1911
0,5403	0,5575	84,98	67,95	0,1832	0,2947
0,6914	0,5817	88,28	63,94	0,0927	0,4414
0,8450	0,6423	93,34	52,39	0,0298	0,6541
0,9676	0,8369	100,40	19,64	0,0025	0,4704
1,0000	1,0000	102,70	0,00	—	—

Berechnete Daten ($q = 0{,}80$, $K_a = 260$).

X_B	X_A	P_A	p_B	$1 - x_e$
0,0	0,0601	102,70	0,00	0,000
0,1	0,0565	98,18	32,73	0,054
0,2	0,0517	95,08	47,87	0,114
0,3	0,0461	93,02	54,46	0,182
0,4	0,0400	91,82	57,16	0,256
0,5	0,0278	91,07	58,34	0,340
0,6	0,0271	90,07	59,32	0,438
0,7	0,0169	87,91	60,81	0,546
0,8	0,0148	82,17	63,43	0,678
0,9	0,0072	67,43	67,45	0,825
1,0	0,0000	0,00	73,62	1,000

des scheinbaren Molenbruches (x_b) der Komponente B nimmt die Differenz zwischen dem berechneten und gemessenen Wert des Partialdruckes des Äthanols bis zum Molenbruch von etwa 0,4 zu. In diesem Bereich beträgt der berechnete Wert des Partialdruckes des Äthanols um etwa 5 mm Hg mehr als der gemessene. Bei Molenbrüchen, die größer als 0,4 sind, nimmt dieser positive Fehler stufenweise ab, bei Molenbrüchen von 0,6—0,7 stimmen die berechneten und gemessenen Partialdrücke überein, während im Bereich von 0,7—1,0 die Abweichung negativ wird.

Tabelle IV

System Äthanol-Toluol, $t = 35°C$

Literaturangaben [6]

x_e	y_e	p_e	p_t	$\lg \gamma_e$	$\lg \gamma_t$
0,0000	0,0000	0,60	46,78	—	0,0 000
0,0330	0,4216	33,47	45,91	0,9926	0,0064
0,0468	0,4749	41,00	45,34	0,9290	0,0073
0,1214	0,5662	57,80	44,29	0,6642	0,0226
0,2079	0,6014	65,61	43,42	0,4850	0,0689
0,3620	0,6346	72,51	41,75	0,2882	0,1458
0,4160	0,6384	73,63	41,71	0,2345	0,1838
0,5930	0,6730	79,35	38,55	0,0530	0,3064
0,7263	0,7164	84,94	33,63	0,0546	0,4194
0,8519	0,7848	91,48	25,08	0,0174	0,5585
0,9701	0,9318	100,29	7,35	0,0012	0,7201
1,0000	1,0000	102,70	0,00	0,0000	—

Berechnete Daten ($q = 0{,}6$, $K_a = 260$).

X_B	X_A	p_A	p_B	$1 - x_e$
0,0	0,0601	102,70	0,00	0,0000
0,1	0,0565	97,92	14,35	0,0542
0,2	0,0518	94,40	21,65	0,114
0,3	0,0464	91,03	27,65	0,1814
0,4	0,0404	88,39	30,80	0,2566
0,5	0,0341	85,83	33,10	0,3414
0,6	0,0277	82,60	35,00	0,4377
0,7	0,0214	78,16	37,10	0,5482
0,8	0,0154	68,83	39,65	0,6765
0,9	0,0093	55,39	43,20	0,8261
1,0	0,0000	0,00	46,80	1,0000

Auch die berechneten und gemessenen Partialdrücke der Komponente B weisen im wesentlichen die gleichen Abweichungen auf. Bei verschiedenen Komponenten B ist die Abweichung von 0 bis zu einem Molenbruch von etwa 0,2—0,3 positiv, um dann allmählich Null zu werden. Bei größeren Molenbrüchen sind die berechneten Werte kleiner als die Meßergebnisse. Der Fehler der berechneten Werte ist auch in diesem Fall von ähnlicher Größe wie der

Tabelle V

Äthanol-Chloroform, $t = 35°C$

Literaturangaben [7]

x_e	y_e	p_e	p_k	$\lg \gamma_e$	$\lg \gamma_k$
1,0000	1,0000	102,70	0,00	—	—
0,9938	0,9746	102,21	2,66	0,0003	0,1628
0,9759	0,9009	102,07	11,03	0,0078	0,1906
0,9703	0,8790	99,86	13,75	0,0005	0,1956
0,9453	0,7846	96,96	26,61	0,0009	0,2170
0,9406	0,7657	95,60	29,48	—0,0048	0,2256
0,8891	0,6115	90,66	57,60	—0,0035	0,2455
0,7639	0,5793	78,01	127,67	—0,0024	0,2630
0,6086	0,3130	71,75	157,49	0,0596	0,2480
0,5652	0,2354	63,00	204,65	0,0351	0,1993
0,3815	0,1819	53,11	238,84	0,1319	0,1167
0,2254	0,1446	43,82	259,23	0,2767	0,0546
0,1517	0,1217	37,27	268,98	0,3786	0,0311
0,0400	0,0597	18,13	285,56	0,6444	0,0034
0,0000	0,0100	0,00	259,11	—	—

Berechnete Daten ($q = 0{,}20$, $K_a = 260$).

X_B	X_A	p_A	p_B	$1 - x_e$
0,0	0,06013	102,70	0,00	0,0000
0,1	0,05679	97,48	42,85	0,0542
0,2	0,05313	92,45	79,27	0,1145
0,3	0,04900	87,30	111,02	0,1817
0,4	0,04634	85,25	139,29	0,2574
0,5	0,03973	75,14	165,56	0,3424
0,6	0,03440	69,33	190,70	0,4393
0,7	0,02883	61,74	215,46	0,5507
0,8	0,02252	51,65	240,57	0,6794
0,9	0,01266	31,39	266,93	0,8277
1,0	0,00000	0,00	295,11	1,0000

Fehler, der bei der Berechnung des Partialdruckes des Äthanols begangen wird. Die angeführten Erscheinungen können beim Partialdruck des Bromoforms im System Äthanol-Bromoform sowie beim Partialdruck des Äthanols im System Äthanol-Heptan, in dem zu kleinen Molenbrüchen des Heptans ge-

Tabelle VI

System Äthanol-Bromoform, $t = 35°C$

Literaturangaben [8]

x_e	y_e	p_e	p_{br}	$\lg \gamma_e$	$\lg \gamma_{br}$
0,000	0,000	0,00	9,80	—	—
0,048	0,759	30,20	9,60	0,7872	0,0124
0,064	0,776	32,59	8,41	0,6953	−0,0600
0,189	0,867	59,99	9,21	0,4907	0,0641
0,211	0,873	60,32	8,78	0,4445	0,0550
0,278	0,900	70,38	7,82	0,3918	0,0434
0,540	0,902	73,87	8,03	0,1245	0,2504
0,580	0,906	74,47	7,73	0,0969	0,2742
0,648	0,912	76,60	7,40	0,0611	0,3314
0,682	0,914	78,14	7,36	0,0472	0,3729
0,846	0,948	88,06	4,84	0,0055	0,5060
0,982	0,994	100,99	0,61	0,0004	0,5386
1,000	1,000	102,70	0,00	0,0000	—

Berechnete Daten ($q = 0{,}6$, $K_a = 260$).

X_B	X_A	p_A	p_B	$1 - x_e$
0,0	0,0601	102,70	0,00	0,0000
0,1	0,0565	97,92	3,00	0,0542
0,2	0,0523	94,40	4,53	0,0114
0,3	0,0471	91,03	5,78	0,1814
0,4	0,0415	88,39	6,43	0,2566
0,5	0,0356	85,83	6,92	0,3414
0,6	0,0295	82,60	7,33	0,4377
0,7	0,0233	78,16	7,77	0,5482
0,8	0,0174	68,83	8,29	0,6765
0,9	0,0106	55,39	8,94	0,8261
1,0	0,0000	0,00	9,80	1,0000

hörigen Bereich, nicht beobachtet werden. Die erstere Erscheinung ist durch den geringen Dampfdruck des Bromoforms, die letztere durch die unverläßlichkeit der Meßergebnisse begründet. (Es ist nämlich nicht möglich, daß der Partialdruck des Äthanols im Gemisch größer wäre als der Gleichgewichtsdampfdruck des reinen Äthanols).

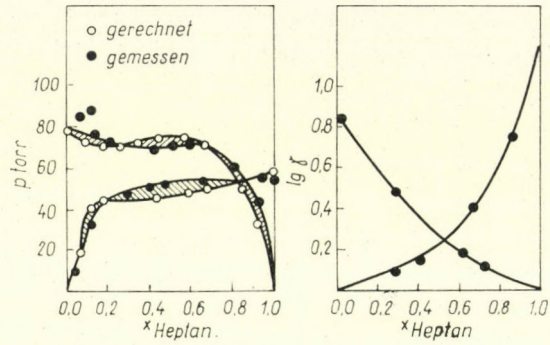

Abb. 1. Äthanol—*n*-Heptan; $p-x$ und $\lg \gamma - x$ Diagramme (30°C)

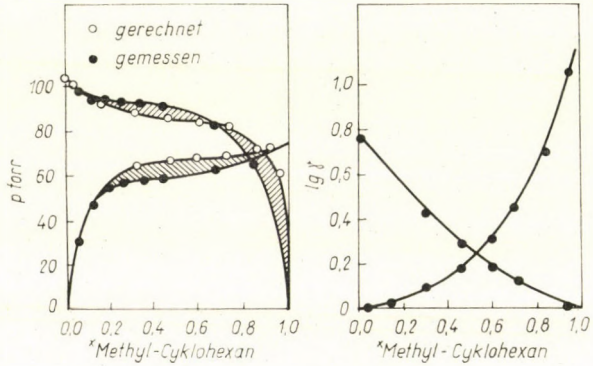

Abb. 2. Äthanol—Methylcyclohexan; $p-x$ und $\lg \gamma - x$ Diagramme (35°C)

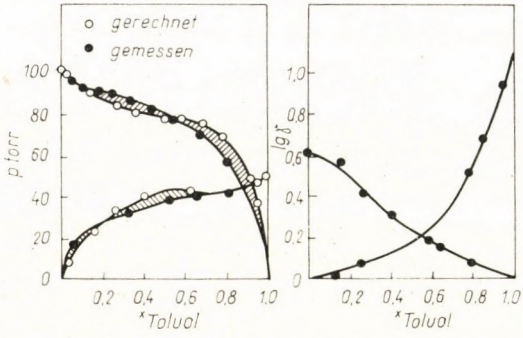

Abb. 3. Äthanol—Toluol; $p-x$ und $\lg \gamma - x$ Diagramme (35°C)

Bei der Ermittlung des Wertes von q verursacht der Umstand Schwierigkeiten, daß bei der Bestimmung eine nichtlineare Extrapolation durchgeführt werden muß, gerade in dem Konzentrationsbereich, wo die Meßergebnisse am meisten streuen. Die Extrapolation kann verläßlicher durchgeführt werden, wenn sie im Diagramm $\lg \gamma_b/x_0^2$ über x_b vorgenommen wird, wo bei Gültigkeit

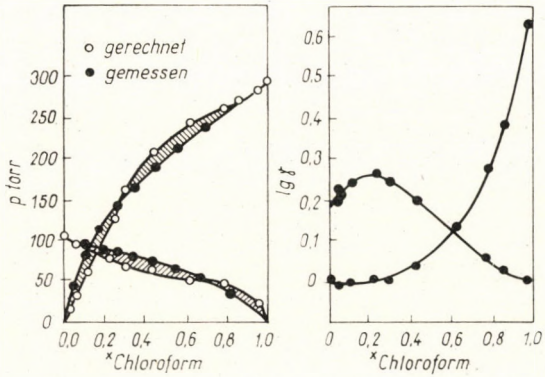

Abb. 4. Äthanol—Chloroform; $p-x$ und $\lg \gamma - x$ Diagramme (35°C)

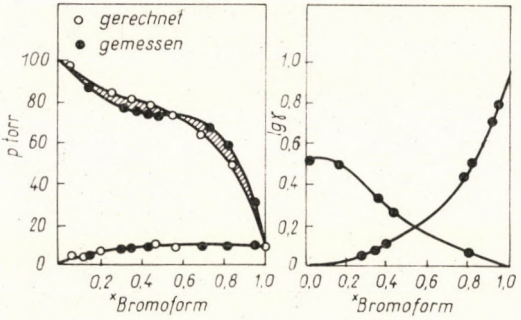

Abb. 5. Äthanol—Bromoform; $p-x$ und $\lg \gamma - x$ Diagramme (35°C)

der Margulesschen Gleichung eine lineare, sonst aber eine nahezu lineare Extrapolation durchgeführt werden kann. Die so bestimmten q-Werte weichen etwa von den Werten ab, die von den Diagrammen $\lg \gamma_b$ über x_b abgelesen werden.

Den Grund des methodischen Fehlers sehen wir darin, daß in unserem Modell die Existenz von Assoziaten, die mehr als zwei Moleküle Äthanol enthalten, nicht berücksichtigt worden ist. Die Berücksichtigung der Existenz solcher Moleküle führt zu Beziehungen, die etwas genauer, aber viel schwieriger zu behandeln sind.

Erklärung der im Text verwendeten Symbole:

A das monomere Molekül irgendeines Alkohols
A_2 das dimere Molekül irgendeines Alkohols
B das Molekül der mit dem Alkohol vermischten anderen Komponente
ΔG^E Zusatz der freien Enthalpie
K_a Gleichgewichtskonstante der Assoziation (ausgedrückt in Aktivitäten)
K_x Gleichgewichtskonstante der Assoziation (ausgedrückt in Molenbrüchen)
K_γ Gleichgewichtskonstante der Assoziation (gebildet aus den Aktivitätskoeffizienten)
P° Gleichgewichts-Dampfdruck
P Druck
p Partialdruck
q Konstante, definiert mit der Gl. (14)
R universelle Gaskonstante
T absolute Temperatur
ΔU° VAN LAARsche Austauschenergie
x Molenbruch in der Flüssigkeitsphase
y Molenbruch in der Dampfphase
γ Aktivitätskoeffizient

Als Indizes wurden die folgenden Bezeichnungen verwendet:

A Monomeres Äthanol in dem als ternär betrachteten Gemisch
A_2 Dimeres Äthanol in dem als ternär betrachteten Gemisch
B die Komponente B in dem als ternär betrachteten Gemisch
e Äthanol in dem als binär betrachteten Gemisch
b die Komponente B in dem als binär betrachteten Gemisch
br Bromoform in dem als binär betrachteten Gemisch
h Heptan in dem als binär betrachteten Gemisch
k Chloroform in dem als binär betrachteten Gemisch
m Methylcyclohexan in dem als binär betrachteten Gemisch
t Toluol in dem als binär betrachteten Gemisch, 1,2 dient im allgemeinen zur Bezeichnung der Komponenten.

ZUSAMMENFASSUNG

Bei der Untersuchung der Anwendbarkeit des Modells des regulären ternären Gemisches vom Typ A-A_2-B sind wir zu der Schlußfolgerung gelangt, daß das Modell bei Gemischen aus Äthanol und 6 verschiedenen Komponenten B gleicherweise angewandt werden kann. Aus den Ergebnissen geht hervor, daß die Abweichungen der berechneten von den gemessenen Partialdrücken in jedem Fall die gleiche Tendenz zeigen. Der Fehler der gezeigten Berechnungsmethode übertrifft in keinem Fall den Fehler der Berechnung, die auf Grund von empirischen Gleichungen mit zwei Konstanten vorgenommen wird. Ein Vorteil unserer Methode der letztgenannten gegenüber besteht darin, daß unsere Gleichung eine einzige Konstante enthält,

die von der stofflichen Beschaffenheit der mit dem Äthanol gemischten Komponente abhängt. Die in den Beziehungen vorkommende Dimerisationsgleichgewichtskonstante hängt nur von der Temperatur ab und kann aus den gaschromatographischen Daten des reinen Äthanols bestimmt werden. Der methodische Fehler der Berechnung findet seine Erklärung darin, daß das Modell A-A_2-B die Existenz von Assoziaten, die mehr als zwei Äthanol-Moleküle enthalten, nicht berücksichtigt.

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DAMPF-FLÜSSIGKEITSGLEICHGEWICHT ALKOHOLHALTIGER BINÄRER GEMISCHE

ÜBER DIE ANWENDBARKEIT DES A-A_2-B REGULÄREN TERNÄREN MISCHUNGSMODELLS, II

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In unserer vorangegangenen Mitteilung [1] zeigten wir die Verwendbarkeit des Modells regulärer Dreistoffgemische von Typ A-A_2-B im Falle einiger Systeme, die neben Äthanol als Komponente B Verbindungen enthielten, deren physikalisch-chemische Eigenschaften voneinander abweichend waren. Die vorliegende Arbeit befaßt sich nun mit dem Problem, wie für ein gegebenes Äthanol-Komponente-B-Gemisch aus den für eine gegebene Temperatur bekannten Dampfdruck-Daten der Dampfdruck des Systems für irgendeine andere Temperatur zu berechnen ist. Es wird eine Berechnungsmethode dargestellt, mit deren Hilfe diese Aufgabe gelöst werden kann.

In der ersten Mitteilung dieser Reihe wurde das Modell des regulären ternären System A-A_2-B von alkoholhaltigen Gemischen diskutiert. Nach der van Laarschen Theorie der regulären Gemische wurde die Abweichung vom idealen Verhalten mit der Austauschenergie charakterisiert. Es wurde der folgende Zusammenhang zwischen den Molenbrüchen und den Aktivitätskoeffizienten der Komponenten in der flüssigen Phase aufgeschrieben:

$$\ln \gamma_1 = \frac{\Delta U^0}{RT} x_2^2 \text{ bzw. } \ln \gamma_2 = \frac{\Delta U^0}{RT} x_1^2, \tag{1}$$

worin x_1 und x_2 die Molenbrüche der Komponenten in der Flüssigkeitsphase,

γ_1 und γ_2 die Aktivitätskoeffizienten der Komponenten in der Flüssigkeitsphase,

ΔU° die van Laarsche Austauschenergie,

R die universale Gaskonstante und

T die absolute Temperatur

bedeuten. Nach Gl. (1) kann geschrieben werden:

$$\lim_{x_B \to 0} \lg \gamma_B = \frac{\Delta U^0}{4{,}57\, T} = q. \tag{2}$$

Die Größe der van Laarschen Austauschenergie kann experimentell bestimmt werden [1]. Wenn nämlich die Konzentration der Komponente B

im Alkohol zu Null konvergiert, so konvergiert die Austauschenergie unabhängig vom Dimerisationsgrad des Alkohols zur wahren Austauschenergie.

Die Zusammenhänge, mit deren Hilfe in der ersten Mitteilung [1] die Dampf-Flüssigkeit-Gleichgewichtsdaten der Gemische von Äthanol und irgendeiner Komponente B berechnet wurden, enthalten zwei Konstanten. Unter diesen Konstanten ist die Assoziationsgleichgewichtskonstante des Äthanols unabhängig von der Natur der Komponente B, jedoch eine Funktion der Temperatur. Der Wert der die Austauschenergie enthaltenden Konstante q hängt sowohl von der Natur der Komponente B als auch von der Temperatur ab. Nach unserer Annahme können nun in Kenntnis der Temperaturabhängigkeit der beiden Konstanten die Dampf-Flüssigkeitsgleichgewichtsdaten von der Temperatur T_1 auf die Temperatur T_2 umgerechnet werden.

Die Temperaturabhängigkeit der Gleichgewichtskonstante der Assoziationsreaktion wird von der VAN'T HOFFschen Gleichung angegeben:

$$\frac{\mathrm{d} \ln K_a}{\mathrm{d}T} = \frac{\Delta H}{RT^2}, \tag{3}$$

worin K_a die Reaktionsgleichgewichtskonstante,
T die absolute Temperatur, K°,
ΔH die Reaktionswärme, kcal/mol, und
R die universelle Gaskonstante, kcal/mol. K° bedeuten.

Wenn die Reaktionswärme der Assoziationsreaktion im gegebenen Temperaturabschnitt als konstant zu betrachten und der Wert von K_a für eine Temperatur bekannt ist, so kann der Wert der Gleichgewichtskonstante innerhalb des gegebenen Temperaturintervalls für eine beliebige Temperatur bestimmt werden. In unserer Mitteilung über die gaschromatographische Bestimmung der Gleichgewichtskonstante der Äthanol-Dimerisation [2] wurde der Beweis dessen erbracht, daß die Reaktionswärme der Dimerisation im Temperaturabschnitt von 20 bis 120°C mit guter Annäherung als konstant betrachtet werden kann. Nach unseren Messungen ist im Temperaturintervall, zwischen 20 und 120°C der Logarithmus der Gleichgewichtskonstante der Äthanol-Dimerisation eine lineare Funktion des reziproken Wertes der absoluten Temperatur (Abb. 1). Der entsprechende Wert von K_a kann daher aus Abb. 1 oder mit Hilfe der VAN'T HOFFschen Gleichung bestimmt werden. Der zur Berechnung der Tensionen benötigte Wert q ist von der Austauschenergie und der Temperatur abhängig.

$$q = b = \frac{\Delta U^\circ}{RT}. \tag{4}$$

Es wurde bereits von HILDEBRANDT festgestellt, daß die Austauschenergie ΔU° von der Temperatur praktisch unabhängig ist [3].

Auf Grund der Gl. (3) besteht also zwischen den zu den Werten T_1, T_2 gehörigen q_1, q_2-Werten der folgende Zusammenhang:

$$\frac{q_1}{q_2} = \frac{T_2}{T_1}.$$

Die Leistungsfähigkeit unserer Berechnungsmethode wird an Hand der Dampf-Flüssigkeitsgleichgewichtsdaten des Systems Äthanol-Toluol gezeigt.

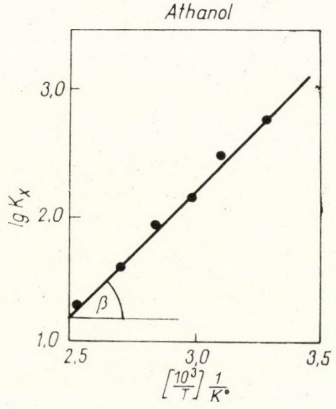

Abb. 1. Die Temperaturabhängigkeit der Gleichgewichtskonstante der Äthanol-Dimerisation

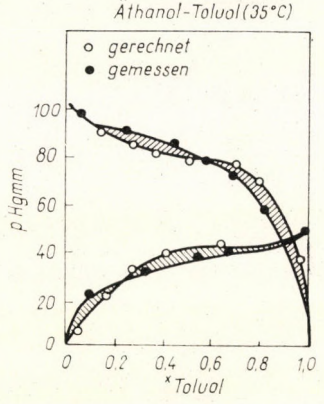

Abb. 2. $p-x$ Diagramm des Systems Äthanol—Toluol bei 35°C

In Kenntnis der bei 35°C gemessenen Versuchsdaten [4] wurde der Partialdruck der Komponenten in Abhängigkeit von der Zusammensetzung der Flüssigkeitsphase bei 40, 60 und 70°C bestimmt. Die Gleichgewichts-Dampfdrücke der reinen Komponenten wurden der Literatur entnommen [4]. In Abb. 2, 3, 4 und 5 sind die entsprechenden $p-x$ Diagramme dargestellt, wobei x die gemessenen und 0 die berechneten Werte bezeichnet. Abb. 2 zeigt vergleichs-

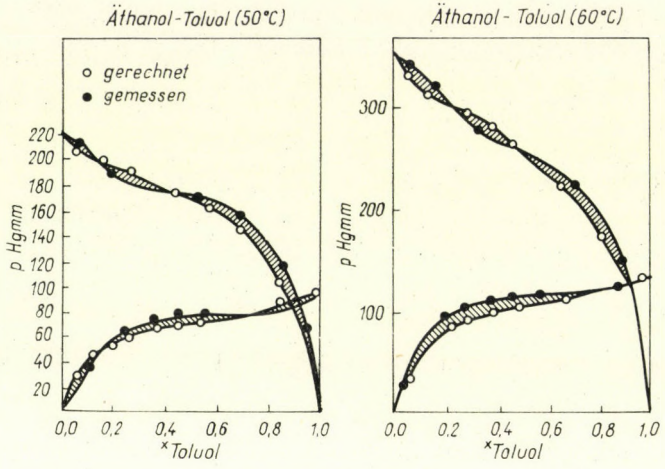

Abb. 3. $p-x$ Diagramm des Systems Äthanol—Toluol bei 50°C
Abb. 4. $p-x$ Diagramm des Systems Äthanol—Toluol bei 60°C

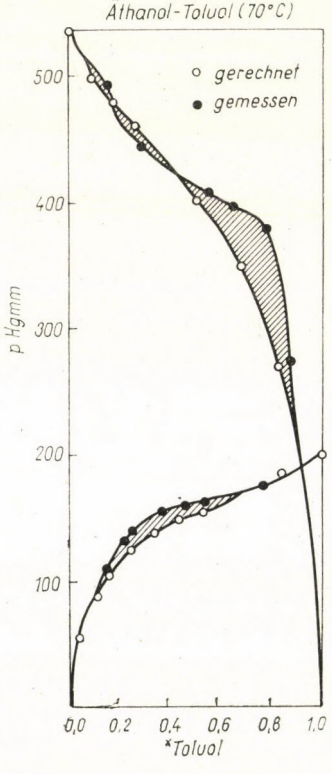

Abb. 5. $p-x$ Diagramm des Systems Äthanol—Toluol bei 70°C

weise die Verwendbarkeit des Modells des regulären ternären Gemisches A-A_2-B für das System Äthanol-Toluol bei 35°C. Diese Daten wurden mit Hilfe der aus den bei 35°C gemessenen Daten bestimmten q- und K_a-Werten berechnet.

Tabelle I

System Äthanol-Toluol, $t = 35°C$

Daten aus der Literatur

x_e	y_e	p_e	p_t	$\lg \gamma_e$
0,0000	0,0000	0,00	46,78	—
0,0330	0,4216	33,47	45,91	0,9926
0,0468	0,4749	41,00	45,34	0,9290
0,1214	0,5662	57,80	44,29	0,6642
0,2079	0,6014	65,61	43,42	0,4850
0,3620	0,6346	72,51	41,75	0,2882
0,4160	0,6384	73,63	41,71	0,2345
0,5930	0,6730	79,35	38,55	0,0530
0,7263	0,7164	84,94	33,63	0,0546
0,8519	0,7848	91,48	25,08	0,0174
0,9701	0,9318	100,29	7,35	0,0012
1,0000	1,0000	102,70	0,00	0,0000

Berechnete Daten ($q = 0{,}6$).

X_B	X_A	p_A	p_B	$1 - x_e$
0,0	0,0601	102,70	0,00	0,0000
0,1	0,0565	97,92	14,35	0,0542
0,2	0,0518	94,40	21,65	0,0114
0,3	0,0464	91,03	27,65	0,1814
0,4	0,0404	88,39	30,80	0,2566
0,5	0,0341	85,83	33,10	0,3414
0,6	0,0277	82,60	35,00	0,4377
0,7	0,0214	78,16	37,10	0,5482
0,8	0,0154	68,83	39,65	0,6765
0,9	0,0093	55,39	43,20	0,8261
1,0	0,0000	0,00	46,80	1,0000

wo x den Molbruch der Flüssigkeit,
y den Molbruch der Dampfphase und
p den Partialdruck bedeuten.

Bedeutung der Indexe:

e Äthanol in dem als binär betrachteten Gemisch,
t Toluol in dem als binär betrachteten Gemisch,
A Äthanol Monomer in dem als ternär betrachteten Gemisch,
B Toluol in dem als ternär betrachteten Gemisch.

Tabelle II

System Äthanol-Toluol, $t = 50°C$

Daten aus der Literatur

x_e	y_e	p_e	p_t
0,000	0,000	0,00	93,00
0,138	0,591	117,90	81,60
0,334	0,695	154,86	80,14
0,437	0,681	164,12	76,88
0,533	0,705	172,72	72,28
0,634	0,713	176,11	70,89
0,736	0,739	184,01	64,99
0,806	0,766	188,82	57,68
0,885	0,839	202,62	37,53
0,946	0,902	212,95	20,55
1,000	1,000	219,50	0,00

Berechnete Daten ($q = 0{,}5729$).

X_B	X_A	P_A	P_B	$1 - x_e$
0,0	0,06511	219,5	0,00	0,0000
0,1	0,06118	208,9	26,85	0,0543
0,2	0,05650	200,7	43,25	0,1147
0,3	0,05102	193,5	52,23	0,181o
0,4	0,04505	187,3	59,82	0,2572
0,5	0,03870	177,1	64,64	0,3422
0,6	0,03210	174,0	68,91	0,4385
0,7	0,02550	164,0	73,24	0,5494
0,8	0,01870	146,5	78,42	0,6768
0,9	0,01171	107,7	84,79	0,8310
1,0	0,00000	0,0	93,00	1,0000

Die in Abb. 3, 4 und 5 dargestellten berechneten Partialdruckwerte wurden mit solchen q- und K_a-Konstanten erhalten, die sich in der oben angeführten Weise aus den bei 35° gemessenen Werten ableiten ließen.

Tabelle III

System Äthanol-Toluol, $t = 60°C$

Daten aus der Literatur

x_e	y_e	p_e	p_t
0,000	0,000	0,00	139,5
0,107	0,618	148,32	91,68
0,231	0,675	247,72	119,28
0,352	0,683	254,75	118,25
0,443	0,690	263,58	118,42
0,543	0,711	275,15	111,85
0,625	0,723	281,97	108,83
0,726	0,744	293,88	101,12
0,767	0,758	300,92	96,08
0,845	0,802	318,39	78,61
0,904	0,853	330,96	57,04
0,957	0,922	345,75	29,25
1,000	1,000	352,70	0,00

Berechnete Daten ($q = 0{,}5549$).

X_B	X_A	p_A	p_B	$1 - x_e$
0,0	0,07847	352,7	0,00	0,0000
0,1	0,07376	335,5	39,27	0,0547
0,2	0,06815	322,3	63,19	0,1154
0,3	0,06163	310,8	78,26	0,1831
0,4	0,05452	300,7	87,94	0,2587
0,5	0,04689	290,0	95,98	0,3440
0,6	0,03903	276,5	102,70	0,4408
0,7	0,03100	260,8	109,56	0,5516
0,8	0,02286	232,8	117,40	0,6796
0,9	0,01427	180,6	127,06	0,8289
1,0	0,00000	0,0	139,50	1,0000

Ein Vergleich der Abbildungen zeigt, daß außer den systematischen Fehlern des Modells des regulären ternären Gemisches keine den oben angeführten Berechnungen zuzuschreibenden Fehler auftreten. Das Modell des regulären ternären Gemisches A-A_2-B erscheint also dazu geeignet zu sein, mit seiner Hilfe aus bei einer einzigen Temperatur bestimmten Meßdaten die

Tabelle IV

System Äthanol-Toluol, $t = 70°C$

Daten aus der Literatur

x_e	y_e	p_e	p_t
0,000	0,000	0,00	202,40
0,107	0,620	227,54	139,46
0,231	0,686	382,10	174,20
0,352	0,703	400,00	169,00
0,443	0,710	406,12	165,88
0,543	0,724	422,82	161,18
0,625	0,739	436,01	153,99
0,726	0,760	449,92	142,08
0,767	0,774	462,85	135,15
0,845	0,814	486,77	111,23
0,904	0,861	508,85	82,15
0,957	0,924	531,30	43,70
1,000	1,000	452,50	0,00

Berechnete Daten ($q = 0{,}5388$).

X_B	X_A	p_A	p_B	$1 - x_i$
0,0	0,09200	542,5	0,00	0,0000
0,1	0,08660	516,8	55,27	0,0551
0,2	0,08000	495,8	89,54	0,1162
0,3	0,07237	477,1	111,54	0,1843
0,4	0,06404	460,7	126,54	0,2604
0,5	0,05520	443,9	138,03	0,3461
0,6	0,04476	412,5	148,16	0,4427
0,7	0,03702	401,0	158,40	0,5546
0,8	0,02692	351,1	170,17	0,6819
0,9	0,01684	271,2	184,31	0,8305
1,0	0,00000	0,0	202,40	1,0000

Dampfdrücke von äthanolhaltigen binären Gemischen in einem nicht allzu breiten Temperaturintervall (einige Male 10°C) zu berechnen. Der Fehler der so berechneten Dampfdrücke liegt innerhalb der Grenzen des aus der Unvollkommenheit des Modells stammenden systematischen Fehlers, dessen Wert die übliche Größenordnung der Fehler von zwei Konstanten enthaltenden

Tabelle V

X_e	p_e		p_t	
	Δ_1	Δ_2	Δ_1	Δ_2
0,000	—	—	—	—
0,0330	—27,3	—26,1	—1,2	0,1
0,0468	—21,8	—20,8	—1,2	0,3
0,1214	— 8,0	—15,3	—3,9	—0,7
0,2079	0,7	— 8,1	—5,8	—3,3
0,3620	1,5	— 1,0	—5,2	—7,1
0,4160	1,4	2,8	—4,6	—10,0
0,5930	— 1,8	5,4	1,1	—9,1
0,7264	— 2,8	3,1	5,5	—6,1
0,8519	— 1,7	1,6	3,6	—2,0
0,9701	— 0,7	— 0,3	—2,1	—0,7
1,0000	—	—	—	—

in der Tabelle bedeuten

Δ_1 den prozentuellen Fehler der MARGULESschen Methode und
Δ_2 den prozentuellen Fehler der von uns empfohlenen Methode.

empirischen Gleichungen besitzt. Dies ist auch aus Tabelle V klar ersichtlich, in der die in Tabelle I aus der Literatur angeführten Daten mit den nach der Methode von MARGULES bzw. nach der hier beschriebenen Methode berechneten Resultaten verglichen wurden.

ZUSAMMENFASSUNG

Es wurde die Verwendbarkeit des Modells der regulären Dreikomponentengemisch von Typ A-A_2-B untersucht. Auf Grund von bei einer einzigen gegebenen Temperatur gemes senen Versuchsdaten wurden die Dampf-Flüssigkeitsgleichgewichtsdaten für andere Tem peraturen berechnet. Es wurde festgestellt, daß die Temperaturabhängigkeit der Gleichgewichtskonstante der Äthanol-Dimerisation mit der VAN'T HOFFschen Gleichung zu beschreiben ist, und die Austauschenergie als temperaturunabhängig betrachtet werden kann. Der Fehler der unter solchen Voraussetzungen berechneten Dampfdruckdaten liegt innerhalb des systematischen Fählers des Modells.

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THEORETICAL INTERPRETATION OF THE DIFFUSE STRUCTURE OF ASSOCIATED OH AND NH STRETCHING VIBRATION BANDS WITH SUBMAXIMA (OF THE CHELATE BANDS)*

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Received April 20, 1967

The cases of the appearance of the OH and NH chelate bands

When OH and NH stretching vibration bands are associated, their frequency will be lower, they become broader and more intense as compared to the respective bands of the corresponding free molecules. In the case of intermolecular and intramolecular hydrogen bonds, respectively, the measure of these effects is different. The band corresponding to groups in intramolecular association (in the case of a weak hydrogen bond) undergoes a smaller shift and becomes less broad (curve *B*, see Fig. 1) in comparison with the band of the free (monomeric) groups (curve *A*) [1—3], than the band assigned to groups asso-

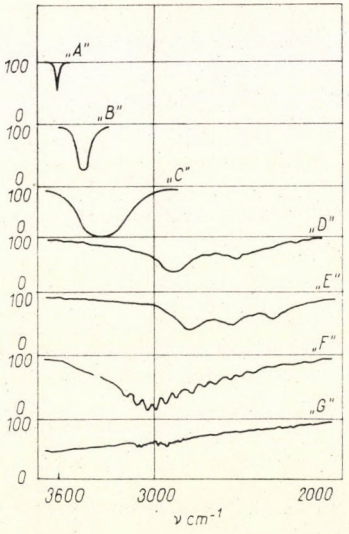
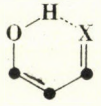


Fig. 1

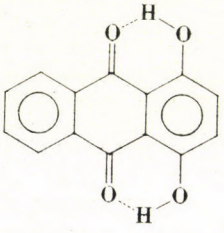
* The paper was presented at the VIIIth European Congress on Molecular Spectroscopy, Copenhagen, 14—20 August, 1965.

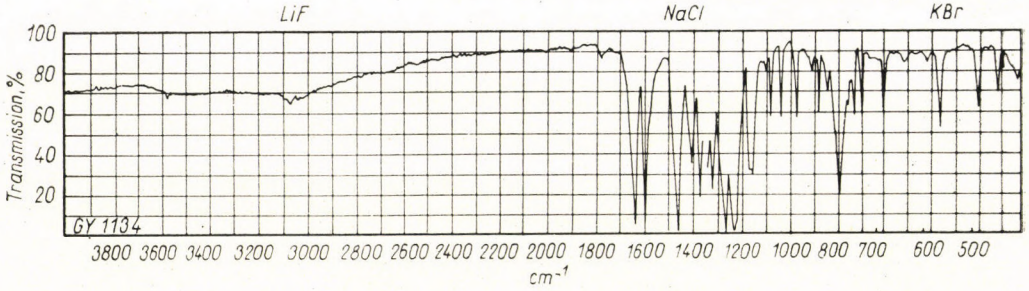
ciated intermolecularly (curve *C*). In the spectra of certain substances the OH stretching band undergoes a double or triple splitting, and the distance between maxima amounts to several hundred cm^{-1} (curves *D* and *E*) [4, 5, 6]. In some cases, presumably in the presence of extremely strong hydrogen bonds, as a particular feature of intramolecular bonds, the OH and NH stretching bands suffer an extremely great shift, sometimes up to 1800 cm^{-1}, and they become diffuse [1, 2, 7—10]. The diffuse band comprises several more or less perceptible submaxima (curve *F*). The submaxima appear contracted but unchanged in structure, in the spectra of the deuterated compounds at lower wave numbers [11, 17]. When the ring carrying the hydrogen bond is continuously conjugated and symmetric, a decrease in intensity may also occur simultaneously with the appearance of the diffuse character, and the absorption of the OH and NH stretching vibrations may disappear in the base line of the spectral curve (curve *G*) [12—15]. The appearance of curves *F* and *G*



I

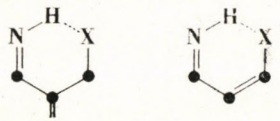
as a characteristic feature of structures expressed by Formula I, as a band of the OH stretching vibration, has often been observed (Spectrum 1). In the case





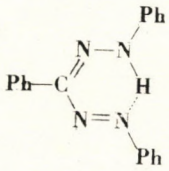
Spectrum 1. 1,4-dioxyanthraquinone

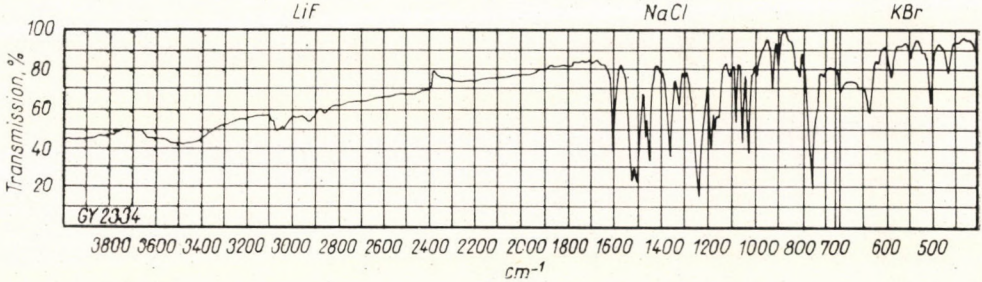
of NH groups, spectra corresponding to curves *F* or *G* were mainly found with compounds where the N atom has planar hybrid electron orbitals [15—17]



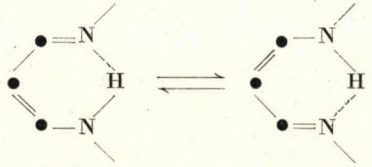
II III

(Structures II and III), or at least the N atom is the member of a mesomeric system the limit structures of which contain a N atom with a planar valence orientation (Formulas IV—XI) (Spectra 2, 3, 4). A completely analogous

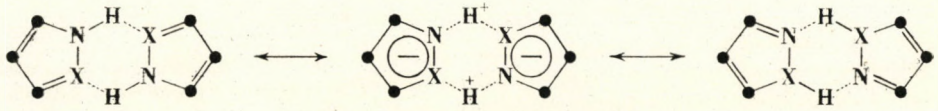




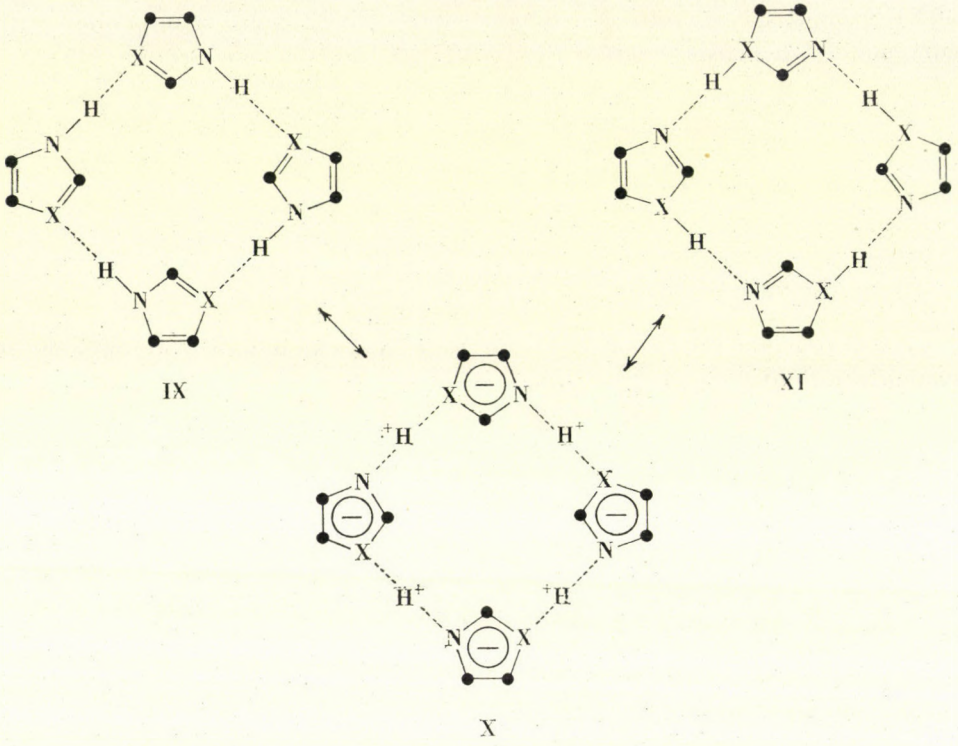
Spectrum 2. Triphenyl formasan

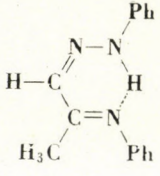


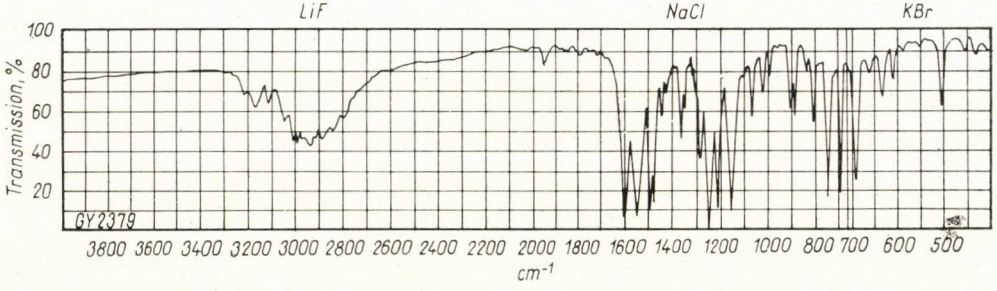
IV V



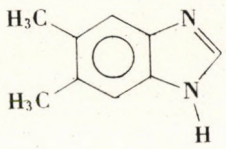
VI VII VIII

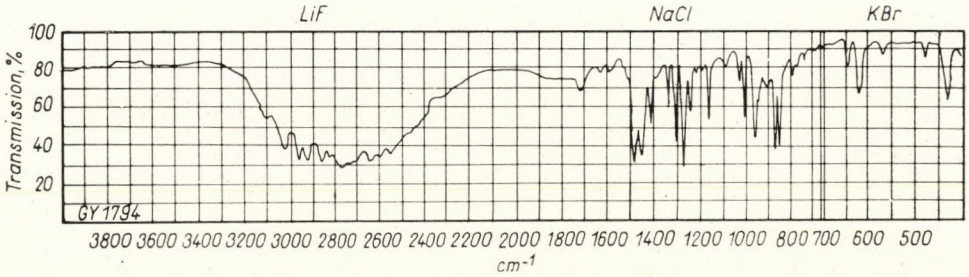






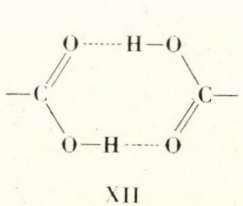
Spectrum 3. Methylglioxale phenyl hydrasone anilide



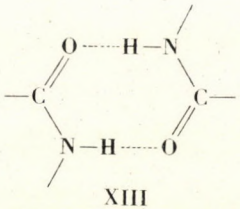


Spectrum 4. 5,6-dimethyl benzimidasole

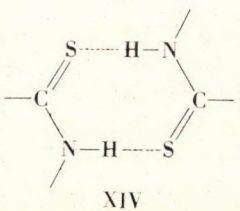
phenomenon (*i. e.* a stretching band according to curve *F*) can also be observed in the spectra of carboxylic acid dimers (XII) (Spectrum 5) [18—23], and according to our own investigations, in the spectra of cyclic amide dimers (Spectrum 6) and analogous compounds (Formulas XIII—XVI); in the latter cases,



XII



XIII



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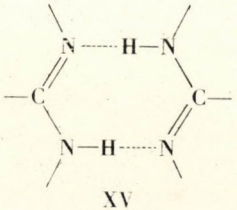

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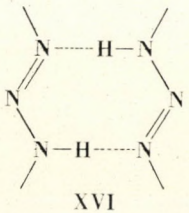

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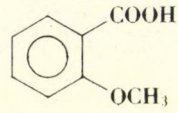
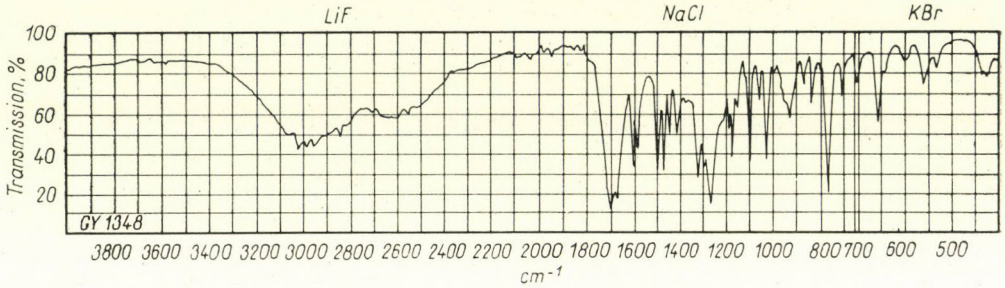
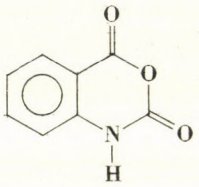
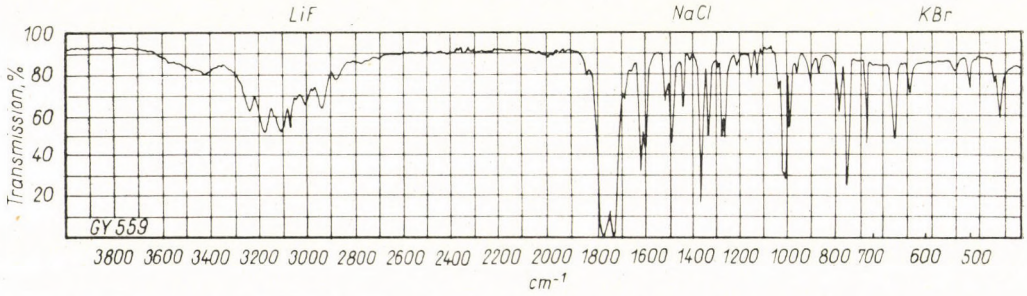




Spectrum 5. *o*-methoxy benzoic acid





Spectrum 6. Isatoic acid anhydride

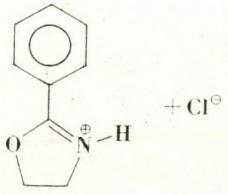
however, the distances between the submaxima are greater [17, 24]. The NH stretching band appears between 3300 and 2700 cm^{-1} (in KBr pellet), in con-

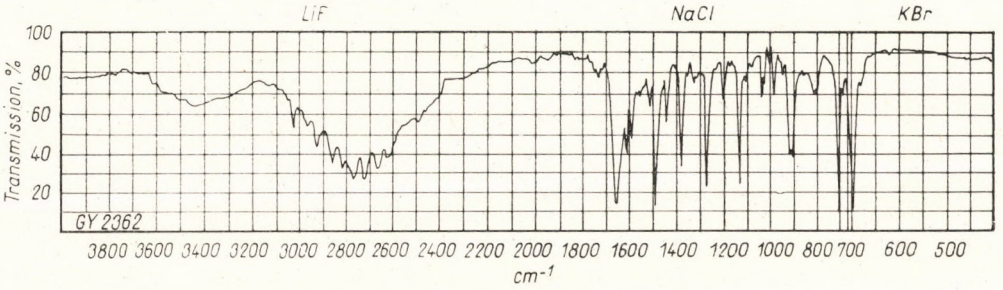
trast to literary data [25, 26] according to which the frequency of this band always exceeds 3050 cm^{-1}. The stretching bands of ionic NH groups also pos-



XVII XVIII

sess a similar structure (Formulas XVII and XVIII) (Spectrum 7) [2, 17]. This





Spectrum 7. Phenyl oxazoline chlorohydrate

absorption of *F* or *G* type commonly denoted as "chelate band", together with the contained submaxima, has been interpreted in several quite different ways such as by the fluctuation theory [27, 28], by the presence of a quasi-aromatic system [29], by the theory of frequency modulation [30, 31], *etc.* The present presumption complements this series with a novel mode of interpretation.

Internal rotation: structure of the γOH band

When a molecule contains two or more identical atoms, their exchange against one another leads to an equilibrium state equivalent to the original one; the molecule has several potential minima. Owing to the resonance among these latter, the energy levels of the molecule are split [32]. Two commonly known examples of this process are inversion and internal rotation.

The term-scheme of the internal rotation is the following [33]:

$$T = BJ(J+1) - BK^2 + A_1 k_1^2 + A_2 k_2^2 \qquad (1)$$

When A_1 and k_1 refer to the hydrogen atom, A_1 is much greater than A_2 and B. Accordingly, the band of the out-of-plane OH deformation vibration (*e. g.* the γOH band of alcohols) becomes markedly broader, and it is divided in submaxima at distances of $2A_1$ corresponding to various values of k_1. Here the value of $2A_1$ is defined by relation (2).

$$2A_1 = \frac{h}{4\pi^2 c\ m_H r^2} = \frac{h}{4\pi^2 c\ I_H} \tag{2}$$

Thus, in first approximation, the structure of the spectrum can be expressed by the formula:

$$\nu = \gamma(\mathrm{OH}) \pm k_1\, 2A_1 \tag{3}$$

Here γ(OH) is the frequency of the out-of-plane OH deformation vibration, m_H is the mass of H atom, r is the radius of the internal rotation, k_1 is the quantum number of partial rotation having values of small whole numbers.

Practically, the consequence of internal rotation is that the γOH band becomes so diffuse that in the majority of cases this band cannot be actually identified. However, when internal rotation is inhibited by an intramolecular or cyclic association, the γOH band has definite contours [3, 8, 17] and it can readily be identified, *e. g.* in the spectra of carboxylic acid dimers (*cf.* Spectrum 5).

Internal oscillation: structure of the νOH and νNH chelate bands

The structure of the bands of the OH and NH stretching vibrations is strikingly similar to that of the νOH bands in the case of formation of strong intramolecular and cyclic dimer associations; namely, the diffuse absorption is distributed into about equidistant submaxima also in this case. Consequently, we attempted for this case the deduction of a formula similar to (3).

Now let us consider the hydrogen bond of Scheme XIX where the hydrogen atom is not in the centre. In that case, provided that $X_1 = X_2$, two completely equivalent equilibrium states may be written: XIX and XX. Motion resulting

$$X_1\text{—}H\text{--------}X_2 \qquad\qquad X_1^-\text{-------}H^+\text{—}X_2$$

XIX XX

in a change of the equilibrium states, namely the internal oscillation of the proton, is possible, when the potential barrier between the equilibrium states is not too high (lower than the excitation energy of the XH stretching vibration). The curve expressing the probability function of the proton has two maxima. This can be quite well approached by the distribution curve of the harmonic oscillator belonging to the first excited quantum state. In this case the proton

performs an essentially independent vibration in the field of the pillar atoms, whose frequency will be the following:

$$kx^2 = hvc \tag{4}$$

where k is the force constant and x is the amplitude.

The amplitude x is equal to the difference of the bond lengths of $X_1—H$ and $H \ldots X_2$. On substituting k from HOOKE's law, we obtain Eq. (5) for the frequency of the proton which has identical form with Eq. (2) that expresses the internal rotation, and determines the distance of the submaxima from each other.

$$\nu(H) = \frac{h}{4\pi^2 cm_H x^2} \tag{5}$$

According to our presumption, when the internal oscillation of the proton is excited, the frequency value and its multiples are superposed on the frequency of the XH stretching vibration. The frequencies of submaxima originated in such a manner can be expressed by formula (6) where n may be a series of small whole numbers.

$$\nu = \nu(XH) \pm n\nu(H) \tag{6}$$

Formula (6) is the analogue of (3).

Consequently, the νXH bands divided into submaxima because of internal oscillation possess structures quite similar to those of the γOH bands split to submaxima owing to internal rotation.

It can be seen from Eq. (5) that the distances of the submaxima are determined by the difference (x) of the $X_1—H$ and $H \ldots X_2$ bond lengths. The smaller the value of x, *i.e.* the nearer are the two potential minima to each other, the higher is the frequency of internal oscillation, and thus the distance of the submaxima. When the bond distance X_1H is 0.95 Å and the length of the hydrogen bond ranges to 1.95 Å (these are the data of ice), the value of 0.5 Å is obtained for the amplitude. From this, the distance of submaxima ($2A_1$) is equal to 130 cm^{-1}. This value agrees fairly well with the experimental results. In an extreme case, x is equal to or shorter than the amplitude of the XH stretching vibration, or it may be even equal to zero when the proton occupies exactly the central position between the atoms X_1 and X_2. In this latter case, internal oscillation is converted into an $X_1—H—X_2$ antisymmetric stretching vibration. The condition of this conversion is the disappearance in the vibrational ground state of the potential barrier separating the two equilibrium positions, *i.e.* instead of the potential curve shown in Fig. 2a, the motion, instead of proton should be described by Fig. 2b. Then the hydrogen bond can be

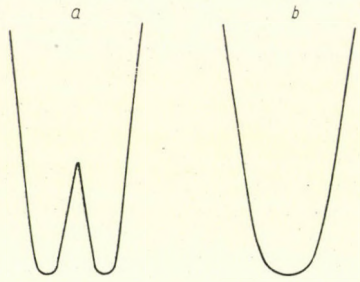
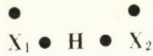


Fig. 2

represented, instead of Formulas XIX and XX, by the electronic structure XXI. In that case, the amplitude of internal oscillation is identical to the ampli-



XXI

tude of the *XH* stretching vibration in the first excited vibrational state, which now does not exceed the value of any common *XH* stretching vibration. When the frequency is 3000 cm^{-1}, the value of 0.11 Å is obtained from Eq. (4) for the amplitude. In this case the submaxima do not separate: the contour of the band of type *F* becomes smooth, and an absorption similar to curve *G* appears; when the *νXH* band is weak, it is not significant.

The above considerations may be generalized for any hydrogen bond, to obtain the following picture:

1. When the potential barrier is high even in an excited vibrational state, the interconversion of the two equilibrium states into each other is impossible. The hydrogen bond exerts only a weak perturbation effect on the term levels and the motion of the hydrogen atom is normal. The probability function of the proton in the vicinity of both possible equilibrium states shows a maximum (Fig. 3a). In the spectrum the *XH* stretching vibration band becomes broad, its frequency decreases, while its intensity rises.

2. When $X_1 = X_2$ the proton can be in both equilibrium positions with a finite probability due to the tunnel effect. In this case, owing to the splitting of the term levels, the *XH* stretching vibration band appears in the spectrum with two maxima (Fig. 3b).

Also cases when the potential minima are not quite symmetrical, the splitting of the term levels may result in three submaxima in the infrared spectrum [6].

3a. When the potential barrier is low in the vibrational ground state, the proton performs an internal oscillation (Fig. 3c). The frequencies of this

internal oscillation are superposed on that of the XH stretching vibration, and the band of the latter is divided in the spectrum into equidistant submaxima.

3b. When there is no potential barrier in the vibrational ground state, the probability function has one maximum in the midpoint of the distance $\overline{X_1X_2}$ (when $X_1 = X_2$), or in the vicinity of this point (when $X_1 \neq X_2$), while

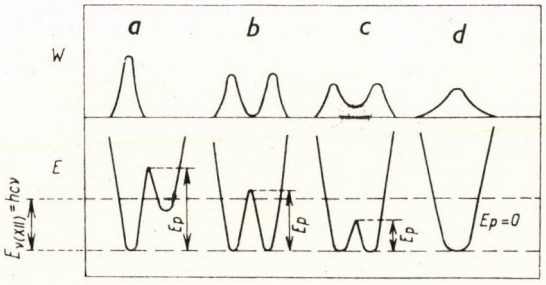


Fig. 3

the internal oscillation of the proton is transformed into an antisymmetric stretching vibration of the group $X_1 - H - X_2$, and no submaxima appear (Fig. 3d).

On applying these considerations, several experimental facts can be interpreted.

The height of the potential barrier, and thus the probability of internal oscillation are determined actually by the strength of the bonds $X_1 - H$ and $H \ldots X_2$. The lower the bond-order X_1H and the higher that of HX_2, the more probable is an internal oscillation. Thus it is readily understood that chelate bands of type F or G can be observed particularly in conjugated systems and in the case of acidic X_1H groups, further when X_2 is a strong electron donor. It is reasonable that no submaxima appear in case of intramolecular hydrogen bonds where the distance of the proton from both pillar atoms is identical, and that a curve of G type is found in the spectrum when the ring is completely symmetrical, and the XH bond is not very polar. In this case, namely, the very diffuse band of smooth contour is of low intensity, and it merges with the base line of the spectrum. Further, it can be understood that the submaxima of the NH stretching band are differentiated to a greater extent than those of the OH stretching bands, since the NH bond is longer, and thus x is shorter;

accordingly the distance of the submaxima is greater from each other. Up to the present, the only interpretation of the equidistant submaxima (apart from the assignment of overtones and combinations strengthened in FERMI-resonance) has been afforded by the theory of frequency modulation. On the basis of this assignment, however, no uniform interpretation of intermolecular and intramolecular associations was possible. Further, it was impossible to explain by the fluctuation theory why splitting to a doublet appears just with the relatively weak hydrogen bonds, while the strongest associations are characterized actually by the appearance of submaxima though fluctuation means a more radical interaction than the anharmonic coupling according to the frequency modulation theory, and thus the inverse of this observation would be expected.

The new theory gives a satisfactory interpretation of some strong deuterium bonds resulting in half-width *F*-type bands with a fine structure in which the distance of submaxima amounts just to the half of the corresponding proton bands [34]. The phenomenon is in agreement with Eq. (5), while it cannot be interpreted by the fluctuation theory.

SUMMARY

The *XH* stretching vibration band of groups present in strong hydrogen bonds is often divided into equidistant, diffuse submaxima of unusually low wave number, or it even disappears. These band types have been observed in case of hydrogen bonds formed by hydroxyl groups. According to our investigations they also appear in hydrogen bonds of the N—H...*X* type. The submaximum structure of the OH and NH stretching vibration bands is very similar to the out-of-plane deformation vibration bands of hydroxyl groups in internal rotation. It has been shown that the OH and NH stretching vibration bands of groups in strong association and the out-of-plane deformation bands of hydroxyl groups in internal rotation may be characterized by analogous mathematical formulas; this is the cause of the similarity of the band structures. These formulas have been obtained by assuming that in the case of a strong hydrogen bond the proton is in a separate vibration between the pillar atoms. This motion is called internal oscillation. Starting with this consideration, the various types of OH and NH stretching vibration bands of spectra taken in the solid phase have been systematized, and the types of hydrogen bonds characterized by them are indicated.

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GENERALIZED MEAN SQUARE AMPLITUDES OF VIBRATION AND SHRINKAGE EFFECT IN $CH_3C{\equiv}CCH_3$ AND $CF_3C{\equiv}CCF_3$

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1. Introduction

MEISTER *et al.* [1] have carried out a normal coordinate treatment of the non-degenerate vibrations of dimethylacetylene, assuming D'_{3h} symmetry. Later DUNCAN [2] evaluated the potential energy constants, CORIOLIS zeta constants and centrifugal stretching constants of the molecule, taking the staggered configuration, belonging to the D_{3d} point group. For hexafluoro-2-butyne, GALASSO and BIGOTTO [3] have evaluated the potential energy constants of G. V. F. F. by a least-square iterative method. They have also evaluated the rotation-distortion constants, mean square parallel amplitudes of vibration, and thermodynamic properties. No attempt has so far been made to compute the generalized mean square amplitudes of vibration for these molecules. In the present investigation the theory of the mean square amplitudes of vibration has been applied to the two molecules; the mean square amplitudes of vibration at 300°K have been determined and used for the evaluation of the perpendicular mean square amplitudes; from them, by applying the theory developed by MORINO, the BASTIANSEN—MORINO shrinkage [4, 5] effect has been calculated.

2. Vibrational frequencies, symmetry coordinates and the kinetic energy matrix

Both dimethylacetylene and hexafluoro-2-butyne have staggered configuration, belonging to the point group D_{3d}. The former has got tetrahedral symmetry while the latter has not. The normal modes of vibration are distributed among the various symmetry species as $4a_{1g} + 1a_{1u} = 3a_{2u} = 4e_a = 4e_g$. In either case, the a_{1u} species torsional vibration has not been reported, hence it is not included in the calculation. The vibrational frequencies and structural parameters used in this investigation are the same as those used by DUNCAN [2] and GALASSO et al. [3] in the case of $CH_3{\equiv}CCH_3$ and $CF_3C{\equiv}CCF_3$ respectively. The symmetry coordinates used by DUNCAN have been taken. The symmetry coordinates are expressed in terms of cartesian displacement coordinates and the elements of the K. E. matrix may be derived using MEAL and POLO's [6] S-vector method. The molecular configuration and the orientation of the principal axes are shown in Fig. 1.

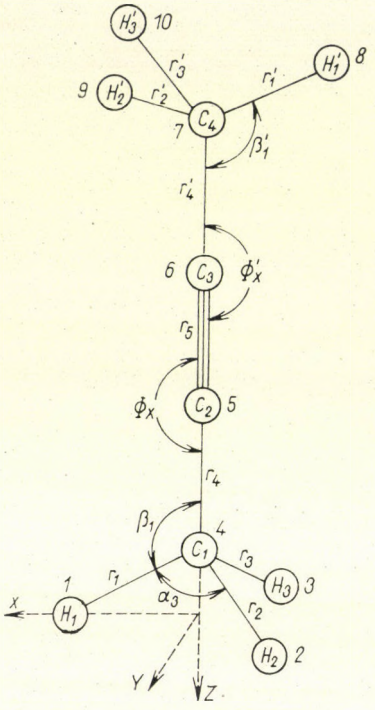

Fig. 1. Notation, numbering of atoms, and orientation of cartesian coordinate axes of $CH_3{\equiv}CCH_3$ and $CF_3C{\equiv}CCF_3$

3. Generalized mean square amplitude matrices

The symmetrized mean square amplitude matrix Σ was calculated by CYVIN's [7] method, solving the secular equation,

$$|\Sigma G^{-1} - \Delta E| = 0,$$

where

$$\Delta = \frac{h}{8\pi^2} \coth \frac{hv}{2kT}.$$

Using the method of MORINO and HIROTA [8], the expressions for the generalized mean square amplitudes of vibration for the various bonded and non-bonded distances were derived. They are the same as in methylacetylenes [9]. The additional expressions for the two non-bonded distances (1 . . . 8) and (1 . . . 9) are given below:

(1 . . . 8)

$$\langle(\Delta z)^2\rangle = \langle[-\sin\psi(x_1 - x_8) + \cos\psi(z_1 - z_8)]^2\rangle$$

$$\langle(\Delta x)^2\rangle = \langle[\cos\psi(x_1 - x_8) + \sin\psi(z_1 - z_8)]^2\rangle$$

$$\langle(\Delta y)^2\rangle = \langle[y_1 - y_8]^2\rangle$$

(1 . . . 9)

$$\langle(\Delta z)^2\rangle = \langle[-\sin\eta(y_1 - y_9) - \cos\eta(z_1 - z_9)]^2\rangle$$

$$\langle(\Delta x)^2\rangle = \langle[-\cos\eta(y_1 - y_9) + \sin\eta(z_1 - z_9)]^2\rangle$$

$$\langle(\Delta y)^2\rangle = \langle[x_1 - x_9]^2\rangle,$$

where (180-ψ) and (180-η) are angles made by the positive Z axis with the (1 . . . 8) and (1 . . . 9) non-bonded distances, respectively.

4. Shrinkage effect

The generalized mean square amplitudes are important in evaluating the shrinkages. The shrinkage is calculated by taking the difference between the mean value of the internuclear distance in the molecule and the sum of the individual bond lengths composing it. In the present case the following shrinkage constants were obtained.

Table I

Elements of the Σ matrices $(\text{Å})^2$ *of* $CH_3C{\equiv}CCH_3$ *and* $CF_3C{\equiv}CCF_3$

Symbol	$CH_3{\equiv}CCH_3$	$CF_3C{\equiv}CCF_3$
$\Sigma_{11} = \Sigma_{66}$	0.006466	0.001786
$\Sigma_{22} = \Sigma_{77}$	0.035501	0.002624
$\Sigma_{33} = \Sigma_{88}$	0.001950	0.001928
Σ_{44}	0.001200	0.001179
$\Sigma_{12} = \Sigma_{67}$	0.001061	0.000601
$\Sigma_{13} = \Sigma_{68}$	−0.000302	−0.000311
$\Sigma_{23} = \Sigma_{78}$	0.000224	0.000231
Σ_{34}	−0.000734	−0.000849
$\Sigma_{99} = \Sigma_{13,13}$	0.005932	0.001965
$\Sigma_{10,10} = \Sigma_{14,14}$	0.022320	0.002104
$\Sigma_{11,11} = \Sigma_{15,15}$	0.045580	0.008570
$\Sigma_{12,12}$	0.116201	0.044921
$\Sigma_{9,10} = \Sigma_{13,14}$	0.000390	0.000381
$\Sigma_{9,10} = \Sigma_{13,15}$	0.001362	0.001050
$\Sigma_{10,11} = \Sigma_{14,15}$	0.000553	0.000549
$\Sigma_{16,16}$	0.007386	0.021312

All other off-diagonal elements are zero.

Table II

Generalized mean square amplitudes of vibration (Å²) of $CH_3C{\equiv}CCH_3$ and $CF_3C{\equiv}CCF_3$

Molecule	Atom pair	$\langle(\Delta z)^2\rangle$	$\langle(\Delta x)^2\rangle$	$\langle(\Delta y)^2\rangle$	$\langle\Delta x\Delta\gamma\rangle$	$\langle\Delta x\Delta y\rangle$	$\langle\Delta y\Delta z\rangle$
$CH_3C{\equiv}CCH_3$	C—H	0.006116	0.021706	0.006482	—0.000296	—	—
	C—C	0.001950	0.014063	0.014063	—	—	—
	C≡C	0.001200	0.020703	0.020703	—	—	—
	$H_2\ldots H_3$	0.015163	0.007260	0.007422	—	—0.001221	—
	$H_1\ldots C_2$	0.018575	0.016284	0.010966	—0.005061	—	—
	$H_1\ldots C_3$	0.020336	0.015296	0.011678	—0.005179	—	—
	$H_1\ldots C_4$	0.021641	0.010043	0.007378	—0.006586	—	—
	$C_1\ldots C_3$	0.002111	0.012456	0.012456	—	—	—
	$C_1\ldots C_4$	0.003023	0.002603	0.002603	—	—	—
	$H_1\ldots H_8$	0.034002	0.021047	0.010687	—0.015114	—	—
	$H_1\ldots H_9$	0.039832	0.005072	0.012416	—0.002901	—0.000504	0.005577
$CF_3C{\equiv}CCF_3$	C—F	0.002025	0.002462	0.003964	0.000951	—	—
	C—C	0.001928	0.018819	0.018819	—	—	—
	C≡C	0.001179	0.012927	0.012927	—	—	—
	$F_2\ldots F_3$	0.003077	0.000876	0.002521	—	—0.000557	—
	$F_1\ldots C_2$	0.005889	0.006259	0.007130	0.000094	—	—
	$F_1\ldots C_3$	0.006098	0.007521	0.007504	0.001582	—	—
	$F_1\ldots C_4$	0.006658	0.005037	0.004029	—0.000622	—	—
	$C_1\ldots C_3$	0.001907	0.016141	0.016141	—	—	—
	$C_1\ldots C_4$	0.002633	0.001062	0.001062	—	—	—
	$F_1\ldots F_8$	0.008297	0.003352	0.000633	—0.002404	—	—
	$F_1\ldots F_9$	0.008961	0.001768	0.001796	—0.001831	—0.000365	—0.000222

$$-\delta_{46} = \frac{\tau_{46}}{r_4 + r_5} - \frac{\tau_{45}}{r_4} - \frac{\tau_{56}}{r_5}$$

$$-\delta_{47} = \frac{\tau_{47}}{2r_4 + r_5} - \frac{2\tau_{45}}{r_4} - \frac{\tau_{56}}{r_5}$$

where τ's represent the perpendicular mean square amplitudes for the corresponding bonds.

$$\tau_{ij} = \frac{<(\Delta x_{ij})^2> + (\Delta Y_{ij})^2>}{2}, \text{ for the linear bonds:}$$

$$\langle(\Delta x_{ij})^2\rangle = \langle(\Delta Y_{ij})^2\rangle.$$

PAULING, SPRINGALL and PALMER [10] found that the C—C bond distance for molecules with resonance structure is shorted. Therefore, the smaller mean amplitude of the C—C bond may be attributed to the shortening of these bonds in molecules with resonant structure. The C≡C mean amplitude value agrees well with that of methylacetylene [9]. The parallel mean square amplitude increases with the distance, as it is seen in the case of the non-bonded distances, (1 . . . 5) (1 . . . 6) and (1 . . . 7). But in the case of the distances (1 . . . 8) and (1 . . . 9), the reverse effect is observed, as it is usually found in *trans* and *cis* cases. As expected, in the same molecule, a larger distance has got a greater shrinkage effect.

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Table III

Shrinkage effect (Å) *in* $CH_3C{\equiv}CCH_3$ *and* $CF_3C{\equiv}CCF_3$ *at 300°K*

Symbol	$CH_3C{\equiv}CCH_3$		$CF_3C{\equiv}CCF_3$	
	distance (Å)	shrinkage	distance (Å)	shrinkage
δ_{46}	2.665	0.02214	2.685	0.01742
δ_{47}	4.123	0.03581	4.150	0.03601

SUMMARY

A theoretical treatment of the generalized vibrational mean square amplitudes of the dimethylacetylene and hexafluoro-2-butyne molecules is presented. The numerical values computed for the parallel and perpendicular mean square amplitudes for all bonded and non-bonded distance deviations are reported. Using the perpendicular mean square amplitudes, the shrinkage constants have been evaluated. All these values are reported at 300°K.

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GENERALIZED MEAN SQUARE AMPLITUDES AND CORIOLIS COUPLING COEFFICIENTS OF PYRAMIDAL XYZ_2 MOLECULES

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1. Introduction

Characterized, as they are, by a low symmetry, C_s pyramidal XYZ_2 molecules provide an interesting problem. The generalized mean square amplitudes and CORIOLIS coupling coefficients of the fluoro- and chloroamines (NF_2H, NF_2D, NH_2Cl and NCl_2H) which belong to this type have been obtained in this investigation. The fluoroamines were first prepared by KENNEDY and COLBURN [1]. LIDE's [2] microwave study threw light on their structure. COMEFORD *et al.* [3] have reported the infrared spectra of these molecules and SUNDARAM, SARMA and PIOTROWSKI [4] have recently made a normal coordinate analysis. The chloroamines have received somewhat less attention. The spectral assignment due to MOORE and BADGER [5] is incomplete but VENKATESWARLU, THIRUGNANASAMBANDAM and BALASUBRAMANIAN [6] as well as THIRUGNANASAMBANDAM [7] have calculated the missing frequencies using the general valence force field.

2. Generalized mean square amplitudes

The symmetry coordinates employed in the present work were taken from Reference [6] after modifying the angle coordinates as usual. The notation is explained in Fig. 1.

The elements of the symmetrized mean square amplitude matrix Σ are defined by $\Sigma_{ij} = \langle S_i S_j \rangle$ where the S_s' are symmetry coordinates whose numbering is the same as in Reference [6], and the brackets denote averaging. The secular equation $|\Sigma G_1^- - E\Delta| = 0$ where G is the kinetic energy matrix and the Δ_s' are mean square values of the normal coordinates, was solved by the method of successive approximations and the Σ-matrix elements were obtained.

MORINO and HIROTA's theory [10] has been applied to evaluate the generalized mean square amplitudes. The mean square amplitude of an atom pair, *ijf*, in a direction specified by the unit vector n_ξ, is given by

$$\langle \Delta\xi^2 \rangle = \langle [\vec{n}\,\xi\,(\vec{\varrho}_i - \vec{\varrho}_j)]^2 \rangle$$

where the ϱ's are the $\vec{\varrho}$-vectors [11] for the atoms i and j. The $\vec{\varrho}$-vector components have been obtained by means of CRAWFORD and FLETCHER's [12] well-known relation,

$$X = \mu B G^{-1} S$$

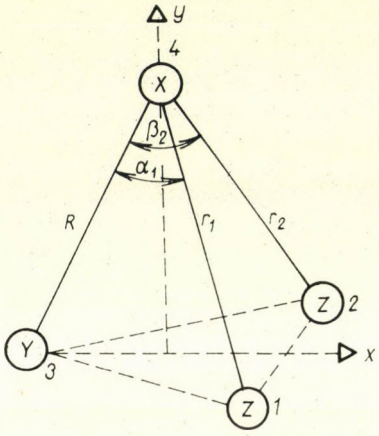

Fig. 1. Pyramidal XYZ_2 molecule: Internal coordinates, numbering of atoms and orientation of principal axes

3. Coriolis coupling coefficients

According to MEAL and POLO [13] the CORIOLIS coupling coefficients are expressed by $\zeta^\alpha = L^{-1} C^\alpha L^{-1}$ where L is the normal coordinate transformation matrix and C^α is a matrix whose elements depend on the masses of the atoms and geometry of the molecule, and $\alpha = x, y, z$ represents the principal axis system. In the present case both ζ^z and ζ^y exist, thus accounting for the vibrational coupling of the species a' and a'' through rotations R and R_y. The C^α-elements were derived by MEAL and POLO's vector method [13].

4. Results and discussion

The structural parameters and fundamental frequencies adopted for the present calculation were taken from References [1—3 and 5].

The Σ-matrix elements are given in Table I. It is seen from Table II which gives the generalized mean square amplitudes that, whereas the parallel values, $\langle \Delta\zeta^2 \rangle$, of characteristic bonds remain more or less constant, the perpendicular values vary considerably in the different molecules. The $\langle \Delta Y^2 \rangle$-value is found to be most affected by the environment. It may be noted that the N—F bond has nearly the same value for the generalized mean square amplitudes and mean

Table I

Σ-Matrix elements of NF_2H, NF_2D, NH_2Cl and NCl_2H at 300°K. Units: 10^{-4} Å^2

Σ_{ij} / Molecule	NF_2H	NF_2D	NH_2Cl	NCl_2H
Σ_{11}	56.16	41.11	24.21	54.93
Σ_{22}	73.87	75.23	246.30	198.80
Σ_{33}	22.61	15.90	57.42	25.91
Σ_{44}	238.70	188.70	272.00	255.30
Σ_{55}	16.29	23.14	54.05	23.02
Σ_{66}	367.40	202.80	287.40	338.60
Σ_{12}	−2.13	1.78	1.51	6.28
Σ_{13}	−7.90	−1.16	−5.38	−4.94
Σ_{14}	−3.33	−8.54	−10.97	−1.72
Σ_{23}	−19.07	−12.65	6.36	11.79
Σ_{24}	−6.83	−5.43	−31.60	81.94
Σ_{34}	−4.13	−1.32	23.34	−26.79
Σ_{56}	−18.31	−21.94	−4.84	−12.00

Table II

Generalized mean square amplitudes of NF_2H, NF_2D, NH_2Cl and NCl_2H at 300°K. Units: 10^{-4} Å^2

Molecule	Atom pair	$\langle \Delta z^2 \rangle$	$\langle \Delta x^2 \rangle$	$\langle \Delta y^2 \rangle$	$\langle \Delta y \Delta z \rangle$	$\langle \Delta z \Delta x \rangle$	$\langle \Delta x \Delta y \rangle$
NF_2H	N—H	56.16	249.97	149.92	..	−65.51	..
	N—F	19.45	16.39	21.76	7.57	−9.13	11.28
	H...F	138.38	171.17	318.70	−103.62	−52.05	−76.38
	F...F	55.22	1.47	0.85	..	..	−0.78
NF_2D	N—D	41.11	142.29	59.49	..	−34.78	..
	N—D	19.52	14.51	18.86	9.80	−7.80	12.88
	D...F	100.63	84.42	193.22	−44.47	−14.95	−61.12
	F.. F	59.22	2.29	1.18	..	..	−1.02
NH_2Cl	N—H	55.00	149.00	8.10	..	9.90	..
	N—Cl	24.00	2.69	1.20	..	4.55	..
	H...Cl	101.00	46.50	68.20	38.80	23.20	7.8
	H...H	146.20	238.90	68.80	15.40	15.10	46.3
NCl_2H	N—H	54.70	123.20	28.40	..	3.20	..
	N—Cl	24.50	1.90	55.10	..	0.60	..
	H...Cl	97.75	42.20	121.10	22.20	..	6.60
	Cl...Cl	75.90	0.70	0.30	..	..	0.40

Table III

Coriolis coupling coefficients (ζ^x and ζ^y) of NF_2H, NF_2D, NH_2Cl and NCl_2H

ζ_{ij}^{α}	NF_2H	NF_2D	NH_2Cl	NCl_2H
ζ_{15}	−0.0521 0.0593	−0.0319 0.0425	0.0792 −0.0943	−0.0337 0.0738
ζ_{25}	0.3846 0.6763	0.5536 −0.2966	0.6075 0.7678	0.4533 0.6565
ζ_{35}	−0.4994 −0.4023	0.2726 0.6357	−0.0651 −0.0498	0.3110 0.4709
ζ_{45}	0.2316 −0.1649	0.5081 −0.2505	0.7101 −0.2296	0.1055 −0.2923
ζ_{16}	0.5549 −0.6708	0.5262 −0.6759	0.0281 −0.2296	0.2808 −0.6025
ζ_{26}	−0.2905 0.2522	−0.1822 0.2581	−0.0266 0.4512	−0.1299 −0.1515
ζ_{36}	0.0396 0.1765	−0.3523 0.0453	−0.1706 0.7605	−0.0760 −0.0014
ζ_{46}	0.6132 −0.7975	0.5441 −0.5054	−0.2357 0.2296	−0.5120 −0.2421

cross products in both NF_2H and NF_2D. The N—Cl parallel mean square amplitude is greater than the N—F value, but the perpendicular amplitudes do not vary according to a definite pattern.

The Coriolis coupling coefficients given in Table III showing the strength of vibrational coupling do not seem to vary according to fixed rules. Both ζ_{15}^z and ζ_{15}^y are of the same order of magnitude in all molecules studied here.

SUMMARY

The generalized mean square amplitudes and Coriolis coupling coefficients of some molecules of the pyramidal XYZ_2 type have been evaluated. It has been found that the value is most sensitive to the environment. Higher halogen substitution leads to an increased $\langle \Delta z^2 \rangle$ value.

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INVESTIGATION OF THE REACTIVITY OF ORGANIC COMPOUNDS IN LIQUID PHASE FREE-RADICAL REACTIONS, II*

THE RELATIVE REACTIVITIES OF ORGANIC ACIDS WITH METHYL RADICALS IN LIQUID PHASE

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Owing to the special electron structure of organic acids, the reactivities of these compounds are influenced by several combined factors. In our present work the relative reactivities of homologues of saturated organic acids have been investigated in liquid phase, in an apolar solvent, according to the reaction equation

$$RCOOH + CH_3^{\cdot} \rightarrow CH_4.$$

The tritium isotope-kinetic method was employed in the experiments, following the methodical principles described in Part I. *n*-Heptane was used as the solvent, the ratio of labelled and non-labelled solvent molecules being $\frac{[RT]}{[RH]} \sim 10^{-6}$. The methyl radicals were obtained from the thermal decomposition of diacetyl peroxide. The free radicals produced participate in the investigated kinetical system in the following concurrent reactions:

$$\begin{aligned} RH + CH_3^{\cdot} &\xrightarrow{k_{st}^{H}} CH_4 \\ RT + CH_3^{\cdot} &\xrightarrow{k^{T}} CH_3T \\ RCOOH + CH_3^{\cdot} &\xrightarrow{k_{\sigma}^{H}} CH_4 \end{aligned} \qquad \text{(I)}$$

where the molecular reactivity of the carboxylic acid, k_{σ}^{H}, may be described related to the reactivity of a secondary C—H bond of *n*-heptane by the expression given in Part I:

$$\frac{k_{\sigma}^{H}}{k_{st}^{H}} = n \cdot \frac{I_0 - I}{I} \cdot \frac{[RH]}{[RCOOH]} \qquad (1)$$

where $n = 10.5$ for the molecule of *n*-heptane. The ratio $k_{\sigma}^{H}/k_{St}^{H}$ is used to characterize the molecular reactivity of the acid.

* Part I: Acta Chim. Acad. Sci. Hung. **54**, 377 (1967).

As it has been proved in Part I, in the reactions of hydrocarbons with methyl radicals, the relative molecular reactivity calculated from Eq. (1) depends on the concentration. For the time being, there is no reliable explanation for this concentration dependence and, thus, we cannot take a definite standpoint concerning its general form. However, we suppose — mainly on the basis of several experiments with hydrocarbons — that the concentration dependence is linear, *i.e.* it may be written as follows:

$$\frac{k_\sigma^{\mathrm{H}}}{k_{st}^{\mathrm{H}}} = ax + b \tag{2}$$

where a and b are constants, and x is the concentration of the investigated compound, in our case that of the acid, in the system (expressed in mole per cent). By converting Eqs (1) and (2), the change of the radioactivity (I) of the formed methane is obtained as a function of the acid concentration:

$$I = \frac{100 - x}{\frac{a}{n I_0} x^2 + x\left(\frac{b}{n I_0} - \frac{1}{I_0}\right) + \frac{100}{I_0}} \cdot \tag{3}$$

For a more simple determination of the constants figuring in Eq. (3), the transformation

$$\bar{I} = \frac{100 - x}{I}$$

is introduced; then from the equation

$$\bar{I} = \frac{a}{n I_0} x^2 + x\left(\frac{b}{n I_0} - \frac{1}{I_0}\right) x + \frac{100}{I_0}. \tag{4}$$

When $\bar{I}$ and x are known, the constants a, b and I_0 may be calculated by employing the method of the least squares. Thus, I_0 may be obtained without measuring its value experimentally or using graphic extrapolation of the function $I = \mathrm{f}(x)$ with $x \longrightarrow 0$. This possibility decreases the number of necessary measurements. It is evident that the specific radioactivity of n-heptane has to be the same in all measurements made with reaction mixtures of different concentrations.

In the case of acids, the experiments have shown [1] that the concentration dependence of $k_\sigma^{\mathrm{H}}/k_{st}^{\mathrm{H}}$ is indeed linear, *i.e.* our supposition expressed in the form of Eq. (2) corresponds to the facts; the slope is zero in the case of acetic acid and cyclohexane-carboxylic acid, in other cases it is different from zero.

As it has been shown [1] in the case of hydrocarbons as well as in that of acids the measured $k_\sigma^{\mathrm{H}}/k_{st}^{\mathrm{H}}$ values are independent of the initial radioactivity of n-heptane, *i.e.* of the extent of labelling of the solvent.

The relative molecular reactivities of carboxylic acids

The above method was used to investigate the molecular reactivities of the following *n*-carboxylic acids: acetic acid, propionic acid, butyric acid, valeric acid, caproic acid, enanthic acid; of the isocarboxylic acids, isobutyric acid and cyclohexylic acid were studied. The dependence of the relative molecular reactivities on the acid concentration of the mixture has been stated for each of the above acids. This dependence is linear in every case; with acetic acid and cyclohexane-carboxylic acid k_σ^H/k_{st}^H is independent of the concentration over the range measured; for the other acids, negative slopes have been found. Furthermore, the ARRHENIUS parameters of the relative reactivities were calculated from the k_σ^H/k_{st}^H ratio measured at four different temperatures, namely at 60, 70, 80 and 90°C. The results are summarized in Table I, where two values of k_σ^H/k_{st}^H are given, namely those extrapolated to the limits $x \to 0$ and $x \to 100\%$, on the basis of the relation $k_o^H/k_{st}^H = f(x)$. The ΔE activation energy differences calculated for $x \to 0\%$ and the A_σ^H/A_{st}^H action constant ratios are also indicated. The relative error of the values shown in Table I is less than 5%. The k_σ^H/k_{st}^H values listed in Table I were measured at 80°C.

Table I

Reactivities extrapolated to 0 and 100 mole% of n-heptane at 80°C and the Arrhenius parameters

Acid	$\left(\frac{k_\sigma^H}{k_{st}^H}\right)_{x\to 0}$	$\left(\frac{k_\sigma^H}{k_{st}^H}\right)_{x\to 100}$	$\Delta E_{x\to 0}$ cal/mole	$\left(\frac{A_\nu^H}{A_{st}^H}\right)_{x\to 0}$
Acetic acid	2.24	2.24	—2080	40.10
Propionic acid	21.75	16.51	2020	1.28
Butyric acid	18.70	14.60	1370	2.58
Valeric acid	20.00	15.25	— 970	5.00
Caproic acid	16.38	13.92	—	—
Enanthic acid	22.20	16.39	—	—
Isobutyric acid	62.93	36.71	— 720	19.56
Cyclohexane-carboxylic acid	38.59	38.59	1260	6.57

It is seen from Table I that in the first members of the homologous series of normal carboxylic acids, k_σ^H/k_{st}^H changes according to a "saw-tooth" diagram, depending on the number of CH_2 groups (N_{CH_2}) present in the carboxylic acid (Fig. 1). From preliminary considerations it would be expected that the relation $k_\sigma^H/k_{st}^H = f(N_{CH_2})$ is linear or nearly linear, with a positive direction factor, but as it is seen in Fig. 1, this is not so in the case of the first members of the homologous series of *n*-carboxylic acids. This fact is possibly explained by the fine structure of the acids, and perhaps by a special order prevailing in the systems consisting of acid and apolar solvents.

As it is well known, the introduction of a carboxyl group increases the reactivity of the carbon chain. This can be explained qualitatively with the electron-withdrawing effect resulting from the electrophilic character of the carboxyl group and affecting the electron cloud of the neighbouring C—H bonds. This effect may act upon the C—H bonds near the carboxyl group, but occasionally on the whole carbon chain. One purpose of our work with carboxyl-

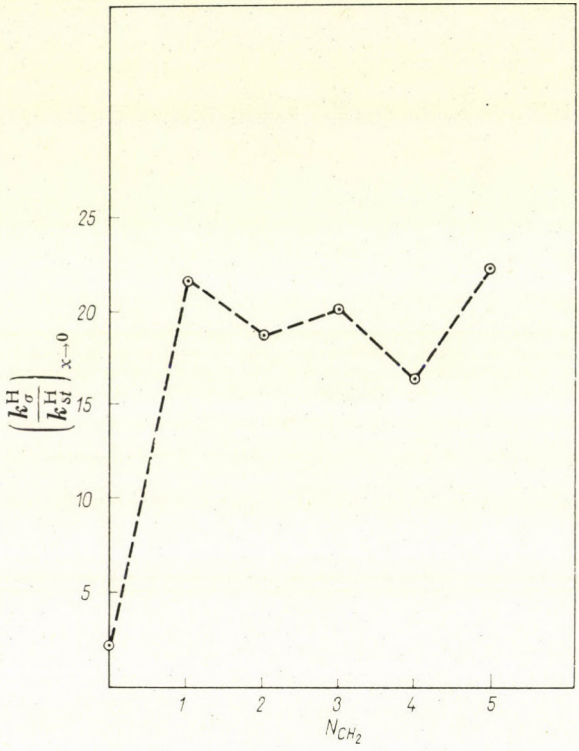

Fig. 1. The relative molecular reactivities of carboxylic acids as a function of the number of CH_2 groups of the carbon chain at 80°C

ic acids has been the quantitative determination of this effect. Using the data of TROTMAN-DICKENSON [2], the ratio of the partial reactivities of the C—H bonds in ethane and methane may be calculated (at 80°C) for a gas-phase reaction of the following type:

$$RH + CH_3^{\cdot} \rightarrow CH_4.$$

This ratio is as follows:

$$\frac{k_\sigma^H\, C_2H_6}{6} : \frac{k_\sigma^H\, CH_4}{4} = 16.3.$$

In our case the ratio of the partial reactivities of the C—H bonds in α-positions in propionic and acetic acid is 15. In other words, it can be supposed on the basis of the satisfactory agreement between the two partial reactivity ratios that the reactivities of the neighbouring C—H bonds are increased to the same extent by the carboxylic group in acetic acid and propionic acid. (It has to be noted, however, that this conclusion has involved a considerable neglection; namely, it has been supposed that in propionic acid, the reactivity-increasing influence of the carboxylic group on the β—C—H bonds is negligible as compared with the effect exerted on the neighbouring α—C—H bonds.) A total evaluation of the electron-withdrawing effect of the carboxyl group becomes possible only after the partial reactivities, constituting the molecular reactivity additively have been determined in adequately chosen members of the homologous series.

Partial reactivity of the hydrogen atom of the carboxyl group

Experiments were also carried out in a system in which the solvent, *n*-heptane was not labelled, but the hydrogen atom of the carboxyl group of acetic acid was substituted by tritium. In this case, the following reactions take place:

$$\begin{aligned} CH_3COOT + CH_3^{\cdot} &\xrightarrow{k_{OT}} CH_3T \\ CH_3COOH + CH^{\cdot} &\xrightarrow{k_{\sigma}^{H}} CH_4 \\ RH + CH_3^{\cdot} &\xrightarrow{k_{st}^{H}} CH_4. \end{aligned} \qquad \text{(II)}$$

The rates of formation of methane and tritiated methane, respectively, are as follows:

$$\frac{d[CH_3T]}{d\tau} = k_{OT} \cdot [CH_3COOT] \cdot [CH_3^{\cdot}] \qquad (5a)$$

$$\frac{d[CH_4]}{d\tau} = k_{\sigma}^{H} \cdot [CH_3COOH] \cdot [CH_3^{\cdot}] + n \cdot k_{st}^{H} [RH] \cdot [BH_3^{\cdot}] \qquad (5b)$$

where n is the number of the equivalent secondary C—H bonds in the *n*-heptane molecule. From Eqs (5a) and (5b) we get:

$$\frac{d[CH_3T]}{d[CH_4]} = \frac{k_{OT}[CH_3COOT]}{k_{\sigma}^{H}[CH_3COOH] + n \cdot k_{st}^{H}[RH]}. \qquad (6a)$$

As long as the conversions are low, the initial concentrations may be written on the right-hand side, and the quantities of $[CH_3T]$ and $[CH_4]$ are proportional to the reaction time; thus, on the left-hand side, instead of the differential quotient the change ratio can be written:

$$\frac{[CH_3T]}{[CH_4]} = \frac{k_{OT}\,[CH_3COOT]}{k_\sigma^H\,[CH_3COOH]_0 + n \cdot k_{st}^H\,[RH]_0} \tag{6b}$$

where the subscripts relate to the initial concentrations in the mixture. However, as the ratio of tritiated and non-tritiated acid concentrations is proportional to the initial radioactivity of the acid, *i.e.*:

$$\frac{[CH_3COOT]_0}{[CH_3COOH]_0} = \gamma I_o$$

and similarly, the ratio of the formed labelled and non-labelled methane is proportional to the measured radioactivity: $\frac{[CH_3T]}{[CH_4]} = \gamma I$, thus, introducing the symbol

$$\frac{[CH_3COOH]_0}{[RH]_0} = \alpha^* \tag{6c}$$

from Eq. (6b), the following equation is obtained:

$$\frac{k_{OT}}{k_{st}^H} = \frac{I}{I_0}\left(\frac{k_\sigma^H}{k_{st}^H} + \frac{n}{\alpha^*}\right). \tag{7}$$

(In the above expressions γ is the so-called proportionality factor, characteristic of the method of measuring the radioactivity.)

If the molecular reactivity belonging to a given value of α^* is known, the ratio k_{OT}/k_{st}^H can be calculated from Eq. (7).

On the basis of thermochemical calculations [3] the energy of the O—H bond in carboxylic acids is ~110 kcal/mole, which is definitely higher than the energy of a C—H bond (85—100 kcal/mole [5]); therefore, the reactivity of the O—H bond is expected to be low in carboxylic acids. Furthermore, it is well known that carboxylic acids are present in a strongly associated form in solution; the hydrogens of the O—H groups are involved in hydrogen bridges, and do not react with free methyl radicals. Consequently, in the case of not too dilute acid solutions, the relative and "apparent" reactivity of the O—H bonds (apart from dimerization) should be low. This assumption was checked in our experiments with acetic acid labelled with tritium in the hydroxyl group [4]. The change of the k_{OT}/k_{st}^H ratio as a function of the acid concentration was determined (Fig. 2), and it could be observed that with an increase of the mole% concentration of the acid, the k_{OT}/k_{st}^H ratio rapidly decreased in the mixture; thus, in the case of 0.2 mole% acid concentration $k_{OT}/k_{st}^H = 2 \cdot 10^{-2}$ and at 12 mole% it is $6 \cdot 10^{-4}$; with a further increase of the acid concentration the ratio remains with good approximation constant. These data unequivo-

cally show that the molecular reactivity of acetic acid, when acted upon by methyl radicals, is primarily given by the partial reactivity of the C—H bonds. This conclusion, however, involves considerable approximation similarly to the case reported previously [4], and a quantitative statement cannot be made until the exact values of the kinetic isotope effect appearing on the O—H and O—T bonds of the carboxyl group of acetic acid are known.

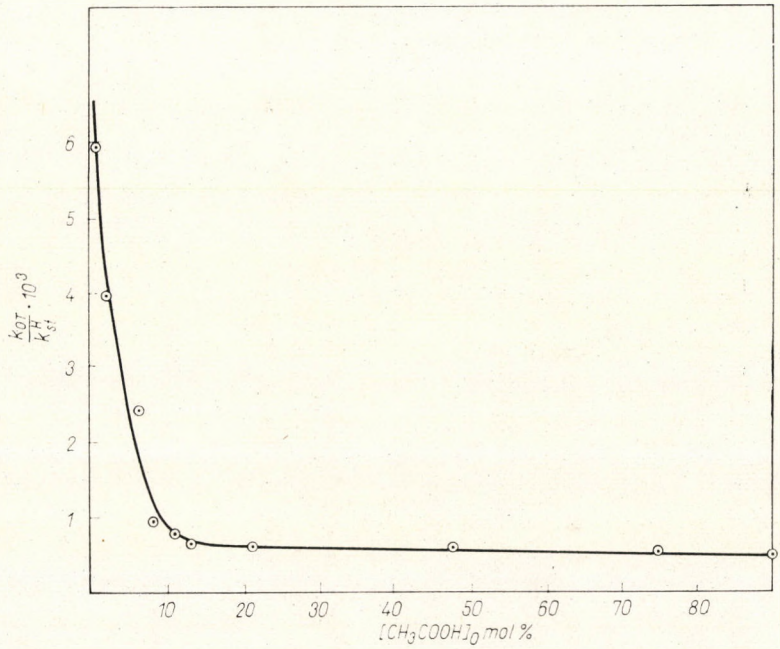

Fig. 2. Reactivity of the hydrogen atom of the carboxyl group as a function of the acetic acid concentration at 80°C

The determination of the value of k_{OT}/k_{st}^{H} at different temperatures and acid concentrations in the system *n*-heptane—acetic acid offers a possibility to establish the dimerization constant and the degree of dimerization of acetic acid.

a) *Determination of the dimerization constant*

The system acetic acid—*n*-heptane is considered to contain only the monomer and complete dimer molecules of acetic acid, and it is also assumed that dimeric molecules consist only of unlabelled acetic acid, or of one labelled and one unlabelled acetic acid. (The concentration of such dimers which are formed from two labelled acetic acid molecules can be neglected owing to the low con-

centration of [CH_3COOT].) Then, the formation of the following hydrogen bonds are to be taken into consideration:

$$CH_3COOH + CH_3COOH \overset{K_d^H}{\rightleftharpoons} (CH_3COOH)_2$$

$$CH_3COOH + CH_3COOT \overset{K_d^T}{\rightleftharpoons} \begin{pmatrix} CH_3COOH \\ CH_3COOT \end{pmatrix} \qquad \text{(III)}$$

where K_d is the dimerization constant, and the superscripts indicate whether only the H, or also the T atom takes part in the formation of the hydrogen bond.

For the total acid concentration the following relation holds:

$$[CH_3COOH]_0 = [CH_3COOH] + 2\,[(CH_3COOH)_2] + \begin{pmatrix} CH_3COOH \\ CH_3COOT \end{pmatrix}.$$

Using this expression, for K_d^H we have:

$$K_d^H + \frac{[(CH_3COOH)_2]}{[CH_3COOH]^2} = \frac{[CH_3COOH]_0 - [CH_3COOH] - \begin{bmatrix} CH_3COOH \\ CH_3COOT \end{bmatrix}}{2\alpha^2 \cdot [CH_3COOH]_0^2} \qquad (8)$$

where $1 - \alpha$ is the degree of dimerization, and

$$\alpha = \frac{[CH_3COOH]}{[CH_3COOH]_0}.$$

After rearrangement of Eq. (8) and supposing that

$$1 - \alpha \gg \frac{\begin{bmatrix} CH_3COOH \\ CH_3COOT \end{bmatrix}}{[CH_3COOH]_0},$$

the following expression is obtained:

$$K_d^H\,[CH_3COOH]_0 = \frac{1-\alpha}{2\alpha^2}.$$

Taking the logarithm of this equation the presentation of $\lg [CH_3COOH]_0$ *vs.* $\lg \frac{1-\alpha}{2\alpha^2}$ gives a straight line with the intercept $\lg K_d^H$:

$$\lg K_d^H + \lg [CH_3COOH]_0 = \lg \frac{1-\alpha}{2\alpha^2} \qquad (9)$$

from which K_d^H can be determined, if α is known as a function of the concentration.

b) *Determination of the degree of dimerization*

If the experimentally determined values of K_{OT}/k_{st}^{H} are represented as lg k_{OT}/k_{st}^{H} *vs.* the acid concentration, we can extrapolate with good approximation to those values of k_{OT}/k_{st}^{H}, where the acid concentration approximates zero or 100 mole%, respectively. Let us use the symbols $k_{OT}/k_{st}^{H} = k_0$ when $[CH_3COOH] \to 0$; and $k_{OT}/k_{st}^{H} = k_{100}$ when $[CH_3COOH] \to 100$ mole%. Then, taking into account dimerization, the following differential equations may be written for reaction system (II):

$$\frac{d[CH_3T]}{d\tau} = k_0 \cdot k_{st}^{H} \cdot \alpha \cdot [CH_3COOT] + k_{100} \cdot k_{st}^{H} \left(\frac{1-\alpha}{2}\right) [CH_3COOT]_0 \qquad (10)$$

$$\frac{d[CH_4]}{d\tau} = n\, k_{st}^{H} [n\text{-hept.}] + k_{\sigma}^{H} [CH_3COOH].$$

By employing once more the assumptions used in the deduction of Eq. (6b), from equation system (10) we get:

$$\frac{[CH_3T]}{[CH_4]} = \frac{k_0 \alpha [CH_3COOT]_0 + k_{100}^{H} \left(\frac{1-\alpha}{2}\right) [CH_3COOT]_0}{\left(\frac{n}{\alpha^*} + \frac{k_{\sigma}^{H}}{k_{st}^{H}}\right) [CH_3COOH]_0}, \qquad (11)$$

where the symbol expressed in (6c) has been taken into account.

Similarly to the process employed for the deduction of Eq. (7), from Eq. (11) we get:

$$2.\frac{I}{I_0}\left(\frac{n}{\alpha^*} + \frac{k_{\varrho}^{H}}{k_{st}^{H}}\right) = 2k_0\alpha + k_{100} - \alpha \cdot k_{100}. \qquad (12)$$

Taking into consideration Eq. (7) and employing on the left-hand side of Eq. (12) the symbol $k_{OT}/k_{st}^{H} = k_x$ to denote partial rate constants belonging to the acid concentration of $[CH_3COOH]_0 = x$, we obtain:

$$2k_x = 2k_0 \alpha_x + k_{100} - \alpha_x k_{100}. \qquad (13)$$

The subscript x for α in Eq. (13) indicates that α here denotes the value belonging to the acid concentration x. Eq. (13) gives on simple algebraic rearrangement:

$$\alpha_x = \frac{k_x - \frac{k_{100}}{2}}{k_0 - \frac{k_{100}}{2}}. \qquad (14)$$

When the α values are determined for different acid concentrations by means of Eq. (14), K_d^H can be calculated from Eq. (9), and if the temperature dependence of this latter is known, the energy of the hydrogen bond may be obtained. In Fig. 3 the graphic determination of K_d^H at 80°C is shown on the basis

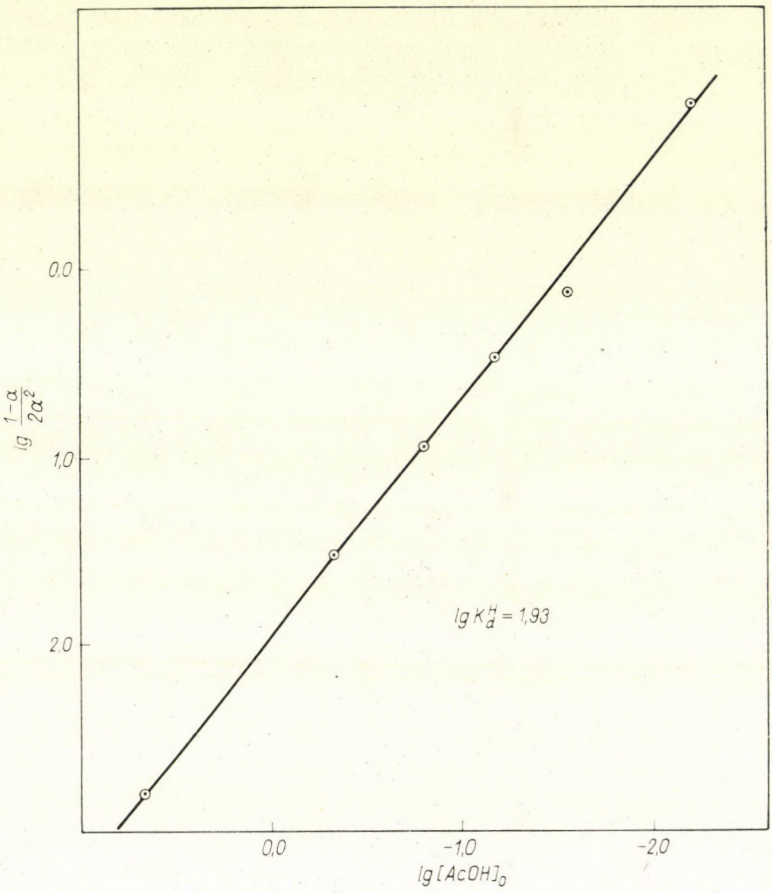

Fig. 3. Determination of the equilibrium constant of dimerization at 80°C

of Eq. (9). From the K_d^H values obtained at different temperatures $\Delta H = 8.83$ kcal/mole; this result is in good agreement with the reported [6] value of 8.53 kcal/mole which was obtained for the energy of the hydrogen bond by determining the temperature dependence of the dimerization constant of acetic acid according to Equations (III), by means of measuring the ultrasonic sound relaxation in a mixture of acetic acid—carbon tetrachloride; according to the EYRING relation, for the same a value of 8.09 kcal/mole has been obtained.

SUMMARY

The relative reactivities of aliphatic monocarboxylic acids have been determined in elementary free-radical reactions of the type RCOOH + CH_3 in liquid phase, by employing the isotope kinetic method.

It has been found that the molecular reactivities of aliphatic monocarboxylic acids are independent of the number of CH_2 groups present in the carbon chain in the first six members of the homologous series, and the molecular reactivities of the acids change according to a "saw-tooth" diagram at a given temperature depending on the number of CH_2 groups present in the carboxylic acids.

After substitution by tritium of the hydrogen atom of the carboxyl group, the equilibrium constant of dimerization and the energy of the hydrogen bond in acetic acid have been determined in *n*-heptane solution.

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INVESTIGATION OF THE REACTIVITY OF ORGANIC COMPOUNDS IN LIQUID PHASE FREE-RADICAL REACTIONS, III

INVESTIGATION OF THE ASSOCIATION OF ALCOHOL-WATER MIXTURES

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Increasing interest has been attached recently to the investigation of hydrogen bonds formed in solutions between the molecules of different substances. A number of papers have been published in which the association process is described qualitatively or quantitatively, and connections are given between the association constant and the concentration of the dissolved substance, or the concentration of the free, non-associated molecules in inert solvents [1, 2, 3]. However, these papers deal with such cases only, where the solvent is not associated, but it forms complexes with the dissolved and associated substances (*e. g.*, solutions of hydroxyl containing substances in acetone, dioxan, or chloroform).

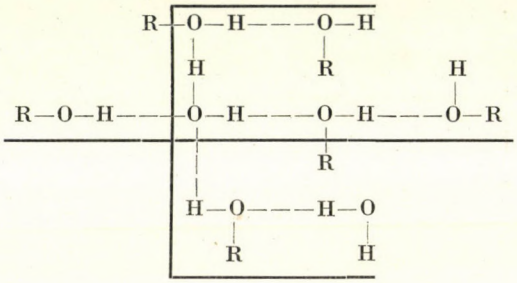
In our present work we investigated the association problems of water-alcohol mixtures, that is, such a system in which both components can form associates with themselves and with each other as well.

In the literature no generally accepted models can be found to describe the structures of pure water, pure alcohol, and water-alcohol mixtures. It has been pointed out repeatedly that in pure alcohols the molecules are present as polymeric chains, but the existence of cyclic associates has also been suggested [4]. The structure of pure water, according to the present view, can be described by a three-dimensional lattice model [5], where a water molecule can form 4, 3, 2, 1 hydrogen bonds, or it appears as a monomeric molecule in the system. The extension of this lattice model for the interpretation of water-alcohol solutions is complicated. However, by introducing certain assumptions, we have obtained a structure model which allows the investigation of water-alcohol solutions as a set of polymeric chains, with the exclusion of cyclic complexes. At the same time, this model is a good approximation of the most probable lattice structure, and its mathematical description does not present difficulties.

We started from the assumption that each alcohol molecule contains a hydroxyl group which can form a pair of hydrogen bonds; the water molecule was considered as if consisting of two such OH groups, each of which can form a pair of hydrogen bonds. Then the number of OH groups, capable of forming two hydrogen bonds, each will be $e + 2m$ mole in a solution which consists of

e mole of alcohol and *m* mole of water. Supposing that the formation of every hydrogen bond is independent of the fact whether the oxygen or hydrogen taking part in it belongs to a monomeric molecule or to the end of a polymeric chain [6, 7] (*i.e.*, that the association constant is independent of the degree of association), the actually branched can be regarded as a set of linear, non-branching chains. These chains may be linked with one another through the oxygen of water.

For example, an arbitrary associate, such as can be regarded (see the drawn lines) as two linear, non-branched chains.



In working out the physical model — for the sake of a more simple mathematical description, and since this does not contradict the experimental data — it has been assumed that in an alcohol-water mixture every possible arrangement of the alcoholic, and aqueous hydroxyl groups is realized, *i.e.* there is no preferred structural orientation of the linear associates.

In our deductions the following symbols have been employed:

A_0 — total concentration of the alcoholic OH groups (all concentrations are given in mole fractions),

V_0 — total concentration of the OH groups of water (if the solution contains *m* mole of water and *e* mole of alcohol, then

$$A_0 = \frac{e}{e + 2m} \quad \text{and} \quad V_0 = \frac{2m}{e + 2m})$$

A — concentration of monomeric alcohol,

V — concentration of monomeric water,

a — concentration of the free protons of alcohol (forming no hydrogen bond),

v — concentration of the free protons of water,

n — total number of molecules in the given associate,

k — number of alcohol molecules in the given associate,

K_a — association constant of the hydrogen bond formed between alcoholic oxygen and alcoholic hydrogen,

K_v — association constant of the hydrogen bond formed between the oxygen of water and the hydrogen of water,

K_{av} — association constant of the hydrogen bond formed between the hydrogen of alcohol and the oxygen of water,

K_{va} — association constant of the hydrogen bond formed between the hydrogen of water and the oxygen of alcohol.

(In our approximate calculations we assumed that $K_{av} = K_{va}$; accordingly, further on the symbol K_{av} will be used only.)

$AA \ldots VVAVA \ldots$ denotes an arbitrary linear chain associate, which contains k alcoholic OH groups and $n-k$ aqueous OH groups, in which the hydrogen of the preceding molecule forms a bridge with the oxygen of the next molecule. Namely, from the point of view of reaction kinetics, the free hydrogen of the hydroxyl group of an alcohol is not equivalent with that of water (see Groups Ic and IIc).

For the sake of a clear-cut mathematical treatment, the possible associates in the given solutions were divided into two main groups, namely:

I) associates in which the terminal group is an alcoholic OH;

II) associates in which the terminal group is the OH of a water molecule.

Both groups can be divided into three sub-groups which are as follows:

Ia) associates in which only alcohol molecules take part $(AA \ldots A)$,

b) associates in which water molecules also take part in the chain $(A \ldots V \ldots A)$,

c) associates in which alcohol and water molecules take part in an arbitrary arrangement in the chain, but the chain begins with a water molecule and ends with an alcohol molecule $(VAV \ldots A)$,

IIa) associates in which only water molecules are present $(VV \ldots V)$,

b) associates in which alcohol molecules also take part in the chain $(V \ldots AAV \ldots V)$,

c) associates in which alcohol, and water molecules take part in an arbitrary arrangement, but the chain begins with an alcohol molecule and ends with a water molecule $(AVA \ldots V)$.

The formal mathematical deduction had the following purposes:

1. A relation had to be found between the association constants and the initial alcohol and water concentrations, and the monomeric alcohol and water concentrations; that is, we had to seek the following function:

$$A_0 = f(A, V, K_a, K_{av}) \text{ and } V_0 = F(A, V, K_a, K_{av}).$$

2. A connection had to be found between the free alcoholic proton concentration and A_0 and A, further between the free aqueous proton concentration and V_0 and V, represented by the functions:

$$a = a(A_0, A) \text{ and } v = v(V_0, V).$$

3. Finally, a relation had to be found between the total alcohol concentration and proton concentrations, and between the initial water concentration of the mixture and the proton concentrations; *i.e.* we had to seek the explicit forms of the functions

$$A_0 = t(a, v, K_a, K_v, K_{av}) \text{ and } V_0 = T(a, v, K_a, K_v, K_{va}).$$

In order to solve these problems, taking into account the above classification of the associates, the following factors had to be determined in every sub-group:

a) the concentration of the associates,
b) the concentration of alcohol, and water in a given sub-group,
c) the concentration of protons bound in hydrogen bridges of the types $A \ldots A$, $A \ldots V$, $V \ldots A$, $V \ldots V$.

In the first step the concentration of the monomeric alcohol or that of monomeric water is applied, because the concentrations of the different associates are expressed by means of the equilibrium constant, as for example:

$$\text{ROH} + \text{HOH} \xrightarrow{K_{av}} \text{ROH} \ldots \text{HOH}$$

$$[\text{ROH} \ldots \text{HOH}] = K_{av} \cdot A \cdot V$$

The theoretical scheme of our calculations is illustrated on the example of investigating associates of Group Ib. It may be seen immediately that in the concentration expression of associates of this types, K_{av} can only take even numbers as its exponent. This exponent, being the number of hydrogen bonds of the type $A \ldots V$ or $V \ldots A$, will be denoted below by $2p$, where $p = 1, 2, 3 \ldots$ is an integer. Thus the number of bonds of the types $A \ldots V$ and $V \ldots A$ being fixed, and knowing that the first and terminal units of the chain can only be alcohol molecules in this group, we may put now k number of alcohol molecules in $p + 1$ places in an arbitrary associate, while maintaining the fixed arrangement of the $n-k$ water molecules. Changing the number of alcohol molecules in every $p + 1$ position so that at least one alcohol molecule should be present in each position, we obtain different associates whose concentration expressions will be identical. Let us take an example:

An associate $AVAAVA$ is given, the concentration of which is $K_{av}^4 A^4 V^2 K_a$. Then, according to the above principles, in this case, where $p = 2$, the arrangements $AAVAVA$, and $AVAVAA$ are also possible; the concentration expressions remain identical. In general, if $x_1, x_2 \ldots x_{p+1}$ denote the number of alcohol molecules in the allowed places in an associate, *i. e.* in the first, second, etc., $p + 1$ places, then the number of all positive-whole solution systems of the equation

$$x_1 + x_2 + \ldots + x_{p+1} = k \tag{1}$$

gives the member of all possibilities of placing k alcohol molecules in $p + 1$ places. However, the number of the positive-whole solution systems of Eq. (1) is:

$$\binom{k-1}{p}$$

When the alcohol molecules are fixed, $n - k$ water molecules can be placed to p places; the number of such arrangements — according to the above considerations if we write the equation analogous with Eq. (1) — will be $\binom{n-k-1}{p-1}$. Thus, the number of all possible associates of identical concentration expressions where K_{av} takes the $2p$-th power with fixed p, will be:

$$\binom{k-1}{p} \cdot \binom{n-k-1}{p-1}$$

Further on the exponents of the association constants K_a and K_v have to be determined in the expression of a generally given associate concentration, again with n, k, and p being fixed. In a given linear associate the sum of hydrogen bonds is $n - 1$, of which $k - 1$ are supplied by alcoholic protons, and $(n - k)$ by protons of water. At the same time the number of the bonds of types $V \ldots A$ and $A \ldots V$ is $2p$: this requires p alcoholic protons and protons of the water, therefore $n - p - 1$ protons are left for bonds of type $A \ldots A$, and $n - k - p$ protons for bonds of type $V \ldots V$. In this way the exponents of K_a and K_v are obtained. Then at fixed n, k and p, the general concentration expression for the associates of group Ib will be as follows:

$$S_{Ib}^{(n,k,p)} = \binom{k-1}{p}\binom{n-k-1}{p-1} A^k \cdot K_a^{k-p-1} \cdot V^{n-k} \cdot K_v^{n-k-p} \cdot K_{av}^{2p} \tag{2}$$

The concentration of the associates classified in group Ib is obtained by performing the following summation:

$$S_{Ib} = \sum_{n=k+p}^{\infty} \sum_{k=p+1}^{\infty} \sum_{p=1}^{\infty} S_{Ib}^{(n,k,p)} \tag{3}$$

The concentration of the associates is equal to the concentration of the alcoholic protons in the group.

The above-mentioned concentrations may be calculated in Group Ib in the following way: the expression $S_{Ib}^{(n,k,p)}$ under the symbol of summation has to be multiplied by a $Z(n, k, p)$ function defined always equivocally by the concentration to be calculated, that is, a sum of the form

$$\sum_{n}\sum_{k}\sum_{p} Z(n,k,p),\, S_{Ib}^{(n,k,p)} \tag{4}$$

has to be composed. The values of the expression $Z(n, k, p)$, depending on the concentration to be calculated, will be the following:

a) $Z(n, k, p) = k$, for the calculation of the alcohol concentration of the group,

b) $Z(n, k, p) = n - k$, for the calculation of the water concentration,

c) $Z(n, k, p) = p$, for the calculation of the concentration of the protons bound in the hydrogen bridges of types $A \ldots V$ and $V \ldots A$,

d) $Z(n, k, p) = k - p - 1$, if we want to determine the concentration of protons bound in the hydrogen bridges of the type $A \ldots A$,

e) $Z(n, k, p) = n - k - p$, for the determination of the concentration of protons bound in the hydrogen bridges of the type $V \ldots V$.

In order to determine the triple summation, the following relation, which can be readily proved by total induction for α, has been employed:

$$\sum_{r=0}^{\infty} \binom{r+\alpha}{\alpha} x^r = \frac{1}{\alpha!} \cdot \frac{d^\alpha}{dx^\alpha} \cdot \left(\frac{x^\alpha}{1-x}\right) \tag{5}$$

where $\alpha \geqslant 0$ is an integer and $|x| < 1$.

If the calculations illustrated by the example of group Ib are made for every sub-group, either according to the above mental process, or by establishing an unequivocal analogy between the associates of the sub-group already calculated and the associates of a sub-group to be calculated, the following relations are obtained:

1) The concentration of the protons bound in the hydrogen bridges of different types, from the monomeric concentrations, will be:

$$\text{a)}\ [A \ldots A] = A_0 A K_a$$

$$\text{b)}\ [A \ldots V] = K_{av} \sqrt{A_0 V_0 A V}$$

$$\text{c)}\ [V \ldots A] = V_0 V K_v$$

$$\text{d)}\ [V \ldots V] = K_{av} \sqrt{A_0 V_0 A V}$$

2) The expression of A_0 and V_0, from the monomeric concentrations and the association constants is:

$$A_0 = \sqrt{A_0 A} + A A_0 A_a + \sqrt{A_0 V_0 A V} \cdot K_{av}$$

$$V_0 = \sqrt{V_0 V} + V_0 V K_v + \sqrt{A_0 V_0 A V} \cdot K_{av} \tag{6}$$

3) For the expression of the free proton concentrations from the monomeric concentrations we get:

$$a = \sqrt{A_0 A}$$
$$v = \sqrt{V_0 V} \tag{7}$$

4) By employing Eqs (6) and (7), the equation system describing the structural model outlined in connection with the association of alcohol-water mixtures is obtained:

$$A_0 = a + a^2 K_a + avK_{av}$$
$$V_0 = v + v^2 K_v + avK_{av} \tag{8}$$

Equation system (8) gives the connection of the free "alcoholic" and "aqueous" protons for solutions of different compositions at known values of K_a, K_v and K_{av}. Using these results, the concentrations of alcohol and water monomers can also be calculated.

When equation system (8) is solved for a, a fourth-degree polynome is obtained. Accepting for its coefficients different initial concentrations, A_0 and V_0, at a definite selection of the value system of the association constants, we determined the roots of a of this polynome which is of fourth degree for a, using an *Eliot—803* computer. In our practical calculations these data have been applied, and they are at our disposal in the form of tables.

The chemical shifts (δ_{OH}) of the hydroxyl protons of *t*-butyl alcohol were measured by NMR spectroscopy at different temperatures (25, 68, 98°) in the aqueous solutions of *t*-butanol [8]. It has been found that the over-all chemical shift of the hydroxylic protons depends in a complicated manner on the composition of the mixture and on the temperature. Starting with Eq. (8), the following expression is obtained concerning the dependence of the chemical shift (δ_{OH}) on the mixture composition and on the association constants:

$$\delta_{OH} = \delta_a \cdot a + \delta_v \cdot v + \delta_{aa}\, a^2 K_a + \delta_{vv}\, v^2 K_v + 2\delta_{av}\, av\, K_{av} \tag{9}$$

where δ_v, δ_x, δ_{aa}, δ_{vv}, δ_{av} stand for the chemical shifts of the free and hydrogen-bonded protons of alcohol and water, respectively (the subscripts indicating the type of the associate). The experimental data obtained by the magnetic resonance method in aqueous solution of butyl alcohol were evaluated by means of Eq. (9).

The calculated values of the association constants for pure water and pure alcohol and for their mixture are summarized in Table I.

We have employed in the calculations the literary data [9—12] concerning the enthalpy of hydrogen bridges in pure *t*-butanol and pure water. The results show that the formation of mixed associates is energetically favoured. However, owing to the great entropy change, the values of the association

Table I

Type of associate	Association constant (at 24°C)	$-\Delta H$ cal/mole	$-\Delta S$ e.u.
Alcohol...alcohol	7.01 ± 0.15	5000	12.97
Water...water	26.37 ± 0.15	4200	7.64
Alcohol...water			
Water...alcohol	15.00 ± 0.15	5600 ± 200	13.44 ± 0.15

constants of the water and alcohol associates are between the values relating to the pure compounds.

For a study of the associates formed in the aqueous solutions of *t*-butyl alcohol also the method of concurrent reactions with tritium labelling was employed. In an aqueous solution of *t*-butanol labelled with tritium in the OH group, we determined at 140° the hydroxylic proton concentration of the alcohol molecules which did not take part in the hydrogen bonds. This was possible by virtue of the well-known fact [13] that water has very low reactivity towards methyl radicals; therefore, in an aqueous solution of *t*-butyl alcohol, the free methyl radicals practically react only with the alcohol molecules. Consequently, our kinetic system may be considered to consist, in good approximation, of the following [14]:

$$(CH_3)_3\,COH + CH_3^{\cdot} \xrightarrow{k_{OH}} (CH_3)_3\,CO^{\cdot} + CH_4$$

$$(CH_3)_3\,COT + CH_3^{\cdot} \xrightarrow{k_{OT}} (CH_3)_3\,CO^{\cdot} + CH_3T$$

$$(CH_3)_3\,COH + CH_3^{\cdot} \xrightarrow{k_{CH}} (CH_3)_2\,CH_2^{\cdot}COH + CH_4$$

As the source of methyl radicals the thermal decomposition of *t*-butyl peroxide was employed, analogously to diacetyl peroxide.

The examination of this system shows that the value of a decreases when the *t*-butanol is diluted with water, consequently the association water-alcohol is indeed greater than that of alcohol-alcohol.

Using the corresponding enthalpy and entropy differences listed in Table I, we calculated the values of K_a and K_v for 140° ($K_a = 0.64$; $K_v = 3.78$), the temperature of the kinetic measurements. From these results and from the a values obtained by the kinetic measurements, the association constant of the water-butanol associates was determined according to Eq. (8) to give $K_{av} = 3.5$. From the data of nuclear magnetic resonance measurements the equilibrium constant of the mixed associates at 140° is $K_{av} = 1.2$. Although the value obtained for K_{av} with some simplifications of the kinetic equations [14] is higher, the results and their combinations derived by two different methods equally prove the higher stability of the mixed associates.

SUMMARY

The structure of the liquid system alcohol-water is described using a lattice model approximation, regarding the system to consist of linear polymeric chains, excluding the possibility of ring structure. On the basis of the model, a relation was statistically derived between the total concentration of the OH groups and the concentration of the free protons (which do not form hydrogen bonds) in alcohol and water.

By means of the obtained equations, the equilibrium constants of the alcohol-alcohol, alcohol-water and water-water associates have been calculated from the chemical shifts measured with the NMR method, and their dependence on the temperature in the system butanol-water has been determined. In the same system the equilibrium constants of the mixed associates were calculated from the data measured at 140°C by means of the isotope-kinetic method.

The equilibrium constants and the equilibrium enthalpy and entropy differences show that the formation of mixed associates is energetically more probable.

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THE CHEMISTRY OF HETEROCYCLIC PSEUDOBASIC AMINO ALCOHOLS, XXXIII*

A NEW METHOD OF BUILDING UP THE BENZO(A)QUINOLIZIDINE SKELETON

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Received April 14, 1967

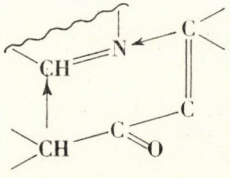
In recent years, the interest for methods aimed at the synthetic building up of the benzo(a)quinolizidine skeleton has been greatly increased by the remarkable physiological effects of Ipecac alkaloids [1] and of azasteroids [2].

In the majority of the reported methods a 3,4-dihydroisoquinoline derivative is used as the starting material. If synthetic approaches consisting of several steps (*e.g.* [3, 4]) are not considered, the reactions accomplishing the desired end in one single operation may be divided according to the character of the other component, or components, as shown in the schemes below.

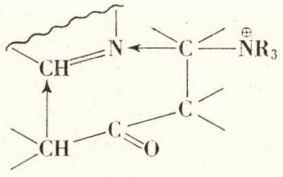
It is possible to react isoquinoline derivatives with α, β-unsaturated ketones [5, 6, 7] (*A*), with salts of β-trialkylaminoketones [8] (*B*), with β-diketones [9] (*C*), or simultaneously with formaldehyde and derivatives of acetoacetic acid [10, 11] (*D*).

All these methods lead to derivatives which carry a carbonyl group in position 2 of the benzo(a)quinolizidine skeleton. By means of the syntheses presented in Schemes *A*—*D*, it is difficult to obtain derivatives disubstituted in position 1 (*cf.* [7]).

It is also possible to react 3,4-dihydroisoquinoline with derivatives of acetylenecarboxylic acids, according to Scheme *E*. However, this reaction is accompanied by the formation of 2 : 1 adducts [12, 13].



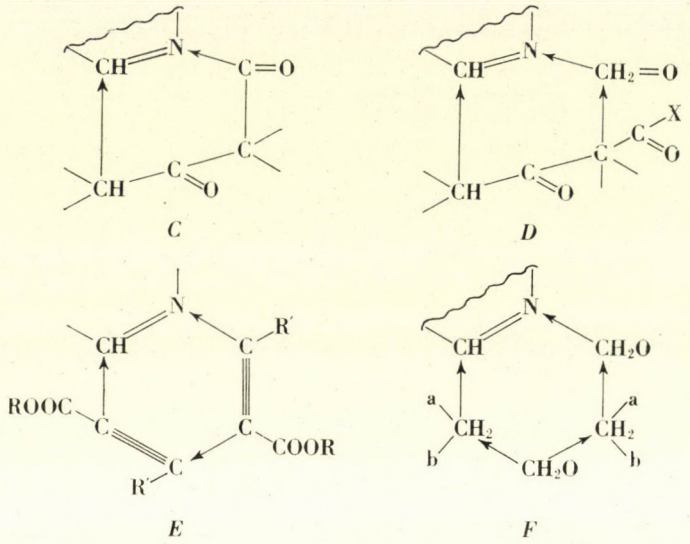
A



B

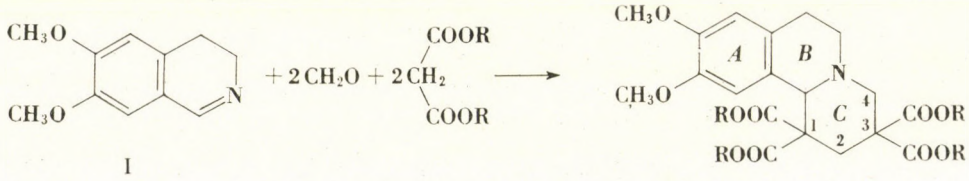
* Part XXXII: Szántay, Cs. and Novák, L.: Chem. Ber. **100**, 2038 (1967).

** The present paper consists of a part of the dissertation of Gy. Kalaus submitted in order to obtain the title of Dr. Techn.



Thus, a novel approach of building up the benzo(a)quinolizidine skeleton has been attempted in the way shown by Scheme *F*, *i.e.* by the simultaneous reaction of 3,4-dihydroisoquinolines with two molecules of formaldehyde and with two molecules of a derivative containing an active methylene group.

When the base **I** was reacted with malonic ester and formaldehyde, derivatives **IIa** or **IIb** were obtained in good yields.



I

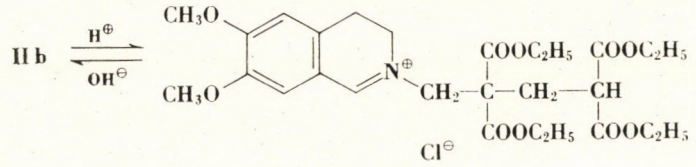
II a $R=CH_3$

b $R=C_2H_5$

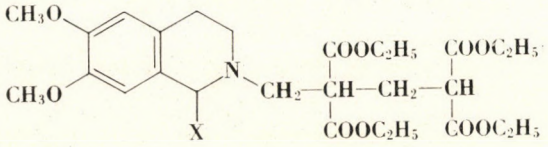
The ultraviolet spectrum of the ethanolic solution of **II** shows the band system characteristic of dimethoxytetrahydroisoquinolines, with a peak appearing at 287 nm. In 1.0 *N* hydrochloric acid solution, the band very characteristic of a C=N bond of positive charge is found at 374 nm. The intensity of this band attains maximum after keeping the solution for 10 minutes at 70°. On the basis of intensity, the presence of one such chromophoric group in each molecule can be concluded.

The change observed in the ultraviolet spectrum on the effect of acid points thus to ring cleavage which has also been proved in a preparative way. Starting with compound **IIb**, we succeeded in isolating the salt **III** from the

reaction mixture and in identifying it in the form of the pseudocyanide (**IV**). One of the characteristic features of salt **III** is that in alkaline medium it is reconverted into the initial cyclic compound **IIb**, and on catalytic hydrogenation (Pd-catalyst), it gives the tetrahydro derivative, **V**.



III



IV X=CN

V X=H

The infrared spectra of these substances are also consistent with the assumed structures (see *Experimental*).

The nuclear magnetic resonance spectra of the compounds furnish particularly much and useful information.

Two distinct triples are to be seen in the spectrum of the ester **IIb** (Fig. 1). The signal which can be attributed, on the basis of integration, to three protons appears at an unusually low value of δ (0.79), while further 9 protons are shown at $\delta = 1.29$, as expected. This phenomenon can only be interpreted if it is assumed that one of the ester groups occupies a position markedly different from those occupied by the three other such groups, and furthermore, that it is subjected to considerable shielding by the electron sextet of the aromatic ring.

This structure has been perfectly confirmed by studies carried out with molecular models. In position 1 of the benzo(a)quinolizidine skeleton, the two rather bulky substituents can find a strainless arrangement only if ring *B*/*C* is cis-annelated, and consequently the axial ester group occupies to a significant extent a position parallel to the plane of the benzene ring, being thus subjected to an extremely strong shielding effect (Fig. 2).

These assumptions are further confirmed by the fact that in the spectrum of the pseudocyanide **IV** the protons of the methyl radicals of the four ester groups merge into a single broad triplet whose centre is found at $\delta = 1.3$, *i.e.* the signal of the shielded protons can be found no longer. The peaks of the two methoxy groups ($\delta = 3.89$ and 3.96) which are clearly discernible in the

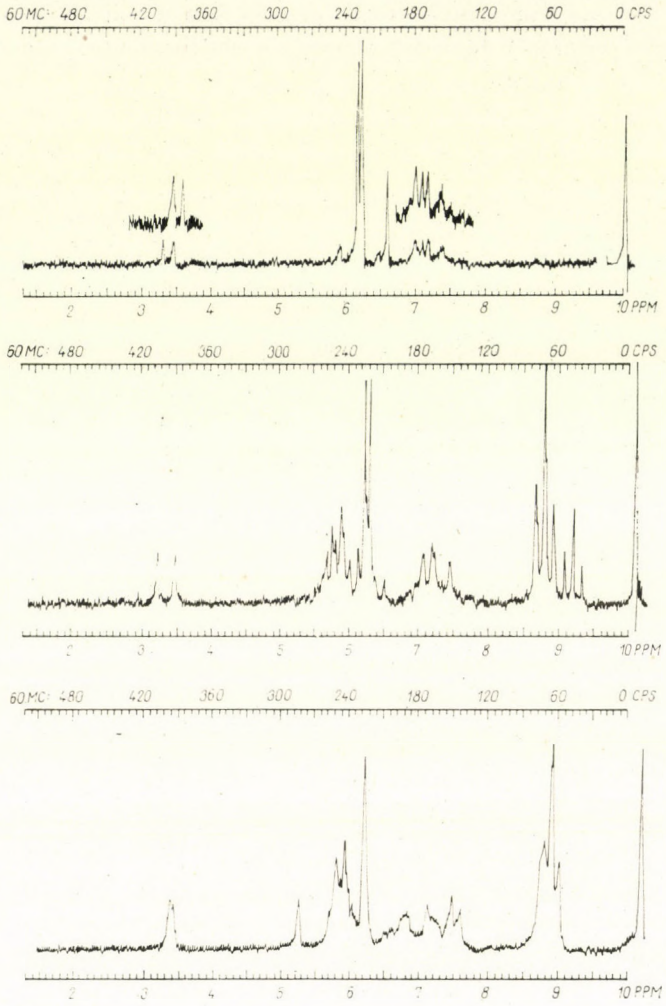


Fig. 1. Nuclear magnetic resonance spectra of compounds **IIa, IIb** and **IV**

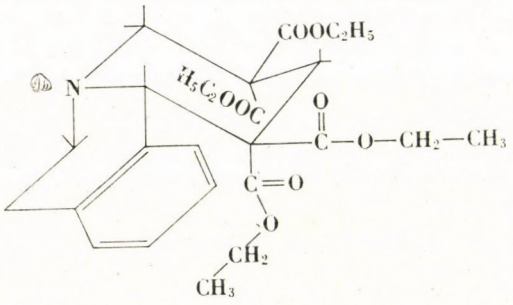


Fig. 2. Steric structure of compound **IIb**

spectrum of the ester **IIb**, merge in the case of derivative **IV**. Also the signals of the aromatic protons ($\delta = 6.72$ and 6.96) which are located far from each other in the cyclic compound approach each other very closely ($\delta = 6.80$ and 6.85).

In accordance with those described above, the spectrum of the methyl ester derivative **IIa** (*cf.* Fig. 1) similarly discloses the signal of a preferred, strongly shielded methyl group, at $\delta = 3.4$.

The existence of a steric structure containing cis-fused *B*/*C* rings (Fig. 2), an arrangement very rarely occurring in benzo(a)quinolizidine derivatives, is further confirmed by the fact that the so-called Bohlmann band group, characteristic of the trans form, is completely absent in the infrared spectra of compounds **II** (*cf.* [1]).

On the analogy of the reactions carried out with malonic ester derivatives and compound **I**, we succeeded in preparing derivatives with structures analogous to that of compound **II**, by reacting 3,4-dihydroisoquinolines with derivatives of cyanoacetic acid, with malonitrile and with ethyl benzoylacetate. The characteristic properties of the derivatives prepared in this way are summarized in Table I.

Our attempts to conduct this reaction with diethyl succinate, diethylaminoacetonitrile, 1-phenyl-2-benzoylpropionitrile, benzyl cyanide and with ethyl nitroacetate failed, since these derivatives did not react at all, or gave reactions quite different from the expected route.

Experimental

1. 1,1,3,3-Tetra-(ethoxycarbonyl)-9,10-dimethoxy-1,2,3,4,5,7-hexahydro-11bH-benzo(a)quinolizine (IIb)

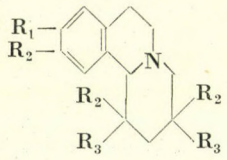
1.7 g of diethyl malonate (10.6 mmoles) and 1.2 ml (11.2 mmoles) of a 26% aqueous solution of formaldehyde were added to a solution of 1.0 g (5.23 mmoles) of 6,7-dimethoxy-3,4-dihydroisoquinoline in 4 ml of ethanol, and the reaction mixture was boiled 2 hrs. on a water bath. The precipitated white crystals were filtered off, washed with 3×5 ml of ethanol and dried to obtain 2.25 g of a product (m. p. 125—127°) which, on recrystallization from 22 ml of ethanol yielded 2.1 g (74.8%) of white platelets of the crystalline **IIb**, m. p. 131—132°.
$C_{27}H_{37}NO_{10}$ (535.57). Calcd. C 60.55; H 6.96; N 2.62. Found C 60.60; H 7.06; N 2.67%.
Molecular weight: 558 (in benzene at 37°, determined by the isotherm distillation method).
Ultraviolet spectrum: $\lambda_{max}^{Methanol}$: 287 nm (log $\varepsilon = 3.608$); $\lambda_{max}^{1.0NHCl}$ (after keeping for ten minutes at 70°)
248 nm (log $\varepsilon = 4.103$)
316 nm (log $\varepsilon = 3.986$)
374 nm (log $\varepsilon = 3.993$)
Infrared spectrum: ν_{max}^{KBr} 1735 cm^{-1} (>C=O).
Nuclear magnetic resonance spectrum: see Fig. 1.

2. 2-[2,2,4,4-Tetra-(ethoxycarbonyl)-butyl]-6,7-dimethoxy-3,4-dihydroisoquinolinium chloride (III)

6 ml of ethanol saturated with hydrogen chloride was added to the solution of 2.0 g (3.73 mmoles) of ester **IIb** in 20 ml of hot ethanol, the solution boiled 30 minutes, and evaporated in vacuum. Crystallization of the residue from a mixture of 2 ml of ethanol and 10 ml

Table 1

Characteristic data of the newly prepared



No.	R_1	R_2	R_3	Yield %	Time (min) and teumpera-ture (°C) of reac-tion	M. p. °C (solvent)
1	OCH_3	COOnPr	COOnPr	41.9	180 78°	87—88 (ethanol)
2	OCH_3	COOnBu	COOnBu	37.1	240 78°	57—59 (ethanol)
3	OCH_3	COOiBu	COOiBu	32.6	240 78°	92—93 (ethanol)
4	OCH_3	$COOCH_2CCl_3$	$COOCH_2CCl_3$	61.2	10 25°	161—162 (methanol)
5	OCH_3	CN	$COOCH_3$	94.6	60 25°	164—165 (methanol)
6	OCH_3	CN	$COOCH_2CH_3$	95.3	60 78°	142—143 (ethanol)
7	OCH_3	$CONH_2$	CN	59.8	60 25°	164—165 (methanol)
8	OCH_3	CN	CN	91.1	10 25°	184—185 (acetone-water)
9	OCH_3	 —CO	$COOCH_2CH_3$	77.2	60 78°	154—155 (ethanol)
10	H	$COOCH_3$	$COOCH_3$	29.7	120 64°	159—160 (methanol)

derivatives of benzo(a)quinolizidine

Molecular formula (molecular weight)	Analytical data						ν_{max}^{KBr} (cm^{-1})	λ_{max}^{MeOH} (nm)
	%C		%H		%N			
	Calcd.	Found	Calcd.	Found	Calcd.	Found		
$C_{31}H_{45}NO_{10}$ (591.68)	62.92	63.07	7.67	7.72	2.37	2.32	1725 (C=O)	
$C_{35}H_{53}NO_{10}$ (647.77)	64.87	64.97	8.24	8.26	2.16	2.18	1728 (C=O)	
$C_{35}H_{53}NO_{10}$ (647.77)	64.87	65.09	8.24	8.23	2.16	2.18	1730 (C=O)	
$C_{27}H_{25}NO_{10}Cl_{12}$ (948.96)	34.16	34.34	2.65	2.57	1.47	1.85	1750 (C=O)	
$C_{21}H_{23}N_3O_6$ (413.42)	61.01	60.83	5.61	5.69	10.16	10.17	1738 (C=O) 1748 (C=O) 2251 (C≡N)	286 (log ε = 3.708)
$C_{23}H_{27}N_3O_6$ (441.47)	62.57	62.54	6.16	6.32	9.52	9.49	1745 (C=O) 2252 (C≡N)	287 (log ε = 3.568)
$C_{19}H_{21}N_5O_4$ (383.40)	59.52	59.72	5.52	5.43	18.27	18.17	1660 (C=O) 1692 (C=O) 2233 (C≡N)	
$C_{19}H_{17}N_5O_2$ (347.37)	65.69	65.64	4.93	5.01	20.16	20.34	2258 (C≡N)	243 (log ε = 4.311)
$C_{35}H_{37}NO_8$ (599.65)	70.10	70.10	6.22	6.04	2.34	2.59	1688 (C=O) 1730 (C=O)	283 (log ε = 3.761)
$C_{21}H_{25}NO_8$ (419.42)	60.13	60.09	6.01	6.05	3.34	3.27	1730 (C=O) 1740 (C=O)	

of anhydrous ether gave 1.5 g of product. Recrystallization from a 1 : 4 mixture of ethanol and ether afforded 0.6 g (28.2%) of yellow crystals of the salt **III**, m. p. 136—137°.
$C_{27}H_{38}NO_{10}Cl$ (572.02). Calcd. C 59.68; H 6.68; N 2.44. Found 59.58; H 6.69; N 2.5%.
Ultraviolet spectrum: $\lambda_{max}^{Methanol}$:

249 nm (log ε = 4.097)
314 nm (log ε = 3.987)
374 nm (log ε = 3.989)

Infrared spectrum: ν_{max}^{KBr}:
1645 cm^{-1} ($\overset{(+)}{>C=N<}$)
1742 cm^{-1} (>C=O)

3. 1-Cyano-2-[2,2,4,4-tetra-(ethoxycarbonyl)-butyl]-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline (IV)

The solution of 1.0 g (1.87 mmoles) of the ester **IIb** in 50 ml of 0.5 *N* HCl was heated 30 minutes on a water bath. After cooling, the solution was made alkaline to p_H 10 with a 5% aqueous solution of potassium cyanide. A white, oily precipitate appeared immediately. This was extracted with 3×15 ml of benzene, the solvent dried and evaporated in vacuum. Crystallization of the oily residue (1.10 g) from 4 ml of ethanol gave 0.9 g (85.7%) of white crystalline **IV**, m. p. 63—64°.
$C_{28}H_{38}N_2O_{10}$ (562.60). Calcd. C 59.77; H 6.81; N 4.98. Found C 59.66; H 6.83; N 4.87%.
Infrared spectrum: ν_{max}^{KBr}:
1735 cm^{-1} (>C=O)
2222 cm^{-1} (—C≡N)

4. 2-[2,2,4,4-Tetra-(ethoxycarbonyl)-butyl]-6,7-dimethoxytetrahydroisoquinoline (V)

The solution of 1.0 g (1.75 mmoles) of the ammonium salt **III** in 15 ml of ethanol was subjected to hydrogenation in the presence of a palladium catalyst (8% Pd) on bone black. After the theoretical amount of hydrogen had been absorbed (90 minutes), the catalyst was filtered off, the filtrate evaporated, the residue dissolved in 5 ml of water and made alkaline to p_H 11 with a 10% solution of Na_2CO_3. The oil which solidified on standing was filtered off, washed with water and dried. The substance (0.6 g) was recrystallized from 5 parts of petroleum ether to afford 0.55 g (58.8%) of white crystals of derivative V, m. p. 66—67°.
$C_{27}H_{39}NO_{10}$ (537.59). Calcd. C 60.32; H 7.31; N 2.61. Found C 60.23; H 7.37; N 2.67%.
Ultraviolet spectrum: $\lambda_{max}^{Methanol}$ 284 nm (log ε = 3.583).
Infrared spectrum: ν_{max}^{KBr} 1735 cm^{-1} (>C=O).

5. 1,1,3,3-Tetra-(methoxycarbonyl)-9,10-dimethoxy-1,2,3,4,6,7-hexahydro-11bH-benzo(a)-quinolizine (IIa)

On the analogy of the preparation of the ester **IIb** (*cf.* the reaction described under 1), the isoquinoline derivative **I** was allowed to react with dimethyl malonate. Yield 81.8%, m. p. 152—153° (from methanol).
$C_{23}H_{29}NO_{10}$ (479.47). Calcd. C 57.61; H 6.10; N 2.92. Found C 57.48; H 5.95; N 2.89%.
Ultraviolet spectrum: $\lambda_{max}^{Methanol}$ 286 nm (log ε = 3.673)
$\lambda_{max}^{1.0N\,HCl}$ 248 nm (log ε = 4.127)
(after keeping ten 319 nm (log ε = 4.021)
minutes at 70°) 376 nm (log ε = 4.012)
Infrared spectrum: ν_{max}^{KBr} 1742 cm^{-1} (>C=O)
Nuclear magnetic resonance spectrum: see Fig. 1.

The new benzo(a)quinolizidine derivatives which are listed in Table I were prepared similarly, on the analogy of the synthesis of the ester **IIb**.

The reagents used were products reported in the literature, with the exception of trichloroethyl malonate which was prepared as follows.

6. Di-(2,2,2-trichloroethyl) malonate

A solution of 6.3 g (60.6 mmoles) of malonic acid and 27.0 g (181 mmoles) of 2,2,2-trichloroethanol in 50 ml of benzene was boiled in the presence of 1 ml of concentrated sulphuric acid. The formed water was continuously removed by azeotropic distillation. After a reaction time of 2 hrs., the solution was poured in ice-water and extracted with benzene layer was washed with 5% Na_2CO_3, dried, evaporated, and the residue fractionated in vacuum to obtain 12.7 g (57.2%) of a colourless liquid of characteristic smell, b. p. 178—179° at 16 mm; $n_D^{22} = 1.4948$.

The ultraviolet spectra were established by means of a *Unicam SP—700*, the infrared spectra with a *Perkin—Elmer 221 G* and the nuclear magnetic resonance spectra with a *J.N.M.—C.—60* instrument.

Thanks are due to Dr. P. SOHÁR *(Pharmaceutical Research Institute, Budapest)* for establishing the nuclear magnetic resonance spectra, and to Mrs. J. VISZT, Mrs. K. ZAUER and Miss K. ÓVÁRI for the microanalyses.

SUMMARY

A new method is described for the preparation of 1,1,3,3-tetrasubstituted benzo(a)-quinolizidines which are otherwise accessible with difficulty. The method consists in the simultaneous reaction of 3,4-dihydroisoquinoline derivatives, formaldehyde and compounds containing an active methylene group. The structures of the compounds formed in these reactions have been proved by chemical and physical methods.

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RINGISOMERISATION VON ISOFLAVON-GLUCOSIDEN, III*

SYNTHESE DES 7-METHYL-TEKTORIGENIN-4'-GLUCOSIDS *(KURZMITTEILUNG)*

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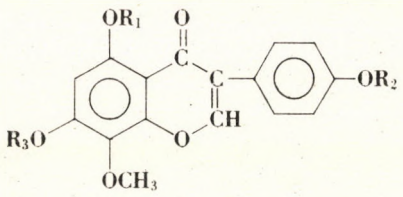
Eingegangen am 27. Mai 1966

Seshadri und Mitarbeiter [1] berichten in einer vorläufigen Mitteilung über die Entdeckung von zwei neuen Glucosiden, Sissotrin und 7-Methyltektorigenin-4'-glucosid (**IId**) in *Dalbergia sissoo*. Bisher erschien jedoch keine ausführliche Mitteilung der Autoren [2] über die Eigenschaften und die Untersuchung der Struktur des letzteren Glucosids.

Wir berichteten bereits in zwei Mitteilungen [3, 4], daß Isoflavon-Glucoside vom Tektoridin-Typ leicht mit unserer auch für Glucoside ausgearbeiteten Ringisomerisationsmethode dargestellt werden können.

Nun soll kurz darüber berichtet werden, daß auf ähnliche weise auch die Synthese des 7-Methyl-tektorigenin-4'-glucosids mittels Ringisomerisation durchgeführt werden konnte.



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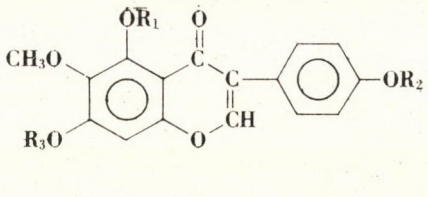

II

a) $R_1=R_2=H$, $R_3=CH_3$
b) $R_1=H$, $R_2=$Tetraacetyl-β-D-glucosyl, $R_3=CH_3$
c) $R_1=$ Acetyl, $R_2=$ Tetraacetyl-β-D-glucosyl, $R_3=CH_3$
d) $R_1=H$, $R_2=\beta$—D-Glucosyl, $R_3=CH_3$
e) $R_1=R_2=R_3=CH_3CO$

Das zur Glucosid-Kopplung benötigte 7-Methylisotektorigenin [6] (**Ia**) wurde aus Isotektorigenintriacetat [5] (**Ie**) durch partiale Desacetylierung in Stellung 7, Methylierung der freien Hydroxyl-Gruppe 7 der erhaltenen Verbindung und nachfolgende vollständige Desacetylierung des Moleküls dargestellt.

* Mitteilung II s. Ref. [4].
** Die Mitteilung bildet einen Teil der Diplomarbeit (Mai 1966) von A. Szőke.

Ia wurde in acetonhaltigem Medium, in Gegenwart von wäßriger Kaliumhydroxydlösung mit Tetraacetyl-α-D-glucosylbromid zu 5-Hydroxy-7,8-dimethoxy-4'-(tetraacetyl-β-D-glucosiloxy)-isoflavon gekoppelt (**Ib**). Die vollständige Acetylierung des rohen **Ib** führte zu 7-Methyl-isotektorigenin-4'-glucosid-pentaacetat (**Ic**, Schmp. 181—182°). Die schonende alkalische Hydrolyse von **Ic** ergab 7-Methyl-isotektorigenin-4'-glucosid (**Id**, Schmp. 198—199°, Monohydrat), seine saure Hydrolyse lieferte das Aglikon, 7-Methyl-isotektorigenin (**Ia**, Schmp. 181—182°; Literatur Schmp. 181°) und seine Ringisomerisation — in Alkohol, in Gegenwart von Natriumäthylat-7-Methyl-tektorigenin-4'-glucosid (**IId**, Schmp. 229—230°, Dihydrat).* Die vollständige Acetylierung von **IId** ergab Glucosidpentaacetat (**IIc**, Schmp. 164—165°), seine saure Hydrolyse das Aglikon, 7-Methyl-tektorigenin (**IIa**, Schmp. 230—231°; Literatur Schmp. 226—227°) [6, 7, 8].

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Budapest XI., Gellért tér 4

* Der Schmelzpunkt des aus natürlicher Quelle isolierten **IId** [1] wurde von den indischen Forschern bisher nicht angegeben.

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POLAROGRAPHY OF THE β- AND γ-PICOLINE COMPLEXES OF CADMIUM IN AQUEOUS MEDIUM

J. N. GAUR and V. K. SHARMA

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Received June 26, 1966

Polarography is so well recognized a technique for the study of complexes that it hardly needs an introduction. Pyridine forms weak complexes with zinc and cadmium as revealed in an earlier study by us [1], but it was found from a survey of the literature [2] that complexes of substituted pyridine have received little attention. BRUEHLMAN and VERHOEK [3] studied the α- and γ-picoline complexes of Ag^+ and the γ-picoline complexes of Cu^{2+}, and MURMANN and BASOLO [4] the β-and γ-picoline complexes of Ag^+ by pH titration technique, using a glass electrode. Polarography of picoline complexes has not been reported. A study of the β- and γ-picoline complexes of cadmium is reported in the present communication.

Theory

DEFORD and HUME in their original article [5] on the mathematical analysis of the waves of complex metal ions, defined an experimentally determinable function, $F_0(x)$, which depends on the concentration of the ligand (x) and the various overall formation constants, β_1, β_2, β_4, etc., of the complex ions:

$$F_0(x) = \text{antilog}\left\{\frac{0.4343\ nF}{RT} \cdot \Delta E_{\frac{1}{2}} + \log\frac{I_s}{I_c}\right\} =$$

$$= 1 + \beta_1(x)\frac{f_M f_x}{f_{Mx}} + \beta_2(x)^2\frac{f_M (f_x)^2}{f_{Mx_2}} + \beta_j(x)^j\frac{f_M(f_x)^j}{f_{Mxj}}$$

where $E_{\frac{1}{2}}$ is the shift in the half-wave potential of the simple metal ion by the addition of (x) moles per litre of the complexing ligand; I_s and I_c denote the experimental diffusion constants for the simple and complex ions; f_M and f_x are the activity coefficients of the metal ion and the ligand; f_{Mxj} denotes the activity coefficient of the jth complex; R, T and F have their usual significance, and n is the number of electrons required for the electrode reaction.

If the ionic strength of the solutions is maintained constant, the activity coefficient term can be dropped to a good approximation [6]. The resulting polynomial equation can be solved graphically for the various values of β_1, β_2, β_3, etc., if the values of $F_0(x)$ are known for a number of different (x) values [5]. This is achieved by measuring the half-wave potentials of a number of solutions containing different amounts of the complexing ligand and a constant concentration of the metal ion under identical conditions of ionic strength, temperature, etc.

Further calculations make it possible to evaluate the percentage composition of the various species, at different ligand concentrations. For details of such calculations the useful review by IRVING [6] may be consulted.

Experimental

An *LP-55* polarograph was operated manually for obtaining the current potential curves. Capillary characteristics for open circuit were m = 1.76 mg per sec and t = 3.6 sec. A constant temperature of 30° ± 01 °C was maintained. Purified nitrogen, presaturated with the solution to be polarographed, was used for removing oxygen from the solutions.

$Cd(NO_3)_2$ concentrations were kept at $1 \cdot 10^{-3}$ *M*. 0.1 *M* KNO_3 was used as the base electrolyte. An overall concentration of 0.001% *Triton X-100* was used in the study of β-picoline complexes, but no suppressor was necessary in the case of γ-picoline complexes. Plots of $\log \frac{i}{i_d - i}$ versus the applied potential were used to test the reversibility of the electrode reaction and for obtaining the half-wave potentials. Polarographic characteristics of the cadmium β-picoline and cadmium γ-picoline systems are given in Tables I and II.

Table I

Polarographic characteristics of the β-picoline complexes of cadmium in aqueous medium

No.	β-picoline conc. (*M*)	$E_{\frac{1}{2}}$ *vs. S. C. E.* (*V*)	i_d (μA)	$F_0(x)$	$F_1(x)$	$F_2(x)$
1.	0.0	−0.5786	6.12	1.0	—	—
2.	0.1	−0.5978	5.26	5.06	40.6	221.0
3.	0.2	−0.6100	4.95	13.72	63.6	225.5
4.	0.3	−0.6185	4.77	27.08	86.9	228.0
5.	0.4	−0.6241	4.59	43.54	106.3	224.5
6.	0.5	−0.6292	4.50	65.69	129.4	222.0
7.	0.6	−0.6332	4.32	92.96	153.3	224.5
8.	0.8	−0.6395	4.23	153.6	190.7	215.4
9.	1.0	−0.6449	4.05	242.9	241.9	223.4

Table II

Polarographic characteristics of the γ-picoline complexes of cadmium in aqueous medium

No.	γ-picoline conc. (*M*)	$E_{\frac{1}{2}}$ *vs.* S. C. E. (*V*)	i_d (μA)	$F_0(x)$	$F_1(x)$	$F_2(x)$	$F_3(x)$
1.	0.0	−0.5692	6.40	1.0	—	—	—
2.	0.05	−0.5835	5.90	3.243	44.86	237.2	—
3.	0.1	−0.5950	5.65	8.177	71.77	387.7	—
4.	0.2	−0.6089	5.30	25.28	121.4	442.0	660
5.	0.3	−0.6185	5.15	54.25	177.5	482.0	573
6.	0.4	−0.6269	5.00	106.4	263.5	576.2	665
7.	0.5	−0.6331	4.80	178.2	354.4	643.0	666
8.	0.6	−0.6372	4.35	268.9	446.5	689.5	665
9.	0.8	−0.6464	4.15	570.5	711.8	850.0	675

Results and discussion

The polarograms of all solutions were well defined, and the reduction process was found to be diffusion-controlled, by plotting i_d *vs.* $\sqrt{h}$, which resulted in straight lines passing through the origin. Straight line plots be-

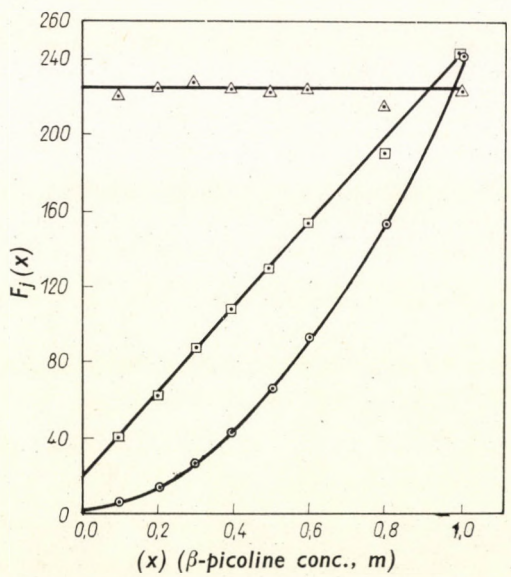

Fig. 1. $F_j(x)$ plots for the cadmium β-picoline complexes (○), $F_0(x)$; (□), $F_1(x)$; (△), $F_2(x)$

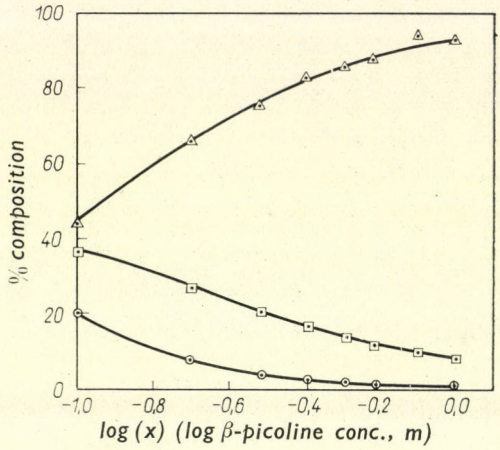

Fig. 2. Percentage composition of various species for the cadmium β-picoline system (○), Cd^{2+}; (□), $ECd(\beta\text{-pic.})]^{2+}$; (△), $[Cd\ (\beta\text{-pic.})_2]^{2+}$

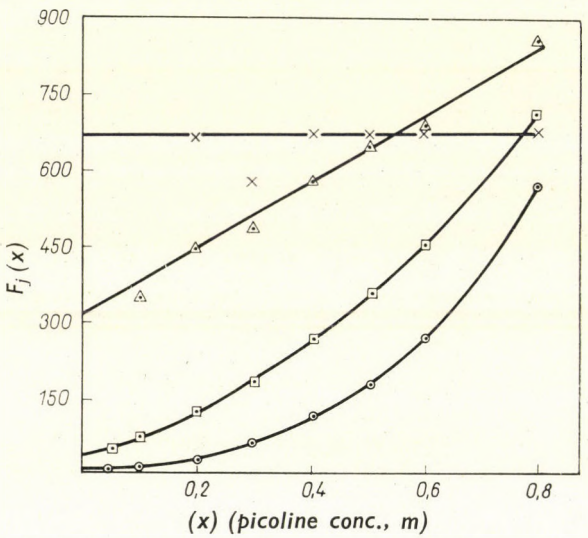

Fig. 3. $F_j(x)$ plots for the cadmium γ-picoline system (○), $F_0(x)$; (□), $F_1(x)$; (△), $F_2(x)$, $F_3(x)$

tween $\log \frac{i}{i_d - i}$ *vs.* the applied potential with a slope varying between 0.030 V and 0.034 V showed a reversible two-electron reduction for all the complex species of both systems.

Cadmium β-picoline system:

The $F_j(x)$ *vs.* (x) plots (Fig. 1) for the cadmium β-picoline system showed the presence of two complex species having the overall formation constants: $\beta_1 = 18.5 \pm 2$ and $\beta_2 = 224 \pm 5$. The percentage composition of Cd^+ and the two complex species are plotted against log (x) in Fig. 2.

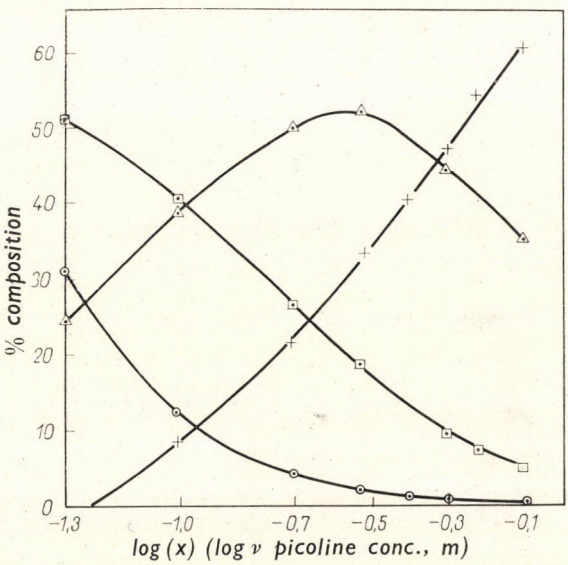

Fig. 4. Percentage composition of various species for the Cd^{2+} γ-picoline system (○), Cd^{2+}; (□), [Cd(γ-pic.)]; (△), [Cd (γ-pic.)$_2$]$^{2+}$ (x) [Cd (γ-pic.)$_3$]$^{2+}$

Cadmium γ-picoline system:

The plot of $F_1(x)$ *vs.* (x) is a smooth curve, but $F_2(x)$ plotted against (x) gives a straight line. The $F_3(x)$ plot is a straight line parallel to the axis of (x) showing the presence of three complex species in solution (Fig. 3). The overall formation constants for these ions are $\beta_1 = 33 \pm 3$; $\beta_2 = 310 \pm 5$ and $\beta_3 = 665 \pm 10$. In Fig. 4 the percentage compositions of the various species present in solution are plotted against log (x).

The only data available for comparison are those from a potentiometric study by DESAI and KABADI [7]. They detected the presence of three complex species in both systems; the overall formation constants for the cadmium β-picoline system were $\beta_1 = 25.5$; $\beta_2 = 146$ and $\beta_3 = 345$, whereas for the cadmium γ-picoline system the constants were $\beta_1 = 31.5$; $\beta_2 = 147$ and $\beta_3 = 941$. The first constants, β_1, for both systems are similar to those obtained by us,

but the others are different. This may be due to the fact that DESAI and KABADI used $NaClO_4$ for maintaining the ionic strength which is not a suitable medium for the study of the complexes of ligands such as pyridine, picoline, etc.

SUMMARY

The complexes of cadmium with β- and γ-picoline have been studied polarographically, using the method of DEFORD and HUME. Two complex species having the overall formation constants $\beta_1 = 18.5 \pm 2$ and $\beta_2 = 224 \pm 5$ were found to be present in the cadmium β-picoline system. In the case of the cadmium γ-picoline system three complex species were found to be present having the formation constants $\beta_1 = 33 \pm 3$, $\beta_2 = 310 \pm 5$ and $\beta_3 = 665 \pm 10$. The percentage composition of the various complexed and uncomplexed species for both systems are presented.

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REAKTIONEN EINIGER EINFACHER ORGANISCHER VERBINDUNGEN MIT HEISSER, KONZENTRIERTER SCHWEFELSÄURE

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Die zur Bestimmung des Stickstoffgehaltes organischer Verbindungen am häufigsten verwendete Methode knüpft sich an den Namen von KJELDAHL [1]. Aus den seit der ersten Mitteilung KJELDAHLs in der Literatur veröffentlichten Angaben geht hervor, daß die sich bei der Zerstörung der organischen Verbindungen nach der KJELDAHLschen Methode abspielenden Prozesse noch ungeklärt sind. Unter den zahlreichen über das Thema veröffentlichten Arbeiten findet man nur vereinzelt solche, die sich mit dem Mechanismus des Zerstörungsprozesses beschäftigen.

Nach L. ROSENTHALER [2] beginnt der Prozeß mit der Oxydation des Stoffes und endet mit Hydrolyse. Das gebildete Ammoniak ist das Produkt dieser Hydrolyse. Auch A. QUARTAROLI [3] hatte festgestellt, daß sich während der Zerstörung zwei Prozesse abspielen, und zwar die Oxydation des organischen Stoffes und die Reduktion des Stickstoffes. E. KAHANE und J. G. CARRERO [4] untersuchten die sich zwischen einfachen Aminen und Schwefelsäure abspielende Reaktion und gelangten zu der Feststellung, daß die Stelle der stickstoffhaltigen, kontinuierlich zerstörten organischen Moleküle von Wasserstoff eingenommen wird, womit sich die Bildung des Ammoniaks erklären läßt. P. BAUMGARTEN [5] untersuchte die Reaktion des Harnstoffs mit konzentrierter Schwefelsäure und fand, daß sich der Prozeß in mehreren Phasen abspielt. Im Intermediärprozeß bildet sich wahrscheinlich Carbaminsäure und in Abhängigkeit vom Überschuß der angewandten Schwefelsäure auch Amino- bzw. Iminosulfonsäure. G. M. SCHWAB und Mitarb. [6] unterzogen die durch BAUMGARTEN untersuchte Reaktion einem kinetischen Studium und nahmen an, daß sich die Reaktion nach einem Kettenmechanismus abspielt. Der Prozeß wird durch die Aminosulfonsäure und möglicherweise auch durch das sich in Abhängigkeit vom Schwefelsäure-Carbamid-Molverhältnis bildende Zwischenprodukt, Iminosulfonsäure, katalysiert. Die genannten Autoren stellten die Zwischenprodukte separat her und beobachteten bei deren Zugabe zum schwefelsauren Reaktionsgemisch ihre katalytische Wirkung. Bei anderen Stoffen (z. B. Salicylsäure, *o*-Phthalsäure, Anilin) konnten sie den eindeutigen katalytischen Effekt der Aminosulfonsäure jedoch nicht feststellen.

Auf Grund der in der Literatur bisher veröffentlichten Angaben bzw. der Ergebnisse jener wenigen Versuche, die zur Erhellung der sich während der Zerstörung nach KJELDAHL abspielenden Prozesse unternommen wurden, hielten wir es für zweckmäßig, die Aufklärung des Mechanismus dieser wichtigen und häufig angewandten Methode zu versuchen. Der Prozeß ist auch eine Funktion der charakteristischen Eigenschaften der zur Zerstörung gelangenden Stoffe, die Feststellung eines einheitlichen Mechanismus konnte also nicht angestrebt werden. Im Interesse einer Lösung dieses Problems stellten wir vorderhand nur die Klärung jener Fragen in den Vordergrund, die wir für grundlegend hielten.

In erster Linie versuchten wir jene Frage zu klären, ob die heiße, konzentrierte Schwefelsäure mit den organischen Verbindungen als

1. oxydierende bzw. reduzierende,
2. wasserentziehende,
3. solvolysierende oder
4. sulfonierende Komponente reagiert.

Um dem gesteckten Ziel näher zu kommen, versuchten wir die Bestimmung einiger solcher, sich bei der Zerstörung einfach zusammengesetzter Stoffe mit konzentrierter Schwefelsäure bildenden Produkte, die bei der Zerstörung der meisten Organika entstehen. Diese Stoffe waren: das Kohlendioxyd, Kohlenmonoxyd und das als Zersetzungsprodukt der in Reaktion tretenden Schwefelsäure entstehende Schwefeldioxyd, mit deren quantitativer Bestimmung darauf geschlossen werden konnte, welche Prozesse sich auf Wirkung der heißen, konzentrierten Schwefelsäure bei den einzelnen Verbindungen abgespielt haben.

Als Modellsubstanzen zur Untersuchung der Reaktionsprodukte wurden die einfachsten, den Kohlenstoff mit verschiedener Oxydationszahl enthaltenden Verbindungen ausgewählt, namentlich Carbamid, Natriumoxalat und Bariumformiat, in denen der Oxydationszustand des Kohlenstoffs $+IV$, $+III$ bzw. $+II$ ist. Keine dieser Verbindungen enthält Kristallwasser, mit einer Verdünnung der Schwefelsäure während der Untersuchung mußte also nicht gerechnet werden.

Von diesen drei Stoffen ist unserer Ansicht nach das Verhalten des Natriumoxalats heißer, konzentrierter Schwefelsäure gegenüber am interessantesten, da man die Oxalsäure, als Endprodukt, beim oxydativen Abbau der Kohlenhydrate sehr oft antrifft. Mit der Bildung dieses Stoffes kann also auch bei komplizierter zusammengesetzten, mehr Kohlenstoffatome enthaltenden Verbindungen gerechnet werden.

Vom Gesichtspunkt der praktischen Durchführung der KJELDAHLschen Zerstörung halten wir das Verhältnis zwischen dem zu zerstörenden Stoff und der konzentrierten Schwefelsäure für überaus wichtig [7], daher berücksichtigten wir dieses Moment bei unseren Versuchen in jedem Falle.

Experimenteller Teil

Die Menge des zu den Untersuchungen verwendeten Stoffes betrug nur in Ausnahmefällen mehr als 40 mg. Zu den Zerstörungen wurden in jedem Falle 3 ml Schwefelsäure verwendet.

Vor der eingehenden Beschreibung unserer Untersuchungen möchten wir die praktische Methode der Bestimmung der Reaktionsprodukte kurz beschreiben.

Die Versuche wurden in dem auf der nachstehenden Abbildung gezeigten Apparat durchgeführt.

Die Vorrichtung besteht aus folgenden Teilen:

1. Waschflasche mit Glasfritte, beschickt mit ca. 30 ml einer mit 70%iger Schwefelsäure hergestellten 0,1 *n* Bichromatlösung, zur Reinigung der in das System geleiteten Luft.

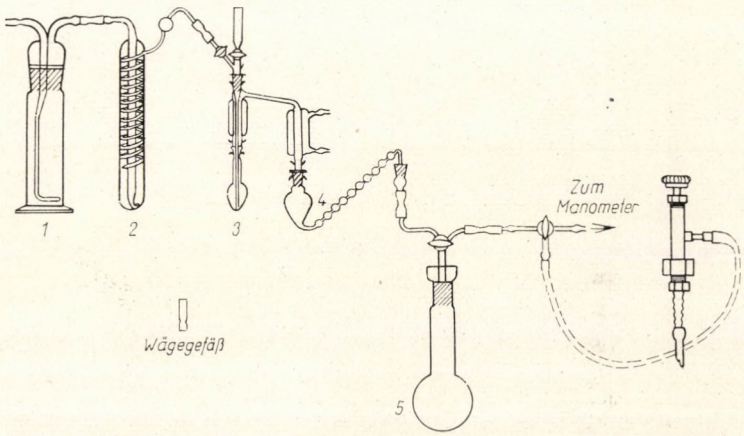

Abb. 1

2. Spiral-Gaswaschflasche, beschickt mit 28%iger Kaliumhydroxydlösung, zur Bindung des Kohlendioxydgehaltes der Luft. Diese Waschflasche ist über ein Gummirohr mit der Fritten-Waschflasche und über ein zweites Gummirohr mit dem Gaseinleitungsrohr des Kolbens verbunden.

3. Das Gesamtvolumen des mit zwei Kühlern versehenen Destillationsapparates beträgt ca. 20 ml. Die beiden Kühler verhindern, daß die beim Kochen der konzentrierten Schwefelsäure entstehenden Schwefelsäuredämpfe in den Titrationskolben gelangen.

4. Die an den zweiten Kühler des Destillationsapparates über einen Schliff angeschlossene Kugelröhre mit zehn Kugeln enthält 2 ml 80%ige Schwefelsäure. Nach den Ergebnissen unserer Untersuchungen ist nämlich eine weniger konzentrierte Schwefelsäure zum Abfangen der eventuell dorthin gelangten Schwefelsäuredämpfe nicht geeignet.

5. 250 ml fassender, mit einem Karlsruher Hahn versehener Schliff-Rundkolben, der über einen Gummischlauch mit einem Dreiweghahn und mit einem zur Regelung der durchströmenden Gasmenge dienenden Nadelventil bzw. mit der Wasserstrahlpumpe in Verbindung steht.

Zu den Schliffen wurde kein Dichtungsmittel verwendet; der Apparat wurde vor jeder Bestimmung sorgfältig ausgewaschen und getrocknet.

Der Prüfstoff wurde in das auf der Abbildung gezeigte kleine Wägegefäß eingewogen und in den kleinen eiförmigen Kolben des Destillationsapparates gebracht. Der Kolben wurde am Apparat befestigt und dieser wurde durch Einsaugen eines mäßigen Luftstromes 5 Minuten hindurch gespült. In den 250-ml-Rundkolben wurde dann die zur Absorption des zu bestimmenden Produktes dienende, in bekanntem Überschuß angewandte Meßlösung eingefüllt, der Kolben wurde am Apparat befestigt und durch entsprechende Verstellung seines Hahnes mit der Wasserstrahlpumpe evakuiert. Nachdem dies geschehen war, wurde der Kolben mit Hilfe des Hahnes wieder mit dem Destillationsapparat verbunden, dann ließen wir durch den Hahntrichter des Apparates 3 ml destillierte, konzentrierte Schwefelsäure auf den eingewogenen

Stoff einlaufen. Durch vorsichtiges Öffnen des Hahnes des Gaseinleitungsrohres wurde ein schwacher Luftstrom in den Apparat gesogen, der gleichzeitig auch für das entsprechende Mischen der schwefelsauren Lösung sorgte. Hierauf begannen wir die Erwärmung des das Reaktionsgemisch enthaltenden Kolbens mit Hilfe eines elektrischen Heizkörpers. Nach 10 Minuten wurde das Kochen der Schwefelsäure unterbrochen, jedoch noch weitere 5 Minuten hindurch wurde Luft durchgesaugt, um auch eventuelle Reste der gebildeten Gase in den Titrationskolben zu spülen. Nachdem dies beendet war, verschlossen wir den Rundkolben, montierten ihn vom Apparat ab, schüttelten mehrmals energisch und titrierten schließlich, nach vorsichtigem Öffnen des Kolbens, den Überschuß der Meßlösung auf entsprechende Weise zurück.

Die Bestimmung des in der konzentriert schwefelsauren Lösung gebildeten Kohlendioxyds führten wir nach der von uns bereits früher ausgearbeiteten Methode [8] bzw. mit einigen unwesentlichen Modifikationen derselben durch.

Die Menge des bei der Zerstörung gebildeten Schwefeldioxyds bestimmten wir gleichzeitig bzw. nach der Kohlendioxydbestimmung. Nach erfolgter Rücktitration des Überschusses der Bariumhydroxyd-Meßlösung titrierten wir die unter einer Pentan-Sperrschicht befindliche Lösung unmittelbar mit Jodlösung. Durch Subtraktion der Milliliter der verbrauchten Jodlösung aus dem Verbrauch der Bariumhydroxydlösung ergibt sich die Menge des Kohlendioxyds.

Zur Bestimmung des Kohlenmonoxyds arbeiteten wir eine, unseren Zwecken entsprechende, neue Methode aus [9], die an anderer Stelle ausführlich beschrieben wurde.

Die quantitative Bestimmung der als Reaktionsprodukte gebildeten drei gasförmigen Komponenten konnten wir nur aus zwei Einwaagen durchführen. Aus der einen bestimmten wir das gebildete Kohlendioxyd und Schwefeldioxyd nebeneinander und aus der zweiten Einwaage das Kohlenmonoxyd.

Experimentelle Ergebnisse und deren Auswertung

Untersuchung der Reaktion zwischen Carbamid und konzentrierter Schwefelsäure

Als erste untersuchten wir die in der Reaktion des Carbamids mit konzentrierter Schwefelsäure gebildeten Produkte. Der in der Verbindung vorhandene Kohlenstoff mit der Oxydationszahl +IV wurde im Laufe der Reaktion quantitativ zu Kohlendioxyd umgewandelt, wie dies auf Grund der Oxydationszahl auch zu erwarten war. Dementsprechend lieferten unsere Versuche zum Nachweis des Kohlenmonoxyds und Schwefeldioxyds negative Ergebnisse (siehe Tabelle I). Auf Grund der Resultate kann eindeutig festgestellt werden, daß sich im Falle des Carbamids auf Wirkung von konzentrierter Schwefelsäure die folgende Solvolyse abspielt:

$$NH_2(CO)NH_2 + 3\ H_2SO_4 = CO_2 + 2\ NH_4HSO_4 + SO_3 \qquad (1)$$

Tabelle I

Untersuchung der Reaktion zwischen Carbamid und konzentrierter Schwefelsäure

Einwaage $(NH_2)_2CO$ mg	Berechnet CO_2 mg	Verbrauch 0,1 *n* $Ba(OH)_2$-Lösung, ml	Gefunden CO_2 mg	CO_2 %
15,2	11,15	5,01	11,03	98,9
14,3	10,49	4,73	10,41	99,3
14,9	10,93	5,11	10,84	99,2

Untersuchung der Reaktion zwischen Oxalsäure und konzentrierter Schwefelsäure

Im weiteren Verlauf unserer Arbeit untersuchten wir das Verhalten des Natriumoxalats konzentrierter Schwefelsäure gegenüber. Es ist seit langem bekannt, daß sich die Oxalsäure auf Einwirkung konzentrierter Schwefelsäure unter Bildung von Kohlendioxyd und Kohlenmonoxyd zersetzt. Nach den Angaben der Literatur bilden sich diese beiden Produkte im Verhältnis von 1 : 1. Bei gleichem Verhältnis spielt die in der Reaktion teilnehmende konzentrierte Schwefelsäure gemäß der nachstehenden Gleichung die Rolle des Wasserbindungsmittels:

$$(COOH)_2 + H_2SO_4 = CO_2 + CO + H_2SO_4 \cdot H_2O \qquad (2)$$

Der obige Prozeß kann eigentlich als eine infolge von Wasserentzug aufgetretene Disproportionierung aufgefaßt werden. Setzt man also diesen Prozeß voraus, so bildet sich aus der Oxalsäure 48,9% Kohlendioxyd und 31,1 % Kohlenmonoxyd.

Das Ziel unserer diesbezüglichen Untersuchung war in erster Linie die Feststellung dessen, ob dieses allgemein angenommene Verhältnis mit quantitativen Messungen bestätigt werden kann. Die Ergebnisse unserer Bestimmungen führten indessen zu der Feststellung, daß die Menge des gebildeten Kohlendioxyds in jedem Falle über 48,9% liegt, während die entstehende Kohlenmonoxydmenge weniger als 31,1% beträgt (siehe Tabelle II). Für das Kohlendioxyd—Kohlenmonoxyd-Molverhältnis ergab sich im Durchschnitt ein Wert von 1,2 : 0,8. Demnach können unsere Ergebnisse mit der Gleichung (2) nicht befriedigend erklärt werden.

Unsere weiteren Untersuchungen ergaben, daß sich im Laufe der Reaktion neben dem Kohlendioxyd und Kohlenmonoxyd auch Schwefeldioxyd bildet, die Reaktion spielt sich also bei der Oxalsäure nach folgendem Schema ab:

$$(COOH)_2 + H_2SO_4 = 2\ CO_2 + SO_2 + 2\ H_2O \qquad (3)$$

demnach ist also die Bildung des Schwefeldioxyds und der zusätzlichen Menge an Kohlendioxyd das Ergebnis einer Redoxreaktion. Es soll jedoch bemerkt werden, daß zu den bei der Bestimmung des Kohlenmonoxyds erhaltenen Ergebnissen auch jene Tatsache berücksichtigt werden muß, daß das Kohlenmonoxyd mit dem Schwefeldioxyd gemeinsam bestimmt wird, da mit der angewandten Kaliumpermanganat-Meßlösung beide Komponenten in gleicher Weise reagieren. Dies beeinflußt die experimentellen Ergebnisse jedoch nicht wesentlich.

Ferner ist auch zu bemerken, daß die Temperaturabhängigkeit der parallel ablaufenden Reaktionen unserer Ansicht nach eine sehr weitgehende ist.

Demnach wird es auch von der Geschwindigkeit der Erreichung der gegebenen Temperatur (des Siedepunktes der konzentrierten Schwefelsäure) abhängen, inwieweit die nebeneinander ablaufenden Reaktionen zur Geltung gelangen, und es ist daher verständlich, daß die Ergebnisse der parallelen Bestimmungen stark unter der in der Analytik üblichen Genauigkeit liegen.

Tabelle II

Mengenverhältnis des in der Reaktion zwischen Oxalsäure und konzentrierter Schwefelsäure gebildeten Kohlendioxyds, Schwefeldioxyds und Kohlenmonoxyds

Nr.	Einwaage $Na_2C_2O_4$, in $H_2C_2O_4$ ausgedrückt, mg	Berechnet CO_2 mg*	Verbrauch 0,1 *N* $Ba(OH)_2$-Lösung, ml		Gefunden CO_2 mg	CO_2 %**	Verbrauch 0,1 *N* J_2-Lösung, ml	SO_2 %***	Bemerkung
			CO_2+SO_2	CO_2					
1.	21,3	10,41	6,52	5,47	12,04	56,5	1,05	10,8	
2.	21,0	10,27	6,57	5,57	12,26	58,3	1,00	10,5	
3.	20,8	10,14	—	5,54	12,20	58,8	—	—	Das gebildete Schwefeldioxyd wurde mit Wasserstoffperoxyd oxydiert
4.	18,7	9,12	—	5,29	11,65	62,4	—	—	

Nr.	Einwaage $Na_2C_2O_4$, in $H_2C_2O_4$ ausgedrückt, mg	Berechnet CO mg*	Verbrauch 0,1 *N* $KMnO_4$-Lösung, ml	Gefunden CO mg	CO %****
5.	22,6	7,02	4,01	5,61	24,9
6.	21,8	6,79	4,04	5,66	25,9

* Auf Grund der Gleichung $(COOOH)_2 + H_2SO_4 = CO_2 + CO + H_2SO_4 \cdot H_2O$.

** Die auf Grund der Disproportionierung gebildete Kohlendioxydmenge sollte 48,9% betragen.

*** In Kohlendioxyd-Prozenten ausgedrückt.

**** Die auf Grund der Disproportionierung gebildete Kohlenmonoxydmenge sollte 31,1% betragen.

Untersuchung der Reaktion zwischen Ameisensäure und konzentrierter Schwefelsäure

In unseren weiteren Versuchen stellten wir fest, daß die konzentrierte Schwefelsäure auf die ein Kohlenstoffatom im Oxydationszustand +II enthaltende Ameisensäure — ähnlich wie bei der Oxalsäure — sowohl dehydratierend als auch oxydierend wirkt.

Bekanntlich bildet sich aus der Ameisensäure bzw. aus ihren Salzen auf Wirkung von konzentrierter Schwefelsäure Kohlenmonoxyd:

$$HCOOH + H_2SO_4 = CO + H_2SO_4 \cdot H_2O \qquad (4)$$

Neben der Dehydratationsreaktion spielt sich nach den Ergebnissen unserer Versuche — wenn auch nur in sehr geringem Maße — auch noch der nachstehend veranschaulichte Prozeß ab:

$$HCOOH + H_2SO_4 = CO_2 + SO_2 + 2\ H_2O \qquad (5)$$

Der Ameisensäure gegenüber gelangt also in erster Linie die wasserentziehende Wirkung der Schwefelsäure zur Geltung; wenn man aber die Oxydationszahl der Kohlenstoffatome der Verbindung in Betracht zieht, so ist auch das Auftreten des Redoxprozesses keineswegs überraschend. Es sei bemerkt, daß die auf der wasserentziehenden Wirkung der Schwefelsäure beruhende Reaktion fast quantitativ und viel schneller verläuft als der Oxydationsprozeß, dessen Produkt, das Kohlendioxyd, mengenmäßig nicht über zwei Prozent lag. Unsere diesbezüglichen Meßergebnisse sind in Tabelle III zusammengefaßt. Neben dem Kohlendioxyd bestimmten wir auf die bereits beschriebene Weise auch das Schwefeldioxyd. Ferner untersuchten wir auch, ob die bei der Destillation eventuell in die Vorlage gelangte Ameisensäure bzw. das Kohlenmonoxyd unter den gegebenen Bedingungen mit Jod reagieren. Diese Untersuchungen führten zu einem negativen Ergebnis, d.h. also, daß der Jodverbrauch ausschließlich dem Schwefeldioxyd entspricht.

Tabelle III

Mengenverhältnis des in der Reaktion zwischen Ameisensäure und konzentrierter Schwefelsäure gebildeten Kohlendioxyds, Schwefeldioxyds und Kohlenmonoxyds

Nr.	Einwaage $Ba(HCOO)_2$, in HCOOH ausgedrückt, mg	Berechnet CO_2 mg*	Verbrauch 0,1 *N* $Ba(OH)_2$-Lösung, ml		Gefunden CO_2 mg	CO_2 %	Verbrauch 0,1 *N* J_2-Lösung, ml	SO_2 %**
			CO_2+SO_2	CO_2				
1.	14,41	13,78	0,33	0,13	0,29	2,10	0,20	3,27
2.	32,06	30,66	0,38	0,18	0,40	1,31	0,20	1,44

Nr.	Einwaage $Ba(HCOO)_2$, in HCOOH ausgedrückt, mg	Berechnet CO mg***	Verbrauch 0,1 *N* $KMnO_4$-Lösung, ml	Gefunden CO mg	CO %
3.	6,96	4,24	3,01	4,21	99,5
4.	8,14	4,95	3,53	4,94	99,8
5.	9,42	5,74	4,09	5,73	99,8

* Auf Grund der Gleichung $HCOOH + H_2SO_4 = CO_2 + SO_2 + 2\ H_2O$.
** In Prozenten des Kohlendioxyds ausgedrückt.
*** Auf Grund der Gleichung $HCOOH + H_2SO_4 = CO + H_2SO_4 \cdot H_2O$.

Auf Grund der Gleichung (5) müßten sich Kohlendioxyd und Schwefeldioxyd in äquivalenter Menge bilden, in unseren Versuchen erwies sich die Menge des Schwefeldioxyds jedoch als größer. Bei diesen Ergebnissen muß jedoch berücksichtigt werden, daß die Bestimmung des in sehr geringen Mengen gebildeten Kohlendioxyds und Schwefeldioxyds schon an und für sich mit einem großen Fehler verbunden ist, und daß der Unterschied zwischen den Mengen der beiden Produkte auch dadurch noch gesteigert wird, daß die Bestimmung des Schwefeldioxyds direkt, die des Kohlendioxyds hingegen durch Rücktitration erfolgt. Unter Berücksichtigung all dieser Tatsachen, kann die ablaufende Oxydationsreaktion nur qualitativ gewertet werden (siehe Tabelle III).

Zusammenfassend kann auf Grund unserer mit den drei einfachen Modellsubstanzen durchgeführten Versuche festgestellt werden, daß die auf Wirkung der heißen konzentrierten Schwefelsäure ablaufenden Prozesse bzw. die Entfaltung der verschiedenen Eigenschaften der konzentrierten Schwefelsäure außer den strukturellen und sonstigen Eigenheiten der einzelnen Verbindungen in entscheidendem Maße durch die Oxydationszahl ihrer Kohlenstoffatome beeinflußt werden.

Eine Verbindung, die den Kohlenstoff mit der Oxydationszahl +IV enthält, kann naturgemäß weiter nicht oxydiert werden, mit einem solchen Stoff kann die Schwefelsäure daher nur unter Entfaltung ihrer solvolysierenden Eigenschaft reagieren. Liegt der Kohlenstoff in der Verbindung jedoch in einem niedrigeren Oxydationszustand vor, so muß mit der Redoxreaktion unserer Ansicht nach unbedingt gerechnet werden. Das Maß, in welchem die Redoxreaktion zur Geltung gelangt, kann in diesem Falle indessen verschieden sein. Bei der den Kohlenstoff im Oxydationszustand +III enthaltenden Oxalsäure ist die Redoxreaktion beträchtlich, während das mit der Oxydationszahl +II vorliegende Kohlenstoffatom der Ameisensäure nur in sehr geringem Maße oxydiert wird. Die Ursache dieses Unterschiedes dürfte mit der Geschwindigkeitsdifferenz zwischen den beiden parallel ablaufenden Reaktionen zu erklären sein. Die bei der Oxalsäure infolge des Wasserentzuges auftretende Disproportionierung ist ein langsamerer Prozeß als die Dehydratation der Ameisensäure. Dies bedeutet jedoch, daß sich die Oxydationsfähigkeit der Schwefelsäure im ersten Falle in höherem Maße entfalten kann, während diese Möglichkeit bei der Ameisensäure infolge der sehr raschen Dehydratation kaum besteht.

Unsere weiteren Versuche werden die Untersuchung der sulfonierenden Eigenschaft der konzentrierten Schwefelsäure zum Gegenstand haben, die bei den aromatischen Verbindungen eine entscheidende Rolle spielen kann.

ZUSAMMENFASSUNG

Mit Hilfe der quantitativen Bestimmung der als Reaktionsprodukte gebildeten gasförmigen Stoffe (Kohlendioxyd, Kohlenmonoxyd und Schwefeldioxyd) wurden die sich zwischen heißer, konzentrierter Schwefelsäure und einigen organischen Verbindungen abspielenden Reaktionen untersucht.

Es wurde festgestellt, daß im Falle des Carbamids, in welchem der Kohlenstoff mit der Oxydationszahl +IV vorliegt, die solvolysierende Eigenschaft der konzentrierten Schwefelsäure zur Geltung gelangt; es spielt sich hier keine Redoxreaktion ab. Beim Natriumoxalat und Bariumformiat, die den Kohlenstoff im Oxydationszustand +III bzw. +II enthalten, wirkt die konzentrierte Schwefelsäure nicht nur wasserentziehend, sondern auch oxydierend. Im Falle der Ameisensäure geht die Redoxreaktion nur in sehr geringem Maße vor sich, während sie bei der Oxalsäure schon ein beachtliches Maß erreicht.

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STUDIUM DER KATALYTISCHEN WIRKUNG DES SELENDIOXYDS IM PROZESS DER KJELDAHL-ZERSTÖRUNG

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Bei der Anwendung der KJELDAHLschen Methode ist es wichtig, einen solchen entsprechenden Katalysator zu wählen, der die zur Zerstörung benötigte Zeit reduziert, die Überführung des in der organischen Verbindung gebundenen Stickstoffs in Ammoniak jedoch nicht nachteilig beeinflußt. Zur KJELDAHLschen Bestimmung wurden zu Beginn verschiedene Metallkatalysatoren verwendet, von denen sich die Literatur in erster Linie mit der Anwendung des Quecksilbers und Kupfers beschäftigt. Nach Ansicht zahlreicher Autoren [1, 2, 3, 4] wirkt nämlich unter sämtlichen Metallen das Quecksilber am günstigsten und verursacht gleichzeitig keinen Stickstoffverlust. Sein Nachteil besteht jedoch darin, daß es die Destillation des Ammoniaks stört und deshalb vor Beginn der Destillation gefällt werden muß. Die Anwendung von Katalysatorgemischen ist ziemlich verbreitet und wird vielfach empfohlen, da ihre Komponenten sich in der Wirkung gegenseitig verstärken.

Die Anwendung des erstmals von LAURO [5] empfohlenen Selens ist heute bereits allgemein verbreitet und steht — wie aus der Literatur ersichtlich ist — auch heute im Vordergrund des Interesses. Seit der Mitteilung von LAURO haben sich zahlreiche Publikationen mit der praktischen Anwendung des Selens als Katalysator beschäftigt, über die katalytische Wirkung und die Anwendungsweise gehen die in der Literatur geäußerten Ansichten jedoch auseinander. Darin stimmen die Autoren allgemein überein, daß die Zerstörungszeit bei der Anwendung von Metallkatalysatoren in Gegenwart von Selen auf die Hälfte oder sogar auf ein Drittel reduziert wird, und daß das Selen die Destillation und Bestimmung des Ammoniaks nicht stört. Besonders nach langen Zerstörungszeiten haben einige Autoren jedoch Stickstoffverluste festgestellt. Nach den Untersuchungen von BELCHER und GODBERT [6] kann der in Gegenwart von Selen eintretende Stickstoffverlust mit Sicherheit vermieden werden, wenn man die in ihrer Vorschrift angegebene maximale Zerstörungszeit von 75 Minuten nicht überschreitet. Diese Behauptung der Autoren hat sich auch in unserer praktischen Erfahrung bewahrheitet, bei der Zerstörung geringer Mengen von Organika kann nämlich die Zerstörungszeit weitgehend verkürzt werden, und es treten keine Stickstoffverluste auf.

Ähnlich zu den oben bereits erwähnten Katalysatorgemischen wird auch die Anwendung verschiedener Selen—Metall-Gemische empfohlen. Man verwendet häufig Selen—Kupfer-Gemische, noch allgemeiner verbreitet ist jedoch die Anwendung des Selen—Quecksilber-Gemisches. Dieses letztere Gemisch hält man [7] allgemein für den bisher bekannt gewordenen wirksamsten Katalysator bei der KJELDAHLschen Methode.

Die praktische Anwendung des Selen-Katalysators wird in vielen Artikeln besprochen, mit seiner Rolle haben sich bisher jedoch nur wenige Autoren beschäftigt. Nach der Annahme von SNIDER und COLEMAN [8] stimmt die Rolle bzw. Wirkung des Selens mit der des Kaliumsulfats überein, d. h. es beschleunigt den Ablauf des Prozesses durch die Erhöhung der Temperatur der Zerstörungsflüssigkeit. Gleichzeitig haben die genannten Autoren jedoch auf Grund eigener Untersuchungen festgestellt, daß diese Annahme zur völligen Klärung der Rolle des Selens noch nicht ausreicht. Hierzu möchten wir bemerken, daß Selen, nach den Ergebnissen unserer eigenen Untersuchungen, die Temperatur der Zerstörungsflüssigkeit auch in hoher Konzentration nicht ändert bzw. nicht erhöht. ILLARIONOV und SOLOVEVA [9] haben es versucht, den bei der Anwendung von Selen als Katalysator auftretenden Stickstoffverlust zu erklären. Ihrer Ansicht nach kommen dabei die folgenden Prozesse in Frage:

$$(NH_4)_2SO_4 + H_2SeO_3 = (NH_4)_2SeO_3 + H_2SO_4$$

$$3\,(NH_4)_2SeO_3 = 9\ H_2O + 2\ NH_3 + 3\,Se + 4\ N$$

Sie haben die Richtigkeit dieser Annahme jedoch nicht bewiesen. Ferner haben sie festgestellt, daß der aktive Katalysator nicht das elementare Selen selbst, sondern die in der konzentriert schwefelsauren Lösung sich bildende selenige Säure ist. Im Lichte späterer Literaturangaben [10] kann diese Erklärung der genannten Autoren jedoch nicht aufrechterhalten werden. Unter den gegebenen Bedingungen kann sich die Bildung des Ammoniumselenits nämlich nicht abspielen, da ja die selenige Säure in konzentriert schwefelsaurer Lösung nicht existieren kann. Der Stickstoffverlust ist daher auf die obigen Gleichungen nicht zurückführbar.

A. SREENIVASAN und V. SADASIVAN [11] haben die sich zwischen der konzentrierten Schwefelsäure und dem Selen abspielende Reaktion eingehend untersucht. Neben der bereits seit langem bekannten Reaktion $Se + H_2SO_4 = SeSO_3 + H_2O$ muß nach Ansicht der genannten Autoren in heißer, konzentrierter, schwefelsaurer Lösung auch mit der Oxydation des Selens gerechnet werden. Sie nehmen an, daß in der schwefelsauren Lösung zwischen dem elementaren Selen und dem Selenit ein Gleichgewicht besteht. In Gegenwart organischer Stoffe bildet sich das Selenit nur in sehr geringen Mengen, da es durch das Organikum zu elementarem Selen reduziert wird.

Nach Ansicht der obigen Autoren wird das gebildete Selenit bei der Anwendung eines Selen—Quecksilber-Gemisches zu Selenat oxydiert. Zwischen den Selenverbindungen, die das Selen mit verschiedenen Wertigkeiten enthalten, kommt das folgende Gleichgewicht zustande:

$$Se \rightarrow SeO_3^{2-} \rightleftharpoons SeO_4^{2-}$$

Sie konnten neben dem Selenit nur sehr geringe Mengen von Selenat nachweisen. In Gegenwart von organischen Verbindungen und Quecksilber wird das Selen, ihrer Ansicht nach, gleichfalls bis zur Selenat-Stufe oxydiert, da sich die Gleichgewichtsreaktion mit dem Vorwärtsschreiten des Zerstörungsprozesses stark in Richtung des oberen Pfeiles verschiebt und die Reaktion nach Vollständiger Oxydation des Organikums in dieser Richtung auch vollständig abläuft. Sie nehmen an, daß die katalytische Wirkung ohne Quecksilber also gerade deshalb schwächer ist, weil in erster Linie die reduzierende Eigenschaft der organischen Verbindung zur Geltung gelangt und so die Bildung der die Oxydation besser fördernden Selenverbindungen in höherem Oxydationszustand verhindert. Damit erklären sie also jene Tatsache, daß die Anwendung von Selen—Quecksilber-Gemischen günstiger ist, als die Verwendung dieser beiden Stoffe für sich.

Der erwähnte Artikel beschreibt die zum Nachweis der in verschiedenen Oxydationszuständen vorliegenden Selenverbindungen nebeneinander dienende Methode nicht. Nach neueren Literaturangaben [12] kann das Selen in heißer, konzentrierter, schwefelsaurer Lösung jedoch nur in Form von Selen-(IV) existieren. Da diese Frage — in Gegenwart von Quecksilber — bisher noch nicht untersucht wurde, führten wir, durch Zugabe von Quecksilberoxyd zur konzentriert schwefelsauren Lösung des Selendioxyds und nachfolgendem Kochen des Gemisches, Versuche zum Nachweis dessen durch, ob das durch die genannten Autoren nachgewiesene Selenat tatsächlich existiert.* SREENIVASAN und Mitarb. behaupten, daß sich das Selenat neben dem Selenit nur in sehr geringer Menge bildet, zur Kontrolle dieser Behauptung war die durch uns angewandte Methode also besonders gut geeignet. Wir stellten fest, daß sich in konzentriert schwefelsaurer Lösung Selen(VI) selbst in Gegenwart von Quecksilber nicht bildet. Demnach kann auch in Gegenwart eines Organikums kein Selenat vorhanden sein, und daher kann die Wirksamkeit des Selen—Quecksilber-Katalysatorgemisches mit der oxydierenden Eigenschaft des Selenats nicht erklärt werden.

Erwähnenswert sind auch die durch G. M. SCHWAB [14] im Zusammenhang mit dem Selen-Katalysator durchgeführten kinetischen Untersuchungen. Der genannte Autor untersuchte die Oxydation des Anilins in konzentriert

* Die Untersuchung wurde nach der Methode von L. BARCZA und E. SCHULEK [13] durchgeführt. Ein großer Vorteil dieses Verfahrens besteht darin, daß mit seiner Hilfe neben viel Selenit noch 0,2 μg Selenat sicher nachgewiesen werden können.

schwefelsaurer Lösung in Gegenwart von Selen und fand, daß die Reaktion heterogen ist. Das organische Molekül reagiert scheinbar mit dem elementaren Selen, SCHWAB konnte jedoch nachweisen, daß das Anilin unmittelbar mit der gebildeten selenigen Säure in Reaktion tritt.

Schließlich möchten wir noch die Untersuchungen BAKERS [4] erwähnen, der sich mit der Wirksamkeit von Selenverbindungen verschiedener Oxydationszustände als Katalysatoren beschäftigt hat. Er gelangte dabei zu dem Ergebnis, daß elementares Selen, Selenit und Selenat als Katalysatoren vollkommen gleichwertig sind. Diese Erfahrung BAKERS ist jedoch eine direkte Folge des Verhaltens des Selens in konzentrierter, heißer Schwefelsäure, zumal dieses Element nach der bereits erwähnten Mitteilung [10] unter den gegebenen Bedingungen nur in Form von Selen(IV) existieren kann.

In unseren Versuchen setzten wir uns im Zusammenhang mit der katalytischen Rolle des Selens die eingehende Klärung von zwei Fragen zum Ziel:

1. Änderung der Wirkungen der konzentrierten, heißen Schwefelsäure auf organische Verbindungen in Gegenwart von Selen.

2. Untersuchung der Funktion des Selen-Katalysators bei der KJELDAHLschen Zerstörung.

Als Modellsubstanzen verwendeten wir zu unseren mit Selen-Katalysator durchgeführten Versuchen, auf Grund der bereits beschriebenen Überlegungen [15], Natriumoxalat und Bariumformiat, während das Selen in Form von festem Selendioxyd angewandt wurde.

Die technische Durchführung unserer Untersuchungen stimmte mit der in der ersten Mitteilung dieser Serie [15] bereits eingehend beschriebenen Methode vollständig überein. Das eingewogene Selendioxyd (ca. 4 cg) wurde mit dem Natriumoxalat gleichzeitig in den Destillationskolben gebracht, und die Produkte der katalysierten Reaktion wurden quantitativ bestimmt.

Das in der Reaktion der heißen, konzentrierten Schwefelsäure mit Natriumoxalat festgestellte CO_2 : CO Verhältnis von 1,2 : 0,8 erfuhr in Gegenwart von Selendioxyd eine starke Verschiebung. Mit zunehmender Menge nahm die Kohlenmonoxydmenge selbstverständlich ab und entsprach in der katalysierten Reaktion schließlich dem Verhältnis 1,8 : 0,2. Unsere diesbezüglichen Ergebnisse sind in der Tabelle I zusammengefaßt. Wie ersichtlich, steigert der Katalysator die Oydationsbereitschaft der Schwefelsäure und in der sich zwischen Oxalsäure und konzentrierter Schwefelsäure abspielenden Reaktion erlangt der Dehydratation gegenüber die Redoxreaktion die Oberhand. In diesem Falle war logischerweise auch eine Zunahme der Menge des gebildeten Schwefeldioxyds zu erwarten, und diese Annahme konnte mit unseren Meßergebnissen auch bestätigt werden. Ohne Katalysator betrug nämlich die Menge des gebildeten Schwefeldioxyds ca. 10%, erreichte jedoch bei Anwendung von Selendioxyd ca. 40%. Die Schwefeldioxydmenge stieg also mit der Menge des gebildeten Kohlendioxyds proportional an.

Nach den Ergebnissen unserer früheren Untersuchungen gelangt die wasserziehende und oxydierende Eigenschaft der heißen, konzentrierten Schwefelsäure auch der Ameisensäure gegenüber zur Geltung. Im Vergleich zur Oxalsäure spielt sich die Redoxreaktion hier nur in sehr geringem Maße ab, wir hielten es daher für zweckmäßig, die Wirkung des Selens auch in diesem Falle zu untersuchen. Auf Grund der durchgeführten Untersuchungen (siehe Tabelle I) kann festgestellt werden, daß das Selendioxyd die oxydierende Eigenschaft der Schwefelsäure auch hier — wenn auch nur in geringem Maße — steigert. Die Menge des gebildeten Schwefeldioxyds bzw. Kohlendioxyds stieg von ca. 2% auf über 5%.

Die Untersuchung der katalysierten Reaktionen zeigt, daß sich die Geschwindigkeit der infolge der verschiedenen Eigenschaften der konzentrierten Schwefelsäure parallel ablaufenden Reaktionen in Gegenwart von Selendioxyd ändert. Bei der Oxalsäure gelangt, ohne Katalysator, in erster Linie die dehydratierende Eigenschaft der konzentrierten Schwefelsäure zur Geltung, gleichzeitig wirkte die Säure nur wenig oxydierend, während in Gegenwart von Selen

Tabelle I

Wirkung des Selendioxyd-Katalysators auf die Reaktion zwischen Oxalsäure bzw. Ameisensäure und konzentrierter Schwefelsäure

Nr.	Einwaage $Na_2C_2O_4$ in $H_2C_2O_4$ ausgedrückt, mg	Einwaage $Ba(HCOO)_2$ in HCOOH ausgedrückt, mg	Berechnet CO_2 mg*	Verbrauch 0,1 *N* $Ba(OH)_2$-Lösung, ml		Gefunden CO_2 mg	CO_2 %	Verbrauch 0,1 *N* J_2-Lösung, ml	SO_2 %**
				CO_2+SO_2	CO_2				
1	13,3		6,50	7,94	5,24	11,53	86,7	2,70	44,7
2	21,8		10,65	11,23	8,21	18,07	82,9	3,02	30,5
3	20,6		10,07	10,36	6,47	14,24	69,1	3,89	41,5
4	13,4		6,57	7,30	5,10	11,23	83,5	2,20	36,0
5		13,72	13,12	0,92	0,47	1,03	7,85	0,45	7,55
6		18,02	17,23	0,72	0,38	0,84	4,88	0,34	4,15

Nr.	Einwaage $Na_2C_2O_4$, in $H_2C_2O_4$ ausgedrückt, mg	Berechnet CO mg*	Verbrauch 0,1 *N* $KMnO_4$-Lösung, ml	Gefunden CO mg	CO %
7	21,8	6,77	0,99	1,39	6,39
8	21,0	6,54	0,92	1,29	6,14

* Auf Grund der Gleichungen $(COOH)_2 + H_2SO_4 = CO_2 + CO + H_2SO_4 \cdot H_2O$ bzw. $HCOOH + H_2SO_4 = CO_2 + SO_2 + 2\ H_2O$.

** In Prozenten des Kohlendioxyds ausgedrückt.

als Katalysator die Lage gerade umgekehrt war. Die Redoxreaktion wird hier so stark beschleunigt, bzw. die Oxydationsbereitschaft der Schwefelsäure in solchem Maße gesteigert, daß die Möglichkeit der auf Wirkung der wasserentziehenden Eigenschaft eintretenden Disproportionierung auf das Minimum herabsinkt. Im Falle der Ameisensäure ändert sich die Lage auch in Gegenwart des Katalysators nicht wesentlich. Zwar nahm das Maß der Oxydation im Vergleich zur katalysatorlosen Reaktion zu, jedoch gelangte auch in Gegenwart des Katalysators in erster Linie die wasserentziehende Wirkung der Schwefelsäure zur Geltung. Das abweichende Verhalten dieser beiden einfachen Verbindungen dem Selen-Katalysator gegenüber ist auch in diesem Falle auf die charakteristischen Eigenschaften und auf die Struktur der Verbindungen zurückzuführen.

Den Ausgangspunkt unserer im Zusammenhang mit der Funktion des Selen-Katalysators durchgeführten Untersuchungen bildeten unsere bei der mit Selendioxyd katalysierten Reaktion zwischen Oxalsäure und konzentrierter Schwefelsäure gemachten Erfahrungen.

Bei den mit Selendioxyd katalysierten Reaktionen organischer Verbindungen mit konzentrierter Schwefelsäure konnten wir die Bildung der in der Literatur mit der Formel $(SeSO_3)_x$ bezeichneten dunkelgrünen Verbindung in jedem Falle beobachten. Die grüne Farbe erschien beim Beginn des Temperaturanstieges und verschwand wieder, nachdem die Flüssigkeit einige Minuten hindurch im Sieden gehalten worden war. Auf Grund unserer Beobachtungen könnte sich im Falle von Oxalat die nachstehende Reaktionsreihe abspielen.

$$2\ (COOH)_2 + SeO_2 = 4\ CO_2 + Se + 2\ H_2O \tag{1}$$

$$Se + H_2SO_4 = SeSO_3 + H_2O \tag{2}$$

$$SeSO_3 + H_2SO_4 = SeO_2 + 2\ SO_2 + H_2O \tag{3}$$

Unser Ziel war weiters, den mit Hilfe der obigen Gleichungen beschriebenen bzw. erklärten Funktionsprozeß des Katalysators auch experimentell zu bestätigen. Um dies zu erreichen, gingen wir auf folgende Weise vor. Wir begannen das zu den Untersuchungen auf die übliche Weise vorbereitete Reaktionsgemisch im Apparat zu erwärmen, stellten die Wärmezufuhr jedoch beim Erscheinen des grünen Produktes sofort ein. An Stelle des mit der zur Bindung des gebildeten Kohlendioxyds und Schwefeldioxyds dienenden Lösung beschickten Kolbens wurde nun ein anderer, gleichfalls mit Meßlösung beschickter Kolben gebracht, und das Kochen der schwefelsauren Lösung wurde noch weitere 5 Minuten hindurch fortgesetzt. Nach Beendigung der Reaktion führten wir die quantitative Bestimmung der in die beiden Kolben gelangten Reaktionsprodukte durch und fanden, daß sich in der ersten Phase der Reaktion praktisch die gesamte Menge des Kohlendioxyds und nur ca. 5% der — auf

Grund der vorangehenden Untersuchungen gleichfalls bekannten — Menge des Schwefeldioxyds bildet. Die restlichen 95% des Schwefeldioxyds entstehen in der zweiten Phase der Reaktion (siehe Tabelle II).

Tabelle II

Untersuchung der katalytischen Wirkung des Selendioxyds

Einwaage $Na_2C_2O_4$, mg	Verbrauch 0,1 *N* $Ba(OH)_2$-Lösung, ml	Verbrauch 0,1 *N* J_2-Lösung, ml	Für CO_2 verbrauchte 0,1 *N* $Ba(OH)_2$-Lösung, ml	CO_2 mg	SO_2 mg
33,2	I. 9,54	I. 0,20	I. 9,34	I. 20,56	I. 0,64
	II. —	II. 4,07	II. —	II. —	II. 13,04
32,0	I. 7,92	I. 0,28	I. 7,64	I. 16,82	I. 0,90
	II. —	II. 2,72	II. —	II. —	II. 8,71

Es gelang mit diesen Versuchen also, zwei Phasen der Reaktion zu unterscheiden und damit die Gültigkeit der obigen Gleichungen auch experimentell zu beweisen. Das Organikum tritt also unmittelbar mit dem in konzentrierter Schwefelsäure allein stabilen vierwertigen Selen in Reaktion und reduziert dieses vorübergehend zu elementarem Selen. Das elementare Selen bildet mit der Schwefelsäure $(SeSO_3)_x$, welches beim Erwärmen mit konzentrierter Schwefelsäure leicht zu Selen im Oxydationszustand +IV oxydiert wird und als solches im Prozeß wieder teilnimmt.

ZUSAMMENFASSUNG

Es wurde die in Gegenwart von Selendioxyd als Katalysator zwischen heißer, konzentrierter Schwefelsäure und organischen Verbindungen ablaufende Reaktion untersucht. Bei Oxalsäure und Ameisensäure wird die Oxydationsfähigkeit der Schwefelsäure durch den Katalysator gesteigert, gelangt jedoch den parallel ablaufenden Reaktionen gegenüber in jedem Falle nur in einem durch die charakteristischen und strukturellen Eigenschaften dieser Verbindungen beeinflußten Maße zur Geltung.

Hinsichtlich der Funktion des Selen-Katalysators bei der KJELDAHLschen Zerstörung wurde experimentell nachgewiesen, daß das Selendioxyd die organische Verbindung oxydiert und gleichzeitig zu elementarem Selen reduziert wird, welches mit der konzentrierten Schwefelsäure vorübergehend $(SeSO_3)_X$ bildet. Das gebildete Produkt wird durch die Schwefelsäure wieder zu Selenit oxydiert und nimmt im Prozeß erneut teil.

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INVESTIGATION OF DEHYDROCYCLIZATION ON METAL CATALYSTS, IV

PARALLELISM OF THE DEHYDROGENATION OF CYCLOHEXANE AND DEHYDROCYCLIZATION

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In a previous communication [1] the authors have stated that unsaturated open-chain hydrocarbons (olefins and diolefins) are formed in the course of the dehydrocyclization of hexane, in the presence of metal catalysts. Olefins and diolefins themselves are also readily aromatized under the given experimental conditions, at a higher rate than paraffinic hydrocarbons. The dehydrocyclization of olefins was shown to take place *via* dienic intermediates [2, 3]. On this basis the conclusion has been drawn that unsaturated compounds are intermediates of paraffin dehydrocyclization; this statement has also been supported by radioactive tracer studies [1]. A similar mechanism was found for the dehydrocyclization of heptane on oxide catalysts [4]. According to these assumptions, cyclization results in the formation of unsaturated cyclic compounds. This observation is in contrast with the statement regarded in the literature so far as proved, according to which no olefins would be formed during dehydrocyclization on metal catalysts, and the only intermediates of the reaction would be cycloparaffinic hydrocarbons [5]. Our previous investigations have cleared up another reaction path of dehydrocyclization, but have not answered the question whether stepwise dehydrocyclization is the only course of the reaction, or there is also a dehydrocyclization process taking place *via* cyclohexane, and if so, what is the ratio of these two processes. This is a question to be answered by the present work.

For the sake of completeness, the aromatization reactions of cyclic and open-chain hydrocarbons were compared in a pulse system, the same as used previously, between 300—400 °C, the temperature range in which detailed studies on dehydrocyclization have most often been carried out. The individual reaction steps were investigated by reacting mixtures of radioactive and inactive hydrocarbons, similarly to our previous communication [1]. The apparatus, experimental technique, catalysts and starting materials have been described in previous publications [1—3].

Results

Cyclic hydrocarbons were dehydrogenated at a high rate using nickel and platinum catalysts under the conditions of the pulse technique. In our previous investigations it was shown that the dehydrogenation of cyclohexane on metal catalysts did not necessarily follow the sextet mechanism generally accepted in the literature [6], since the formation of cyclohexane must also be taken into

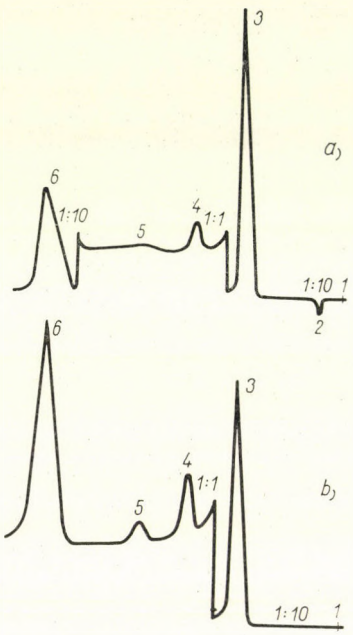


Fig. 1. a) Chromatogram of the dehydrogenation of cyclohexane (Catalyst: 1.07 g of Pt; t = 405 °C); *b)* Chromatogram of a model mixture

Conditions of analysis: t = 25 °C; 100 cm of triethylene glycol dibutyrate, 20% on Chromosorb W. 1 — sample introduction; 2 — hydrogen; 3 — cyclohexane; 4 — cyclohexene; 5 — cyclohexadiene-1,3; 6 — benzene

account [7]. This observation could be confirmed by experiments carried out by means of the pulse technique, too: when platinum catalyst was used, cyclohexene and moreover, at higher temperatures, cyclohexadiene-1,3 were detected among the products (Fig. 1).

The product composition in the dehydrogenation of identical pulses of cyclohexane was plotted as a function of the contact time (the active proportion of the catalyst) expressed in a way described previously [2]. The concentration of cyclohexene was characterized by a very flat maximum, unambiguously indicating that this compound was an intermediate (Fig. 2). Low concentrations throughout the experiment indicated that the rate of formation of cyclohexene was considerably less than that of its further dehydrogenation. In fact,

the rates of benzene formation from cyclohexene and cyclohexadiene exceeded by about an order of magnitude that from cyclohexane, while the cyclohexane content of the product was negligible as compared to the quantity of benzene

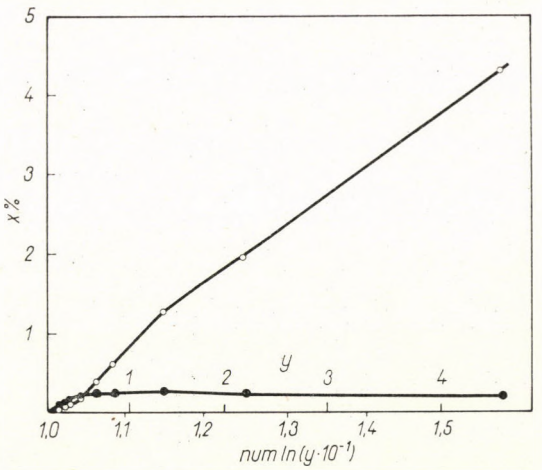


Fig. 2. Formation of benzene and cyclohexene in the dehydrogenation of cyclohexane as a function of catalyst activity (overall conversion)

t = 360 °C; catalyst: 0.011 g of Pt; x: benzene or cyclohexene content of the product, % (w/w); y: overall conversion, 100% — (cyclohexane%); ○: benzene; — ●: cyclohexene

Table I

Product composition in the course of the dehydrogenation of cyclic hydrocarbons of various unsaturation

Catalyst: 0.11 g of Pt; carrier gas: He, 55 NTP ml/min; charge: 3 μl of hydrocarbons

Starting hydrocarbon	Product composition, %(w/w)			
	cyclohexane	cyclohexene	cyclohexadiene-1,3	benzene
t = 300 °C				
cyclohexane	98.9	0.2	—	0.9
cyclohexene	6.8	61.7	0.5	31.0
cyclohexadiene-1,3 ...	0.7	6.7	42.9	49.8
t = 330 °C				
cyclohexane	98.6	0.3	—	1.1
cyclohexene	4.5	63.0	0.4	32.0
cyclohexadiene-1,3 ...	0.4	4.8	39.2	55.7
t = 360 °C				
cyclohexane	95.7	0.5	—	3.8
cyclohexene	2.3	62.4	0.5	34.8
cyclohexadiene-1,3 ...	0.1	2.9	37.0	60.0

[11]. This fact suggested that disproportionation had a subordinate role under our experimental conditions (Table I).

When the rates of aromatization of open-chain and cyclic hydrocarbons are compared, it is obvious that cyclic hydrocarbons react by about an order of magnitude faster than normal ones, except in the presence of pure nickel catalyst. In this case the rate of the dehydrogenation of cyclohexane was similar to that of dehydrocyclization, while an extremely large difference was observed between the rates of aromatization of cyclohexane and cyclohexene. The apparent activation energies of dehydrocyclization and cyclohexane dehydrogenation were close to each other only in the presence of platinum catalyst (Table II).

Table II

Comparison of catalyst activities in the dehydrocyclization of open-chain hydrocarbons and the dehydrogenation of cyclic hydrocarbons

t = 360 °C; carrier gas: helium, 55 NTP ml/min; charge: 6 μl of hydrocarbon
Catalysts: 0.16 g of Pt (9.1 m^2/g)
0.59 g of Ni (3.5 m^2/g)
0.16 g of Ni. Al_2O_3 (266 m^2/g)

Starting hydrocarbon	Relative amount (weight-% of the catalysate)			Absolute amount (μg)		
	of benzene formation					
on:	Pt	Ni	Ni.Al_2O_3	Pt	Ni	Ni.Al_2O_3
n-hexane	1.4	0.4	2.8	0.03	0.008	0.06
hexene-1	1.7	1.5	6.2	0.04	0.03	0.11
cyclohexane	57	1.6	41.2	1.36	0.05	1.28
cyclohexene	98.4	69.7	93.5	2.04	1.67	2.1

Starting hydrocarbon	Specific value, $\mu g/m^2$ catalyst surface			Apparent activation energy, kcal/mol		
	of benzene formation					
on:	Pt	Ni	Ni.Al_2O_3	Pt	Ni	Ni.Al_2O_3
n-hexane	21	3.9	1.4	10	—	22
hexene-1	28	14.6	2.6	8	18	21
cyclohexane	940	24	30	6	7	9
cyclohexene	1400	810	50	—	—	—

On the basis of the known rates of dehydrogenation of the cyclic hydrocarbons, the compositions of the mixtures of radioactive and inactive, open-chain and cyclic hydrocarbons were chosen so as to obtain comparable quantities of the aromatic products formed from each component. The question whether the

transition hexane → cyclohexane takes place or not in the presence of nickel or platinum catalyst was studied by using mixtures of radioactive *n*-hexane-1-^{14}C [3] and inactive cyclohexane, as well as of inactive *n*-hexane and radioactive cyclohexane-1-^{14}C. The results are shown in Tables III—V.

It can be seen from the Tables that no change in the specific radioactivity of the cyclohexane fraction could be detected within the limits of experimental error, indicating that no measurable conversion of *n*-hexane into cyclohexane took place in the presence of either platinum or nickel catalyst. Table III shows that deactivation of the catalyst had a negligible effect on the specific radioactivity of benzene, *i.e.* it did not affect the ratio of the dehydrocyclization of *n*-hexane and dehydrogenation of cyclohexane.

The argument might be raised that there is a possibility of actual cyclohexane formation from *n*-hexane during the reaction, and it is only its unability to desorb from the surface which causes the specific radioactivity of cyclohexane to remain unchanged. Literature data suggest that a considerable exchange takes place between cyclohexane and deuterium on metal surfaces [8], which reaction requires the same initial step, *i.e.* dissociative adsorption, as the dehydrogenation of cyclohexane [9]. This phenomenon was checked under our own experimental conditions by means of a catalyst covered with tritium. This was prepared by regenerating the catalyst with hydrogen containing tritium, according to the standard method described previously, before the introduction of the hydrocarbon [3]. Each fraction — cyclohexane, cyclohexene and benzene — were found to contain considerable amounts of tritium, provided that a sufficient quantity of tritium had been adsorbed on the catalyst surface. The specific activities of cyclohexane and benzene were in the same order of magnitude, indicating that the cyclohexane molecules adsorbed in a dissociative manner on the surface are not necessarily converted into benzene, but they may desorb unchanged, with a commensurable probability, as well. The unchanged specific radioactivity of cyclohexane is therefore actually due to the lack of the reaction hexane → cyclohexane, and not to the hindered desorption of the latter compound.

Several authors, though they do not mention the direct conversion of hexane into cyclohexane, are of the opinion that the olefinic intermediate of the reaction is converted into cyclohexane. This assumption is included even in manuals (*e.g.* [10]).

The detection of *n*-hexene in the dehydrocyclization of hexane [1], together with the unchanged specific radioactivity of cyclohexane, suggest that this transition is highly improbable. Nevertheless, assuming that the rate of this reaction is very slow, owing to the low concentration of hexene, while any cyclohexane formed may rapidly react further without desorption, experiments were made to this possibility by means of the dehydrocyclization of a mixture of radioactive *n*-hexene-1-(1-^{14}C) and inactive cyclohexane. The data in Table VI

Table III

Dehydrocyclization of a mixture of radioactive n-hexane(-1-^{14}C) and inactive cyclohexane

Catalyst: 0.76 g of Pt; t = 360 °C; carrier gas: helium, 55 NTP ml/min.
Separating columns: for Mixture 1: 120 cm of triethyleneglycol dibutyrate, 20% on Chromosorb W; for Mixture 2: as before and in addition 35 cm of silicon oil, 30% on Celite

Ser. No.	Fraction											
	hexane			hexene			cyclohexane			benzene		
	peak area, mm²	activity, tpm	spec. activity, tpm/mm²	peak area, mm²	activity, tpm	spec. activity, tpm/mm²	peak area, mm²	activity, tpm	spec. activity, tpm/mm²	peak area, mm²	activity, tpm	spec. activity, tpm/mm²
Starting mixture 1	5400	396 990	74	—	—	—	2510	2 035	0.8[3]	—	—	—
	7000	524 080	75	—	—	—	3320	10 590	3.1	—	—	—
1307[1]	3880	239 850	62	100	8 600	86	1280	1 900	1.5	1520	43 575	29
1308[2]	3600	358 150	64	210	16 800	80	2160	3 370	1.6	850	23 030	27
1309[2]	3880	234 360	61	140	10 880	78	1460	1 290	0.9	625	18 590	29
1310[2]	6200	404 370	65	230	16 800	81	2600	2 980	1.2	590	17 950	30
Starting mixture 2	5730	214 670	37.5	tailing	6 400	—	3500	1 100	0.3	—	—	—
1684[1]	2180	60 420	36	40	1 800[4]	45	1380	250	0.2	380	4 880	12.5
1685[1]	2920	103 240	35.5	40	820[4]	21	1380	470	0.3	325	6 100	18.5
1686[1]	5220	203 440	39	120	5 300[4]	44	3000	1 070	0.3	765	13 240	17.5

[1] Regenerated catalyst.
[2] Non-regenerated catalyst.
[3] The small deviation from zero of the specific activity of the cyclohexane fraction is due to minor contamination of the radioactive *n*-hexane by *n*-heptane. It is obvious from the chromatograms that in case of a less complete separation, a higher specific activity of cyclohexane is observed.
[4] The separation of hexane and hexene is not complete; the radioactivity of hexene is corrected taking into account the "tailing" of the hexane.

Table IV

Dehydrocyclization of a mixture of inactive n-hexane and radioactive cyclohexane(-^{14}C)

Catalyst: 0.29 g of Pt; t = 360 °C; carrier gas: helium, 55 NTP ml/min

Ser. No.	Fraction								
	hexane			cyclohexane			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 mixture	2550	background	—	800	30 000	37.5	—	—	—
1100	2800	background	—	720	27 300	38	700	11 500	16.5
1101	4180	background	—	1250	47 400	38	260	3 900	15

Table V

Dehydrocyclization of a mixture of radioactive n-hexane(-1-^{14}C) and inactive cyclohexane

Catalyst: 0.35 g of Ni/Al_2O_3; t = 360 °C; carrier gas: helium, 55 NTP ml/min

Ser. No.	Starting hydrocarbon	Fraction								
		hexane + hexene			cyclohexane			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 *n*-hexane		5 400	276 640	51	—	—	—	—	—	—
1335	*n*-hexane	3 500	181 150	52	—	—	—	160	7 400	47
Starting mixture of *n*-hexane and cyclohexane		3 520	163 830	47	1870	2600	1.4	—	—	—
1337	mixture	1 670	87 180	53	960	800	0.8	460	4 320	9.4
1338	of *n*-hexane	2 580	135 900	52	1480	1310	0.9	620	6 170	10
1340	and cyclo-	4 190	221 550	53	2430	2180	0.9	900	7 860	8.8
1341	hexane	10 700	550 700	51	5510	3920	0.7	1090	11 200	10

Table VI

Dehydrocyclization of a mixture of radioactive n-hexene-1-(1-^{14}C) and inactive cyclohexane

Catalyst: 0.76 g of Pt; t = 360 °C; carrier gas: helium, 55 NTP ml/min

Ser. No.	Fraction														
	hexane			hexene			cyclohexane			cyclohexene + hexadienes			benzene		
	peak area, mm²	activity, tpm	spec. activity, tpm/mm²	peak area, mm²	activity, tpm	spec. activity, tpm/mm²	peak area, mm²	activity, tpm	spec. activity, tpm/mm²	peak area, mm²	activity, tpm	spec. activity, tpm/mm²	peak area, mm²	activity, tpm	spec. activity, tpm/mm²
Starting	150	—	—	4630	485 520	105	5850	3540	0.6	—	—	—	—	—	—
material	165	—	—	5350	544 250	102	6740	4680	0.7	—	—	—	—	—	—
1231	1430	159 300	112	720	88 140	122	3400	1430	0.4	85	3610	42	1220	100 710	82
1232	1950	183 410	94	1510	147 550	94	5800	2700	0.5	55	1230	22	1220	76 930	63
1233	1920	184 100	96	900	88 354	98	4700	2020	0.4	70	2380	35	1080	63 260	59

Table VII

Dehydrocyclization of a mixture of radioactive n-hexene-1-(1-^{14}C) and inactive cyclohexene

Catalyst: 0.76 g of Pt; t = 360 °C; carrier gas: helium, 55 NTP ml/min

Ser. No.	Fraction														
	hexane + hexene			hexadiene-1,3			cyclohexene			hexadiene-2,4			benzene		
	peak area, mm²	activity, tpm	spec. activity, tpm/mm²	peak area, mm²	activity, tpm	spec. activity, tpm/mm²	peak area, mm²	activity, tpm	spec. activity, tpm/mm²	peak area, mm²	activity, tpm	spec. activity, tpm/mm²	peak area, mm²	activity, tpm	spec. activity, tpm/mm²
Starting material	9000	712 350	79	—	—	—	2340	11 080	4.7	—	—	—	—	—	—
1245	5810	477 500	82	160	9 600	60	1380	5 880	4.3	150	12 580	84	1360	62 850	46
1246	4800	360 810	75	153	7 080	47	910	3 860	4.3	120	9 020	75	1440	61 410	42.5
1247*	7480	553 440	74	270	23 710	88	2300	13 945	6	290	20 800	72	580	30 920	52

* The catalyst was not regenerated.

Table VIII

Dehydrocyclization of a mixture of radioactive hexene-1(-1-^{14}C) and inactive cyclohexadiene-1,3

Catalyst: 0.055 g of Pt; t = 360 °C; carrier gas: helium, 55 NTP ml/min

Ser. No.	Fraction											
	hexane + hexene			cyclohexane + hexadiene-1,3 + cyclohexene			cyclohexadiene-1,3			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, tpm	activity, tpm	spec. activity, tpm/mm^2
Starting material	2560	924 500	362	100*	65 070	65	7920	9 400	1.2	—	—	—
	2620	975 580	373	104*	46 450	46	8030	9 320	1.2	—	—	—
1848	3070	1 088 200	355	724	45 220	16.5	2010	12 610	6.3	7900	20 350	2.6
1849	2650	1 001 200	377	490	36 290	13,5	2310	9 250	4.0	5900	16 420	2.8
1850	2500	930 600	373	540	36 550	14,8	2240	10 240	4.6	5720	16 900	3.0

* Cyclohexene only

show no sign of transfer of the radioactivity between hexene and cyclohexane. Thus, the generally accepted mechanism should be corrected in this respect as well: our experiments suggest no cyclohexane formation at all in the course of the dehydrocyclization either of hexane or hexene.

According to recent concepts about the mechanism of dehydrocyclization in the presence of oxide catalysts, ring closure is associated with the formation of an unsaturated cyclic compound — probably a homologue of cyclohexadiene [4]. In order to check this assumption, the aromatization of a mixture of *n*-hexene-1-(1-^{14}C) and unsaturated cyclic hydrocarbons (cyclohexene and cyclohexadiene-1,3, respectively) was investigated. The results are summarized in Tables VII and VIII.

The measurements encountered in both cases certain experimental difficulties. The separation of cyclohexene from the hexadiene-2,4 *trans-trans* isomer, and that of cyclohexadiene-1,3 from the hexadiene-2,4 *cis-cis* isomer were incomplete on the chromatographic column employed. Thus it cannot be decided whether the radioactivity found in the cyclic hydrocarbons was due to chemical reaction or to an overlapping of that inactive and radioactive peaks. On the basis of the considerations mentioned [3, 4], the reaction steps leading to cyclohexene are improbable; uncertain data concerning cyclohexene are in agreement with the hypothesis, indicating that unexpected reaction steps resulting in cyclohexene did not occur. The specific radioactivity of cyclohexadiene-1,3 after the reaction exceeded considerably the value measured in the starting mixture, however, the quantity of the compound decreased to about the same extent. A comparison of the specific radioactivities of benzene and the starting hexene showed that only as little as 1% of the benzene was formed *via* the dehydrocyclization of hexene. The large difference (about two orders of magnitude) between the rates of formation and decomposition of a possible cyclohexadiene intermediate may result in the accumulation of only a negligible amount of radioactivity in this compound, which cannot be unambiguously distinguished from minor quantities of inseparable radioactive hexadiene, or even from the background.

Discussion

Considering the results of the present and previous communications, it appears that a new view is necessary about the mechanism of the dehydrocyclization of hexane in the presence of metal catalysts. Hypotheses assuming the formation of cycloparaffinic intermediates in either the primary or any further reaction step, cannot be supported any more. It has been proved that dehydrocyclization may be regarded to occur according to a common mechanism in the presence of both oxide and metal catalysts. Saturated hydrocarbons lose their hydrogen atoms successively to give olefins and diolefins, and cycli-

zation takes place only as one of the last stages of the reaction, resulting in the formation of unsaturated cyclic products. This assumption is also supported by a communication reporting that the aromatization of hexane takes place in homogeneous phase at 550 °C, in the presence of vapours of iodine, *via* hexene, hexadiene and hexatriene as intermediates [15].

Unsaturated and cyclic hydrocarbons are aromatized at a higher rate than saturated and open-chain ones (Table II). Using a platinum catalyst, the differences between the rates of aromatization of hexane and hexene and of cyclohexane and cyclohexene are considerably smaller than in the presence of a nickel catalyst, so that in the latter case the reaction rate of cyclohexane dehydrogenation is close to the rate of the dehydrocyclization of hexene. With platinum, however, there is a large gap between the aromatization rates of open-chain and cyclic hydrocarbons. Nickel-on-carrier occupies a medium position between these pure metals.

These facts are to be explained by considering the elementary processes in the aromatization of each types of hydrocarbons. In the course of stepwise aromatization, saturated starting compounds must be adsorbed in every case in a dissociative way; therefore the rates of aromatization of hexane or cyclohexane are smaller than those of the corresponding unsaturated compounds, which can be adsorbed through their π-electron bonds. This fact can be best proved by the difference observed between the isotopic exchange of hydrogen atoms of CH_4 or C_2H_4, respectively. The starting temperature of the exchange reaction between hydrogen and tritium in ethylene in the presence of a nickel catalyst is about 200 °C lower, and its apparent energy of activation is about 20 kcal/mol less than the corresponding values of methane and ethane [16, 17].

The main difference between the aromatization of open-chain and cyclic hydrocarbons consists in the necessity of a step of ring closure.

The facts mentioned above can be summarized by the following scheme:

	Necessity of		Aromatization rate on	
	dissociative adsorption	ring closure	platinum	nickel
n-hexane	+	+	slow	very slow
n-hexene	—	+	slow	slow
cyclohexane	+	—	rapid	slow
cyclohexene	—	—	rapid	rapid

The parallelism suggests that in the presence of platinum it is ring closure, while in the presence of nickel it is dissociative adsorption which represents the slowest step of the reaction; however, neither of these can be regarded as the exclusive step determining the overall rate of the process.

The fact that ring closure is involved in the dehydrocyclization process makes the energetical and geometrical problems different as compared with those of the dehydrogenation of cyclohexane. Investigations reported in the literature have not decided whether the formation of heptatriene is necessary during the dehydrocyclization of heptadiene, or dienes may undergo direct aromatization. From the point of view of the overall mechanism, it is not the formation of hexatriene which is to be proved or disproved; main interest is attached to the fact that the formation of a conjugated double bond system (either of a π-quartet or π-sextet) is a necessary previous step of the path leading to aromatic compounds. Such a conjugated system may stabilize the molecules, and thus promote aromatization [3]. For example the hydrogen atoms attached to C-1 and C-6 in hexadiene-2,4 are in α-position to the double bonds, thus π-σ conjugation provides energetically more favourable conditions for the elimination of hydrogen, followed by cyclization, than in the case of the hexane molecule.

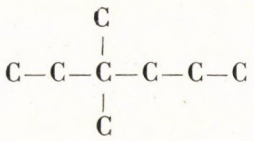
Unsaturated compounds make also possible the fulfilment of some important geometrical conditions. Ring closure requires the adsorption at two sites of the same molecule in a given favourable orientation. If unsaturated bonds are formed possibilities of free rotation are lost, and molecules of the required hexagonal steric structure are obtained (*cis*-stereoisomers). At the same time, the corresponding *trans*-isomers cannot undergo cyclization. These molecules are practically equivalent to the *cis*-isomers from the energetic point of view; their adsorption followed by formation of intermolecular C—C bonds may produce high polymers (coke). If the statistical weight of these two isomers (which is probably near to unit) is not taken into account, according to the above considerations no more than one half of the elementary reactions may result in ring closure; it is obvious that molecules having already a complete six-membered naphthenic ring will be able to aromatize at a much higher rate. These considerations are valid for dienes as well as for trienes.

The step of ring closure itself has not been elucidated on the basis of our experiments. The reaction hexadiene → cyclohexene seems to be improbable; the process hexadiene (or hexatriene) → cyclohexadiene has a greater probability. The formation of benzene after ring closure is certainly a very rapid reaction, so that it is dubious whether any unsaturated cyclic compound is able to desorb at all.

Our experiments do not preclude the possibility of the formation of nonsix-membered rings, either; however, if such compounds are formed, they may not have saturated rings; for example the reaction hexadiene → methylcyclopentadiene can be supposed. The process termed C_5 in the literature as dehydrocyclization [18] might be explained by a similar process.

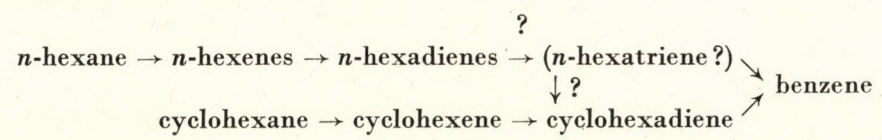
In the literature the formation of seven- and eight-membered rings has also been reported [13, 14]; it may be supposed that these are formed similarly, *via* intermediates with conjugated double bonds.

KAZANSKII, LIBERMAN and BATUEV [5] intended to prove the direct reaction paraffin → cycloparaffin, using 3,3-dimethylhexane as the starting material, which has the following carbon skeleton:



No conjugated double bond system can be formed from this compound, and its aromatization takes place with simultaneous demethylation. It is obvious that this is not a typical compound to study dehydrocyclization, and the results obtained with this hydrocarbon may be generalized with great caution only. It is possible that this compound is dehydrocyclized when forced only *via* a naphthenic intermediate, but we cannot exclude either the possible formation of some isolated double bond system followed by a ring closure to an unsaturated cyclic intermediate, which is partly aromatized, accompanied by simultaneous demethylation, and partly hydrogenated to a cyclohexane derivative.

Since the experiments have shown that the sex tetmechanism cannot be regarded as absolutely valid in the dehydrogenation of cyclohexene, it was not *a priori* necessary (and moreover, not possible) to insist that the formation of an intermediate with six-membered ring is a decisive step, facilitating dehydrocyclization as a consequence of its distinguished manner of adsorption. The present experimental results are in full agreement with our previous considerations: the actual mechanism of dehydrocyclization of *n*-hexane is a stepwise dehydrogenation followed by ring closure, where the decisive step consists, instead of the formation of a six-membered ring, in the consecutive formation of conjugated double bond systems which are eventually transformed into an aromatic π-electron cloud. When there is no steric hindrance in the process, it is regarded as a paramount reaction path. The dehydrogenation of cyclohexane is not a "continuation" of dehydrocyclization; these are parallel reactions having analogous stepwise reaction mechanism and meeting only in some of the last steps:



The exact mechanism of the ring closure step can be elucidated only by further experiments.

*

The authors are grateful to Dr. T. SZARVAS for kindly accomplishing radioactivity measurements.

SUMMARY

The dehydrogenation of six-membered cyclic hydrocarbons was compared with the previously reported dehydrocyclization of *n*-hydrocarbons, using the pulse technique. Additional direct experimental evidence has been obtained to show that the stepwise dehydrogenation of cyclohexane takes place *via* cyclohexene and cyclohexadiene intermediates. In the conversions of various mixtures of open-chain and cyclic hydrocarbons where one of the components was radioactive, no detectable transfer of radioactivity has been found to occur either from *n*-hexane or *n*-hexene to cyclohexane, indicating that the probabilities of the reaction steps *n*-hexane → cyclohexane and *n*-hexene → cyclohexane assumed heretofore are negligible. Uncertain transfer of the radioactivity was shown to take place between radioactive *n*-hexene and inactive cyclohexene or cyclohexadiene-1,3. Our results show that the formation of cycloparaffinic compounds need not be taken into account during dehydrocyclization, thus the stepwise mechanism described previously can be regarded as an exclusive reaction path. The dehydrogenation of cyclohexane and the dehydrocyclization of *n*-hexane are considered parallel reactions, possessing similar, stepwise mechanisms, concurring only in some of the ultimate reaction steps.

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DIPHENYLPROPYLAMINE DERIVATIVES, II*

3,3-DIPHENYLPROPYLAMINE DERIVATIVES WITH NITRO- OR AMINO-SUBSTITUTION ON THE AROMATIC RING

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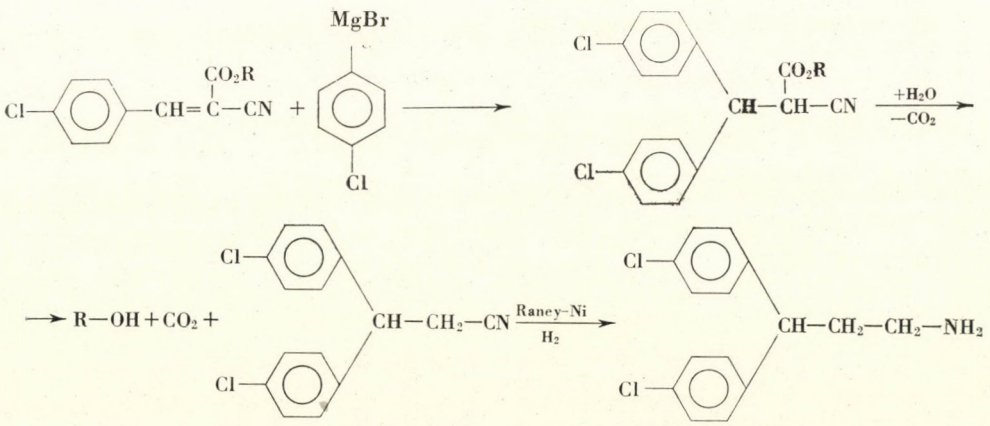
In Part I we have reported our investigations concerning N-substituted 3,3-diphenylpropylamine derivatives; this work has led to new substances with significant coronary dilating effect. In the same paper we have mentioned some attempts made to increase the water solubility of the reaction products, which would result in preparation of better absorption characteristics with the consequent possibility of administration in forms other than solid powders.

The present work concerning the preparation of 3,3-diphenylpropylamine derivatives with basic substituent groups on the aromatic ring had essentially the same objectives.

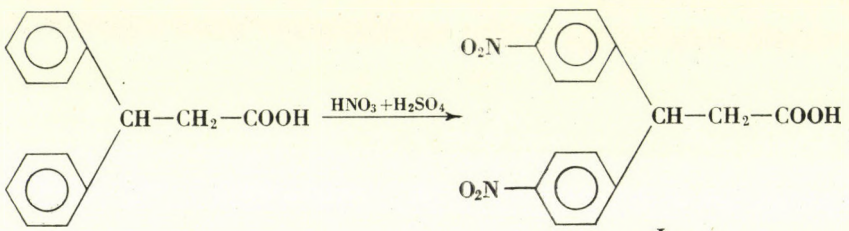
It appears from a survey of the literature of 3,3-diphenylpropylamine derivatives [1] that in spite of the pharmacologically interesting properties of this group of compounds, only very little work has been devoted to the preparation of 3,3-diphenylpropylamine derivatives with substituents on the aromatic ring, and even then the synthesis started from compounds which were originally substituted on the ring. Thus, *e.g.* LEDITSCHKE *et al.* [2] synthesized 3,3-bis-(4-chlorophenyl)-propylamine by a process which might be illustrated with the following sequence of formulas



* Part I, see K. HARSÁNYI, D. KORBONITS, P. KISS: J. Med. Chem. **7**, 623 (1964).

The synthesis of 3,3-diphenylpropylamine derivatives containing amino substituents on the aromatic ring has not been reported in the earlier literature so far.

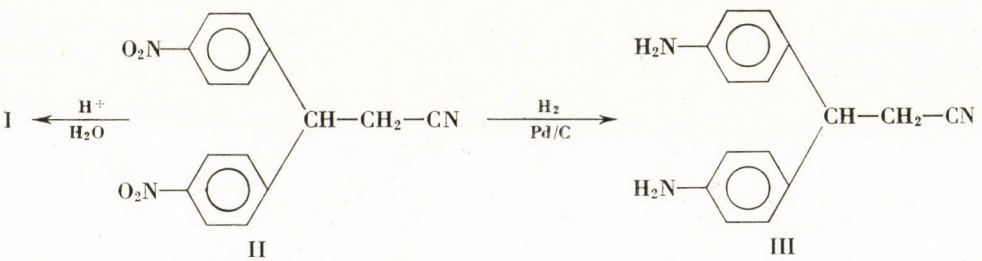
The starting point of our syntheses was the conception that both 3,3-diphenylpropionitrile and 3,3-diphenylpropylamine are benzene derivatives substituted by groups promoting electrophilic displacement (essentially diphenylmethane derivatives), where the most direct way to introduce an amino group is nitration and subsequent reduction. This conception is supported by PFEIFFER *et al.* [3] who reported the nitration of 3,3-diphenylpropionic acid to 3,3-bis-(4-nitrophenyl)-propionic acid with a mixture of concentrated sulphuric acid and nitric acid.



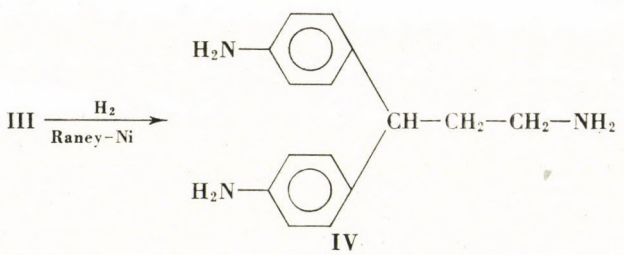
I

In our experiments, 3,3-diphenylpropionitrile has been nitrated under similar conditions without any signification hydrolysis of the cyano group. The 3,3-bis-(4-nitrophenyl)-propionitrile **(II)** structure of the product is unequi. vocally confirmed by its hydrolysis to **I**.

Compound **II** is reduced in alcoholic solution with Pd/C catalyst to 3,3-bis-(4-aminophenyl)-propionitrile. The cyano group in compound **III** is also liable to reduction, so a primary amine could be obtained in the presence of Raney nickel catalyst at low pressure in alcoholic ammonia solution.



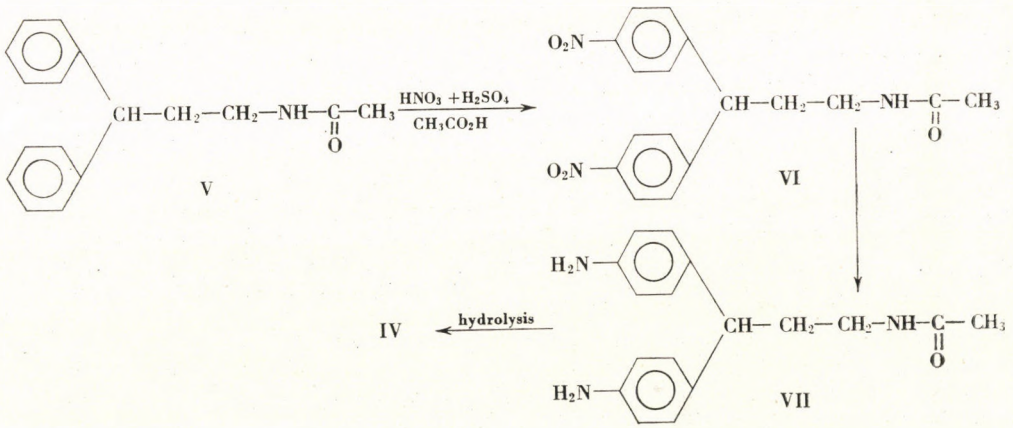
II III



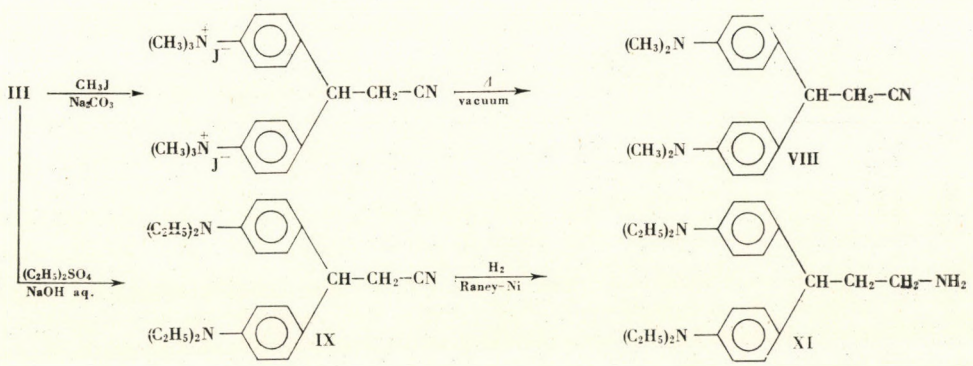
IV

It was not possible to convert **II** in a single reduction step into 3,3-bis-(4-aminophenyl)-propylamine **(IV)**.

The synthesis of **IV** has also been achieved in another way showing at the same time that favourable yields of the *p,p'*-isomer **(VI)** can be obtained by the nitration of N-acetyl-3,3-diphenylpropylamine **(V)**. The catalytic reduction of **VI** leads to **VII**, and hydrolysis of the latter gives **IV**.

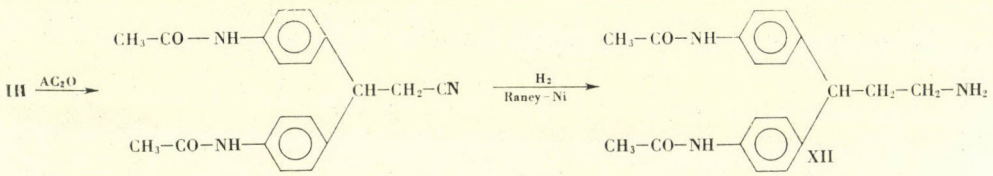


III could also be employed for some conversions not affecting the cyano group to be used at a later stage for obtaining the aliphatic amino group. The N,N-dialkylation of the aromatic amino groups has been effected by two methods. Thermal decomposition of the quaternary salt as described by BOYER *et al.* [4] has been found to be the most suitable method for the preparation of the N,N-dimethyl derivative, while the N,N-diethyl derivative may directly be obtained by diethylation of the primary amine, either according to WEISSBERGER *et al.* [5] with ethyl iodide, or according to HÜNIG [6] with diethyl sulphate. The nitriles **VIII** and **IX** thus prepared are converted into the 3,3-diphenylpropylamine derivatives (**X** and **XI**), by reduction in the presence of Raney nickel.



Owing to the different reactivities of the primary and tertiary amino groups, compounds **X** and **XI**, obtained by the dialkylation of **III**, appear suitable for the preparation of other compounds also included in our later research program.

Diacetylation of **III** and subsequent reduction gives 3,3-bis-(4-acetylaminophenyl)-propylamine **(XII)**, a substance useful in further conversions in which temporary blocking of the amino group is necessary (see Part III).



The results of the pharmacological testing of **III** and **IV** were reported in an earlier communication [7].

Experimental*

3,3-bis-(4-Nitrophenyl)-propionitrile (II)

A mixture of 1120 ml of nitric acid (sp.gr. 1.29 : 45.95% w/w) and 1600 ml of conc. H_2SO_4 was cooled to +3—+5°, and 115.0 g (0.55 mole) of 3,3-diphenylpropionitrile was added in small portions under constant stirring, over a period of 2 hrs. The reaction mixture was stirred for 3 more hrs at 0—+5°, then it was poured on 6 kg of crushed ice and allowed to stand overnight. Next day the crude product was filtered off, washed with water and dried. Recrystallization from a hot mixture of 280 ml of benzene and 190 ml of anhydrous alcohol gave 92.0 g (57%) of **II**, m. p. 144—146°, after repeated recrystallizations 149°. $C_{15}H_{11}N_3O_4$ (297.26). Calcd. N 14.13. Found N 14.24%.

When 1.1 g (3.3 mmole) of **II** was refluxed for 2 hrs with 5 ml of 60% H_2SO_4, 1.0 g of **I** was obtained. Recrystallization from aqueous alcohol yielded a product melting at 188° which showed no m.p. depression when mixed with the product prepared by the method described in the literature [3].

3,3-bis-(4-Aminophenyl)-propionitrile (III)

In an autoclave of 1100 ml 80.0 g (0.27 mole) of **II** was hydrogenated in the presence of 5 g of palladium catalyst (8% Pd on charcoal) in 600 ml of anhydrous alcohol, at 2—10 atm. pressure and 60—70°. After hydrogen absorption had been completed, the solution was filtered from the catalyst while still hot, and evaporated to 150 ml. On cooling 58.5 g (91%) of **II** crystallized from the solution. After recrystallization from methanol the m.p. of the product was 139°.

$C_{15}H_{15}N_3$ (237.29). Calcd. C 75.92; H 6.37; N 17.71. Found C 75.96; H 6.46; N 17.85%.

3,3-bis-(4 Aminophenyl)-propylamine (IV)

In the above autoclave, 30.0 g (0.13 mole) of **III** was hydrogenated at 10—15 atm. pressure and 60° in the presence of 440 ml of alcohol which had been saturated at 0° with ammonia, 10.0 g of Raney nickel catalyst, and 0.5 g solid NaOH. After the hydrogenation had been

* Some of the compounds reported here are patented [8]. All melting points reported are uncorrected.

completed, the solution was freed from the catalyst by filtration, and the solvent evaporated in vacuum. The residue was dissolved in hot benzene, treated with decolourizing carbon and crystallized to obtain 24.66 g (81%) of **IV**, m.p. 122—123°.

$C_{15}H_{19}N_3$ (241.32). Calcd. C 74.65; H 7.93; N 17.41. Found C 74.80; H 7.80; N 17.32%.

N-Acetyl-3,3-diphenylpropylamine (V)

To 31.13 g (0.15 mole) of 3,3-diphenylpropylamine, 15.5 ml of acetic anhydride was added, and the mixture was heated on a hot water bath for 30 min. The reaction product was poured on ice, and the precipitated crude product filtered off dried and recrystallized from a 1 : 1 mixture of hot benzene and petrol ether, to give 31.85 g (85%) of **V**, m.p. 106°.

$C_{17}H_{19}NO$ (253.33). Calcd. C 80.57; H 7.56; N 5.53. Found C 80.49; H 7.48; N 5.54%.

N-Acetyl-3,3-bis-(4-nitrophenyl)-propylamine (VI)

105.0 g (0.5 mole) of 3,3-diphenylpropylamine was dissolved in 160 ml of glacial acetic acid under cooling, and 53 g of acetic anhydride was added dropwise over a period of 0.5 hr., under constant stirring. The reaction mixture was allowed to warm up to 40—50°, and after the addition of the anhydride, it was stirred for 1 hr. at 70°. To the cooled reaction mixture first 160 ml of conc. H_2SO_4 was added at +10—+15° over a period of 1 hr., followed by the addition of a cooled mixture of 108 ml of nitric acid (sp.gr. 1.40) and 54 ml of conc. H_2SO_4 at +3—+5° over a period of 3 hrs. The reaction mixture was stirred at the same temperature for 3 hrs, and the yellowish brown solution was poured on 3 kg of ice. A yellowish mass separated which was separated from the aqueous acid and washed repeatedly with water. The crude product solidified under water. After standing for one day it was filtered off and recrystallized from butanol to yield 115.0 g (67%) of **VI**, m.p. 156—159°.

$C_{17}H_{17}N_3O_5$ (343.33). Calcd. C 59.47; H 4.99; N 12.24. Found C 59.45; H 4.70; N 12.26%.

N-Acetyl-3,3-bis-(4-aminophenyl)-propylamine (VII)

A solution of 30.0 g (0.09 mole) of **VI** in 250 ml of anhydrous ethanol was hydrogenated at room temperature and atmospheric pressure in the presence of 2 g of palladium catalyst (8% Pd on charcoal). When the hydrogenation had been completed the catalyst was removed by filtration at 60°, and the filtrate evaporated to 50 ml. After cooling 23.67 g (95%) of **VII** crystallized from the solution, m.p. 119—121°.

$C_{17}H_{21}N_3O$ (283.36). Calcd. C 72.05; H 7.47. Found C 72.30; H 7.12%.

3,3-bis-(4-Aminophenyl)-propylamine (IV)

To 40.0 g(0.14 mole) of **VII**, 200 ml of ethanol and 500 ml of 10% NaOH solution were added and the mixture was refluxed for 20 hrs. The solution was then evaporated to 200 ml in vacuum. The initially oily crude reduction product was allowed to solidify, it was filtered off, dried, and finally recrystallized from benzene to obtain 26.4 g (78%) of **IV**, m.p. 121°. The product was identical with **IV** obtained by the catalytic reduction of **III**.

7.23 g (0.03 mole) of **IV** was dissolved in 100 ml of hot anhydrous ethanol, and 1.8 g of acetic acid was added to the hot solution. On cooling 6.7 g (74%) of the monoacetate of **IV** crystallized from the solution, m.p. 180—182°.

$C_{17}H_{23}N_3O_2$ (301.37). Calcd. N 13.94. Found N 14.20%.

3,3-bis-(4-Dimethylaminophenyl)-propionitrile (VIII)

To 70.0 g (0.30 mole) of **III**, 85 ml of water, 64.0 g of sodium carbonate, 340 ml of ethanol and 290 g of methyl iodide were added. The mixture was refluxed for 1 hr. After cooling 165.0 g of the quaternary salt crystallized from the solution, m.p. 192—196° (d.).

The quaternary salt was fused in a vacuum distillation apparatus at 80—100 mm Hg pressure on an oil bath of 220—230°, and kept at this temperature till foaming subsided (about

15 min.). After cooling 300 ml of water was added, the crude product filtered off, dried, and recrystallized from methanol to yield 54.70 g (63%) of **VIII**, m.p. 103—105°.

$C_{19}H_{23}N_3$ (293.40). Calcd. N 14.32. Found N 14.56%.

The dihydrochloride of **VIII** can be precipitated from a solution in anhydrous ethanol, m.p. 212° (d.).

$C_{19}H_{25}N_3Cl_2$ (366.32). Calcd. N 11.47. Found N 11.33%.

3,3-bis-(4-Diethylaminophenyl)-propionitrile (IX)

To a mixture of 118.5 g (0.5 mole) of **III**, 400 ml of diethylsulphate and 500 ml of water, 140 g of NaOH in 400 ml of water was added by drops, at 52—56° over a period of 4 hrs. The mixture was stirred at 52° for 30 min. and then allowed to cool under continued stirring. The crude product was filtered off, dried and recrystallized from 350 ml of hot ethanol to give 132.0 g (75%) of **IX**, m.p. 78—80°.

$C_{23}H_{31}N_3$ (349.50). Calcd. N 12.02. Found N 12.15%.

3,3-bis-(4-Diethylaminophenyl)-propylamine (XI)

122.5 g (0.35 mole) of **IX** was hydrogenated in 600 ml of 20% alcoholic ammonia at 55—60° and 5—12 atm. pressure, in the presence of 17.0 g of Raney nickel catalyst and 0.5 g of solid NaOH. The catalyst was removed by filtration, the solvent evaporated and the residual oil subjected to vacuum distillation to yield 105.0 g (85%) of pale yellow, oily **XI**, b.p. 252—254° at 0.4 mm Hg.

The trihydrochloride of **XI** can be precipitated from an alcoholic solution, m.p. 240° (d.).

$C_{23}H_{38}N_3Cl_3$ (462.92). Calcd. C 59.67; H 8.27; N 9.07. Found C 59.50; H 8.18; N 9.24%.

3,3-bis-(4-Dimethylaminophenyl)-propylamine (**X**) was prepared, in an analogous way to **XI**, from **VIII**; b.p. 224—226° at 0.2 mm Hg, m.p. 55—60°.

3,3-bis-4-(Acetylaminophenyl)-propionitrile

7.52 g (0.03 mole) of **III** was heated on a hot water bath with 9 ml of acetic anhydride for 30 min. The solution was then poured into 100 ml of water to obtain 9.6 g (94%) of a product which was recrystallized from aqueous alcohol, m.p. 188°.

$C_{19}H_{19}N_3O_2$ (321.36). Calcd. N 13.08. Found N 13.18%.

3,3-bis-(4-Acetylaminophenyl)-propylamine (XII)

25.0 g (0.08 mole) of 3,3-bis-(4-acetylaminophenyl)-propionitrile was hydrogenated at 55—60° and 10—15 atm. pressure in 250 ml of anhydrous ethanol saturated at 0° with ammonia, in the presence of 10.0 g of Raney nickel catalyst and 0.5 g of solid NaOH. The catalyst was removed by filtration, and the filtrate evaporated in vacuum. The residue was suspended in 50 ml of light petrol, filtered off and dried to give 24.0 g (95%) of **XII**, m.p. 203° which remained unchanged after recrystallization from a mixture of pyridine—petrol ether.

$C_{19}H_{23}N_3O_2$ (325.39). Calcd. N 12.91. Found N 12.76%.

The authors wish to express their thanks to Mrs. I. BALOGH-BATTA and to Mr. I. REMPORT for the microanalyses, and to Miss É. KOVÁCS and Miss Á. MÉSZÁROS for their assistance in the experimental work.

SUMMARY

3,3-bis-(4-Nitrophenyl)-propionitrile has been prepared by the nitration of 3,3-diphenyl-propionitrile. Selective reduction of the nitrogroups can be achieved in the presence of Pd/C catalyst. Direct reduction of the 3,3-bis-(4-aminophenyl)-propionitrile obtained in this way, in the presence of Raney nickel catalyst, gives 3,3-bis-(4-aminophenyl)-propylamine, the former of which can be converted by acetylation or dialkylation of the aromatic amino groups into the

corresponding 3,3-bis-(4-aminophenyl)-propylamine derivatives. The nitration of N-acetyl-3,3-diphenylpropylamine can also be readily carried out. Thus alternative reaction schemes have been worked out for the synthesis of 3,3-bis-(4-aminophenyl)-propylamine, and it has been shown that in this case, too, nitration proceeds mainly on the *p,p'*-positions of the aromatic rings.

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DIPHENYLPROPYLAMINE DERIVATIVES, III*

N-SUBSTITUTED 3,3-BIS-(4-NITROPHENYL)- AND (4-AMINOPHENYL)-PROPYLAMINE DERIVATIVES

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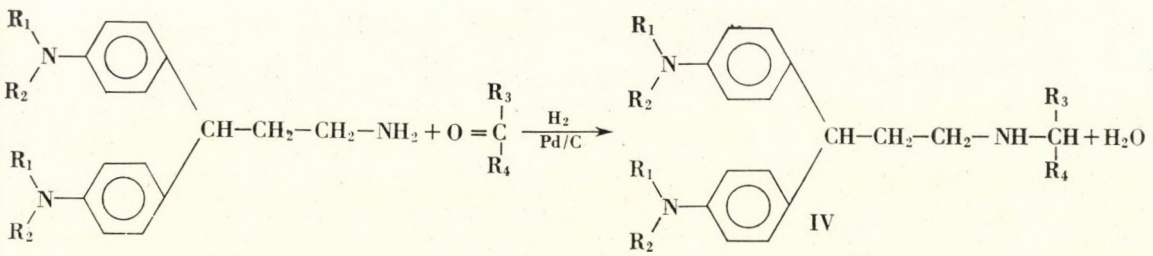
Received April 15, 1967

In Part II we have reported the synthesis of 3,3-bis-(4-acetaminophenyl)-propylamine **(I)**, and 3,3-bis-(4-dimethyl- and diethylaminophenyl)-propylamine **(II** and **III)**. Owing to the presence of primary amino groups, these compounds were considered suitable starting materials for the preparation of derivatives containing N-substituted aliphatic amino groups.

With the aim to prepare secondary amines [1] potentially useful as coronary dilators, we investigated the reductive alkylation reaction of compounds **I, II** and **III** with ketones.

Our program included the preparation of N-substituted 3,3-diphenylpropylamine derivatives, starting from **I**, which would give on reductive alkylation and subsequent hydrolysis compounds containing primary amino groups in the *para* positions of the aromatic rings. Though the hydrogen uptake observed in the course of the catalytic reduction of the acetyl derivative **I** in the presence of ketones suggested that reductive alkylation had taken place, no uniform reaction products could be obtained in this way.

Compounds **II** and **III** gave products corresponding to the general formula **IV**, in good yields.



where:

$R_1 = H$, $R_2 = COCH_3$ **(I)**
$R_1 = R_2 = CH_3$ **(II)**

* Part II, see preceding paper.

Table I

No.	Amine	Ketone	Salt forming acid	M. P. of salt °C	Analysis							
					Molecular formula	Molecular weight	Calculated			Found		
							C%	H%	N%	C%	H%	N%
1	II	Cyclohexanone	3 HCl	223 (d.)	$C_{25}H_{40}N_3Cl_3$	448.96	61.41	8.24	8.59	61.31	8.29	8.56
2	II	Acetophenone	3 HCl	224 (d.)	$C_{27}H_{38}N_3Cl_3$	510.96	63.46	7.49	8.22	63.29	7.38	8.67
3	II	Benzyl methyl ketone	3 HCl	230 (d.)	$C_{28}H_{40}N_3Cl_3$	524.99	63.98	7.68	7.95	64.02	7.64	8.07
4	II	4-Methoxy benzyl methyl ketone	3 HCl	232 (d.)	$C_{29}H_{42}N_3OCl_3$	555.02	62.75	7.63	7.56	62.83	7.51	7.70
5	II	3,4-Dimethoxybenzyl methyl ketone	3 HCl	192 (d.)	$C_{30}H_{44}N_3O_2Cl_3$	585.04			7.18			7.45
6	II	4-Phenylbutanone-2	3 HCl	230 (d.)	$C_{29}H_{42}N_3Cl_3$	539.02	64.61	7.85		64.41	7.55	
7	II	4-(4-Hydroxyphenyl)-butanone-2	3 HCl	127 (d.)	$C_{29}H_{42}N_3OCl_3$	555.02			7.57			7.33
8	III	Cyclopentanone	3 HCl	253 (d.)	$C_{28}H_{46}N_3Cl_3$	531.04			7.91			8.54
9	III	Cyclohexanone	3 HCl	257 (d.)	$C_{29}H_{48}N_3Cl_3$	545.06			7.71			8.28
10	III	Acetophenone	3 HCl	247 (d.)	$C_{31}H_{46}N_3Cl_3$	567.07	65.65	8.17	7.41	65.80	7.94	7.63
			HCl	241 (d.)	$C_{31}H_{44}N_3Cl$	494.14	75.34	8.97	8.50	75.23	8.98	8.47
11	III	Benzyl methyl ketone	HCl	210 (d.)	$C_{32}H_{46}N_3Cl$	508.17	75.63	9.12	8.27	75.84	9.22	8.17
12	III	4-Methoxybenzyl methyl ketone	HCl	218 (d.)	$C_{33}H_{48}N_3OCl$	538.19	73.64	8.99	7.81	73.80	8.90	8.13
13	III	4-(4-Hydroxyphenyl)-butanone-2	HCl	215 (d.)	$C_{33}H_{48}N_3OCl$	538.19	73.64	8.99	7.81	73.23	8.90	8.21
14	III	Indanone-1	3 HCl	254 (d.)	$C_{32}H_{46}N_3Cl_3$	579.09	66.36	8.00		65.98	8.03	

$R_1 = R_2 = C_2H_5$ **(III)**
$R_1 = R_2 = CH_3$ **(IV)**
$R_1 = R_2 = C_2H_5$ **(IV)**
$R_1 = R_2 = H$ **(V)**

The compounds of type **IV** prepared by us are shown in Table I.

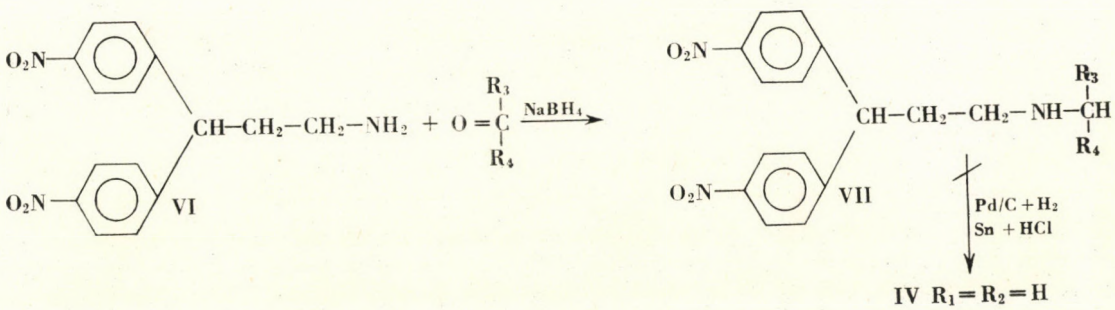
It is characteristic of the compounds of type **IV** that the difference between the basicity of the aliphatic and aromatic amino groups is shown also by the salt formation reactions with mineral acids. Equivalent quantities of mineral acids bring about exclusively the protonation of the secondary alkylamino groups. The monohydrochlorides formed in this way are sparingly soluble in water. Owing to this property, salt formation with these compounds is possible by means of aqueous ammonium chloride solution accompanied by the liberation of ammonia, when there is no danger of an inaccurate precipitation of the monohydrochloride.

When an excess of mineral acid is used, the aromatic amino groups will also participate in salt formation leading to water-soluble products.

Considering the fact that the reductive condensation of **I** with ketones failed to give uniform products, it was impossible to synthesize analogues of **IV** containing primary amino groups attached to the aromatic rings. The use of 3,3-bis-(4-aminophenyl)-propylamine **(V)** for this purpose seemed hopeless.

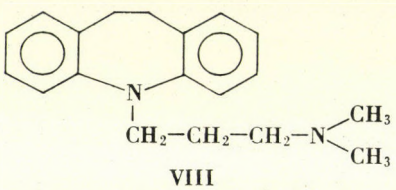
Because of these difficulties, another way was sought for the synthesis of N^1-substituted 3,3-bis-(4-aminophenyl)-propylamines **(IV**; $R_1 = R_2 = H$). In Part II of this series we have described N-acetyl-3,3-bis-(4-nitrophenyl)-propylamine as an intermediate of the synthesis of **V**. When this compound is deacetylated, 3,3-bis-(4-nitrophenyl)-propylamine **(VI)** is obtained. Selective reductive alkylation of the amino group of **VI** can be successfully effected with the aid of sodium borohydride. Table II lists the N-substituted 3,3-bis-(4-nitrophenyl)-propylamine derivatives **(VII)** prepared by us.

Certain representatives of type **VII** were catalytically hydrogenated in the presence of Pd/C catalysts, but no homogeneous products were obtained. Neither could the analogues of **IV**, containing primary aromatic amino groups, be prepared by the use of chemical reducing agents (Sn—HCl).

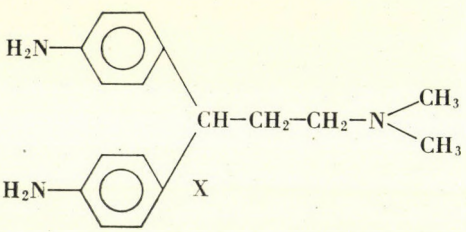


As it is seen from what has been said above the reductive condensation proceeds without difficulty and unequivocally if the aromatic rings are substituted by tertiary amino groups. This led to the idea that the preparation of 3,3-diphenylpropylamine derivatives containing amino groups attached to the aromatic rings might be possible with reduction as the final step, if the aliphatic amino group were first converted by N,N-disubstitution into a tertiary amino group.

This objective had also a pharmacological justification. The noradrenaline potentiating action of compound **V** surpasses that of Imipramine **(VIII)** [2]. To enhance the common structural elements it seemed expedient to prepare the N^1-dimethyl derivative of **V** (compound **X**).

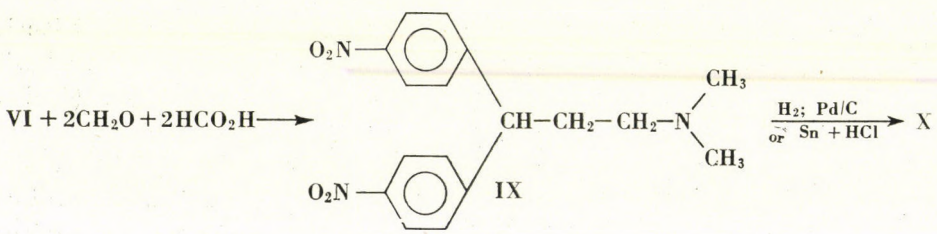


VIII



X

Compound **X** was synthesized from **VI** by means of ESCHWEILER-CLARKE methylation, followed by catalytic or chemical reduction. The yield was satisfactory.



IX

Experimental*

General method for the preparation of compounds of type IV

To a solution of 0.02 mole of **II** or **III** in 120 ml of methanol, 0.02 mole of ketone and 3.0 g of a palladium-carbon catalyst (8% Pd) were added, and the mixture was hydrogenated at 60° and 5—10 atm. pressure for 6 hrs. The catalyst was removed by filtration, and the solvent evaporated in vacuum. The products were identified in the form of their salts.

* Some of the compounds reported here are patented [3]. All melting points reported are uncorrected.

Table II

No.	Amine	Ketone	Salt forming acid	M. p. of salt °C	Analysis							
					Molecular formula	Molecular weight	Calculated			Found		
							C%	H%	N%	C%	H%	N%
1	VI	Acetone	maleic acid	187	$C_{22}H_{25}N_3O_8$	459.44	57.51	5.48	9.14	57.92	5.82	9.49
2	VI	Cyclopentanone	maleic acid	197	$C_{24}H_{27}N_3O_8$	485.48			8.65			8.43
3	VI	Cyclohexanone	maleic acid	207	$C_{25}H_{29}N_3O_8$	499.50			8.41			8.32
4	VI	Methyl benzyl ketone	HCl	235	$C_{24}H_{24}N_3O_4Cl$	453.91	63.50	5.33		63.19	5.72	
5	VI	4-Phenylbutanone-2	HCl	180	$C_{25}H_{28}N_3O_4Cl$	469.96	63.89	6.00	8.94	63.64	6.19	8.58

The trihydrochlorides of the compounds of type **IV** were separated by dissolving the base (0.02 mole) in 15 ml of anhydrous ethanol, followed by the addition of a 25% alcoholic solution of hydrochloric acid.

The monohydrochlorides of compounds **IV** were prepared by one of the following methods:

(a) To a solution of 0.02 mole of the base **IV** in 20 ml of anhydrous ethanol, a solution of 0.73 g (0.02 mole) of hydrogen chloride gas in 10 ml of anhydrous ethanol was added; the monohydrochloride of **IV** crystallized from the solution.

(b) To a solution of 0.02 mole of the base **IV** in 60 ml of ethanol, 20 ml of aqueous 1 *N* HCl was added; the monohydrochloride crystallized from the solution.

(c) To a solution of 0.02 mole of the base **IV** in 30 ml of ethanol, 2.17 g (0.04 mole) of ammonium chloride was added in 20 ml of water, under constant stirring by drops; the monohydrochloride of **IV** crystallized from the solution.

3,3-bis-(4-nitrophenyl)-propylamine (VI)

To 34.33 g (0.1 mole) of N-acetyl-3,3-bis-(4-nitrophenyl)-propylamine (see Part II), 170 ml of conc. HCl and 170 ml of ethanol were added and the reaction mixture was refluxed for 20 hrs, clarified while hot with charcoal, filtered, and the filtrate evaporated in vacuum. The residue was taken up in 300 ml of hot water, and the solution made alkaline with 10% NaOH solution. The precipitated crude product was filtered off, dried, and recrystallized from light petrol to obtain 23.8 g (79%) of **VI**, m.p. 121°.

$C_{15}H_{15}N_3O_4$ (301.29). Calcd. C 59.79; H 5.02; N 13.94. Found C 59.52; H 4.93; N 13.78%.

General method for the preparation of compounds of type VII

To a solution of 6.02 g (0.02 mole) of **VI** in 50 ml of benzene, 0.02 mole of the ketone was added, and the reaction mixture refluxed for 1 hr. The benzene was evaporated in vacuum, and the residue dissolved in 60 ml of methanol. Three drops of water and 0.8 g of sodium borohydride were added, this latter in small portions over a period of 1 hr., at room temperature. The mixture was allowed to stand for another hour, the methanol evaporated in vacuum, and the residue dissolved in 50 ml of water. The oily substance was extracted with ether, and, after drying, the solvent was evaporated. The compounds of type **VII** were obtained as oily products whose salts could be prepared from the alcoholic solutions with a solution of hydrogen chloride or maleic acid in ethanol.

N,N-Dimethyl-3,3-bis-(4-nitrophenyl)-propylamine (IX)

Twenty grams (0.07 mole) of **VI** were dissolved in 23 ml of 85% formic acid under cooling, and 20 ml of 36% aqueous formaldehyde was added. The reaction mixture was heated on a water bath for 8 hrs. After the addition of 15 ml of conc. HCl, the solution was evaporated to dryness in vacuum. The residue was dissolved in 120 ml of water, the solution clarified, filtered and the filtrate made alkaline with 10% NaOH solution. The precipitated crude product was filtered off, dried, and recrystallized from aqueous methanol to obtain 14.5 g (66%) of **IX**, m.p. 130°.

$C_{17}H_{19}N_3O_4$ (329.34). Calcd. N 12.76. Found N 12.86%.

N,N-Dimethyl-3,3-bis-(4-aminophenyl)-propylamine (X)

(a) To a solution of 9.9 g (0.03 mole) of **IX** in 200 ml of anhydrous ethanol, 2 g of palladium-charcoal catalyst (8% Pd) was added, and the compound hydrogenated at 60° and atmospheric pressure. After the absorption of hydrogen had been completed, the solution was filtered from the catalyst, the solvent evaporated, and the residue distilled in vacuum. The main fraction was collected at 222° at 0.2 mm Hg pressure. The yield was 4.6 g (56%) of **X** in the form of a pale-yellow oil. This was then dissolved in 50 ml of anhydrous ethanol, and a solution of 4.0 g of maleic acid in 40 ml of anhydrous alcohol was added; 6.3 g of the dihydrogen-maleate of compound **X** crystallized from the solution, m.p. 148—150°.

$C_{25}H_{31}N_3O_8$ (501.52). Calcd. C 59.87; H 6.23; N 8.38. Found C 59.78; H 6.26; N 8.71%.

(b) To a solution of 3.30 g (0.01 mole) of **IX** in a mixture of 20 ml of conc. HCl and 15 ml of water, 5.0 g of tin powder was added in small portions over a period of 1 hr. under constant stirring. The mixture was stirred for another hour and made strongly alkaline with 40% NaOH solution under cooling. The reaction product was extracted with three 40-ml portions of benzene, the combined benzene solution dried over $MgSO_4$ and the solvent evaporated. The residue was then dissolved in 20 ml of anhydrous ethanol and a solution of 1.5 g of maleic acid in 10 ml of anhydrous ethanol was added. The dihydrogen-maleate of **X** (2.6 g; 52%) crystallized from the solution; the properties of this product were the same as those of the product obtained by method (a).

*

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SUMMARY

N-substituted 3,3-bis-(4-dialkylaminophenyl)-propylamines have been synthesized by the reductive condensation of the corresponding primary amines with ketones. The preparation of N^1-substituted 3,3-bis-(4-aminophenyl)-propylamines was attempted by two methods, but homogeneous product was obtained in either case. Introduction of a tertiary aliphatic amino group renders possible the preparation by reduction of the derivative containing primary amino groups in the aromatic ring. N-substituted 3,3-bis-(4-nitrophenyl)-propylamine derivatives can be obtained by reductive condensation in the presence of $NaBH_4$.

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CONSTITUENTS OF LOCAL PLANTS, XII

THE STEROIDAL ALKALOIDS OF SOLANUM MACROCARPUM L. UNRIPE FRUITS

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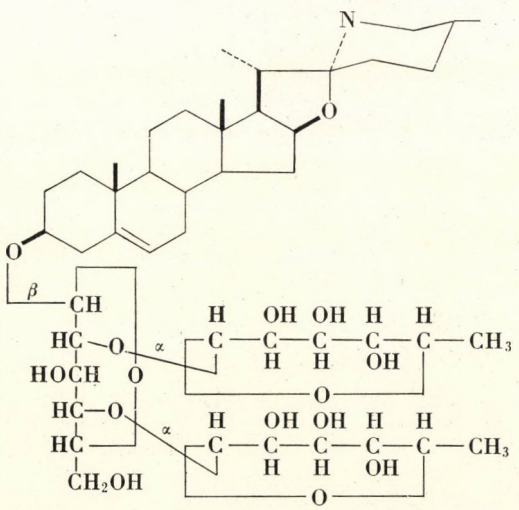
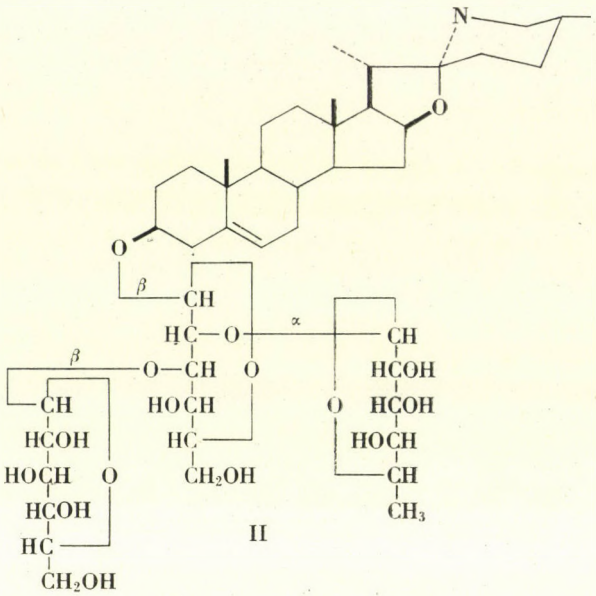
This is a further contribution in an efford made for the systematic investigation of Egyptian solanaceous plants to elucidate their steroid alkaloidal contents. The unripe fruits of *Solanum macrocarpum* L. of German origin were previously examined by SCHREIBER [1, 2] who found them to contain only solasonine. BOGNÁR and MAKLEIT [3] investigated the leaves but found them to be devoid of any alkaloids.

In the present study, the green unripe fruits of this plant were extracted with methanol, containing acetic acid, to take up glycoalkaloids and saponins, and the extract, after defatting with benzene-ether, was made alkaline to give a fraction of alkaloid matter. The latter was shown in silica gel chromatoplates to contain four alkaloidal glycosides in additon to a fifth product which was a steroidal saponin (see below). The mixture was resolved by partition chromatography on a column of alumina. One of the earlier fractions afforded a product which was identified as solamargine **(I)**, m.p. 294—296°, $[\alpha]_D$ — 100° (methanol). The later fractions gave solasonine **(II)**, m.p. 282—285°, $[\alpha]_D$ — 74° (pyridine). Other fractions of the chromatogram were combinations of these two products and two other alkaloid glycosides and a steroid saponin.

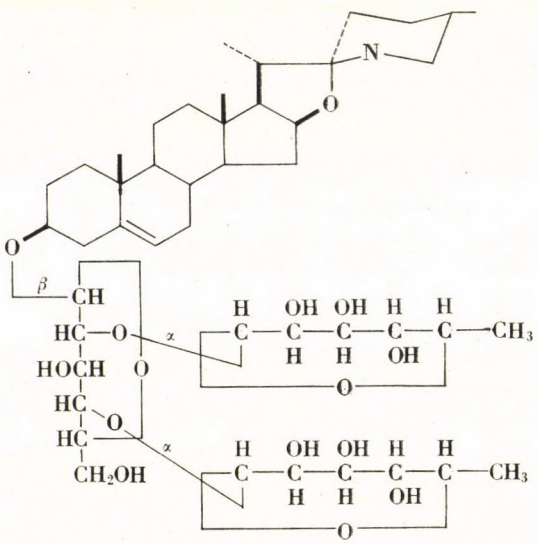


I

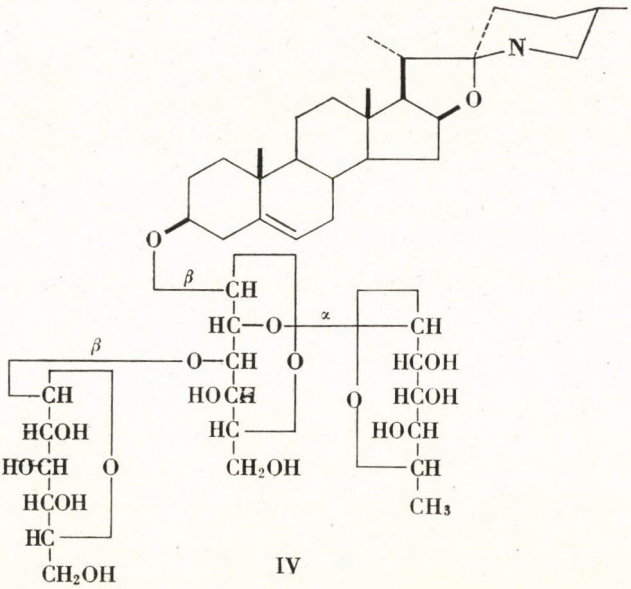


II

The identities of the isolated solamargine and solasonine were established, apart from direct comparison and their behaviour on the chromatoplates, by acid hydrolysis which afforded the same aglycone, solasodine, (25R)-22α-N-spirosol-5-en-3β-ol [4], m.p. 196—199°, $[\alpha]_D$ — 100° (methanol), from both. The aqueous hydrolysate from **I** contained glucose and rhamnose, and that from **II** contained glucose, galactose and rhamnose which were identified on silica gel thin-layers.

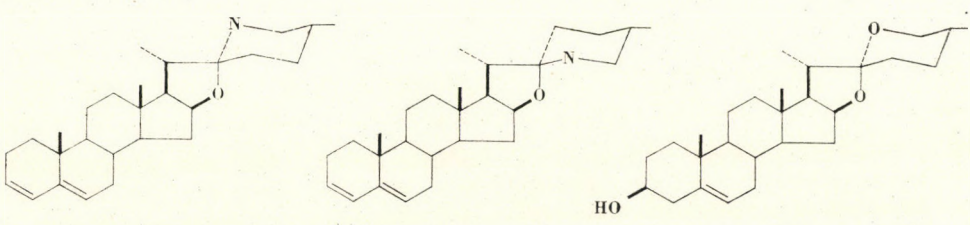


III



IV

The two other gylcoalkaloids present in the natural mixture were identified in the mixed column chromatogram fractions and isolated by preparative layer chromatography. Thus a purified sample, m.p. 269—271°, was shown to be identical with β-solamarine **(III)** which, after acid hydrolysis, afforded the aglycone tomatid-5-enol, (25S)-22-β-N-spirosol-5-en-3β-ol, and the sugars glucose and rhamnose. Another sample, m.p. 274—277°, was identified as α-solamarine **(IV)** giving, by hydrolysis, the same aglycone along with glucose, galactose and rhamnose. Besides the aglycones solasodine (from **I** and **II**) and tomatid-5-enol (from **III** and **IV**), the formation of (25R)-22α-N-spirosola-3,5-diene **(V)** and (25S)-22β-N-spirosola-3,5-diene **(VI)** was established. The latter two compounds are artefacts resulting by acid-induced dehydration of solasodine and tomatid-5-enol, respectively, during the hydrolysis of the natural glycosides. They were identified together with solasodine, tomatid-5-enol (which were actually isolated) and a monohydroxylic steroid sapogenin in the chromatogram fractions obtained during the resolution of the aglycone mixture, resulting after the acid hydrolysis of the total glycosides, on a column of alumina. One of them, **V**, was also obtained in crystalline state, m.p. 165—70°, $[\alpha]_D$ — 176° (chloroform).



V VI VII

It is interesting to observe that the tissue of the same plant source, *S. macrocarpum* L. unripe fruits, contains simultaneously glycosides derived from both the solasodane (**I** and **II**) and tomatidane (**III** and **IV**) types of the spirosolane class of steroidal alkaloids.

The alkaline filtrate, obtained after precipitation of the glycoalkaloids, was processed by extraction of the saponins with *n*-butanol, followed by acid hydrolysis and treatment of the resulting sapogenin matter with alkali in the manner recommended by WALL *et al.* [5] for the isolation of steroid sapogenins. The obtained sapogenin corresponded to the same aglycone previously detected in the alkaloid aglycone mixture, and was found to be contaminated with solasodine, tomatid-5-enol, and their dehydration products (**V** and **VI**), as revealed by inspection on the chromatoplates. The basic contaminants were eliminated by treatment with hydrogen chloride gas in a dry ethereal solution to form the hydrochloride salts. In this manner the pure sapogenin was isolated, m.p. 189—192°, $[\alpha]_D$ — 121° (chloroform), and identified as diosgenin (**VII**). We have previously shown [6] that steroid sapogenins may conveniently be differentiated from steroidal alkaloids on silica gel thin-layers by the use of *p*-anisaldehyde—acetic acid—sulphuric acid mixture as spray reagent. It gives a yellow colour (non-fluorescent in ultraviolet light) with all sapogenins and various colours (fluorescent in ultraviolet light) which change upon heating from pink to dark blue with the steroidal alkaloids.

The literature contains several examples of the joint occurrence of spirostanes and spirosolanes in the same plant. The obvious structural and stereochemical relationship between diosgenin and its ring-F nitrogenous counterpart, solasodine, may suggest that common biogenetic pathways are involved in the formation of their glycosides and probably also those of tomatid-5-enol; all being 5,6-unsaturated products glycosidically linked at C-3 different sugars.

The fatty matter, contained in the benzene—ether extract during the initial processing of plant material, was saponified and the unsaponifiable fraction resolved on a column. A sterol, m.p. 132—134°, $[\alpha]_D$ — 34° (chloroform), was isolated and shown to be β-sitosterol.

Experimental

Thin-layer chromatography

The plates (7 × 13 cm) used were prepared in the usual manner by slurrying silica gel *G Merck* (1 g) in water (3 ml) followed by manual application and drying at 110° for 1 hr.

The following solvent systems were used:

A: benzene—methanol (10 : 7.5), for alkaloidal glycosides.

B: isopropanol—ethyl acetate—toluene—water (10 : 2 : 5 : 2.5), for sugars.

C: benzene—methanol (5 : 1), for alkaloidal aglycones.

D: *n*-hexane—ethyl acetate (10 : 3), for sterols.

After drying the chromatoplates, they were sprayed with the suitable reagent, dried again at 110° for a few minutes, and the developed colours observed in daylight and under an

ultraviolet lamp. The following spray reagents were used for alkaloidal and neutral glycosides and aglycones: DRAGENDORFF's; antimony trichloride [7] (25% solution in chloroform); 10% aqueous sulphuric acid; *p*-anisaldehyde [8] (in acetic acid containing sulphuric acid); and CLARKE's [9] (1% paraformaldehyde in 80% phosphoric acid). The diphenylamine—aniline—phosphoric acid reagent [10] was used for sugars, and antimony trichloride for sterols.

The steroidal alkaloid content

The fresh unripe fruits (6 kg) of *S. macrocarpum* L. were minced in 5% acetic acid in methanol (6 l), the mixture was allowed to stand for 48 hrs, filtered, and the marc re-extracted with the same solvent (3 l). After concentration (to about 1 l), the extract was treated with 10% acetic acid (1 l), allowed to stand overnight, and freed from the deposited resinous matter. After defatting with benzene—ether (1 : 1) (see later), the aqueous solution was heated to about 70° adjusted with ammonia solution to pH 10, then allowed to stand overnight. The deposited mixture of alkaloid glycosides was separated (filtrate examined later) and refined by repeated dissolution in 5% acetic acid and precipitation with ammonia, to give 25 g of crude material. The latter was further refined by repeated extraction with boiling methanol which removed 15 g of the purified basic glycoside mixture. The latter was shown on the chromatoplates (solvent system A) to consist of 4 DRAGENDORFF-positive products (R_f 0.25, 0.34, 0.40 and 0.52), corresponding — according to location and the colours developed with the antimony trichloride, 10% sulphuric acid, *p*-anisaldehyde and CLARKE's reagents — to solasonine, α-solamarine, solamargine and β-solamarine, respectively. A fifth product (R_f 0.60) was DRAGENDORFF-negative and gave with the *p*-anisaldehyde reagent a saponin colour reaction [6].

The alkaloidal glycoside mixture (7 g) was fractionated on an alumina (1.4 kg) column packed in *n*-butanol saturated with water. Elution was made with the same solvent and the course of fractionation followed on the chromatoplates using solvent system A. The following fractions were obtained successively: i) a mixture (193 mg; uncrystallizable) comprising the saponin (R_f 0.60); ii) a mixture (3.18 g) comprising three products (R_f 0.60, 0.52 and 0.40); iii) a mixture (664 mg) containing two products (R_f 0.40 and 0.34); iv) a mixture (237 mg) comprising two constituents (R_f 0.34 and 0.25), and v) a product (1.11 g) with R_f 0.25.

Solamargine (I)

It was obtained from fraction ii (above) by repeated recrystallizations from aqueous methanol. A pure sample (R_f 0.40) had m.p. 294—296° (undepressed), $[\alpha]_D$ — 100° (methanol); lit. [11] m.p. 301°, $[\alpha]_D$ — 105°. Hydrolysis of this material (0.5 g) by refluxing an ethanolic (5 ml) solution with 2 *N* HCl (5 ml) for 3 hrs afforded a crude hydrochloride salt which was treated with ammonia in hot ethanol solution. The resulting aglycone (103 mg) was recrystallized from aqueous methanol to give hexagonal plates, m.p. 196—199° (undepressed by authentic solasodine), $[\alpha]_D$ — 100° (methanol), R_f 0.38 (solvent system C); lit. [12] m.p. 201°, $[\alpha]_D$ — 100°. The following derivatives were prepared: N-nitroso, m.p. 260—262°, $[\alpha]_D$ — 52.3° (pyridine) (lit. [13] m. p. 260—262.5°), N,O-diacetate, m.p. 155—157° (lit. [14] m.p. 164—166°) and picrate, m.p. 144—146° (lit. [13] m.p. 144°). The sugars in the acid hydrolysate were obtained in the usual manner and examined on silica gel thin-layers (solvent system B) to show the presence of glucose (R_f 0.45) and rhamnose (R_f 0.78).

Solasonine (II)

Repeated recrystallizations of fraction v (above) from aqueous methanol gave colourless needles (R_f 0.25), m.p. 282—285° (undepressed by authentic solasonine), $[\alpha]_D$ — 74° (pyridine) lit. [13] m.p. 284—5°, $[\alpha]_D$ — 68.7 (ethanol). Hydrolysis of this material with ethanolic hydrochloric acid (as above) afforded solasodine, m.p. 201—203° (undepressed), $[\alpha]_D$ — 105° (methanol), R_f 0.38 (solvent system C). The sugars in the acid hydrolysate were identified (as before) as galactose (R_f 0.37), glucose (R_f 0.45) and rhamnose (R_f 0.78).

β-Solamarine (III)

This compound (R_f 0.52) was isolated from the column chromatographic fraction ii by a process of preparative layer chromatography on silica gel using solvent system A for develop-

ment. The isolated material (6 mg) was identical with β-solamarine, m.p. and mixed m.p. 269—271°; lit. [15] m.p. 275—277°. Hydrolysis with ethanolic hydrochloric acid gave tomatid-5-enol which was identified on the chromatoplates (R_f 0.50, solvent system C) by direct comparison with authentic material. The aqueous hydrolysate was shown on the chromatoplates (solvent system B) to contain glucose (R_f 0.45) and rhamnose (R_f 0.78).

α-Solamarine (IV)

Preparative layer chromatography of the column fractions iii and iv gave the product with R_f 0.34 in pure state (3.4 mg) which was shown by direct comparison to be identical with α-solamarine, m.p. and mixed m.p. 274—277°; lit. [15] m.p. 278—281°. Hydrolysis with ethanolic hydrochloric acid yielded an aglycone fraction which were identified on the chromatoplates (R_f 0.50, solvent system C) as tomatid-5-enol. The sugars in the aqueous hydrolysate were identified on the chromatoplates as galactose (R_f 0.37), glucose (R_f 0.45) and rhamnose (R_f 0.78).

The total aglycone mixture

The total alkaloid glycoside mixture (R_f 0.25, 0.34, 0.40, 0.52 and 0.60; 4 g) was refluxed in ethanol (40 ml) with 2 *N* HCl (40 ml) for 3 hrs. After the usual work-up and treatment of the mixed hydrochloride salts with ammonia, the total free aglycone mixture (665 mg) was inspected on chromatoplates (solvent system C) to reveal the presence of 5 products (R_f 0.38, 0.50, 0.55, 0.70 and 0.82). All spots gave pink changing to dark blue colours (daylight) and yellow fluorescence (ultraviolet) with CLARKE's spray reagent and pink changing to blue colours (daylight) and yellow fluorescence (ultraviolet) with the *p*-anisaldehyde reagent except one spot (R_f 0.70), which gave with the latter reagent a distinct yellow colour in daylight (no ultraviolet fluorescence), as expected for a steroidal sapogenin [6].

Column chromatography of the obtained aglycone mixture on alumina (60 g) gave: i) a mixture (91 mg) containing one product (R_f 0.82, solvent system C) identified on the chromatoplates as tomatid-3,5-diene **(VI)**; ii) a mixture (44 mg) containing two products (R_f 0.82 and 0.70) of which that at R_f 0.70 was a monohydroxylic steroid sapogenin (see later); iii) a mixture (91 mg) containing two products (R_f 0.70 and 0.55); iv) a single product (R_f 0.55, 127 mg), which was obtained on crystallization from aqueous methanol as colourless plates, m.p. 168—170° (undepressed by an authentic sample of solaso-3,5-diene, **V**) $[\alpha]_D$ — 176° (chloroform), giving an orange tetranitromethane reaction; lit. [12] m.p. 170°, $[\alpha]_D$ — 180° (chloroform). The chromatogram subsequently gave: v) a single product (R_f 0.50, 38 mg) which was recrystallized from acetone to give needles, m.p. 236—239° (undepressed by authentic tomatid-5-enol), $[\alpha]_D$ — 36.5° (methanol); vi) a mixture (39 mg) containing two products (R_f 0.50 and 0.38) of which the latter was identical with solasodine; vii) a single product (R_f 0.38; 198 mg) which was crystallized from aqueous methanol to give plates, m.p. 196—198° (undepressed by authentic solasodine), $[\alpha]_D$ — 104° (methanol). The above mentioned chromatographic fractions were eluted successively with benzene (i, ii), 10% chloroform in benzene (iii), 20% chloroform in benzene (iv), 40% chloroform in benzene (v, vi), 60% chloroform in benzene and chloroform alone (vii).

The steroid sapogenin content

The ammoniacal filtrate (above) resulting after the precipitation of the glycoalkaloids was concentrated and repeatedly extracted with *n*-butanol saturated with water. The extract was concentrated, then hydrolyzed by refluxing with 2 *N* HCl for 3 hrs. The aglycone fraction was extracted with chloroform to afford 0.88 g of a brownish residue which was dissolved in benzene (50 ml) and refluxed with a strong methanolic potassium hydroxide solution for 30 min. After the addition of water, the benzene layer was freed from alkali and examined on the chromatoplates (solvent system C) to show the presence of a main product (R_f 0.70) and 4 minor alkaloidal companions (R_f 0.82, 0.55, 0.50 and 0.38). The residue (0.35 g) from the benzene extract was treated with ammonia in a methanolic solution. The resulting deposit (160 mg) was dissolved in dry ether and treated with hydrogen chloride gas. After elimination of the precipitated hydrochloride salts, the solution was evaporated to give 78 mg of a solid which was crystallized from chloroform—methanol to obtain needles, m.p. 189—192° (undepressed by authentic dios-

genin, **VII**), $[\alpha]_D$ — 121° (chloroform); lit. [16] m.p. 204—207°, $[\alpha]_D$ — 129°. Acetylation (pyridine—acetic anhydride), yielded a substance, m.p. 185—187° (undepressed), which was identical with diosgenin acetate; lit. [16] m.p. 195—198°.

Unsaponifiable fraction of the fatty matter

The residue (6.08 g) obtained from the benzene—ether extract (above) was saponified by refluxing in ethanol (36 ml) with caustic potash (6 g). The resulting soap solution was worked up in the usual manner, and the isolated unsaponifiable fraction (600 mg) was fractionated on a column of alumina (30 g). After the removal of much waxy and resinous matter by elution with non-polar solvents, a solid fraction (174 mg) was removed in the later zone of the benzene eluate. The material was repeatedly recrystallized from chloroform—methanol to give plates, m.p. 132—134° (undepressed by authentic β-sitosterol) $[\alpha]_D$ — 34° (chloroform) R_f 0.39 (solvent system D); lit. [17] m.p. 136—137°, $[\alpha]_D$—36.5°. The acetyl derivative (pyridine—acetic anhydride), m.p. 123—125° (undepressed), $[\alpha]_D$ — 38° (chloroform) was found to be identica with β-sitosterol acetate; lit. [17] m.p. 134° $[\alpha]_D$ — 38.5°.

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SUMMARY

The unripe fruits of *Solanum macrocarpum* L. were found to contain the glycoalkaloids solasodine, solamargine, α-solamarine and β-solamarine. The neutral glycoside fraction afforded, after hydrolysis, one steroid sapogenin, diosgenin. The unsaponifiable fraction of the fatty matter was found to contain β-sitosterol.

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A NEW SYNTHESIS OF 5,7-DIHYDROXY-3,4',8-TRIMETHOXYFLAVONE AND 4',5-DIHYDROXY-3,7-DIMETHOXYFLAVONE

TWO CONSTITUENTS OF BEYERIA SPP.*

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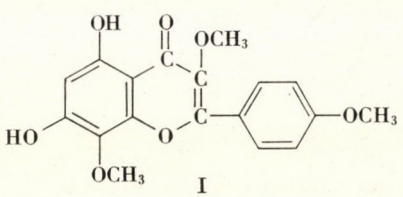
In a series of papers on the chemistry of the *Euphorbiaceae*, JEFFERIES *et al.* reported about investigations on some undescribed species of *Beyeria*, a kind of shrub indigenous to Western Australia [1—3]. Besides diterpenoids, four flavones have been isolated [2, 3]. Two of them, genkwanin (4',5-dihydroxy-7-methoxyflavone) and 5-hydroxy-4',7-dimethoxyflavone, were known compounds that had been isolated previously from several sources [4]. The other two, 5,7-dihydroxy-3,4',8-trimethoxyflavone **(I)** [2] and 4',5-dihydroxy-3,7-dimethoxyflavone **(II)** [3] (the latter being the only one of the six possible dimethyl ethers of kaempferol that had not been described in the literature) were new. The structure of Iδ and IIδ has been elucidated by JEFFERIES and his group [2, 3] by means of UV and NMR spectroscopy, as well as by degradation of both the parent compounds and their ethyl ethers.



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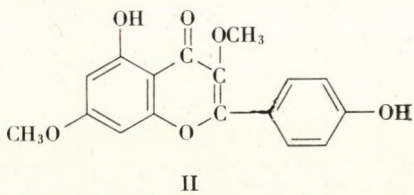


II

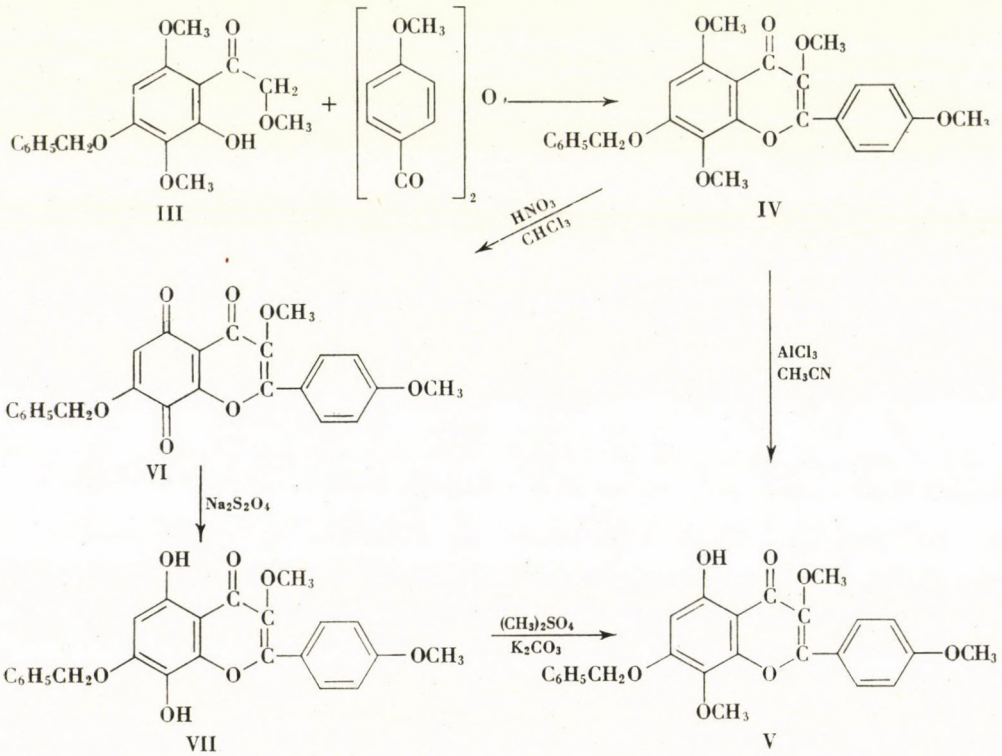
As a continuation of our synthetic investigations in the field of *Euphorbiaceae* flavonoids [5, 6], we undertook the synthesis of **I** and **II**.

Our key intermediate in the sequence leading to 5,7-dihydroxy-3,4',8-trimethoxyflavone was 7-benzyloxy-3,4',5,8-tetramethoxyflavone **(IV)**, prepared by the ALLAN-ROBINSON method [7] from 2-hydroxy-4-benzyloxy-3,6, ω-trimethoxyacetophenone [8] **(III)** and anisic anhydride. The absence of free hydroxyls in **IV** offered considerable advantages in the preparation and purifi-

* Preliminary communication: FARKAS, L., NÓGRÁDI, M.: Tetrahedron Letters 3759 (1965).

fication of this intermediate. Elimination of the methyl group from position 5 has been achieved by two different means. The first one was a modification of the aluminium chloride—acetonitrile method, developed by SESHADRI *et al.* [9]. According to this procedure **IV** was refluxed with a slight excess of anhydrous aluminium chloride in acetonitrile. From the reaction mixture a yellow product could be isolated in fair yield, that was not the expected **I**, but 7-benzyloxy-5-hydroxy-3,4',8-trimethoxyflavone **(V)** [9]. Resistance of the benzyloxy group to the dealkylating action of aluminium chloride under specific conditions has been recently observed in this laboratory [10]. Catalytic debenzylation of **V** afforded 5,7-dihydroxy-3,4',8-trimethoxyflavone **(I)**, identical in every respect with the natural product [3].

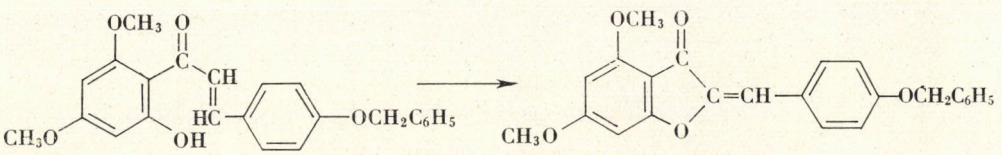
Elimination of the 5-methyl group was alternatively carried out by the oxidation of **IV** with nitric acid to 7-benzyloxy-3,4'-dimethoxy-5,8-quinoflavone **(VI)**. Reduction of **VI** with sodium dithionite in aqueous dimethylformamide afforded a quantitative yield of 7-benzyloxy-5,8-dihydroxy-3,4'-dimethoxy-flavone **(VII)** that was partially methylated to **V**, an intermediate of the previous sequence.



Though at the outset of our investigations no synthesis of **I** had been reported, later we became aware of a paper of SESHADRI *et al.* describing the preparation of this compound by a different route [11].

A number of different approaches have been tried to realize the synthesis of 4',5-dihydroxy-3,7-dimethoxyflavone **(II)**.

First we attempted to build up the flavone molecule by the ALGAR-FLYNN-OYAMADA oxidation [12, 13] of 4-benzyloxy-2'-hydroxy-4',6'-dimethoxychalkone **(VIII)**. Though a close analogue of **VIII**,4-benzyloxy-2'-hydroxy-4',5',6'-trimethoxychalkone gave the corresponding flavonol when oxidized at the boiling point of methanol with alkaline hydrogen peroxide [10], a similar treatment of **VIII** afforded 4,6-dimethoxy-2-(4-benzyloxybenzal)-coumaran-3-one **(IX)** as the only isolable product. The structure of **IX** has been supported by its highly characteristic UV spectrum and the absence of free hydroxyls.

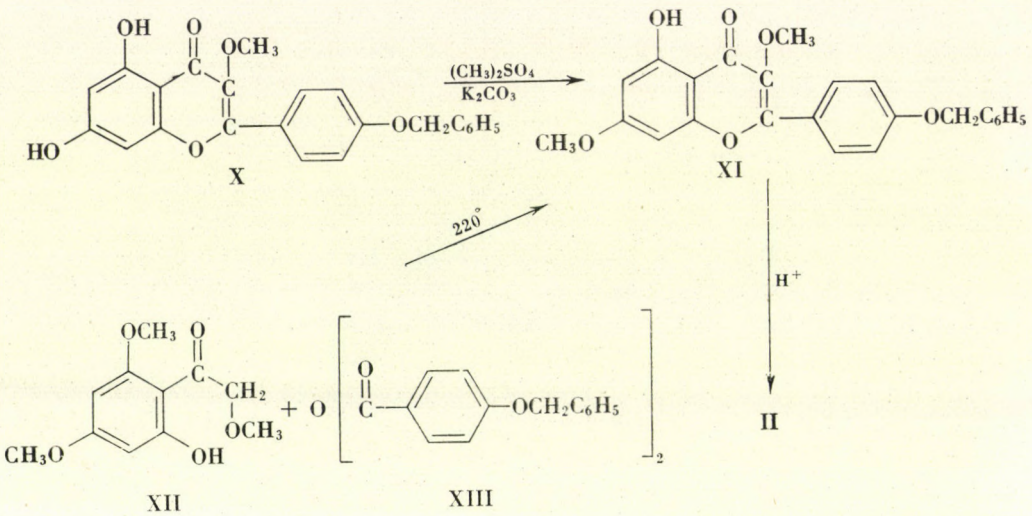


VIII IX

The desired intermediate 4'-benzyloxy-3,5,7-trimethoxyflavone could be, in turn, prepared directly by the ALLAN-ROBINSON method as described by KOBAYASHI [14]; partial demethylation of this compound, however, was found to proceed unsatisfactorily.

After this we turned to the way of partial methylation. 4'-Benzyloxy-5,7-dihydroxy-3-methoxyflavone **(X)** [15] was prepared by the method of SESHADRI *et al.* [17] directly from 2,4,6-trihydroxy-ω-methoxyacetophenone [16] and 4-benzyloxybenzoyl chloride [15] and subsequently partially methylated to 4'-benzyloxy-3,7-dimethoxy-5-hydroxyflavone **(XI)**. **XI** was debenzylated in acetic acid—hydrochloric acid to 4',5-dihydroxy-3,7-dimethoxyflavone **(II)**, being completely identical with the natural compound. **II** was further characterized by its acetate.

A more direct access to the key intermediate **XI** has been found when we investigated the effect of temperature on the ALLAN-ROBINSON reaction of 2-hydroxy-4,6,-$\delta\omega$-trimethoxyacetophenone **(XII)** [18] and 4-benzyloxybenzoic anhydride **(XIII)** [15]. If this reaction was carried out at the conventional temperature of 180°, a yellow by-product appeared that could be avoided when working at 160°. If, in turn, the temperature was raised to 220°, the yellow product became predominant. It could be isolated from the reaction mixture in moderate yield and identified as 4'-benzyloxy-3,7-dimethoxy-5-hydroxyflavone **(XI)**. Demethylation in the ALLAN-ROBINSON reaction has been experienced several times [19, 20].



After this work had been completed, we became aware of a recent short communication by SESHADRI *et al.* [21] describing without experimental details the synthesis of **II**, using the method of partial methylation.

Note: After the submission of our paper, Y. KIMURA *et al.* (Yakugaku Zasshi, **84,** 440 (1967) reported the isolation of 4',5-dihydroxy-3,7-dimethoxyflavone (**II**), from *Alpinia kumatake* Makino.

Disregarding the isolation of **II** by DAWSON *et al.* in 1965 [3], they stated it to be a new flavonoid and coined for it the name "Kumatakenin".

Experimental*

7-Benzyloxy-3,4',5,8-tetramethoxyflavone (IV)

An intimate mixture of 0.5 g of 4-benzyloxy-2-hydroxy-3,6,ω-trimethoxyacetophenone **(III)** [7], 2 g of anisic anhydride and 1 g of sodium anisate was heated for 3 hrs in vacuum in an oil bath of 165°. After cooling, the melt was boiled for 20 min. with a mixture of 20 ml of ethanol and 2 ml of conc. aqueous potassium hydroxyde (60 g KOH/100 ml). After standing overnight, the product (0.42 g: 57%) was filtered off and recrystallized from chloroform—ethanol (1 : 3) to yield colourless prisms of m.p. 178—180°.

UV spectrum: λ_{max}(log ε) 270 (4.19), 311 (4.10) and 347 (4.14). $C_{26}H_{24}O_7$ (448.5). Calcd. C 69.63; H 5.39. Found: C 69.42; H 5.34%.

7-Benzyloxy-5-hydroxy-3,4',8-trimethoxyflavone (V)

(*a*) A solution of 100 mg of 7-benzyloxy-3,4',5,8-tetramethoxyflavone **(IV)** and 58 mg of anhydrous aluminium chloride in 5 ml dry acetonitrile was refluxed for 2 hrs. After the addition of 2 ml of conc. HCl, the solvent was removed by steam distillation, the raw product that precipitated filtered off and recrystallized twice from methanol—chloroform to obtain yellow needles (40 mg) of m.p. 172—174°; lit. [11] m.p. 170—171°. $FeCl_3$ colour reaction green.

UV spectrum: λ_{max}(log ε) 271 (4.26), 318 (4.15) and 362 (4.17).

(*b*) 100 mg of 7-benzyloxy-5,8-dihydroxy-3,4'-dimethoxyflavone **(VII)** 200 mg of anhy-

* M.p.'s are uncorrected. UV spectra were measured with a *Unicam Sp. 700* type spectrophotometer in methanol.

drous potassium carbonate and 22 mg of dimethyl sulphate in 10 ml of dry acetone were refluxed, with stirring, for 90 min. The filtered solution was concentrated to a small volume, whereupon the product crystallized. Recrystallization from acetone afforded 70 mg of V, m.p. 171—173°.

5,7-Dihydroxy-3,4',8-trimethoxyflavone (I)

A solution of 100 mg of 7-benzyloxy-5-hydroxy-3,4',8-trimethoxyflavone **(V)** in acetic acid was hydrogenated in the presence of palladium on charcoal. After the usual work-up, the raw product was crystallized from ethyl acetate to yield yellow needles (50 mg) of m.p. 174—175.5°; lit. [3] m.p. 173—174°.

UV spectrum: λ_{max}(log ε) 274 (4.36), 310 (4.21) and 358 (4.09). $C_{18}H_{16}O_7$ (344.3). Calcd. C 62.79; H 4.68. Found: C 61.89; H 4.70%.

7-Benzyloxy-3,4'-dimethoxy-5,8-quinoflavone (VI)

To an ice-cold solution of 300 mg of 7-benzyloxy-3,4',5,8-tetramethoxyflavone **(IV)** in 20 ml chloroform 4 ml of conc. nitric acid was added with vigorous stirring. Stirring was continued for 20 min., the wine red solution was then washed with aqueous sodium bicarbonate, dried and evaporated. Recrystallization of the residue from a large volume of ethanol afforded carmin red needles (100 mg; 34%) of m.p. 201—204°.

UV spectrum: λ_{max}(log ε) 230 (4.19), 250 (4.11) and 303 (4.27). $C_{24}H_{18}O_7$ (418.4). Calcd. C 68.89; H 4.34. Found C 68.45; H 4.62%.

7-Benzyloxy-5,8-dihydroxy-3,4'-dimethoxyflavone (VII)

To a solution of 150 mg of 7-benzyloxy-3,4'-dimethoxy-5,8-quinoflavone **(VI)** in 2 ml dimethylformamide at water bath temperature, 0.5 ml of water and 200 mg of sodium dithionite were added. The initially deep red solution turned in a few seconds into light yellow. Addition of water precipitated the pure hydroquinone derivative (140 mg). It crystallized from acetone in light yellow rhomboids of m.p. 187—188.5°.

UV spectrum: λ_{max}(log ε) 280 (4.63), 305 (4.30), 324 (infl.) (4.23) and 370 (3.96).

$C_{24}H_{20}O_7$ (420.4). Calcd. C 68.56; H 4.80. Found C 68.87; H 5.00%.

4-Benzyloxy-4',6'-dimethoxy-2'-hydroxychalcone (VIII)

20 g of 4,6-dimethoxy-2-hydroxyacetophenone [22] and 19.2 g of *p*-benzyloxybenzaldehyde [23] were refluxed in ethanol (270 ml) with 14 ml of piperidine for 8 hrs. After standing overnight, a mixture of **VIII** and the corresponding flavone crystallized. This was separated, dissolved in a hot mixture of 150 ml 1 *N* sodium methoxide and 400 ml methanol. Acidification with acetic acid precipitated the chalcone that was recrystallized from benzene to yield 13.85 g (35%) of yellow prisms, m.p. 161—163°.

$C_{24}H_{22}O_5$ (390.4). Calcd. C 73.82; H 5.68. Found: C 73.90; H 5.62%.

4,6-Dimethoxy-2-(4-benzyloxybenzal)-coumaran-3-one (IX)

To a boiling solution of 1 g of 4-benzyloxy-4',6'-dimethoxy-2'-hydroxychalcone **(VIII)** in 200 ml of methanol and 20 ml of 20% aqueous potassium hydroxyde, 4.5 ml of 30% hydrogen peroxide was added. The deep red solution soon became light yellow. After 2 min. the reaction mixture was poured onto ice. After standing overnight, the yellow precipitate was separated and extracted with chloroform. The chloroform solution was washed several times with aqueous Na_2CO_3 solution, finally with water and evaporated. The residue was crystallized from acetone to yield very pale yellow crystals (0.08 g) of m. p. 197°. $FeCl_3$ colour reaction: negative. Treatment with acetic anhydride—sodium acetate resulted in the recovery of starting material.

UV spectrum: λ_{max}(log ε) 224 (infl.) (4.17), 248 (4.11), 342 (infl.) (4.28) and 390 (4.42).

$C_{24}H_{20}O_5$ (388.4). Calcd. C 74.21; H 5.19. Found: C 74.92; H 5.30%.

4'-Benzyloxy-5,7-dihydroxy-3-methoxyflavone (X)

1.0 g of 2,4,6-trihydroxy-ω-methoxyacetophenone [16], 5 g of 4-benzyloxybenzoyl chloride [15] and 6 g of potassium carbonate were refluxed with stirring in 40 ml of dry acetone for 9 hrs. The filtered solution was concentrated, and the residue refluxed for 30 min. with a mixture of 70 ml of methanol and 4 ml of 60% aqueous potassium hydroxyde. The cooled solution was neutralized with acetic acid, the precipitate separated and extracted with ethyl acetate. The raw product that separated on cooling was recrystallized from aqueous ethanol to yield 0.15 g of **(X)**, m.p. 279° (lit. [13] m.p. 280°).

4'-Benzyloxy-3,7-dimethoxy-5-hydroxyflavone (XI)

(a) A vigorously stirred solution of 0.4 g of 4'-benzyloxy-5,7-dihydroxy-3-methoxyflavone **(X)** in 40 ml dry acetone was treated at reflux temperature for 20 min. with 0.4 g of dry K_2CO_3 and 0.13 g of dimethyl sulphate. The reaction mixture was filtered while hot and diluted with water. The precipitate was filtered off, and recrystallized from methanol to obtain yellow needles of m.p. 140—142°; lit. [21] m.p. 131—132°. $FeCl_3$ colour reaction in methanol: green.

UV spectrum: λ_{max}(log ε) 267 (4.09) and 344 (4.07).

$C_{24}H_{20}O_6$ (404.4). Calcd. C 71.27; H 4.98. Found C 71.10; H 5.10%.

(b) 0.5 g of 2-hydroxy-4,6,ω-trimethoxyacetophenone **(XII)** [18], 2 g of 4-benzyloxybenzoic anhydride [15] and 0.5 g sodium salt of the same acid were mixed thoroughly and heated for 6 hrs in vacuum in an oil bath at 220°. The melt was boiled for 20 min. with a mixture of 50 ml of methanol and 2 ml of 60% aqueous KOH. The insoluble residue was filtered off, extracted with chloroform and the chloroform solution evaporated to dryness. Crystallization of the residue from methanol afforded 0.12 g product of m.p. 140—141°. On admixture with the former product no m.p. depression was observed.

5-Acetoxy-4'-benzyloxy-3,7-dimethoxyflavone

0.1 g of 4'-benzyloxy-3,7-dimethoxy-5-hydroxyflavone **(XI)** was heated on the water bath with 2 ml acetic anhydride and 0.5 g of sodium acetate for 1 hr. The cooled reaction mixture was decomposed with water, the precipitate filtered off and recrystallized from ethanol to yield colourless plates, of m.p. 170—172°.

$C_{26}H_{22}O_7$ (446.4). Calcd. C 69.94; H 4.97. Found C 69.81; H 5.08%.

4',5-Dihydroxy-3,7-dimethoxyflavone (II)

0.08 g of 4'-benzyloxy-3,7-dimethoxy-5-hydroxyflavone **(XI)** was heated on a water bath for 1 hr. with a mixture of 4 ml acetic acid and 2 ml conc. HCl. Dilution of the reaction with 10 ml of water precipitated the product, that was recrystallized from aqueous methanol to give yellow needles of m.p. 247° (lit. m.p. 253—254° [2] and 252—253° [21]). $FeCl_3$ colour reaction in methanol: green.

UV spectrum: λ_{max} (log ε) 267 (4.13) and 350 (4.12).

$C_{17}H_{14}O_6$ (314.3). Calcd. C 64.96; H 4.49. Found C 64.78; H 4.56%.

4',5-Diacetoxy-3,7-dimethoxyflavone

25 mg of 4',5-dihydroxy-3,7-dimethoxyflavone **(II)** was acetylated in the usual manner. Repeated recrystallizations of the raw product from ethanol afforded colourless tiny needles, m.p. 165—167° (lit. [3] m.p. 140—143° and 165—167°).

$C_{21}H_{18}O_8$ (398.4). Calcd. C 63.31; H 4.55. Found C 63.96; H 4.91%.

SUMMARY

The synthesis of 5,7-dihydroxy-3,4',8-trimethoxyflavone **(I)** and 4',5-dihydroxy-3,7-dimethoxyflavone **(II)**, two components of *Beyeria*, is reported.

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1,2,4-TRIAZINES AND CONDENSED DERIVATIVES, V* SYNTHESIS OF PYRANO[2,3-e][1,2,4]TRIAZINES AND ATTEMPTED SYNTHESIS OF FURANO[2,3-e][1,2,4]-TRIAZINES**

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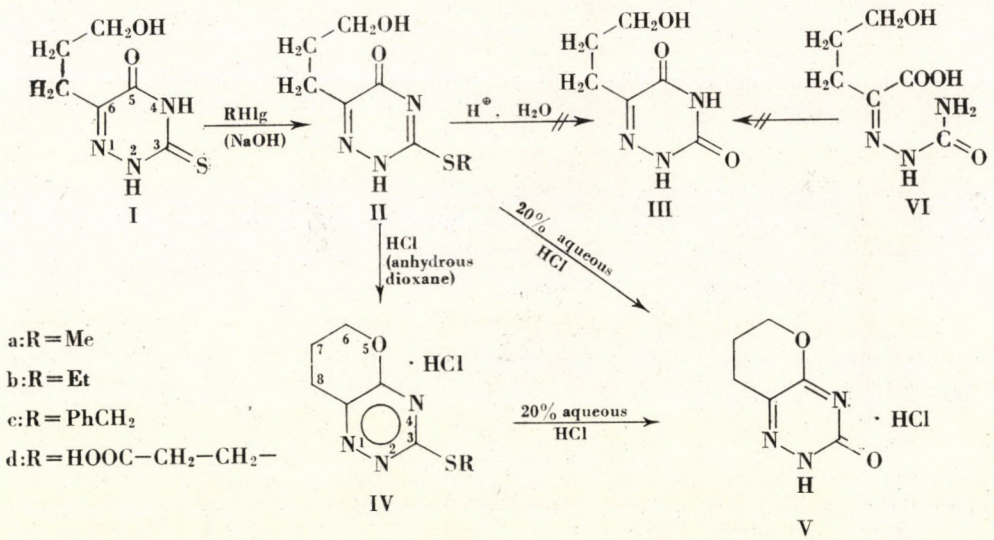
As the starting compound for planned syntheses a quantity of 6-(3-hydroxypropyl)-1,2,4-triazine-3,5(2*H*, 4*H*)-dione **(III)** was required. Since this compound could not be prepared by ring closure of α-oxo-δ-hydroxyvaleric acid semicarbazone **(VI),** we attempted the synthesis starting with the readily accessible [1] 3-thio analogue **(I),** and proceeding as usually (*cf.* [2, 3]) by *S*-methylation and subsequent acid hydrolysis. Hydrolysis of the methylthio

Scheme 1



derivative **IIa,** however, yielded, instead of the expected product **III,** the hydrochloride **(V)** of a sulfur-free base, which contained one molecule of water less than calculated for **III.** By the removal of hydrogen chloride from the salt with diazomethane the free base could also be prepared.

* Part IV: DOLESCHALL, G. and LEMPERT, K., Acta Chim. Acad. Sci. Hung. **53,** 397 (1967).
** Partly based on the thesis of M. H. H. (Technical University, Budapest, 1966)

The elucidation of structure of the product was greatly facilitated by our finding that treatment of an anhydrous dioxane solution of **IIa** with dry hydrogen chloride gave the hydrochloride **IVa,** an intermediate of the reaction leading to **V;** on subsequent treatment with aqueous hydrochloric acid **IVa** was transformed into **V.**

The free base corresponding to the salt **IVa** could not be isolated in crystalline form; based on the analysis figures of its hydrochloride, it could be deduced from **IIa** by the loss of one molecule of water.

Since the IR spectrum of the salt **IVa** does not contain any carbonyl band (the first band of the double bond region appearing at 1620 cm^{-1}), it was obvious that the carbonyl group of **IIa** and the hydroxyl group of its side chain had reacted with each other under elimination of water and aromatization of the triazine ring to form the hydrochloride **(IVa)** of 3-methylthio-7,8-dihydro-6*H*-pyrano[2,3-e][1,2,4] triazine. This structure assignment could be corroborated by the UV spectrum of **IVa** and, especially, by the pH dependence of the spectrum (see below).

As to its type, **IVa** is related to certain non-isolated 3-methylthio-5-ethoxy-1,2,4-triazine salts which were previously [6] suggested as intermediates of the reactions of 3-methylthio-1,2,4-triazin-5(2*H*)-ones, when these compounds were treated first with ethanol in the presence of boron fluoride etherate or sulfuric acid, and then subjected to aminolysis to obtain the corresponding 3-methylthio-5-amino-1,2,4-triazines.

The overall change effected by the hydrolysis of **IVa** with hydrochloric acid consisted in the elimination of the methylthio group and in the simultaneous uptake of one atom each of oxygen and hydrogen. From this and the well-known behaviour of 3-methylthio-triazines and related compounds under the conditions of acid hydrolysis it follows immediately that **V** is the hydrochloride of 7,8-dihydro-6*H*-pyrano-[2,3-e][1,2,4] triazin-3(2*H*)-one, or of the tautomeric 3(4*H*)-one.

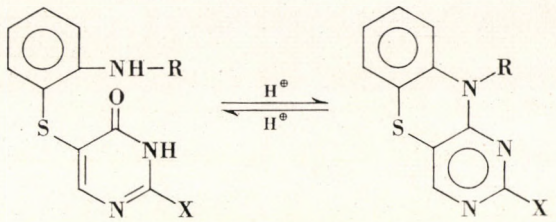
Analogous reactions were observed with the 3-ethylthio **(IIb)** and 3-benzylthio **(IIc)** analogues of **IIa,** while treatment of the 3-(2-carboxyethyl) analogue **(IId)** with hydrogen chloride in anhydrous dioxane did not yield a defined crystalline product.

The acid-catalyzed ring closure of compounds **II** is related to the cyclization of 5-(2'-aminophenylthio)-4-pyrimidinones to yield pyrimido-benzothiazines (see Scheme 2) investigated by Roth *et al.* [4, 5]. While the mechanism of the latter reactions has not been completely elucidated, it follows unequivocally from kinetic measurements that the effective reactants are (doubly) protonated forms of the starting compounds.

Similarly, it is certainly the conjugate acids, protonated at N-2* of the compounds **II** which take part in the transformations **II** → **IV** (see Scheme 3). In these protonated forms, the electron density at the carbonyl carbon atom in

* For the site of protonation, see [6].

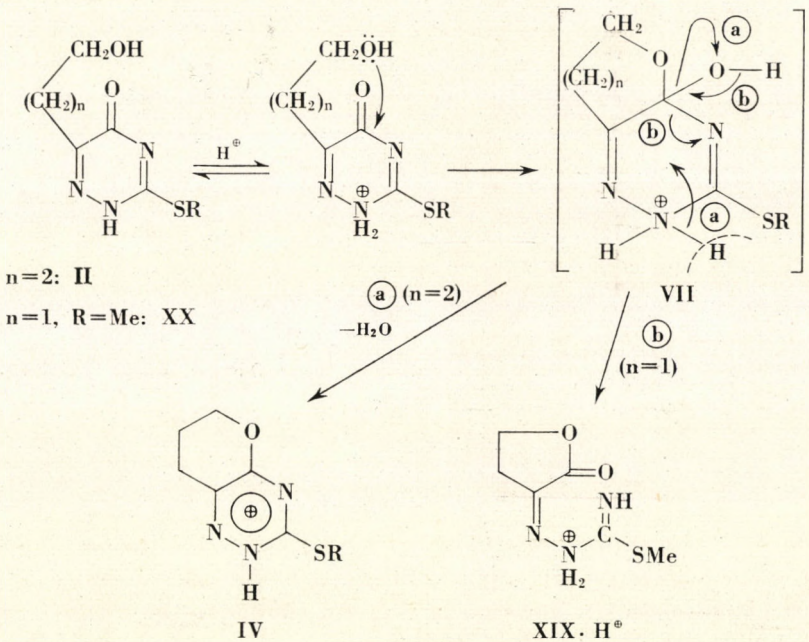
Scheme 2



X=OH*, NH_2, NHR', NR'_2

position 5 is significantly further lowered as compared with the non-protonated compounds **II**,** and thus, the readiness of this atom for the attack by the nucleophilic hydroxyl group of the side chain, to yield the intermediate **VII** ($n = 2$), is increased. The final step of the reaction consists in the stabilization of the unstable intermediate **VII**, one possible path for this — in fact, the only

Scheme 3



n=2: II

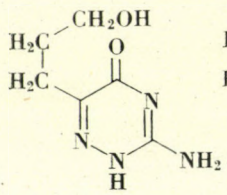
n=1, R=Me: XX

one observed for the case $n = 2$ — being elimination of water (reaction *a*) facilitated by the tendency of aromatization of the triazine ring.

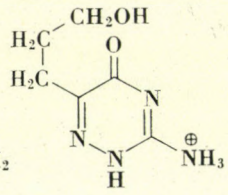
* In this case the compounds exist as the corresponding oxo-tautomers.

** This follows clearly from an inspection of the IR spectrum of the 6-methyl analogue of **IIa** and its hydrochloride. While the carbonyl band of the base appears at 1620 cm^{-1} (the frequency being lowered by hydrogen bonding), that of the salt is found at 1720 cm^{-1} (KBr pellets) [6].

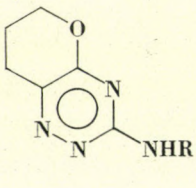
IIa may readily be ammonolyzed to yield the amino derivative **VIII.** However, neither from the latter, nor from compound **I** containing a non-



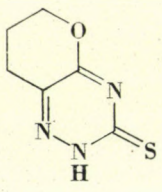
VIII *



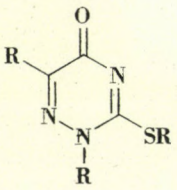
IX



X



XI



XII

alkylated sulfur atom, could the corresponding pyrano[2,3-e][1,2,4]triazines **(X, XI)** be prepared by treatment with hydrochloric acid. While with **VIII** only salt formation occurred, **I** did not react at all.

The negative result of the latter experiments may easily be explained on the basis of the previous considerations. **I,** namely, is non-basic and incapable to form a hydrochloride; consequently, the proneness of its carbonyl carbon atom to react with nucleophilic agents cannot be increased. The amino derivatives **VIII,** on the other hand, are basic and therefore capable to form hydrochlorides, however, consistently with the structure of cation **IX,**** the positive charge affects the carbonyl group less than in the protonated forms of compounds **II.*****

Cyclization of **VIII** could not be effected by thionyl chloride, either; this reagent rapidly converted **VIII** into tars.

Moreover, amino derivatives of type **X** could not be prepared either by the ammonolysis or aminolysis of **IVa.** Although during attempted reactions the evolution of methanethiol could always be detected, no defined products could be isolated from the reaction mixtures.

*

The UV spectrum of an ethanolic solution of the hydrochloride **IVa** contains a single maximum at 236 nm (log $\varepsilon = 4.32$); the spectrum of **IVb** is completely identical with, and that of **IVc** very similar to that ($\lambda_{max} = 240$ nm, log $\varepsilon = 4.28$). Although this type of spectrum is, according to previous studies [7,8], characteristic of the *neutral molecular species* of 3-alkylthio-1,2,4-triazin-

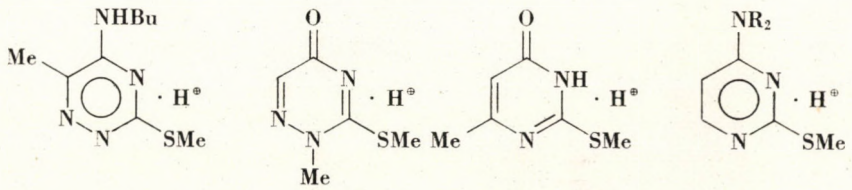
* As to the tautomeric structure, *cf.* [11].

** According to the evidence of the IR spectrum, during salt formation the exocyclic nitrogen atom of **VIII** is protonated.

*** The protonation of **VIII** gives rise to a hypsochromic shift of only 20 cm^{-1} of the carbonyl band. In the IR spectrum of the base this band appears at 1655 cm^{-1}, while in the spectrum of the salt it is found at 1675 cm^{-1} (KBr pellets).

-5(2*H*)-ones **(XII)** containing a cross-conjugated chromophoric system, it nevertheless does not contradict structure **IV** which contains an aromatic triazine ring. It is namely known, partly from our own studies, partly from those of other investigators, that the UV spectra of the *cations* of 1,2,4-triazine (and even of pyrimidine) derivatives related to **IV** have always only a single maximum, irrespectively of whether the corresponding neutral species itself contains a continuous, cross-conjugated, or even aromatic chromophoric system. The spectra of the cations of 3-methylthio-5-butylamino-6-methyl-1,2,4-triazine **(XIII)** [6], 2-methyl-3-methylthio-1,2,4-triazin-5(2*H*)-one **(XIV)** [7], 2-methylthio-6-methyl-4(3*H*)-pyrimidinone **(XV)** [9] and of 2-methylthio-4-aminopyrimidines **(XVI)** [10] may serve as examples.

Scheme 4



	XIII	XIV	XV	XVI
λ_{max} (log ε)	250 (4,28)	235 (4,32)	232 (4,19)	R=H: 241 (4,45) R=Me: 251 (4,41)
ref.:	[6]	[7]	[9]	[10]

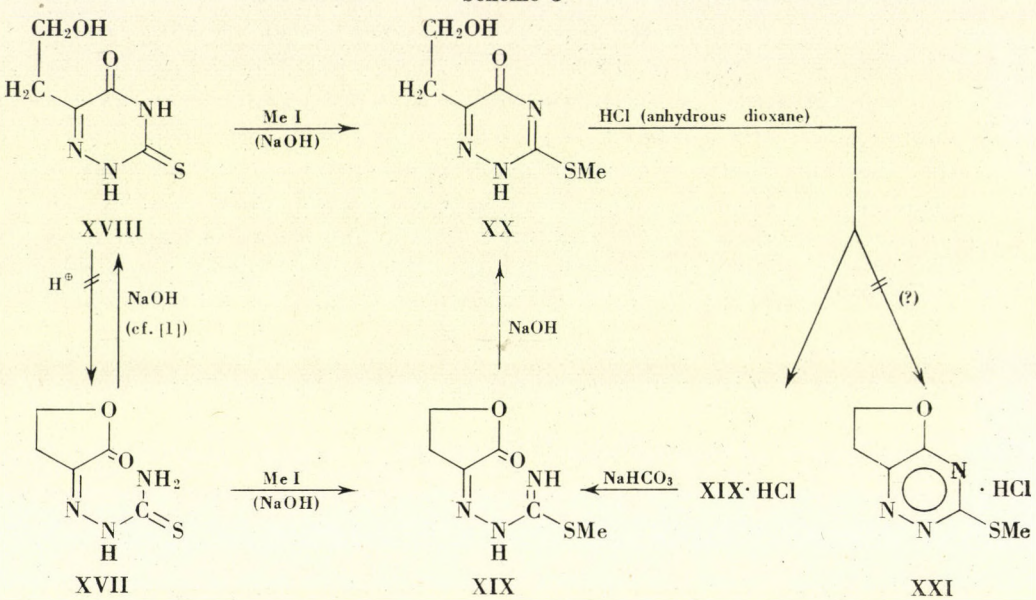
Thus, in order to prove the structures of the hydrochlorides **IV** (or of the analogues), their UV spectra taken in alcoholic or aqueous *alkaline* solutions are to be examined. The spectra obtained in such solutions were found to have changed substantially. In the case of **IVb,** *e.g.*, the following maxima were observed λ_{max} (log ε): 229 (4.23); 242 (shoulder; 4.10); 302 (3.70). This spectrum is practically identical with that of 3-methylthio-5-butylamino-6-methyl-1,2,4-triazine **(XIII)** as the *free base* [6] [λ_{max} (log ε): 234 (4.28); ~250 (shoulder; 4.15); 303 (3.73)], thus it proves that in the *free base* corresponding to **IVb** the triazine ring is, indeed, aromatic. This result is explainable if and only if structures **IV** are correct.

*

In the further work, attempt was made to convert similarly 3-methylthio-6-(2-hydroxyethyl)-1,2,4-triazin-5(2*H*)-one **(XX),** the analogue of **IIa** containing one methylene group less in the side chain, and readily obtainable from **XVII** [1] through **XVIII** (*cf.* [1]) or **XIX,** into the corresponding furo[2,3-e]-[1,2,4]triazine derivative **(XXI).**

Refluxing of **XX** in dry dioxane or dry methanol, while a stream of dry hydrogen chloride was passed through the solution, however, did not give **XXI**

Scheme 5



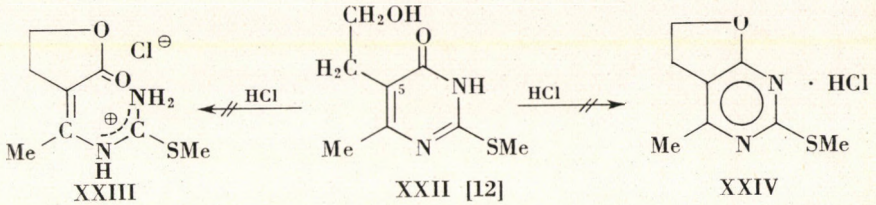
expected by analogy; only the hydrochloride of **XIX** could be isolated besides considerable amounts of unidentified decomposition products. The isomerization **XIX** $\rightleftarrows$ **XX** may, of course, be envisaged as a reversible O $\rightleftharpoons$ N acyl migration; therefore, in accordance with the general experience, the formation of the *N*-acyl derivative **(XX)** is favoured in basic medium, while in acid medium the hydrochloride of the *O*-acyl derivative **(XIX)** is formed preferentially.

The intermediate **VII** ($n = 1$; R = Me) of the conversion **XX** $\rightarrow$ $\rightarrow$ **XIX** · HCl is of the same type as the intermediate **VII** ($n = 2$) of the reaction **II** $\rightarrow$ **IV** discussed above. However, when $n = 1$, only the product originating from the other possible mode of cleavage (see reaction path **b**, Scheme 3) of the intermediate could be isolated.

Again, these considerations furnish an explanation for our experimental finding that **XVIII** may neither by treatment with aqueous hydrochloric acid nor by dry hydrogen chloride in anhydrous dioxane be reconverted into **XVII** but, instead, it is decomposed into unidentifiable products. The cause of the difference between the reactivities of **XVIII** and **XX** lies again in the fact that, in contrast to **XX** and the isomeric **XIX**, neither **XVIII** nor the isomeric **XVII** are basic.

The pyrimidine analogue **XXII** [12] of **XX**, when treated with dry hydrogen chloride in anhydrous dioxane, reacts in an entirely different manner: neither is its pyrimidine ring cleaved to give **XXIII**, nor is the furo[2,3-d]pyrimidine derivative **XXIV**, an analogue of the hypothetical **XXI**, formed. Instead, simple salt formation occurs, although the amino derivative **XXV** (to which

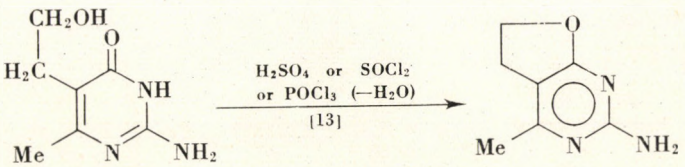
Scheme 6



XXIII XXII [12] XXIV

XXIV would be an analogue) may, according to SCHRAGE and HITCHINGS [13], easily be prepared.

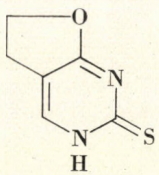
Scheme 7



XXV

Thus, here again a substantial difference is found between the reactivities of a 1,2,4-triazine and its pyrimidine analogue, the cause of this difference being — similarly to a case reported previously [6] — again the different site of protonation of the triazine **XX** and the pyrimidine **XXII.***

Since cyclization according to SCHRAGE and HITCHINGS may be rated as more forceful than our method using hydrochloric acid, the cyclization of **XVIII** to yield **XXVI** by the former technique was also tried. However, none of the recommended reagents (sulfuric acid, thionyl chloride, phosphoryl chloride) proved to be suitable for the preparation of **XXVI,** since **XVIII** was decomposed by all of them.



XXVI

Experimental**

α-Oxo-δ-hydroxyvaleric acid semicarbazone (VI)

Crude α-ethoxalyl-γ-butyrolactone [14] of approximately 90% purity (11 g; 53 mmoles) was refluxed 1 hr. with a mixture of conc. H_2SO_4 (6 ml) and water (24 ml). After cooling, a

* According to the IR spectra, the analogue of **XXII** carrying a hydrogen atom instead of the side chain attached to C-5 is protonated during salt formation at the carbonyl oxygen (and, presumably, this holds also for **XXII** itself). Consequently, a salt containing an aromatized pyrimidine ring and, therefore, less sensitive to nucleophilic attack is formed [6].

** All m.p.'s are uncorrected.

solution of NaOH (8.0 g, in 20 ml of H_2O) and semicarbazide (3.25 g; 43 mmoles) were added and refluxing was continued for 1 hr. The reaction mixture was allowed to stand in a refrigerator, the crystals were filtered off, washed with a small amount of water and dried in air at 80° to yield 3.4 g (41.7%) of **VI**, colourless needles, m.p. 192—193° (dec.; from water).

$C_6H_{11}N_3O_4$ (189.2). Calcd. C 38.09; H 5.86; N 22.21. Found C 38.15, 38.11; H 5.74, 5.83; N 22.15, 22.65%.

The product did not change on refluxing with 1 *N* aqueous NaOH; in contrast to the corresponding thiosemicarbazone [1] it did not cyclize to **III**.

3-Methylthio-6-(3-hydroxypropyl)-1,2,4-triazin-5(2*H*)-one (IIa)

To a mixture, consisting of **I** [1] (8.0 g; 43 mmoles), NaOH (1.8 g; 45 mmoles) and water (50 ml), methyl iodide (7.2 g; 50 mmoles) was added by drops under continuous stirring. Stirring was continued for 2 hrs.; after approximately ½ hr. crystals began to precipitate. The reaction mixture was allowed to stand in a refrigerator, the crystals were filtered off, washed with ice-water and dried over P_2O_5 to yield 8.2 g (94%) of **IIa**, colourless crystals, m.p. 175—176° (from ethanol-petrol ether, 1 : 1).

$C_7H_{11}N_3O_2S$ (201.2). Calcd. C 41.77; H 5.51; S 15.93. Found C 42.06, 41.80; H 4.94, 5.44; S 16.05, 16.04%.

3-Ethylthio-(IIb) and 3-benzylthio-6-(3-hydroxypropyl)-1,2,4-triazin-5(2*H*)-one (IIc)

were prepared analogously;

IIb, yield 61%, colourless crystals, m.p. 133—134° (from acetone). $C_8H_{13}N_3OS$ (215.3). Calcd. S 14.89%. Found 14.61, 14.67%.

IIc, yield 95%, colourless crystalline powder, m.p. 140—141° (from acetone). $C_{13}H_{15}N_3O_2S$ (277.3). Calcd. N 15.61; S 11.56. Found N 15.85; S 11.39, 11.40%.

3-(2-Carboxyethylthio)-6-(3-hydroxypropyl)-1,2,4-triazin-5(2*H*)-one (IId)

To a solution of **I** [1] (3.0 g; 16 mmoles) and NaOH (0.64 g; 16 mmoles) in water (15 ml), a solution of β-bromopropionic acid (3.1 g; 20 mmoles) and NaOH (0.8 g; 20 mmoles) in water (15 ml) was added. The mixture was refluxed 20 minutes and, after cooling, acidified with conc. HCl. The precipitated colourless crystals were filtered off, washed with a small amount of water, and dried in air at 60° to yield 2.6 g (63%) of **IId**, m.p. 197—198° (dec.) (from water).

$C_9H_{13}N_3O_4S$ (259.3). Calcd. N 16.21; S 12.36. Found N 16.42, 16.46; S 11.86%.

3-Methylthio-7,8-dihydro-6*H*-pyrano[2,3-e][1,2,4]triazine hydrochloride (IVa)

Into a solution of **IIa** (10 g; 50 mmoles) in *anhydrous* dioxane (200 ml) a stream of dry HCl was introduced. The oily residue obtained on evaporation of the solvent, was boiled up in water (150 ml) and rapidly cooled. The crystalline product was filtered off and dried over P_2O_5 to yield 6.3 g (58%) of **IVa** as colourless needles, m.p. 155—156° (from acetone).

$C_7H_{10}ClN_3OS$ (219.7). Calcd. Cl 16.14; S 14.59. Found Cl 15.71, 16.27; S 14.12, 14.27%.

3-Ethylthio- (IVb) and 3-benzylthio-7,8-dihydro-6*H*-pyrano[2,3-e][1,2,4]triazine · HCl (IVc) were prepared analogously;

IVb, yield 51%, colourless crystalline powder, m.p. 124—125° (from acetone-water, 1 : 1 v/v). $C_8H_{12}ClN_3OS$ (233.7). Calcd. Cl 15.17; N 17.98; S 13.72. Found Cl 15.11, 15.48; N 18.08, 18.35; S 13.71, 13.37%.

IVc, yield 32%, colourless needles, m.p. 150—151° (from acetone). $C_{13}H_{14}ClN_3OS$ (295.8). Calcd. N 14.21; S 10.84. Found N 14.01, 14.27; S 10.56, 10.43%.

7,8-Dihydro-6*H*-pyrano[2,3,e][1,2,4]triazin-3(2*H*)-one hydrochloride (V)

(a) A mixture of **IIa** (10 g; 50 mmoles) and 20% aqueous HCl (100 ml) was refluxed 3 hrs in a hood (evolution of CH_3SH), and evaporated to dryness in vacuum. The crystalline

residue was boiled with acetic acid (200 ml) until completely dissolved. A stream of dry HCl gas was introduced for a few minutes into the hot solution whereby a colourless crystalline product separated. This was filtered off after cooling, washed with ether and dried over P_2O_5 to yield 6.4 g (74%) of **V**, m.p. 230—232°. The product was pure without further crystallization.

$C_6H_8ClN_3O_2$ (189.6). Calcd. Cl 18.70; N 22.16. Found Cl 18.89, 19.16; N 21.84, 21.70%.

(b) Starting with **IVa** (1.4 g; 6.4 mmoles) and proceeding analogously, 1.09 (82%) of **V** was obtained. M.p. and mixed m.p. with the product prepared according to *(a)*: 230—232°. The products proved to be identical also by the IR spectra.

In order to prepare the corresponding *free base*, an ethereal solution of diazomethane was added by drops, under continuous stirring, to a suspension of the salt **V** (6.5 g; 34 mmoles) in dry dioxane (40 ml) until the diazomethane was just in excess. The colourless crystals were filtered off and washed with ether to yield 5.1 g (97%) of the free base, m.p. 249—251° (dec.) (from aqueous ethanol).

$C_6H_7N_3O_2$ (153.1). Calcd. C 47.05; H 4.61; N 27.44. Found C 46.93, 46.81; H 4.56, 4.56; N 27.49, 27.24%.

3-Amino-6-(3-hydroxypropyl)-1,2,4-triazin-5(2*H*)-one (VIII)

IIa (2.0 g; 10 mmoles) and ethanol (10 ml) saturated previously with NH_3 at 0° were heated in a sealed tube 8 hrs at 120°. After cooling, the mixture, which smelled strongly of CH_3SH, was filtered and the yellowish crystalline product washed with ethanol to yield 1.1 g (65%) of **VIII**, colourless plates, m.p. 267—268° (from water).

$C_6H_{10}N_4O_2$ (170.2). Calcd. C 42.35; H 5.92; N 32.92. Found C 42.66, 42.27; H 5.64, 5.68; N 32.67%.

Hydrochloride

VIII (2.0 g; 11.8 mmoles) was refluxed ½ hr. with 20% aqueous HCl (20 ml). The mixture was evaporated to dryness in vacuum and the solid residue boiled up with a mixture of ethanol (30 ml) and conc. aqueous HCl (3 ml). On cooling 1.5 g (62%) of **VIII** · HCl deposited; it was filtered off and washed with ethanol; colourless crystalline powder, m.p. 183—184° (dec.) (from ethanol containing some HCl).

$C_6H_{11}ClN_4O_2$ (206.6). Calcd. Cl 17.16. Found 16.75, 17.04%.

Treatment with aqueous $NaHCO_3$ reconverted the salt into the base, in approximately 80% yield. (Identification: m.p., mixed m.p., and IR spectrum).

3-Thio-6-(2-hydroxyethyl)-1,2,4-triazine-3,5(2*H*,4*H*)-dione (XVIII)*

α-Oxo-γ-butyrolactone thiosemicarbazone **(XVII)** [1] (1.7 g; 10 mmoles) was refluxed 10 minutes** with a solution of NaOH (0.4 g; 10 mmoles) in water (7 ml); the solution was rapidly cooled to room temperature and acidified with conc. aqueous HCl to Congo indicator. On standing in a refrigerator, crystallization slowly started. The product was filtered off by suction, washed with a small amount of water, and dried in air at 80° to yield 1.6 g (94%) of **XVIII** in form of a colourless crystalline powder, m.p. 194—195° (from water).

$C_5H_7N_3O_2S$ (173.2). Calcd. N 24.27; S 18.51. Found N 24.00, 23.76; S 18.17; 18.19%.

3-Thio-6-(2-benzoyloxyethyl)-1,2,4-triazine-3,5(2*H*,4*H*)-dione

To an aqueous alkaline solution of **XVIII**, prepared from α-oxo-γ-butyrolactone thiosemicarbazone **(XVII)** [1] (1.7 g; 10 mmoles) as above, benzoyl chloride (1.15 ml; 10 mmoles) was added by drops, under continuous stirring at room temperature. Stirring was continued for 2 hrs; after approximately ½ hr. crystallization started. The mixture was allowed to stand overnight in a refrigerator, and the thick crystalline paste thus obtained filtered by suction. The product was washed first with water and then with a small amount of acetone, and dried in air

* For the method of preparation *cf.* [1], in which case, however, **XVIII** was further transformed without isolation.

** By prolonged refluxing the product was damaged and the yield, consequently, was considerably lowered.

at 80° to yield 2.0 g (72%) of a colourless crystalline powder, m.p. 167—168° (from isopropanol).
$C_{12}H_{11}N_3O_3S$ (277.3). Calcd. N 15.15; S 11.56. Found N 14.74, 15.02; S 11.47, 11.25%.

α-Oxo-γ-butyrolactone *S*-methyl-iso-thiosemicarbazone (XIX)

To a mixture of **XVII** [1] (1.7 g; 10 mmoles) and methanol (50 ml), methyl iodide (2.5 ml; 40 mmoles) was added by drops under vigorous stirring. Stirring was continued until a clear solution was obtained (approximately 24 hrs). The solution was subsequently concentrated to approximately 10 ml in vacuum and the product precipitated, after cooling, by adding to the solution twice its volume of ether. The product was dried in air to yield 3.0 g (95%) of **XIX** · HI, m.p. 220—225° (dec.). From this the free base (1.8 g; 96%) was liberated by rubbing with 10% aqueous $NaHCO_3$ solution, m.p. 170—171° (from water).
$C_6H_9N_3O_2S$ (187.2). Calcd. N 22.44; S 17.20. Found N 22.32, 22.34; S 16.63, 16.93%.

α-Oxo-γ-butyrolactone semicarbazone

A mixture, consisting of α-isonitroso-γ-butyrolactone [15] (1.15 g; 10 mmoles), semicarbazide (0.75 g; 10 mmoles), water (5 ml) and acetic acid (2 drops), was refluxed for 20 min. The product which precipitated on chilling in ice-water, was filtered off, washed with a small amount of water, and dried in air at 80° to yield 0.5 g (32%) of the required semicarbazone; colourless crystals, m.p. 232° (dec.) (from water).
$C_5H_7N_3O_3$ (157.1). Calcd. C 38.22; H 4.49; N 26.74. Found C 38.01; H 4.59; N 26.40%.
In contrast to the corresponding thiosemicarbazone **(XVII)**, this compound could not be rearranged by refluxing with alkali into a 1,2,4-triazine derivative, the sulfur-free analogue of **XVIII**. Under these conditions the semicarbazone remained unchanged as proved by the m.p. and the IR spectrum (presence of a single carbonyl band at 1760 cm^{-1}, in accordance with the γ-lactone-like structure).

3-Methylthio-6-(2-hydroxyethyl)-1,2,4-triazin-5(2*H*)-one (XX)

(a) To an aqueous alkaline solution of 3-thio-6-(2-hydroxyethyl)-1,2,4-triazine-3,5-(2*H*,4*H*)-dione **(XVIII)**, prepared as described above from **XVII** (1.7 g; 10 mmoles), methyl iodide (0.63 ml; 10 mmoles) was added at room temperature and the mixture stirred 2 hrs. After ½ hr. crystallization started. The thick crystalline paste, obtained on allowing the mixture to stand in a refrigerator, was filtered off by suction, the product was washed first with a small amount of water and then with acetone, and dried in air at 80° to yield 1.3 g (70%) of **XX** as a colourless crystalline powder, m.p. 184—185° (from water).
$C_6H_9N_3O_2S$ (187.2). Calcd. N 22.30; S 17.20. Found N 22.31, 22.33; S 16.91, 17.19%.

(b) α-Oxo-γ-butyrolactone *S*-methyl-iso-thiosemicarbazone **(XIX)** (0.6 g; 3.2 mmole) was refluxed ½ hr. with 20% aqueous NaOH (15 ml). After cooling, the solution was acidified with acetic acid and concentrated to approximately 5 ml. Overnight an abundant crystallization took place. The product was isolated as above to yield 0.3 g (50%) of a substance which in every respect (m.p., mixed m.p., IR spectrum) proved to be identical with that prepared according to *(a)*.

3-Benzylthio-6-(2-hydroxyethyl)-1,2,4-triazin-5(2*H*)-one was prepared analogously to the method described above under *(a)*, using benzyl chloride (1.15 ml; 10 mmoles) instead of methyl iodide.
The yield was 1.4 g (54%) of a colourless crystalline powder, m.p. 154—155° (from acetone).
$C_{12}H_{13}N_3O_2S$ (266.3). Calcd. N 15.96; S 12.18. Found N 15.77, 15.96; S 12.30, 12.11%.

Reaction of 3-methylthio-6-(2-hydroxyethyl)-1,2,4-triazin-5(2*H*)-one with hydrogen chloride in dioxane

A stream of dry hydrogen chloride was passed into a boiling solution of **XX** (3.6 g; 20 mmoles) in anhydrous dioxane (80 ml). The solution rapidly became deeply coloured and,

after approximately 5 min. it gave a reddish brown precipitate. The introduction of HCl was discontinued and the solvent evaporated in vacuum. The residue* was rubbed with 10% aqueous $NaHCO_3$ solution (15 ml), the insoluble material filtered off, washed with water and dried in air at 80° to yield 1.2 g (33%) of α-oxo-γ-butyrolactone *S*-methyl-iso-thiosemicarbazone **(XIX)** as small yellowish crystals; m.p. and mixed m.p. with an authentic sample (see above): 171—172°.

3-Amino-6-(2-hydroxyethyl)-1,2,4-triazin-5(2*H*)-one

3-Methylthio-6-(2-hydroxyethyl)-1,2,4-triazin-5(2*H*)-one **(XX)** (2.0 g; 11 mmoles) and ethanol (10 ml) saturated previously with ammonia at 0° were heated in a sealed tube for 8 hrs to 120°. After cooling, the reaction mixture smelling strongly of methanethiol was filtered, and the yellowish crystals obtained were washed with ethanol to yield 1.4 g (84%) of the required product. Colourless crystals, after recrystallization from water, m.p. 268—269°.

$C_5H_8N_4O_2$ (156.1). Calcd. C 38.46; H 5.16; N 35.88. Found C 38.46; H 5.17; N 35.46, 35.31%.

Reaction of 2-methylthio-5-(2-hydroxyethyl)-6-methyl-4(3*H*)-pyrimidinone (XXII) with hydrogen chloride in dioxane

Into a boiling solution of **XXII** [12] (2.0 g; 10 mmoles) in anhydrous dioxane a stream of dry HCl was introduced for 20 min. The colourless crystals obtained on cooling were filtered off, washed with ether and dried in air to yield 2.3 g (97%) of **XXII** · HCl, m.p. 194—195° (dec.) (obtained by precipitation from an ethanolic solution containing HCl, by the addition of ether).

$C_8H_{13}ClN_2O_2S$ (236.7). Calcd. Cl 14.98. Found 15.19 and 15.33%.

The fact that the product was really the hydrochloride of the starting compound and not that of a rearranged product produced by some deeper change, was proved by treatment with aqueous $NaHCO_3$ solution which reconverted it into **XXII.**

The UV spectra of some compounds were taken by Dr. L. LÁNG and microanalyses were performed in the Microanalytical Laboratories (Head: Mrs. I. BALOGH-BATTA) of this Institute by Mrs. S. VISZT-SIMON, Mrs. I. ZAUER-CSÜLLÖG and Miss K. ÓFALVI, to whom all the thanks of the authors are due. The authors finally should like to express their thanks to *Egyesült Gyógyszer és Tápszergyár (United Works of Pharmaceutical and Dietetic Products)*, Budapest, for financial support.

SUMMARY

3-Alkylthio-6-(3-hydroxypropyl)-1,2,4-triazin-5(2*H*)-ones **(IIa-c)**, on treatment with hydrogen chloride in anhydrous dioxane, are cyclized to the corresponding 3-alkylthio-7,8--dihydro-6*H*-pyrano[2,3-e][1,2,4]triazine hydrochlorides **(IVa-c)** which may be hydrolyzed by aqueous hydrochloric acid to 7,8-dihydro-6*H*-pyrano[2,3-e][1,2,4]triazin-3(2*H*)-one hydrochloride **(V).** Compounds **IIa-c** may also directly be transformed, by treatment with aqueous hydrochloric acid, into **V.**

Neither the 3-amino analogue **(VIII)** of **IIa-c**, nor compound **I,** which differs from **IIa-c** only by the absence of an alkyl group at the sulfur atom, can undergo a similar cyclization reaction.

3-Methylthio-6-(2-hydroxyethyl)-1,2,4-triazin-5(2*H*)-one **(XX)**, the lower homologue of **IIa,** on the other hand, is isomerized by similar treatment into the *S*-methyl-iso-thiosemicarbazone **(XIX)** of α-oxo-γ-butyrolactone. Again, compound **XVII,** which differs from **XX** only by the fact that it is not alkylated at the sulfur atom, is stable to treatment with hydrochloric acid. The same is true for **XXII,** the pyrimidine analogue of **XX,** which gives only the salt on treatment with hydrochloric acid. An interpretation of these experimental results is suggested.

* This crude material proved to be the hydrochloride of the rearranged product **XIX,** and not that of the starting compound **XX,** because its IR spectrum was completely identical with that of the authentic hydriodide (*cf.* below) of **XIX.**

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STEREOCHEMICAL STUDIES, III* QUATERNIZATION OF 1,2-DISUBSTITUTED-1,2,3,4-TETRAHYDROISOQUINOLINES, I

PREPARATION OF STEREOISOMERIC 1-METHYL-6,7-DIMETHOXY-1,2,3,4-TETRAHYDROISOQUINOLINIUM SALTS

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Introduction

Examination of the quaternization reactions of cyclic tertiary nitrogen compounds is one of the actual problems in organic chemistry. Subsequent to the classical investigations [1—6] and then to the work of FODOR and coworkers concerning mainly the quaternization reaction of tropane alkaloids [7—9], recently an intensive research commenced in this field [10—30]. Despite of the great number of publications, the factors determining the mechanism and stereoselectivity of quaternization reactions have not yet been elucidated [31].

As a continuation of our examinations concerning the quaternization of morphine derivatives [32—34], the quaternization of 1,2-disubstituted-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline derivatives was studied to supply further data for the elucidation of the above problem. Further, the authors wished to obtain data concerning the conformational relations of tetrahydroisoquinoline derivatives, not investigated in detail hitherto.

In the present communication, the synthesis of 1-methyl-2-alkyl-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline derivatives **(IIb-f)** will be described, with the products obtainable from them by "direct" and "reverse" quaternization. We have reported earlier [38, 39] on the paper chromatographic investigation of the above-mentioned compounds, the corresponding hydriodides, and of some related derivatives, in connection with a study of the correlation between R_f values and chemical structure.

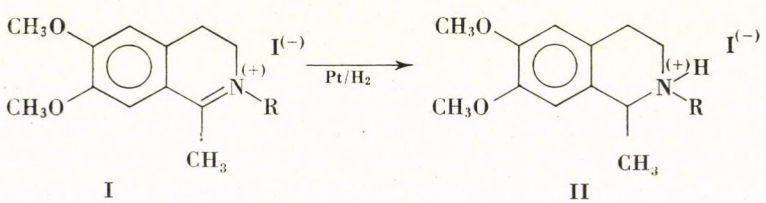
* As Parts I and II of this series are regarded: BERNÁTH, G., SZABÓ, J. A., KOCZKA, K., VINKLER, P.: Acta Chim. Acad. Sci. Hung. **51**, 339 (1967) and [34], respectively.

Synthesis of the tertiary compounds

One of the parent compounds of the series examined by us is 1,2-dimethyl-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline, *i.e.* carnegine (HI = **IIb**), isolated from the cactus species *Carnegiea gigantea* (Engelm.) indigenous to North America [40, 41]. The first synthesis of carnegine was achieved by SPÄTH [42]. Later, in the course of the synthesis of a number of homologous and related compounds prepared mainly for pharmacological examination, several other reaction conditions were tried [43—47]. In the synthesis of 1-methyl-6,7-dimethoxy-3,4-dihydroisoquinoline (HI = **Ia**) we found, in accordance with recent data of literature [43, 46, 47], that ring closure with phosphorus oxychloride is the most suitable method, particularly in the case of preparing larger amounts.

The reaction of 1-methyl-6,7-dimethoxy-3,4-dihydroisoquinoline with methyl iodide was made by refluxing the reagents in methanol for 4—5 hours. With the other alkyl iodides, refluxing was conducted in ethanol. The corresponding quaternary iodides were obtained in each case in satisfactory yields. The only exception was the reaction with isobutyl iodide that gave the hydriodide (**Ia**) of the initial substance. However, this result is in accordance with the observations of KNABE and GRUND [48] made in connection with the attempted quaternization of papaverine with *t*-butyl bromide.

A number of methods are known for the reduction of analogous 3,4-dihydroisoquinoline derivatives [42, 43, 49]. We prepared the N-alkyl-1-methyl-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinolinium iodide derivatives (**IIb-f**) by hydrogenation in ethanolic medium at room temperature and atmospheric pressure, in the presence of ADAMS PtO_2 catalyst (Fig. 1). The homologues prepared in this way (**IIb-f**) are listed in Table II.



I II

a: R = H; b: R = CH_3—; c: R = C_2H_5—; d: R = *n*-C_3H_7—; e: R_2 = *n*-C_4H_9—; f: R = C_6H_5—CH_2—

Fig. 1

The compounds may also be synthesized from salsolidine (HI = **IIa**), obtainable in good yield [50], by reducing the N-acyl derivatives with $LiAlH_4$ [51]. However, owing to the poor yields of the latter reaction, the way of synthesis followed by us appears to be more convenient.

Table I

Melting points and analyses of 1-methyl-2-alkyl-6,7-dimethoxy-3,4-dihydroisoquinolinium iodide homol—ogues **(Ia-f)**[a]

Compound	R	Melting point, °C (solvent)	Formula (molecular weight)	Analytical data, calculated, % found, %		
				C	H	I^-
1-Methyl-6,7-dimethoxy-3,4-dihydroisoquinolinium iodide **(Ia)**	H	218[b] (methanol)	$C_{12}H_{16}O_2NI$ (333.18)	43.26 43.63	4.84 4.94	38.09 37.70
1,2-Dimethyl-6,7-dimethoxy-3,4-dihydroisoquinolinium iodide **(Ib)**	Me	181—182[c] (methanol)	$C_{13}H_{18}O_2NI$ (347.20)	44.97 45.26	5.23 5.40	36.55 36.86
1-Methyl-2-ethyl-6,7-dimethoxy-3,4-dihydroisoquinolinium iodide **(Ic)**	Et	170 (methanol—ether)	$C_{14}H_{20}O_2NI$ (361.23)	46.55 46.23	5.58 5.40	35.14 34.86
1-Methyl-2-*n*-propyl-6,7-dimethoxy-3,4-dihydroisoquinolinium iodide **(Id)**	*n*-Pr	178—179 (ethanol)	$C_{15}H_{22}O_2NI$ (375.26)	48.01 47.85	5.91 6.02	33.81 34.06
1-Methyl-2-*n*-butyl-6,7-dimethoxy-3,4-dihydroisoquinolinium iodide **(Ie)**	*n*-Bu	180—181 (ethanol)	$C_{16}H_{24}O_2NI$ (389.29)	49.38 49.06	6.21 6.42	32.61 32.82
1-Methyl-2-benzyl-6,7-dimethoxy-3,4-dihydroisoquinolinium iodide **(If)**	Bz	171—172 (ethanol)	$C_{19}H_{22}O_2NI$ (423.30)	53.90 53.54	5.20 4.98	29.98 30.22

a) The melting points and analyses refer to substances dried for 2 hrs at 117° and 25 Torr.
b) M. p. of the base: 106—107° [54].
c) Lit. [42]: m. p. 176—178°. The substance obtained from aqueous methanol contains crystal water. M. p. 100—101°; lit. [60] m.p. 98°.

Table II

Melting points and analyses of 1-methyl-2-alkyl-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinolinium iodide homologues **(IIb—f)**[a]

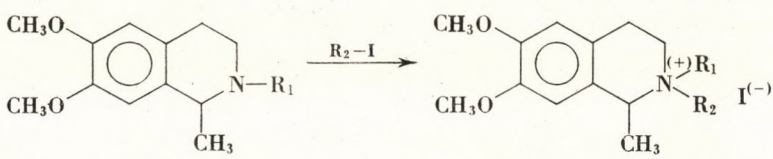
Compound	R	Melting point, °C (solvent)	Formula (molecular weight)	Analytical data, calculated, % found, %			Note
				C	H	I⁻	
Carnegine.HI	Me	220—221 (methanol)	$C_{13}H_{20}O_2NI$ (349.22)	44.71 44.72	5.77 5.52	36.34 36.11	*b)*
N-Ethylsalsolidine.HI	Et	204—205 (methanol)	$C_{14}H_{22}O_2NI$ (363.25)	46.29 46.42	6.10 6.36	35.14 34.93	*c)*
N-*n*-Propylsalsolidine.HI	*n*-Pr	196—197 (methanol)	$C_{15}H_{24}O_2NI$ (377.27)	47.76 48.01	6.41 6.65	33.64 33.75	
N-*n*-Butylsalsolidine.HI	*n*-Bu	133—134 (ethanol—ether)	$C_{16}H_{26}O_2NI$ (391.30)	49.11 48.90	6.70 7.02	32.43 32.47	*d)*
N-Benzylsalsolidine.HCl	Bz	161 (acetone—ether)	$C_{19}H_{24}O_2NCl$ (333.87)	68.34 67.98	7.01 6.93		*e)*

a) The analyses refer to substances dried for 2 hrs at 117° and 25 Torr.
b) Carnegine.HCl, m. p. 210—212° [42].
c) (—)-Base, *cf.* [51].
d) Picrate, m. p. 152—153° (from ethanol). $C_{22}H_{28}N_4O_9$ (492.50). Calculated: C 53.65; H 5.73; N 11.37. Found: C 53.88; H 5.62; N 11.58%.
e) Calculated Cl^-: 10.63, found: 10.32%. M. p. of the base: 66—67 °C (from ether).

The selectivity of quaternization

Already the classical investigations of the stereochemistry of nitrogen [1, 2] and mainly the research works of WEDEKIND and collaborators [3] included model compounds of tetrahydroquinoline and tetrahydroisoquinoline skeleton. Recently again, a great number of tetrahydroisoquinoline derivatives have been prepared, mainly for pharmacological purposes, but the stereochemistry of the quaternization reaction resulting these compounds were not examined in detail, not considering here the hardly evaluable, classical investigations. No attention was paid to the stereohomogeneity of the products, but the pharmacological experiments were carried out with the quaternization products not analysed from a stereochemical point of view, though it was obviously possible and physical data actually indicated that the products used were mixtures of stereoisomeric quaternary salts [35—37]. On the other hand, it is known for more than sixty years [6] that stereoisomeric quaternary salts may have different physiological effect.

In the present series of experiments, simple alkyl and benzyl radicals as substituents were varied on the nitrogen atom of 1-methyl-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline (salsolidine) (HI = **IIa**) used as the model compound. Investigation of systems with other substituents in position 1 is in progress in our laboratory.



IIIa, b; IVa, b;
Va, b; VIa, b.

IIIa: $R_1 = CH_3-$, $R_2 = C_2H_5-$; IIIb: $R_1 = C_2H_5-$, $R_2 = CH_3-$.
IVa: $R_1 = CH_3-$, $R_2 = n\text{-}C_3H_7-$; IVb: $R_1 = n\text{-}C_3H_7-$, $R_2 = CH_3-$.
Va: $R_1 = CH_3-$, $R_2 = n\text{-}C_4H_9-$; Vb: $R_1 = n\text{-}C_4H_9-$, $R_2 = CH_3-$.
VIa: $R_1 = CH_3-$, $R_2 = C_6H_5-CH_2-$; VIb: $R_1 = C_6H_5-CH_2-$, $R_2 = CH_3-$.

Fig. 2

The bases obtained from **IIb-f** by alkaline treatment were quaternized with an excess of the corresponding alkyl iodide in methanol, acetone or ethanol either at room or reflux temperature. The reactions were evaluated by isolating the products and by examining the crude reaction products by means of proton resonance spectroscopy.

In the course of preparative evaluation of quaternization reactions, if carnegine (HI = **IIb**) is quaternized with ethyl iodide or *n*-propyl iodide, and in the quaternization of N-ethyl- and N-*n*-propylsalsolidine (HI = **IIc** and **IId**) with methyl iodide, the quaternary salt which is the nearly homogeneous main product crystallizing first from the solution in yields of 65 to 75%, is in case of "direct" and "reverse" quaternizations in each experiment a different quaternary compound. On subjecting these quaternary salts to two or three crystallizations, products of constant melting point can be obtained. On further recrystallizations no changes in the infrared or NMR spectra were perceptible either. N-ethylsalsolidine methiodide (**IIIb**), carnegine-*n*-propiodide (**IV**), and N-*n*-propylsalsolidine methiodide (**IVb**) proved to be homogeneous compounds also on the basis of their proton resonance spectra. However, from the mother liquors of the reactions yielding the methyl-ethyl (**IIIa, b**) and methyl-*n*-propyl (**IVa, b**) isomeric salt pairs the stereoisomeric quaternary salt could also be isolated as a by-product in each case.

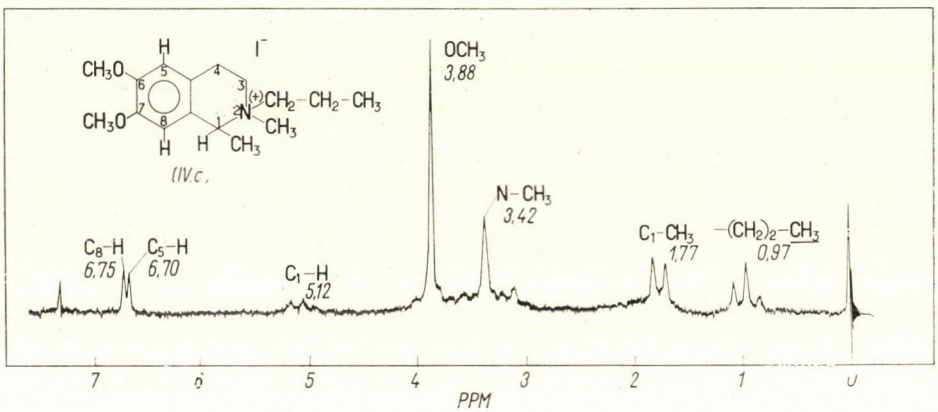


Fig. 3

Also the picrates (*cf.* Table III) of the isomeric salt pairs have been prepared. In several cases these were significantly different in their tendency for crystallization and crystal form, as well.

The accurate quantitative ratios could be established by examining the crude reaction products by NMR spectroscopy.

Fig. 3 shows a typical spectrum of a pure isomeric salt (carnegine-*n*-propiodide, **IVa**), while Fig. 4 that of a crude mixture containing the former isomer together with its diastereomeric pair (**IVb**). Interpretation of spectra of the particular isomers in terms of various protons in the molecule was unambiguous in each case. The chemical shifts of the main assignable protons (in δ ppm) are collected in Table IV. As it is illustrated by Fig. 4, some of the lines in the spectra of reaction mixtures exhibit a resonance doubling due to the

fact that the corresponding protons possess a slightly different chemical shift in the two isomers (see Table IV). The extent and direction of chemical shift differences for a particular proton remained practically unchanged throughout the mixtures of quaternary salts investigated, making thus possible to divide, in accordance with chemical evidences, the isomers into groups A and B.

The relative intensities of lines arising from the two isomers gave a quantitative measure for their proportions in the crude reaction mixtures. In this series of experiments the signals from the C_8 aromatic proton appearing in the spectra of mixtures without overlapping have been chosen as the "analytical" line. Intensity ratios were determined by area measurements with an accuracy of $\pm$ 3%. The results are given in the last column of Table IV.

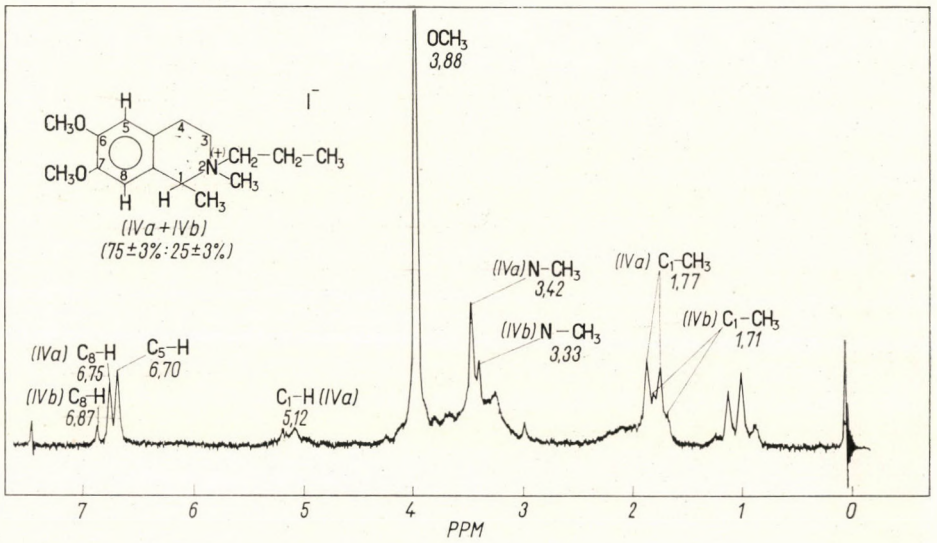


Fig. 4

As it can be seen, the stereoselectivity of both the reaction of carnegine (N-methylsalsolidine) **(HI = IIb)** with alkyl iodides and the quaternization of N-alkylsalsolidine homologues **(HI = IIc-e)** with methyl iodide is moderate. The selectivity of the former reactions is somewhat higher than that of the latter. However, the main product of "direct" and "reverse" quaternizations (quaternary salt type A and B, respectively) is different in case of R_1, R_2 = CH_3—, C_2H_5—, *n*-C_3H_7—, *n*-C_4H_9—.

On the other hand, the quaternization of carnegine with benzyl iodide gave only one quaternary product, at least within the limits of proton resonance spectroscopic evaluation ($\pm$ 3%). The same isomer was formed as main product (55%) in the quaternization of N-benzyl-salsolidine **(HI = IIf)** with methyl iodide, the other isomer being formed in 45% yield. Thus, in contrast to

Table III

Melting points and analyses of carnegine N-alkyl iodides and N-alkylsalsolidine methiodide homologues and of their picrates[a)]

Compound	Melting point, °C (solvent)	Formula (molecular weight)	Analytical data, calculated, % found %			Note
			C	H	I–	
Carnegine ethiodide **(IIIa)**	200—201 (methanol)	$C_{15}H_{24}O_2NI$ (377.27)	47.76 47.89	6.41 6.57	33.64 33.45	*b)*
Carnegine ethiodide picrate	167 (methanol)	$C_{21}H_{26}O_9N_4$ (478.45)	52.72 52.70	5.48 5.05		*d)*
N-Ethylsalsolidine methiodide **(IIIb)**	217—218 (methanol)	$C_{15}H_{24}O_2NI$ (377.27)	47.76 47.61	6.41 6.94	33.64 33.44	*c)*
N-Ethylsalsolidine methiodide picrate	144 (ethanol)	$C_{21}H_{28}O_9N_4$ (478.45)	52.72 52.70	5.48 5.05		*e)*
Carnegine *n*-propiodide **(IVa)**	200—201 (methanol)	$C_{16}H_{26}O_2NI$ (391.30)	49.11 49.28	6.70 6.88	32.43 32.20	*f)*
Carnegine *n*-propiodide picrate	142 (ethanol)	$C_{22}H_{28}O_9N_4$ (492.48)	53.65 54.06	5.73 5.97		*h)*
N-*n*-Propylsalsolidine methiodide **(IVb)**	215—216 (methanol)	$C_{16}H_{26}O_2NI$ (391.30)	49.11 49.42	6.70 6.90	32.43 32.50	*g)*
N-*n*-Propylsalsolidine methiodide picrate	138 (ethanol)	$C_{22}H_{28}O_9N_4$ (492.48)	53.65 54.04	5.73 6.14		*i)*
Carnegine *n*-butiodide **(Va)**	214.5—215.5 (ethanol)	$C_{17}H_{28}O_2NI$ (405.31)	50.37 50.36	6.96 6.90	31.31 31.37	*j)*
N-*n*-Butylsalsolidine methiodide **(Vb)**	213.5—214.5 (ethanol)	$C_{17}H_{28}O_2NI$ (405.31)	50.37 50.53	6.96 6.52	31.31 31.40	*k)*
Carnegine benziodide **(VIa)**	165—166 (ethanol)	$C_{20}H_{26}O_2NI$ (439.35)	54.67 54.38	5.96 5.98	28.88 28.54	*l) m)*

a) The analyses refer to substances dried 2 hrs at 117° and 25 Torr. Stereochemical homogeneity was established by NMR spectroscopy. Chemical shifts are listed in Table **IV.**
b) Contains 20% of **IIIb.** Mixed m. p. of **IIIa** and **IIIb:** 192—196°.
c) Stereochemically homogeneous; the substance contains no **IIIa** isomer.
d) Fine needles tangled up like cotton.
e) Poor crystallizability; lentil-shaped crystals.
f) Stereochemically homogeneous; the product contains no **IVb** isomer. Mixed m. p. of **IVa** and **IVb:** 191—193°.
g) Stereochemically homogeneous; contains no **IVa** isomer.
h) Rapidly crystallizing plates.
i) Poor crystallizability; lentil-shaped crystals.
j) Contains about 5—10% of **Vb.** Mixed m. p. of **Va** and **Vb:** 213—214°.
k) A 1 : 3 mixture of **Va** and **Vb.** The picrate crystallized with difficulty.
l) Stereochemically homogeneous; contains no **VIb** isomer.
m) On reacting N-benzylsalsolidine (HI = **IIf**) with methyl iodide the crude reaction mixture contains 45% of **VIb** (see: Table IV). By repeated recrystallization only the **VIa** could be isolated.

Table IV

Proton chemical shifts in isomeric quaternary salts of carnegine and N-alkylsalsolidine, and fractional yields of the isomers in the crude reaction mixtures

Compound	Chemical shifts (ppm)							Percentage ratios of isomers in reactions	
	C_8—H	C_5—H	C_1—H	O—CH_3	N—CH_3	C_1—CH_3	N—CH_2-Ø	*a)*	*b)*
Carnegine hydriodide **(IIb)**									
stable isomer (65%)	6.59	6.67	4.54	3.88	2.92	1.90			
less stable isomer (35%)	6.53	6.67	4.83	3.88	2.80	1.73			
Carnegine methiodide	6.70	6.70	5.10	3.88	3.53	1.76		—	
Carnegine ethiodide **(IIIa)**	6.78	6.71	5.14	3.88	3.38	1.78		70	35
N-Ethylsalsolidine methiodide **(IIIb)**	6.89	6.72	5.01	3.87	3.28	1.72		30	65
Carnegine *n*-propiodide **(IVa)**	6.75	6.70	5.12	3.88	3.42	1.77		75	35
N-*n*-propylsalsolidine methiodide **(IVb)**	6.87	6.70	5.06	3.88	3.33	1.71		25	65
Carnegine *n*-butiodide **(Va)**	6.77	6.70	5.14	3.88	3.42	1.78		75	45
N-*n*-Butylsalsolidine methiodide **(Vb)**	6.87	6.70	5.04	3.87	3.33	1.72		25	55
Carnegine benziodide **(VIa)**	6.79	6.72	4.83	3.90	3.29	1.82	5.17 4.81	100	55
N-Benzylsalsolidine methiodide **(VIb)**	6.68	6.70	?	3.86	3.12	1.96	5.39 4.83	0	45

Reaction *a)*: carnegine + alkyl iodide ("direct" quaternization).
Reaction *b)*: N-alkylsalsolidine + methyl iodide ("reverse" quaternization).

the above, in this pair of reactions both "direct" and "reverse" quaternization yielded the same main product.

The configurational assignments of isomeric quaternary salts have usually been based on the method suggested by CLOSS [52]. If a protonated cyclic methylamine (of a given fixed, or preferred ring conformation) exists in two configurations at nitrogen, its proton resonance spectrum frequently exhibits two N-methyl signals associated with the two differently oriented (and hence differently shielded) N-methyl groups. Usually one of these signals is more intense, reflecting the greater stability of one configuration. As far as decision can be made as to the relative stability of the two configurations in the protonated base and, furthermore, the possibility of structural (*e.g.* conformational) differences between tertiary and quaternary salts can be excluded, the difference in the shielding of the N-methyl protons, accompanying a given configurational change in the spectrum of the quaternary salts, may be expected of the same sign as in that of the protonated base, *e.g.* the N-methyl line with greater chemical shift corresponds to *axial* position in both cases.

Though the proton resonance spectrum of carnegine hydriodide involves two N-methyl signals, the application of the CLOSS-method presents difficulties in this case. Namely, the proton resonance analysis of carnegine and salsolidine bases [55] indicated that these bases are conformationally unstable, the methyl group in position 1 has no preferred spatial orientation. Further difficulties arise from the fact that the stability relations of 1,2-disubstituted tetrahydroisoquinoline derivatives are not known in the necessary degree (compare to [56—58, 47]), therefore the conformational assignment of the two isomers of carnegine hydriodide cannot be done, *a priori*, with certainty. Because of the above the determination of the steric structure of diastereoisomers was approached on the basis of other experimental results.

As it can be seen from stereoselectivity data presented in Table IV, the quaternization occurring with greater stereoselectivity (in this case the "direct" quaternization) yields predominantly isomers of type A. On the other hand, equilibration of N-methyl-N-benzyl-salts gives 70—75% of isomer A, indicating that in this isomer the benzyl group assumes a less hindered position, *i.e.* isomer A is more stable than isomer B.

Stability considerations, furthermore, suggest the *trans* position of N-benzyl group relative to C_1-methyl to be more favourable than the *cis* one. This expectation is completely supported by the proton resonance spectra of N-methyl-N-benzyl diastereomeric pair. In case of isomer A the benzyl methylene and benzyl aromatic protons exhibit only a slight extent of magnetic nonequivalence, whereas in isomer B the nonequivalence of these protons is considerable. According to [53] this difference is best interpreted in terms of different hindrance to rotation of benzyl group, *i.e.* large nonequivalence is connected with higher barrier to rotation.

If we assume that in the more stable *trans* N-benzyl quaternary salt, *i.e.* carnegine benziodide **(VIa)**, the N-benzyl group occupies *equatorial* position,

we may assign *pseudo-equatorial* orientation for the methyl group at C_1 and an *axial* orientation at the nitrogen respectively.

Owing to the close similarity between the proton resonance spectra of the diastereomeric mixtures investigated in the present work, we may extend with great probability the conclusion found with the N-methyl-N-benzyl isomers to other quaternary salts. In other words, we may assign isomers of types A and B in each case to those diastereoisomers which have their N-methyl group in *axial* and *equatorial* position, respectively.

As far as the formation of quaternary salts is not accompanied by change in conformation, the above considerations mean that in quaternization the approach from the *equatorial* direction is favoured for the entering alkyl group.

The validity of this conclusion is to be proved by further investigations. Experiments with other 1,2-disubstituted tetrahydroisoquinolines are in progress [59].

Experimental

1-Methyl-6,7-dimethoxy-3,4-dihydroisoquinoline

(a) 150 g (1.06 mole) of phosphorus pentoxide was added to a solution of 52.0 g (0.233 mole) of acetylhomoveratrylamine in 1.2 l of toluene in a 2000-ml round-bottomed flask, and the mixture refluxed in an oil bath. After 20 and another 30 minutes of heating, two 100-g portions (0.70 mole) of P_2O_5 were added to the reaction mixture. After a total reflux period of 2 hrs, the reaction mixture was cooled to room temperature, and 800 ml of water was added in small portions, under cooling. The toluene phase was separated, extracted with three 400-ml portions of 5% HCl, and the combined phosphoric acid and hydrochloric acid solutions were washed twice with 500 ml of ether. The aqueous phase was made alkaline with potassium hydroxide under cooling, and extracted four times with 500 ml of ether. The combined ethereal extracts were dried over sodium sulphate. On evaporation, 40.7 g (85.4%) of 1-methyl-6,7-dimethoxy-3,4-dihydroisoquinoline, m.p. 104—105°, was obtained. Repeated recrystallizations from ether gave m.p. 106° (lit. [54] m.p. 106—107°).

(b) 128 g (0.573 mole) of acetylhomoveratrylamine was dissolved in 300 ml of chloroform in a 1500-ml round-bottomed flask. Under cooling and shaking, 220 g (1.43 mole) of phosphorus oxychloride was added to the solution in small portions. The reaction mixture was refluxed 2 hrs, then evaporated to dryness under reduced pressure. The solid residue was dissolved in 500 ml of water under cooling, the solution made alkaline with potassium hydroxide, extracted with five 600-ml portions of ether, and the combined ethereal extracts, after drying over potassium carbonate, were evaporated to about 400 ml. On cooling, 80.8 g of well-developed crystals separated, m.p. 107—108°. Evaporation of the mother liquor gave further 17.0 g of the substance. Total yield: 83.3%.

1-Methyl-2-n-butyl-6,7-dimethoxy-3,4-dihydroisoquinolinium iodide (Ie)

A solution of 6.0 g (0.029 mole) of 1-methyl-6,7-dimethoxy-3,4-dihydroisoquinoline in 40 ml of anhydrous ethanol was refluxed 6 hrs with 8.0 g (0.044 mole) of *n*-butyl iodide. The reaction mixture was evaporated to one third of the original volume. On cooling, 8.65 g (76.1%) of light yellowish needles separated, m.p. 176—178°. Repeated recrystallizations from ethanol gave m.p. 178—179°. After drying for 2 hrs at 117° and 25 Torr, a substance of correct analytical composition (*cf.* Table I) was obtained.

The 2-ethyl **(Ic)** and 2-*n*-propyl **(Id)** derivatives could be prepared by the above method, employing the corresponding alkyl iodides while the 2-methyl compound **(Ib)** was obtainable by quaternization in methanol; the yields varied from 72—94%. The m.p. values and analytical data of the prepared 1-methyl-2-alkyl-6,7-dimethoxy-3,4-dihydroisoquinolinium iodide homologues **(Ia-f)** are listed in Table I.

Reaction of 1-methyl-6,7-dimethoxy-3,4-dihydroisoquinoline with isobutyl iodide

A solution of 8.0 g (0.04 mole) of 1-methyl-6,7-dimethoxy-3,4-dihydroisoquinoline in 30 ml of acetone was refluxed 6 hrs on a water bath with 10 g (0.055 mole) of isobutyl iodide. Cooling gave 10.7 g of greenish needles, m.p. 210—213°. On repeated recrystallizations from methanol, a substance of m.p. 218° was obtained. The analytical data of this substance were correct for 1-methyl-6,7-dimethoxy-3,4-dihydroisoquinolinium iodide **(Ia)** (cf. Table I).

1-Methyl-2-ethyl-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinolinium iodide **(IIc)**

1.5 g (4.15 millimoles) of 1-methyl-2-ethyl-6,7-dimethoxy-3,4-dihydroisoquinolinium iodide **(Ic)** was dissolved in 30 ml of methanol and hydrogenated at room temperature and atmospheric pressure in the presence of 0.1 g of ADAMS PtO_2 catalyst prehydrogenated in 30 ml of methanol. After the absorption of the calculated amount of hydrogen (1 hr.) the reaction mixture was shaken for another 30 minutes, the catalyst filtered off, and the solution evaporated to about 10 ml. On the addition of ether, 1.35 g (89.5%) of slightly yellowish-greenish needles separated, m.p. 203—204°. Recrystallization of a small portion from methanol gave a product of m.p. 204—205° which had correct analytical composition (cf. Table II).

1-Methyl-2-alkyl-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinolinium iodide homologues **(IIb-f)** could be prepared by the above method in nearly quantitative yields. The melting points and analyses of the substances prepared by us are listed in Table II.

Quaternization of N*-alkylsalsolidine homologues*

(a) Preparative isolation of the isomers. The quaternization of carnegine (HI = **IIb**) with alkyl iodides and the reactions of N-alkylsalsolidine homologues (HI = **IIc-f**) with methyl iodide were carried out by treating 3 to 22 g of the initial base with a 30 to 50% excess of the quaternizing agent in methanol, ethanol or acetone at room temperature, or at the boiling point of the mixture. The reaction mixture was then evaporated and the crude product worked up by repeated recrystallizations from the solvents shown in Table III. The quaternary salts were characterized by preparing the picrates. The melting points and analyses are listed in Table III.

In the reactions of carnegine with ethyl iodide and *n*-propyl iodide, and in those of N-ethylsalsolidine and N-*n*-propylsalsolidine with methyl iodide, in addition to the quaternary salts **(IIIa, IVa** and **IIIb, IVb,** respectively) formed as the main product, smaller quantities of the isomeric compounds **(IIIb, IVb** and **IIIa, IVa,** respectively) were also obtained; the latter products were isolated in the purity indicated in Table III. The two-directional nature of these reactions could thus be evaluated also in preparative way. In the case of the methyl-butyl isomers **(Va, Vb)**, in turn, only spectroscopical evaluation was possible, owing to the mixed crystallization of the salts and to the poor crystallizing properties of the corresponding picrates.

(b) Spectroscopical evaluation. Isomeric ratios were quantitatively established by subjecting the evaporated and homogenized reaction mixtures to analysis by NMR spectroscopy. The quaternization reactions were carried out under the conditions specified in point *(a)*, starting with 0.2—0.3 g of the base.

The NMR measurements were made with a 60 Mc/s *AEI RS2* spectrometer. Deuterochloroform was used as solvent of the test samples, and tetramethylsilane was employed as internal standard. Chemical shifts were determined by the conventional side band technique with an accuracy of ±0.01 ppm. The concentrations of the solutions varied according to the solubility of the sample between 2 and 10% (w/v). The results of NMR measurements are shown in Table IV.

Isomerization of N-benzyl quaternary salts

200 mg carnegine benziodide **(VIa)** in 100 ml of anhydrous chloroform was heated in a sealed tube for 20 hrs at 80 ±2°. The homogenized crystalline substance obtained on evaporation was subjected to NMR analysis. The product contained carnegine benziodide **(VIa)** and N-benzylsalsolidine methiodide **(VIb)** in a ratio of about 3 : 1. The equilibration of a sample enriched in N-benzylsalsolidine methiodide **(VIb)** gave the same ratio.

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SUMMARY

Some homologues of 1-methyl-2-alkyl-6,7-dimethoxy-3,4-dihydroisoquinolinium iodide and 1-methyl-2-alkyl-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinolinium iodide have been prepared. The selectivity has been studied in the quaternization reactions of 1,2-dimethyl-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline (carnegine) with alkyl iodides, and of 1-methyl-2-alkyl-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline (N-alkylsalsolidine) homologues with methyl iodide. It has been shown by the preparative processing of the reaction mixtures, and by analysis of the crude reaction products by proton resonance spectroscopy that in the quaternization of both carnegine with alkyl iodides and in that of N-alkylsalsolidine homologues with methyl iodide, only a moderate selectivity can be attained, while the quaternization of carnegine with benzyl iodide occurs entirely selectively. By evaluating the selectivity of the examined quaternization reactions, from NMR data and equilibration of benzyl quaternary salts it seems likely that in the quaternary salts formed as the main products, the substituent introduced by quaternization occupies *equatorial* position on the nitrogen atom.

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STRUCTURE AND SYNTHESIS OF OROBOSIDE AND A NEW SYNTHESIS OF SANTAL

(SHORT COMMUNICATION)

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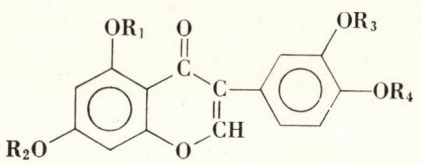
Oroboside was originally isolated from *Orobus tuberosus* L. [1], but subsequently found also in *Lathyrus macrorhizus* [2]. As to its structure, its glycosidic nature was soon established, the sugar portion being D-glucose, the glucosidic bond having β-configuration [1], and the aglycone (orobol) being 5,7,3',4'-tetrahydroxyisoflavone [3, 4]. The structure of orobol (= norsantal) was corroborated first by its synthesis by demethylation of naturally occurring santal [4], and subsequently by its total synthesis [5]. Up to the present, however, the site of attachment of the sugar to the aglycone has been unknown.

Since in naturally occurring isoflavone glycosides known up to the present (daidzin, ononin, genistin



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a: $R_1 = R_3 = R_4$ = acetyl, $R_2 = H$
b: $R_1 = R_3 = R_4$ = acetyl, R_2 = tetraacetyl-β-D-glucopyranosyl
c: $R_1 = R_3 = R_4 = H$, $R_2 = \beta$-D-glucopyranosyl
d: $R_1 = R_2 = R_3 = R_4 = H$ (orobol)
e: $R_1 = R_3 = R_4$ = acetyl, $R_2 = CH_3$
f: $R_1 = R_3 = R_4 = H$, $R_2 = CH_3$

tectoridin, iridin, *etc.*) the sugar is in most cases attached to the hydroxyl group in position 7 of the aglycone, the same mode of attachment has been supposed for oroboside, too. This assumption has been proved by the following synthesis.

* Based on a part of the B. Sc. thesis of ZSUZSANNA LUKA, Polytechnical University, Budapest, May 1966.

7-Hydroxy-5,3',4'-triacetoxyisoflavone (**Ia**; m.p. 192—3°) was prepared by selective deacetylation [6] of orobol tetraacetate* and, subsequently, coupled in acetonic solution in the presence of concentrated aqueous potassium carbonate with tetraacetyl-α-D-glucopyranosyl bromide, yielding thereby crude 5,3',4'-triacetoxy-7-(tetraacetyl-β-D-glucopy-ranosyloxy)-isoflavone (oroboside heptaacetate; **Ib**). Alkaline hydrolysis of the latter yielded 5,3',4'-trihydroxy-7-(β-D-glucopyranosyloxy)-isoflavone (oroboside, **Ic**) as the monohydrate; m.p. 219—20° (KOFLER block) from 40% aqueous ethanol; further heating causes decomposition at 270°; lit. m.p. 220—1° (MAQUENNE block) [1]; $[\alpha]_D^{20°}$ —58.5° (50% aqueous pyridine) lit. $[\alpha]_D^{20°}$ —58.96° [1] (50% aqueous pyridine). Acid hydrolysis of **Ib** gave, as expected, 5,7,3',4'-tetrahydroxy-isoflavone (orobol, **Id**; m.p. 270°, lit. m.p 270.5° [1]).

Methylation of **Ia** with dimethyl sulfate under the conditions applied for its glucosylation gave santal triacetate (**Ie**; m.p. 152°, lit. m.p. 152° [4]) and hydrolysis of the latter santal itself (**If**; m.p. 222°, lit. m.p. 223° [5]). By the latter series of reactions a new synthesis of santal has thus been achieved.

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6. The method applied for this selective deacetylation will shortly be published in detail by one of the authors (J. V.) in Acta Chim. Acad. Sci. Hung.

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* That during deacetylation the acetyl group in position 7 is removed follows from a new synthesis of santal starting from **Ia**

Acta Chimica Academiae Scientiarum Hungaricae Tomus 55 (3), pp. 347—349 (1968)

PREPARATION AND INVESTIGATION OF LEWIS ACID COMPLEXES, II*

THE PREPARATION AND INVESTIGATION OF THE TITANIUM TETRACHLORIDE AND TIN TETRACHLORIDE COMPLEXES OF THE ESTERS OF CYCLOHEXANE DIOLS AND TRIOLS AND OF MONO- AND OLIGOSACCHARIDES

(PRELIMINARY COMMUNICATION)

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In continuation of our earlier investigations [1], we have prepared titanium tetrachloride and tin tetrachloride complexes of a number of compounds, which can be considered polyfunctional from the point of view of electron pair donation. The investigated compounds were: ethylene glycol diacetate and dibenzoate; the diacetates of cyclopentane-1,2-cis- and-trans-diols; cyclohexane-1,2-cis- and -trans-, -1,3-trans-, further -1,4-trans-diol diacetates; the acetates of α-, β- and γ-cyclohexane-1,2,3-triols; 3,4-diacetoxytetrahydrofurane; tetraacetyl-α- and -β-D-xylose; 2,3,4-triacetyl-α-methyl-glucoside; levoglucosan triacetate and tribenzoate; 2,3,4,6-tetraacetyl-α-D-glucose; 1-chloro-2,3,4-triacetylglucose; pentaacetyl-α- and -β-glucose; β-cellobiose octaacetate, and raffinose acetate. The complexes were prepared and investigated under anhydrous conditions, excluding any traces of water. The points of decomposition of the complexes were determined; the compositions were established by elemental analysis, and by a method developed earlier [2], and the IR spectra were recorded in Nujol suspension. In evaluating of the spectra, the findings of Lappert [3] were taken into consideration, and primarily the shifts due to the complexing of the carbonyl band and of the band attributed to the asymmetric stretching vibration of the O—C—C group were studied.
‖

It has been found that in the titanium tetrachloride complex the wave number of the carbonyl band is, in general, by 80—120 cm^{-1} lower, and the ν_{as} (O—C—C) by 50—80 cm^{-1} higher, than in the non-complexed starting com-
‖

pounds. From the splitting of the carbonyl band, conclusions have been drawn

* Part I: Z. Csűrös, Gy. Deák and L. Fenichel: Acta Chim. Acad. Sci. Hung. **21**, 169 (1960).

concerning the steric structures of the complexes. On this basis we suggest that titanium tetrachloride — contrary to data in the literature which are unsupported by experimental results — is able to form both cis and trans complexes, depending on the structure of the starting compound and on the

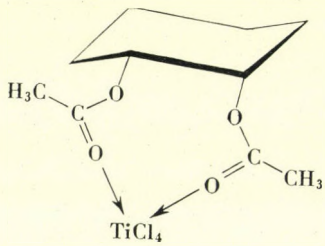

Fig. 1

composition of the complex. The study of the tin tetrachloride complexes yielded similar results.

It has been established in our further work that complexes of cyclic structure are formed, if the ester groups are situated near enough to one

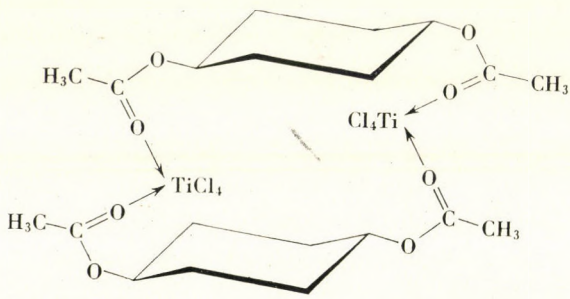

Fig. 2

another (Fig 1), in accordance with an earlier finding of RIVEST *et al.* [4] in the case of aliphatic dicarboxylic esters. If the formation of such cyclic structures is impossible owing to steric factors, intermolecular linkages may give rise to larger cyclic structures, consisting of two molecules each of the substrate and the Lewis acid (Fig. 2).

With a substrate containing a hydroxyl group, such as 2,3,4-triacetylmethyl glucoside, tin tetrachloride and titanium tetrachloride, a chelate-type linkage is formed between the hydroxyl group and tin, which is indicated by the broad band at 2400—2500 cm^{-1} in the infrared spectrum of the perfluorokerosene suspension of the complex. On the other hand, with titanium tetrachloride the corresponding derivative of orthotitanic acid trichloride, $HOTiCl_3$,

i.e. $\underbrace{CH(OMe)CH(OAc)CH(OAc)CH(OAc)CH}_{O}CH_2OTiCl_3$ is formed with the elimination of HCl. In this complex titanium is attached intra- or intermolecularly with a coordinative bond to the carbonyl oxygen of one of the ester groups.

A similar reaction was observed between titanium tetrachloride and 1-chloro-2,3,4-triacetylglucose. On comparing the infrared spectrum of the complex with that of ethoxytitanium trichloride, it has been found that the new, strong band at 1105 cm^{-1} is due to the stretching vibration of the C—O—Ti group. This band is also present in the infrared spectrum of the complex obtainable in the ring cleavage reaction of levoglucosan triacetate [5], which complex yields 1-chloro-2,3,4-triacetylglucose on hydrolysis; this verifies our earlier assumption, according to which no hydroxyl group is present in position 6 in the primary reaction product, this position being occupied by an $-O-TiCl_n$ ($n = 3$ or 4) group. The hydroxyl group is formed only subsequently, in the hydrolysis of the complex.

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РЕЗЮМЕ

Полярография комплексов кадмия с β- и γ-пиколинами в водной среде

ДЖ. Н. ГАУР и В. К. ШАРМА

Комплексы кадмия с β- и γ-пиколинами изучались полярографическим методом Дэфорда и Хьюма. В системе кадмий β-пиколин было обнаружено присутствие двух комплексов с константами стабильности равными $\beta_1 = 18{,}5 \pm 2$ и $\beta_2 = 224 \pm 5$, а для системы кадмий — γ-пиколин три комплекса с константами стабильности $\beta_1 = 33 \pm 3$, $\beta_2 = 310 \pm 5$ и $\beta_3 = 665 \pm 10$. Приводятся данные процентного содержания различных комплексов и свободных составных компонентов для обеих систем.

Реакции некоторых простых органических соединений с горячей концентрированной серной кислотой

Э. ШУЛЕК и М. ФЭХЕР-ГАБОР

За реакцией горячей концентрированной серной кислоты с некоторыми органическими соединениями следили. Путём измерения количества выделяющихся в течение реакции двуокиси и окиси углерода и двуокиси серы.

В то время как карбамид под действием концентрированной серной кислоты подвергается только сольволизу, оксалат натрия и формиат бария окисляются. Муравьиная кислота окисляется в бóльшей степени, по сравнению с щавелевой кислотой.

Изучение каталитического влияния SeO_2 в разложении Кьелдаля

Э. ШУЛЕК, М. ФЭХЕР-ГАБОР и Л. БАРЦА

Изучалась реакция горячей концентрированной серной кислоты с некоторыми органическими соединениями в присутствии двуокиси селена как катализатора. В присутствии двуокиси селена щавелевая и муравьиная кислоты окисляются под действием концентрированной серной кислоты в гораздо бóльшей степени.

Приводится экспериментальное доказательство влияния катализатора, заключающегося в следующем: органические соединения восстанавливают двуокись селена до элементарного селена, образующегося с своей стороны с концентрированной серной кислотой $(SeSO_3)_x$, который окисляется далее серной кислотой до Se(IV).

Исследование дегидроциклизации на металлических катализаторах IV. Сравнение дегидрирования циклогексана с дегидроциклизацией

З. ПАЛ и П. ТЕТЕНИ

С помощью импульсной техники сравнивалось дегидрирование циклических углеводородов с дегидроциклизацией углеводородов с открытой углеродной цепью описанной частично в предыдущих сообщениях. Было получено новое непосредственное доказатель-

ство того, что дегидрирование циклогексана протекает через образование циклогексена и циклогексадиена, как промежуточных продуктов. С помощью введения радиоактивного изотопа (C^{14}) в один из компонентов системы углеводородов с открытой углеродной цепью и циклических углеводородов было обнаружено, что в пределах измеримости переход радиоактивности между гексаном, гексеном и циклогексаном и между гексеном и циклогексеном не происходит. Это, в свою очередь, указывает на то, что ступени реакций н-гексан → циклогексан и н-гексен → циклогексан, предполагавшиеся до сих пор, протекают лишь в степени, достойной пренебрежения. Неопределенный переход радиоактивности наблюдался между радиоактивным н-гексеном и неактивными циклогексеном и циклогексадиеном-1,3 соответственно. Т. о., не нужно считаться с образованием циклопарафиновых соединений в течение дегидроциклизации, и можно считать, что реакция протекает исключительно по ступенчатому механизму, приведенному в предыдущем сообщении. Дегидрирование циклогексана и дегидроциклизация н-гексана рассматриваются параллельными реакциями, которые имеют подобный ступенчатый механизм и встречаются лишь в какой-то последней ступени реакции.

Производные дифенилпропиламина, II. Производные 3,3-дифенилпропиламина с нитро- и амино-заместителями в ароматическом кольце

К. ХАРШАНИ, К. ТАКАЧ и Д. КОРБОНИЧ

С помощью нитрования 3,3-дифенилпропионитрила был синтезирован 3,3-бис-(4-нитрофенил)-пропионитрил. Нитрогруппы восстанавливались избирательно в присутствии катализатора Pd/C. При восстановлении полученного 3,3-бис-(4-аминофенил)-пропионитрила в присутствии никеля Ренея получался 3,3-бис-(4-аминофенил)-пропиламин. После предварительного ацетилирования или диалкилирования ароматической аминогруппы получались соответствующие производные 3,3-бис-(4-аминофенил)-пропиламина. Исходя из N-ацетил-3,3-дифенилпропиламина, также удалось осуществить нитрование. Таким образом, разработан альтернативный путь реакций для синтеза 3,3-бис-(4-аминофенил)-пропиламина и одновременно было доказано, что в данном случае нитрование протекает главным образом в *n,n'*-положениях ароматических колец.

Производные дифенилпропиламина, III. N-Замещенные производные 3,3-бис-(4-нитрофенил) и (4-аминофенил)-пропиламина

К. ТАКАЧ, К. ХАРШАНИ и Д. КОРБОНИЧ

N-замещенные 3,3-бис-(4-диалкиламино-фенил)-пропиламины синтезировались путем восстановительной конденсации соответствующего первичного амина с кетонами. Авторы попытались получить N^1-замещенный 3,3-бис-(4-аминофенил)-пропиламин двумя путями, однако однозначного превращения не удалось добиться. Образование третичной алифатической аминогруппы позволяло получить путем восстановления производные замещенные в ароматическом кольце с первичными аминогруппами. Производные N-замещенного 3,3-бис-(4-нитрофенил)-пропиламина были получены с помощью восстановительной конденсации с $NaBH_4$.

Составные компоненты местных растений, XII. Стероидные алкалоиды недоспелых фруктов Solanum macrocarpum L.

М. Б. Е. ФАЙЕЗ и А. А. САЛЕХ

Было найдено, что недоспелые фрукты *Solanum macrocarpum L.* содержат глюкоалкалоиды соласонин, соламаргин, α-соламарин и β-соламарин. Полученная после гидролиза нейтральная глюкозидная фракция содержит стероид типа сапогенина, диосгенин. Фракция жира, неподвергнувшаяся омылению, содержит β-ситостерол.

Новый синтез двух компонентов Beyeria 5,7-дигидрокси-3,4',8-триметоксифлавона (I) и 4',5-дигидрокси-3,7-диметоксифлавона(II)

Л. ФАРКАШ, А. ГОТТСЕГЕН и М. НОГРАДИ

Указанные соединения были получены однозначным путем и оказались идентичными с соответствующими природными веществами.

1,2,4-Триазины и их конденсированные производные, V. Синтез пирано [2,3-e] [1,2,4] триазинов и попытки получения фуро [2,3-e] [1,2,4]-триазинов

Г. ДОЛЕШАЛ, М. ХОРНЯК-ХАМОРИ и К. ЛЕМПЕРТ

3-(алкилтио)-6-(3-гидроксипропил)-1,2,4-триазин-5/2*H*/-оны **(IIa-c)** циклизируются под влиянием сухого газообразного хлористого водорода в обезвоженном диоксане в соответствующие хлористоводородные 3-(алкилтио)-7,8-дигидро-6*H*-пирано[2,3-e] [1,2,4] триазины **(IVa-c).** Под действием же соляной кислоты последние гидролизуются в хлористоводородный 7,8-дигидро-6*H*-пирано [2,3-e] [1,2,4] триазин-3/2*H*/-он **(V).** Соединения **IIa-c** превращаются под действием соляной кислоты непосредственно в **V.**

Ни 3-амино-аналог **IIa-c (VIII),** ни основное соединение, в котором отсутствует алкильная группа на сере **(I)** не циклизируется под влиянием кислоты.

С другой стороны, 3-(метилтио)-6-(2-гидроксиэтил)-1,2,4-триазин-5/2*H*/-он **(XX)** — т. е. более низкий гомолог **IIa** изомеризуется в подобных условиях в *S*-метил-изотиосемикарбазон α-оксо-γ-бутиролактона **(XIX).** Основное соединение **XX** не алкилированное на сере **(XVIII),** оказалось стабильным под действием солянокислой обработки. Та же самая картина наблюдается и для аналога **XX** содержащего пиримидинний кольцо **(XXII),** который под действием соляной кислоты образует только соль.

Были проведены попытки объяснения наблюдаемых явлений на обобщенной основе.

Получение четвертичных солей 1-метил-6,7-диметокси-1,2,3,4-тетрагидро-изохинолина стереоизомерных на азоте. Исследование селективности кватернизации

Г. БЕРНАТ, К. КОЦКА, Й. КОБОР, Л. РАДИЧ и М. КАЙТАР

Было синтезировано несколько гомологов иодалкилатов 1-метил-2-алкил-6,7-диметокси-3,4-дигидро-изохинолина и гидроиодидов 1-метил-2-алкил-6,7-диметокси-1,2,3,4-тетрагидро-изохинолина. Исследовалась селективность кватернизации гомологов 1,2-диметил-6,7-диметокси-1,2,3,4-тетрагидро-изохинолина (карнегина) с иодалкилатами, а также гомологов 1-метил-2-алкил-6,7-диметокси-1,2,3,4-тетрагидро-изохинолина (*N*-алкилсаль. золидина) с иодметилатом. С помощью препаративной обработки реакционных смесей, а также с помощью инфракрасного и ЯМР спектроскопического анализа сырых продуктов реакции было установлено, что кватернизация карнегина иодалкилатами и гомологов *N*-алкил-сальзолидина иодметилатом обладает лишь средней селективностью. На основе ик-спектров продуктов реакции, а также анализа данных по селективности следует заключить, что вводимый при кватернизации заместитель вероятно занимает экваториальное положение в четвертичных солях, образующихся в качестве главного продукта реакции.

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ON THE SIGN OF INTERACTIONS IN THE THEORY OF THE MEAN SQUARE AMPLITUDES OF VIBRATION

(SHORT COMMUNICATION)

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Introduction

When CYVIN's [1] Σ-matrix formalism is used to compute the mean square amplitudes, one comes across the interactions σ_{ij}, where i and j represent any two internal coordinates. An apparent paradox about such terms is that these are sometimes negative. In this note we attempt to give a simple interpretation of the sign of σ_{ij}. It is also shown that the signs of σ_{ij} and f_{ij} can be correlated in most cases.

We can define σ_{ij} by a relation of the type

$$<\sigma_{ij} = \Delta i \, \Delta j> \tag{1}$$

where Δi and Δj are increments in the internal coordinates; i and j and the brackets denote thermal averaging in the sense introduced in Reference [1]. It follows, therefore, that the sign of σ_{ij} is determined by the relative sign of Δi and Δj. But their relative signs may change with the mode of vibration. So the ultimate value (and hence the sign) of σ_{ij} is some weighted average of σ_{ij} over the various modes.

Though it is not possible to fix *a priori* the sign of σ_{ij}, it may be related to the sign of f_{ij} in several instances. This correlation may be investigated by means of the general quadratic potential function.

$$\text{Let } V = V\,(\Delta r_1, \Delta r_2, \ldots \Delta r_i, \ldots \Delta r_n)$$

be the general quadratic potential function written in terms of the internal coordinates. If we give a small value to Δr_i, the equilibrium is changed, and $\Delta r_j (j \neq i)$ will be different from zero. To determine the new equilibrium we must set

$$\frac{\partial V}{\partial \Delta r_j} = 0\,. \tag{2}$$

Now

$$\Delta r_i \frac{\partial V}{\partial \Delta r_j} = 0\,. \tag{3}$$

We can employ a set of equations of the type (3) and take the averages of the various quantities. This is a generalization of the method used by COULSON, DUCHESNE and MANNEBACK [2] who have shown that f_{12} and $\Delta r_1\,\Delta r_2$ (stretching) are of opposite sign. Whenever necessary, equations $\left\langle \Delta r_i \dfrac{\partial V}{\partial \Delta r_j} \right\rangle = 0$ should be compounded by Lagrange's method of undetermined multipliers.

Bond-bond interaction

Let us take the potential function of a linear XY_2 molecule in the form

$$2V = f_1(\Delta r_1^2 + \Delta r_2^2) + 2f_{12}\,\Delta r_1\,\Delta r_2 + r_1 r_2 f_\alpha \Delta\alpha^2 . \tag{4}$$

Using the "constraint" $\dfrac{\partial V}{\partial \Delta r_2} = 0$, we deduce that

$$f_1 \Delta r_2 + f_{12}\,\Delta r_1 = 0 . \tag{5}$$

Multiplying by Δr_2 and averaging, we get:

$$f_1\,\sigma_r + f_{12}\,\sigma_{rr} = 0 . \tag{6}$$

The positive definiteness of the first term requires that f_{12} and σ_{rr} are of opposite sign.

This may be easily extended to interactions of the type σ_{rR} by considering the potential for a linear XYZ molecule.

Table I

Interactions in bent symmetrical XY_2 molecules [3, 4]

Molecule / Interaction	f_{rr}	σ_{rr}	$f_{r\alpha}$	$\sigma_{r\alpha}$
H_2Se	—0.12000	0.000021	0.00850	—0.00058
D_2Se	—0.12550	0.000115	0.02080	—0.000367
F_2O	1.6540	—0.000313	0.98770	—0.000650
Cl_2O	—1.1220	—0.004668	0.02900	—0.001077
CCl_2	0.01100	—0.004738	0.00800	—0.000749
CBr_2	0.02500	—0.005488	0.04700	—0.001209
CI_2	0.01700	—0.009208	0.03200	—0.001435

Units: f_{ij} md/Å. σ_{ij} Å² (at 300 °K)

Table II

Interactions in pyramidal XYZ_2 molecules [5, 6]

Molecule / Interaction	f_{Rr}/σ_{Rr}	f_{rr}/σ_{rr}	$f_{r\alpha}/\sigma_{r\alpha}$	$f_{r\alpha'}/\sigma_{r\alpha'}$	$f_{\alpha\alpha}/\sigma_{\alpha\alpha}$
$SOBr_2$	0.276/—0.000059	0.296/—0.000603	—	—	—
NH_2Cl [7]	—0.378/+0.00038	—	—	—	—
$NHCl_2$ [7]	—0.284/+0.00034	—	—	—	—
NH_2D	—	—	0.250/—0.00204	—0.027/0.001128	0.005/—0.00662
NHD_2	—	—	0.163/—0.001613	—0.154/0.000629	0.007/—0.0004045

Units: f_{ij} md/Å. σ_{ij} Å² (at 300 °K)

Bond-angle interaction

The potential function for a bent symmetrical XY_2-type molecule is written as

$$2V = f_r(\Delta r_1^2 + \Delta r_2^2) + 2f_{rr}\Delta r_1 \Delta r_2 + r^2 f_\alpha \Delta\alpha^2 + 2rf_{r\alpha}(\Delta r_1 + \Delta r_2)\Delta\alpha\,. \quad (7)$$

Applying the constraint $\left\langle \Delta\alpha \dfrac{\partial V}{\partial \Delta\alpha} \right\rangle = 0$

we obtain the result

$$f_\alpha \sigma_\alpha + 2f_{r\alpha}\sigma_{r\alpha} = 0\,. \quad (8)$$

This shows that $f_{r\alpha}\sigma_{r\alpha}$ is negative.

Table III

Interactions in tetrahedral XY_4 [8, 9]

Molecule / Interaction	$f_{r\alpha}$	$\sigma_{r\alpha}$	$f_{\alpha\alpha}$	$\sigma_{\alpha\alpha}$
$SiCl_4$	0.3737	—0.001508	0.0439	—0.00459
SiB_4	0.4614	—0.001105	0.1679	—0.00542
$SnCl_4$	0.2293	0.000601	0.0297	—0.00924

Units: f_{ij} md/Å. σ_{ij} Å² (at 300 °K)

Angle-angle interaction

To discuss angle-angle interactions we may consider models such as pyramidal XY_3 and pyramidal XYZ_2 which provide examples of the interactions $\alpha\alpha$ and $\alpha\beta$. In the first case we find that

$$f_\alpha \sigma_\alpha + 2f_{\alpha\alpha}\sigma_{\alpha\alpha} + f_{r\alpha}\sigma_{r\alpha} + f'_{r\alpha}\sigma'_{r\alpha} = 0\,. \quad (9)$$

The above analysis of the bond-bond and bond-angle interactions may be applied here. In spite of this, the relative signs of $f_{\alpha\alpha}$ and $\sigma_{\alpha\alpha}$ remain undetermined.

In a similar way, we get the following equations for pyramidal XYZ_2 type molecules:

$$f_\beta \sigma_\beta + 2f_{r\beta}\sigma_{r\beta} + f_{R\beta}\sigma_{R\beta} + 2f_{\alpha\beta}\sigma_{\alpha\beta} = 0 \quad (10)$$

$$f_\alpha \sigma_\alpha + f_{R\alpha}\sigma_{R\alpha} + f_{\alpha\alpha}\sigma_{\alpha\alpha} + f_{\alpha\beta}\sigma_{\alpha\beta} + f_{r\alpha}\sigma_{r\alpha} + f'_{r\alpha}\sigma'_{r\alpha} = 0\,. \quad (11)$$

Neither of these equations helps us to fix the relative signs of angle-angle interactions.

Table IV

Interactions in ethylene oxide, ethylene oxide-d_4 and ethylene sulphide [10]

Molecule / Interaction	V_{rr}/σ_{rr}	V_{DD}/σ_{DD}	V_{Dr}/σ_{Dr}	V_{Rr}/σ_{Rr}	$V_{r\alpha}/\sigma_{r\alpha}$	$V_{r\beta}/\sigma_{r\beta}$	$V_{r\varphi}/\sigma_{r\varphi}$
C_2H_4O	0.045/—0.001041	0.1210/0.000014	0.0892/0.0001997	0.1704/0.000398	0.0907/0.000347	—0.1055/—0.00016	—0.094/—0.010945
C_2D_4O	—0.2510/—0.000859	—0.8385/0.000025	0.1780/—0.0003166	0.2145/–0.0001585	0.2767/–0.0002757	0.1055/—0.001589	0.0951/—0.001510
C_2H_4S	—0.4890/—0.00082	0.3540/—0.00016	—0.2315/0.0004012	—0.0920/0.0003971	—0.00791/0.000178	0.0941/—0.002006	0.0926/—0.002265

Units: f_{ij} md/Å. σ_{ij} $Å_2$ (at 300 °K)

Table V

Interactions in methylacetylenes [11—13]

Interaction / Molecule	$CH_3C{\equiv}CH$	$CH_3C{\equiv}CCl$	$D_3C{\equiv}CCl$	$CH_3C{\equiv}CBr$	$CH_3C{\equiv}CI$
V_{rcra}/σ_{rcra}	0.47059/ 0.000167	0.47059/—0.000772	0.4706/ 0.000479	0.4706/—0.000671	0.4706/—0.000824
V_{rcra}/σ_{rcra}	0 / 0.00019	0 / 0.000803	0 /—0.000509	0.2075/—0.00071	0.5320/—0.000682
V_{rr}/σ_{rr}	0.09457/—	0.0418/—	0.0418/—	0.0418/—	0.0418/—
$V_{\varphi a}/\sigma_{\varphi a}$	0.1289 /0.000321	0.1334/ 0.000321	0.1334/ 0.000321	0.1430/—0.000321	0.1493/—0.000321
$V_{\alpha\beta}/\sigma_{\alpha\beta}$	—0.10761/ 0.000432	—0.1084/ 0.000432	—0.1084/ 0.000432	—0.1076/—0.000432	—0.1076/ 0.000432
$V_{\lambda c\alpha}/\sigma_{\lambda c\alpha'}$	0.14310/—0.000224	0.1431/—0.000355	0.1431/—0.000311	0.1431/—0.000808	0.1431/ 0.000808

$\sigma r_c\alpha'$ is some combination of $\sigma r_c\alpha$ and $\sigma r_c\beta$. Units: f_{ij} md/Å. σ_{ij} $Å^2$ (at 300 °K)

Results

We have collected here (Tables I to V) a number of cases from the literature to show how far the sign correlation between σ_{ij} and f_{ij} is maintained. Some of the "correlation violations" may be ascribed to the uncertainty in the relative sign of angle-angle interactions, though the extent to which the other interactions are affected by these, may be small.

One of the authors (K. B. J.) wishes to thank the Government of India for the award of a Junior Research Fellowship.

SUMMARY

An interpretation of the interaction terms in the theory of mean square amplitudes of vibration has been attempted. It is shown that there exist "sign correlations" between force constant and mean square amplitude interactions.

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A TECHNIQUE OF MEASURING IMPEDANCES WITH SENSITIVITY FOR THE RECORDING OF CHEMICAL REACTIONS

(SHORT COMMUNICATION)

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In recent years several techniques to measure impedances have been developed. Absolute accuracies of 0.1% can be obtained for example with bridges of appropriate construction. In the field of chemistry impedance measurements are used preferentially for the recording of reactions; here bridge methods are not applicable in case of fast reactions, since the measurement proper is very time-consuming and difficult.

This paper presents a technique which records directly and without any delay. When using appropriate cells [1, 2], it is possible to record all kinds of reactions occurring in liquid media on the basis of the change of the dielectrical constant or of conductivity. Both cells with direct electrode contact and so-called electrodeless cells can be used in this case.

From the principle of the measuring circuit (Fig. 1) [3] it can be understood that the relation between the recorded value f_0 and, *e.g.*, the electrical conductivity $\varkappa$ is given by the following equations:

For electrodeless cells $f_0 = K_1 \cdot \sqrt{\dfrac{\varkappa}{1 + \varkappa \cdot K_2}}$

For cells with direct contact $f_0 = K_3 \cdot \sqrt{\varkappa}$.

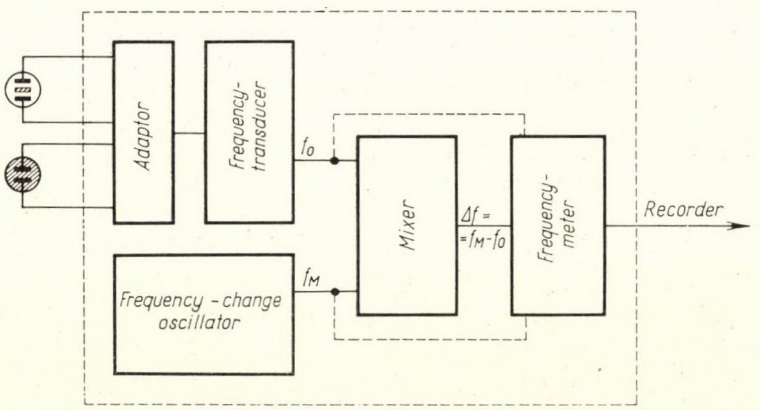

Fig. 1. Schematic circuit diagram

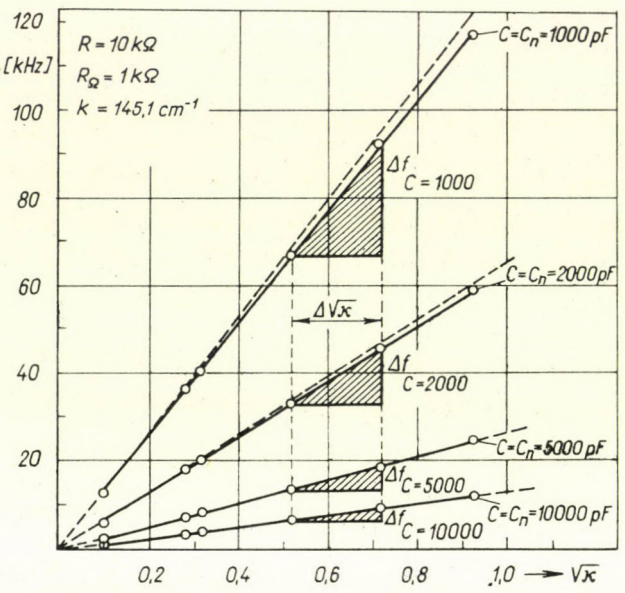

Fig. 2. Comparison of the theoretical and experimental frequency-conductivity curves for cells with direct electrode contact (dotted line: theoretical curve)

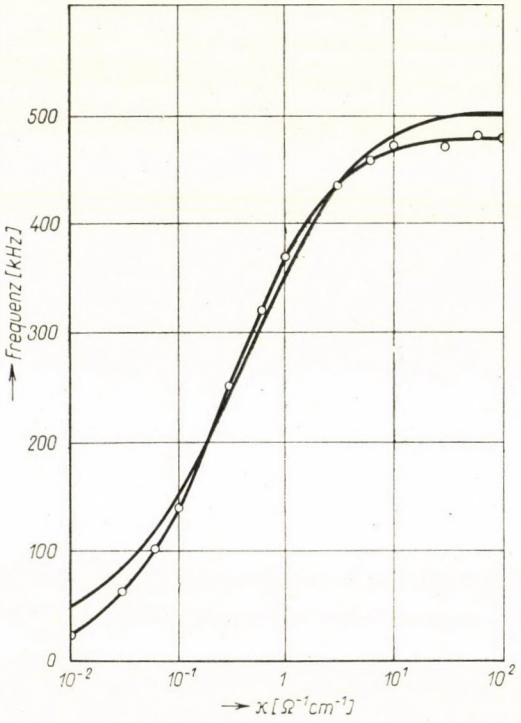

Fig. 3. Comparison of the theoretical and experimental frequency-conductivity curves for electrodeless cells

K_1, K_2 and K_3 are values independent of the medium to be investigated. Comparisons of values calculated on the basis of these equations with values obtained experimentally are shown graphically in Figs 2 and 3. The K values can be varied by changing the cells (different cell constants) and by the variation of additional impedances.

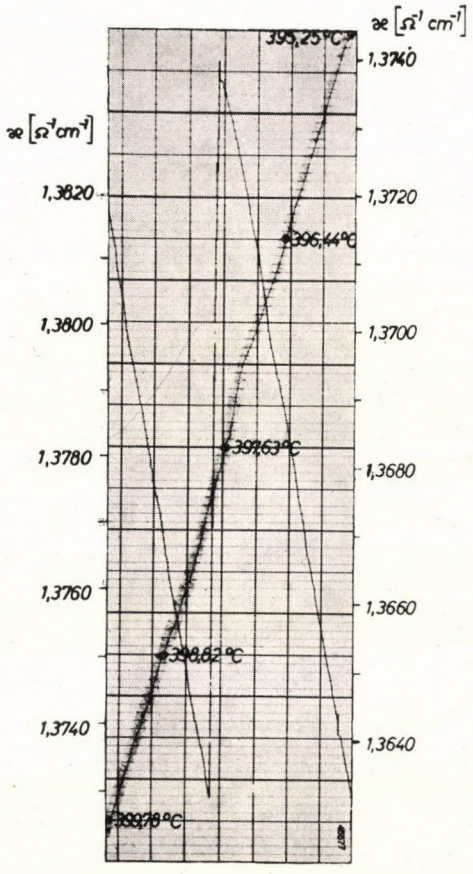

Fig. 4. Uncorrected original curves ($\varkappa$—T)

It can be seen that the slope of the straight line (sensitivity) and the upper limit of frequency are independent of the electrical conductivity of the medium to be investigated in case of electrodeless measurement.

The method has been tested for liquids of low conductivity ($10^{-9}\Omega^{-1}\text{cm}^{-1}$) and also for molten salts of relatively high conductivity (approx. $1\Omega^{-1}\text{cm}^{-1}$).

The efficiency of this method can be seen particularly from the uncorrected original curves (Fig. 4). The sensitivity was selected so that relative differences of $10^{-3}\%$ still can be measured. The temperature has been deter-

mined by thermocouples of very low heat capacity. Consequently, the accuracy was $5 \cdot 10^{-2}$ °C.

Complete measurements over the whole range of liquid electrolytes — from solutions of low conductivity to highly conducting melts [4] — may be performed with ordinary and electrodeless cells by the new method described in this paper.

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DISPLACEMENT SUBSTOICHIOMETRY

(PRELIMINARY COMMUNICATION)

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Received November 20, 1967

The principle of substoichiometry was developed nearly simultaneously by the independent researches of RŮZIČKA and STARÝ [1], ZIMAKOV and ROZHAVSKY [2] and SUZUKI [3]. It was RŮZIČKA and STARÝ who recognized the great potentialities of the method, making it the subject of detailed studies in various respects [4]. We suggest the name "direct substoichiometry" for the original procedure according to which identical quantities of a metal ion are separated in a reproducible way from solutions containing the metal ion in different concentrations, by means of the addition of less than the equivalent quantity of a complexing or precipitating agent.

As a novel method, we suggest a new possibility which is also expected to have extremely wide applicability:

Let us consider an organic reagent, HL, which is able to react with several various metal ions, M_a, M_b, $M_c \ldots M_z$, to give complexes, M_aL, M_bL, $M_cL \ldots M_zL$, that can be extracted by an organic solvent. If, by employing an excess of the reagent HL, the metal ions are transferred from the aqueous into the organic phase, and then excess of the reagent is removed from this latter phase, it is possible to separate the complexes remaining in the organic solvent by means of a "displacement substoichiometric" method:

After the excess of complexing agent has been removed, the organic phase containing the complexes M_aL, M_bL, $M_cL \ldots M_zL$ treated with an aqueous solution that contains ion M_a in substoichiometric quantity as compared to the quantity of ion M_z.

In this case the following reaction will take place:

$$\left[\begin{matrix} M_aL \\ M_bL \\ M_cL \\ \cdot \\ \cdot \\ M_zL \end{matrix}\right]_{\text{org.}} + [M_a]_{H_2O} \rightleftarrows \left[\begin{matrix} M_aL \\ M_bL \\ M_cL \\ \cdot \\ \cdot \\ M_zL \end{matrix}\right]_{\text{org.}} + [M_z]_{H_2O}$$

(provided that $pK_{M_aL}\ pK_{M_cL} > \ldots > pK_{M_zL}$; where K denotes the extraction constant of the complex in question).

In consequence of the reaction, M_a will displace the equivalent quantity of M_z ions, pushing it out from the organic phase. In this way, from a solution containing the complexes of the ions M_a, M_b, $M_c \ldots M_z$, a known substoichiometric quantity of the ion M_z can be separated in the presence of all the other ions.

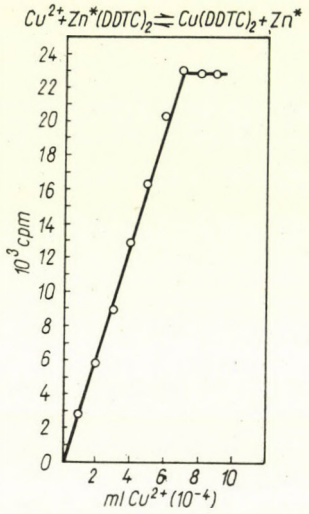

Fig. 1. Reproducibility of the displacement $[Cu^{2+}]_{H_2O} + [{}^*Zn(DDTC)_2]_{org} \rightleftarrows [{}^*Zn^{2+}]_{H_2O} + [Cu(DDTC)_2]_{org}$, using increasing amounts of $[Cu^{2+}]_{org}$; $[Cu^{2+}] = 10^{-4}$ *M*

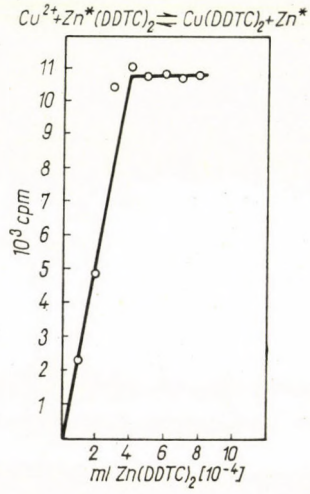

Fig. 2. Reproducibility of the displacement $[Cu^{2+}]_{H_2O} + [{}^*Zn(DDTC)_2]_{org} \rightleftarrows [{}^*Zn^{2+}]_{H_2O} + [Cu(DDTC)_2]_{org}$, using increasing amounts of $[{}^*Zn(DDTC)_2]_{org}$; $[{}^*Zn(DDTC)_2] = 10^{-4}$ *M*

The above considerations have been studied with the following systems:*

$$[^*Pb(DDTC)_2]_{CCl_4} + [Cu^{2+}]_{H_2O} \rightleftarrows [Cu(DDTC)_2]_{CCl_4} + [^*Pb^{2+}]_{H_2O}$$

$$[^*Zn(DDTC)_2]_{CCl_4} + [Cu^{2+}]_{H_2O} \rightleftarrows [Cu(DDTC)_2]_{CCl_4} + [^*Zn^{2+}]_{H_2O}$$

$$[^*As(DDTC)_3]_{CCl_4} + 3[Cu^{2+}]_{H_2O} \rightleftarrows 3[Cu(DDTC)_2]_{CCl_4} + 2[^*As^{3+}]_{H_2O}$$

$$[^*Mn(DDTC)_3]_{CCl_4} + 3[Hg^{2+}]_{H_2O} \rightleftarrows 3[Hg(DDTC)_2]_{CCl_4} + 2[^*Mn^{3+}]_{H_2O}$$

Figs. 1 and 2 present radiometric titration curves showing the displacement of zinc.

Details of this work will be published later.

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* DDTC = diethyl ditiocarbaminate

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CHEMICAL CONVERSIONS OF DIOLS AND CYCLIC ETHERS, XIII*

PREPARATION OF 2,2-DIALKYL- AND ARYL-SUBSTITUTED OXETANES

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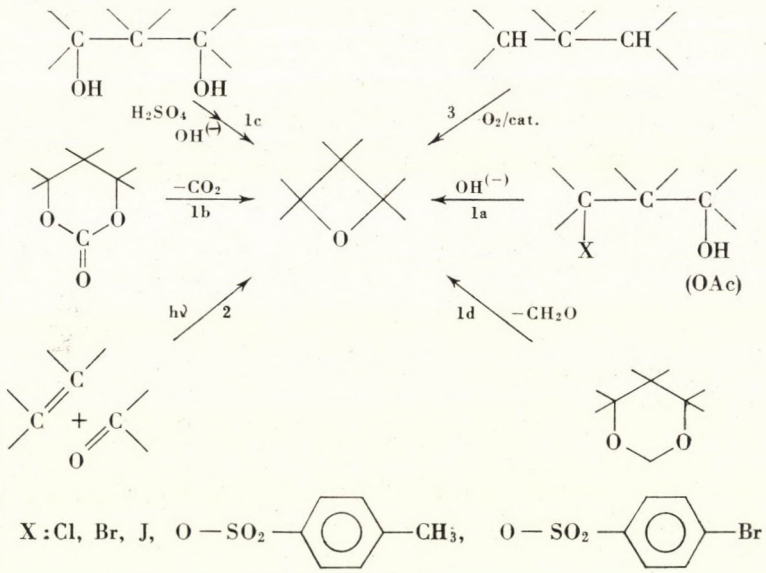
Received February 20, 1967

In earlier communications [1—4], we have dealt with the preparation of trimethylene oxide and its derivatives substituted by 2-mono-, 3-mono-, 3,3-dialkyl and aryl groups. In the course of the experiments reported in this paper, starting with 1,3-chlorohydrins which contained a primary chlorine atom and a tertiary hydroxyl group in suitable positions, we succeeded in preparing the following oxetanes in about 80% yields; 2,2-dimethyl- and 2,2-diethyloxetane, further the new compounds 2-methyl-2-*n*-propyl-, 2-methyl-2-isopropyl- and 2-methyl-2-phenyloxetanes. The preparation of 2,2-diphenyloxetane has also been examined.



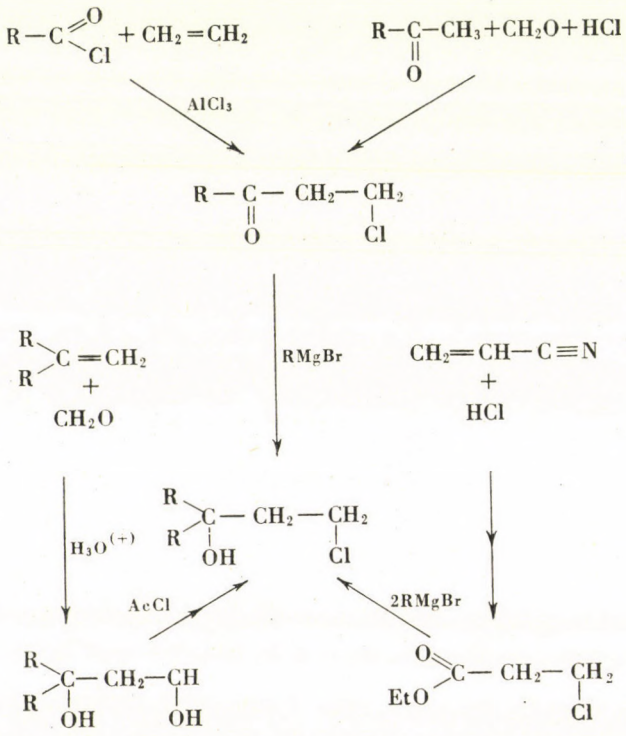
The methods applicable for the synthesis of the above-described oxetanes are summarized in Scheme 1. It appears from Scheme 1 that the methods employed by us for the synthesis of oxetanes may be classified in three main groups.

* Part XII: Acta Phys. et Chem. Szeged **12**, 151 (1966)

The first main group includes the syntheses starting from various 1,3-bifunctional compounds (methods denoted by 1a, 1b, 1c and 1d). The second main group embraces the methods where oxetanes are prepared by the addition reactions of two systems containing $\sigma\pi$ bonds (such as the method denoted by 2). The third main group contains, in addition to the oxidation process shown in Scheme 1, all chemical conversions where the formation of the oxacyclobutane skeleton can be detected, however, the very poor yields prevent the practical application of the methods for the preparation of oxetanes.

The methods outlined in Scheme 1 cannot be equally employed for the preparation of oxetanes of various types. A survey of the literature shows that, up to the present, essentially only method 1a has been applied for the synthesis of 2,2-disubstituted oxetanes [5—10], whereas method 1c proved practically unsuitable for this purpose [11, 12]. The other methods have not been studied as regards their suitability in the synthesis of 2,2-disubstituted oxetanes.

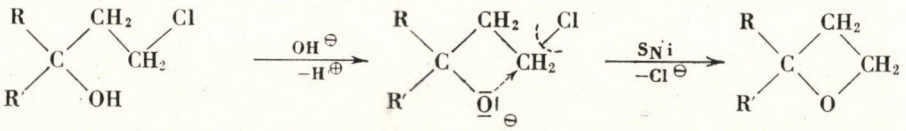
In the present experiments, we have chosen 1,3-chlorohydrins, containing a chlorine atom in the required primary position, as initial substances for the preparation of 2,2-disubstituted oxetanes. The methods used for the synthesis of the mentioned chlorohydrins are summarized in Scheme 2.



The desired chlorohydrins can be obtained from acrylonitrile by the addition of hydrogen chloride, esterification, and subsequent Grignard reaction.

In this way, we prepared 3-methyl-3-hydroxybutyl chloride and 3-ethyl-3-hydroxyamyl chloride. Starting from acetyl chloride, in the mode shown in Scheme 2, we synthesized 3-methyl-3-hydroxyhexyl chloride, 3-isopropyl-3-hydroxybutyl chloride, and 3-phenyl-3-hydroxybutyl chloride. Our studies on the conversions with acetyl chloride of 1,3-diols, which are obtainable by the Prins reaction [13] of olefins containing a quaternary carbon atom will be reported in another paper.

2,2-Disubstituted oxetanes have been prepared in yields of about 80% by the reaction of potassium hydroxide with 1,3-chlorohydrins carrying a chlorine atom in primary position. The general course of this process is presented in Scheme 3.



Where $R\,R'$ denote methyl-methyl, ethyl-ethyl, methyl-*n*-propyl, methyl-isopropyl, or methyl-phenyl groups.

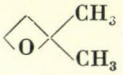
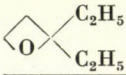
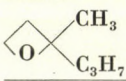
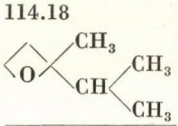
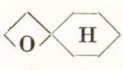
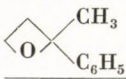
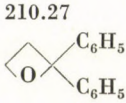
The formation of 2,2-disubstituted oxetanes is, as regards the mechanism of the process, the result of an intramolecular nucleophilic substitution (S_Ni). The conversions of the above-mentioned 1,3-chlorohydrins into oxetane homologues represent at the same time examples of (O^-—4) neighbouring group participation [14]. The structures of the oxetanes were identified by their infrared spectra and by means of their iron(II) cyano oxonium salts, while their purity was checked by microanalysis and gas chromatography. Our attempts to prepare 2,2-diphenyloxetane failed. Namely, instead of the desired product, β-phenylpropiophenone was obtained. This compound was identified by its physical constants, infrared spectrum and by the melting point of the semicarbazone.

Data of literature concerning the preparation of 2,2-disubstituted oxetanes, together with the experimental results of the present work and with some physical constants of oxetanes are summarized in Table I.

As regards the data of literature given in Table I, attention is called to two problems. One of these is that a very simple method had been reported by LOMBARD and ASFAZADOURIAN [15] for the preparation of 2,2-dimethyloxetane; however, in our several attempts aimed at reproducing the reaction of *t*-butanol and formaldehyde under the experimental conditions described by these authors, we did not observe the formation of 2,2-dimethyloxetane. The formation of oxetanes under such conditions would undoubtedly afford essential information about the mechanism of the Prins reaction.

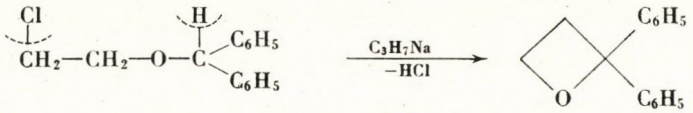
Table I

The preparation and some physical constants of 2,2-disubstituted oxetanes

Formula and molecular weight	Starting compound	Yield, %	Boiling point, °C (torr)	Spec. gravity, d	Refractive index, n_D	Ref.
$C_5H_{10}O$	Chlorohydrin	43	71 (750)	0.8279_4^{20}	—	5
86.13	Chlorohydrin	25[b]	70 (742)	—	1.3907^{20}	6
	*t*-Butanol+CH_2O	9	—	—	—	15
	1,3-Dioxanone-2	0	—	—	—	11
	Chlorohydrin	90	71 (752)	0.829_4^{20}	1.3908^{20}	a
	t-Butanol+CH_2O	0	—	—	—	a
$C_7H_{14}O$	Iodohyrin	—	128—130	—	—	7
114.18	Chlorohydrin	90	129 (760)	0.8525_4^{18}	1.4200^{22}	8
	Chlorohydrin	50[b]	124	—	1.4168^{23}	6
	Chlorohydrin	76	129 (754)	0.8424_4^{20}	1.4190^{20}	a
$C_7H_{14}O$	Chlorohydrin	89	100 (744)	—	1.4142^{20}	a
114.18						
						
$C_7H_{14}O$	Chlorohydrin	82	93 (744)	—	1.4176^{20}	a
114.18						
						
$C_8H_{14}O$	Diolmonobrosylate	62	57 (16)	—	1.458^{23}	9
126.19	Chlorohydrin	55	78 (34)	—	1.4521^{26}	10
						
$C_{10}H_{12}O$	Chlorohydrin	68	70—72 (4)	—	1.5371^{20}	a
126.19						
						
$C_{15}H_{14}O$	Benzhydryl-β-chloro-ethylether+sodium propoxide	44	m. p. 103	—		16
210.27						
	Chlorohydrin	0	—	—	—	a

a See Experimental of the present paper
b Yields are given by SEARLES [17]

The second problem concerns the new method of preparation of oxetanes reported by SEARLES *et al.* [16], who made 2,2-diphenyloxetane from benzhydryl-β-chloroethyl ether in the way shown by Scheme 4.



44%

The mechanism of this process, which can formally be regarded as a 1,4-elimination, has not been studied so far.

Experimental

β-Chloropropionitrile was prepared as described in literature [18]. Starting from 470 g of acrylonitrile (4.7 moles), 660 g (86%) of β-chloropropionitrile was obtained. B. $p._{28}$ 76—77° (lit. [18]: $b.p._{16}$ 71°).
C_3H_4ClN (89.53). Calcd. Cl 39.6. Found Cl 30.3%.

Ethyl β-chloropropionate. Gaseous hydrochloric acid was passed for 3—4 hrs. into a mixture of 376 g (4.2 moles) of β-chloropropionitrile, 734 ml (12.6 moles) of ethanol, and 75.6 ml (4.2 moles) of water. The mixture was heated on a water bath for 30 min., and the excess ethanol removed by distillation. The precipitated ammonium chloride was removed by filtration, and the filtrate distilled under reduced pressure, to yield 400 g (70%) of the product, $b.p._{28}$ 78—80°; n_D^{20} 1.4272 (lit. [19] $b.p._{29}$ 80°; n_D^{20} 1.4269).

3-Methyl-3-hydroxybutyl chloride. To a Grignard reagent prepared from 104.6 g (4.3 moles) of magnesium and 635 g (4.5 moles) of methyl iodide in 1500 ml of anhydrous ether, a solution of 272 g (2 moles) of ethyl β-chloropropionate in 300 ml of anhydrous ether was added dropwise, under continuous stirring and cooling in an ice-salt mixture. The reaction mixture was allowed to stand overnight and the product decomposed, under effective cooling and stirring, by the addition of 240 g (4 moles) of a 25% aqueous acetic acid solution. The ethereal solution of the crude product was purified, the solvent evaporated, and the residue subjected to distillation under reduced pressure, on a column of 10 theoretical plates, packed with glass spirals. The yield was 120 g (50%); $b.p._{28}$ 78°; n_D^{20} 1.4410 (lit. [5] $b.p._{13}$ 72°).
$C_5H_{11}C_{10}$ (122.60). Calcd. Cl 28.92. Found Cl 28.60%.

2,2-Dimethyloxetane. 56 g (1 mole) of potassium hydroxide and 10 ml of water were placed into a flask equipped with a stirrer, dripping funnel and a 20 cm long Vigreux column. The potassium hydroxide melt was heated to 140°, and 40 g (0.3 mole) of 3-methyl-3-hydroxybutyl chloride was added by drops. Meanwhile, 2,2-dimethyloxetane continuously distilled into the receiver chilled in a mixture of acetone and dry ice. When the addition of the reagent was completed, the temperature was to 170° in order to complete the reaction. The crude product was distilled from sodium metal to obtain a yield of 28 g (90%). Physical constants of the product are given in Table I.

3-Ethyl-3-hydroxyamyl chloride. To a Grignard reagent prepared from 162 g (6.67 moles) of magnesium and 750 g (6.95 moles) of ethyl bromide in 2200 ml of dry ether, a solution of 400 g (3 moles) of ethyl 3-chloropropionate in 500 ml of anhydrous ether was added dropwise, under continuous stirring and cooling in an ice-salt mixture. The yield was 182 g (42%) $b.p._{10}$ 82—83°; n_D^{20} 1.4584 (lit. [8] $b.p._{14}$ 89°; n_D^{20} 1.4579).
$C_7H_{15}OCl$ (150,64). Calcd. Cl 23.54. Found Cl 23.4%.

2.2-Diethyloxetane was prepared similarly to 2.2-dimethyloxetane. From 26.6 g (0.17 mole) of 3-ethyl-3-hydroxyamyl chloride. 15.8 (76%) of 2.2-diethyloxetane was obtained. Its physical constants, together with reported data are listed in Table I.

4-Chlorobutanone-2 was prepared as described in literature [20].

3-Methyl-3-hydroxyhexyl chloride. To a Grignard reagent prepared from 73 g (3 moles) of magnesium and 243 g (3.1 moles) of propyl chloride in 1200 ml of anhydrous ether, a solution

of 320 g (3 moles) of 4-chlorobutanone-2 in 300 ml of anhydrous ether was added dropwise under cooling. The yield was 150 g (33%); b.p.$_{28}$ 105—106°; n_D^{22} 1.4510.
$C_7H_{15}OCl$ (150.64). Calcd. Cl 23.54. Found Cl 23.25%.

2-Methyl-2-n-propyloxetane was prepared similarly to 2,2-dimethyloxetane. The cyclix ether obtained was distilled from the alkaline mixture after the removal of the column. From 26.6 g (0.17 mole) of chlorohydrin, 17.4 g (89%) of the product was obtained. The main physical constants are given in Table I. When the formed 2-methyl-2-*n*-propyloxetane was analyzed by gas-liquid chromatography, the peak appeared at a distance of 2.2 cm from the spot of injection. (The conditions of the chromatographic technique were as follows: a column of 200 cm height, containing 15% of silicone grease on sodium chloride as carrier; thermostat temperature 80°; detector current 150 mA; sensitivity of the *Willy Giede GCHF 18/2* type gas chromatograph: 1; carrier gas: 60 ml of hydrogen per minute; running rate of paper: 600 mm/hr.; amount of sample 0.002 ml.)

3,4-Dimethyl-3-hydroxyamyl chloride. To a solution of isopropylmagnesium bromide prepared from 48.6 g (2 moles) of magnesium and 250 g (2.15 moles) of isopropyl bromide in 900 ml of dry ether, a solution of 213 g (2 moles) of 4-chlorobutanone-2 in 200 ml of anhydrous ether was added, by drops under cooling. The reaction mixture was processed as described above. Distillation gave 96 g (31.7%) of the chlorohydrine, b.p.$_{28}$ 102°; n_D^{27}: 1.4544.
$C_7H_{15}OCl$ (150.64). Calcd. Cl 23.54. Found Cl 22.88%.

2-Methyl-2-isoprolypoxetane was prepared in the same way as 2,2-dimethyloxetane. From 13 g (0.08 mole) of chlorohydrine, about 7 g (82%) of 2-methyl-2-isopropyloxetane was obtained. Its physical constants are listed in Table I. When the product was analyzed by gas-liquid chromatography under the conditions stated above, the peak appeared at a distance of 2.2 cm from the spot of injection.

3-Phenyl-3-hydroxybutyl chloride. To a solution of phenylmagnesium bromide prepared from 97.2 g (4 moles) of magnesium and 628 g (4 moles) of bromobenzene in 1200 ml of anhydrous ether, a solution of 410 g (3.86 moles) of 4-chlorobutanone-2 in 400 ml of anhydrous ether was added dropwise under continuous stirring and cooling. After usual processing, fractional distillation under reduced pressure afforded two fractions:
(a) 140 g, between 110 and 130° at 7 torr;
$C_{10}H_{13}OCl$ (184.62). Calcd. Cl 19.2. Found Cl 191.1%;
(b) 78 g, between 130 and 220° at 7 torr; and 116 g of a resinous residue.

Fraction (a) was used for the preparation of 2-methyl-2-phenyloxetane. From fraction (b) 14 g of diphenyl (m.p. 72°) was isolated, leaving unknown condensates of high molecular weight.

2-Methyl-2-phenyloxetane was prepared under conditions similar to those applied in the synthesis of the oxetanes described above, with the difference that, owing to the high boiling point of the product, no Vigreux attachment was used. The reaction product was obtained by subjecting the alkaline melt to steam distillation. Evaporation of the solvent from the ethereal extract of the steam distillate and fraction distillation of the residue under pressure gave, from 14 g of chlorohydrin, 7.6 g of product (68%). Its main physical constants are given in Table I.
$C_{10}H_{12}O$ (148.2). Calcd. C 81.1. Found C 80.96; H 8.16%.

Attempts to produce 3,3-diphenyl-3-hydroxypropyl chloride. To phenylmagnesium bromide prepared from 121.5 g (5 moles) of magnesium and 800 g (5.1 moles) of bromobenzene in the presence of 1500 ml of anhydrous ether, a 1 : 1 solution of 272 g (2 moles) of ethyl β-chloropropionate in anhydrous ether was added by drops, under cooling. The usual processing of the reaction mixture gave 225 g (45.6%) of a viscous product, which was used without further purification.

Attempts to produce 3,3-diphenyloxetane. To 225 g of crude product obtained in the preceding experiment, 112 g (2 moles) of potassium hydroxide was added, the mixture fused at 140°, and the melt stirred for 1 hr. at 160°. After cooling, the melt was mixed with 200 ml of water and repeatedly extracted with ether. The combined extracts were dried over ignited potassium carbonate, the solvent was removed by distillation, and the product subjected to fractional distillation under reduced pressure. Recrystallization of the fractions from aqueous ethanol afforded, besides 8 g diphenyl (m.p. 72°), 60 g ($\sim$30%) of β-phenylpropiophenone which latter was identified by its melting point, microanalysis, infrared spectrum, and by the melting point of its semicarbazone. M. p. 71° (lit. [21] m. p. 72°). $C_{15}H_{14}O$ (210.26). Calcd. C 85.7; H 6.7. Found C 85.8; H 6.8%.
M.p. of the semicarbazone (from aqueous ethanol); 146° (lit. m.p. [22] 144°).

SUMMARY

The synthesis of 2,2-dialkyl- and aryl-substituted oxetanes has been studied. Treatment with potassium hydroxide of 1,3-chlorohydrins carrying a chlorine atom in the required primary position gave the following oxetanes in yields of about 80%; 2,2-dimethyl-, 2,2-diethyl-, and the new compounds 2-methyl-2-*n*-propyl-, 2-methyl-2-isopropyl- and 2-methyl-2-phenyl-oxetanes. These oxetanes are formed by S_Ni mechanism. The synthesis of the above-mentioned cyclic ethers represents new examples of (O^-—4) neighbouring group participation. 3,3-Diphenyl-3-hydroxypropyl chloride gives, when treated in the described way, the isomeric β-phenylpropiophenone instead of the expected 2,2-diphenyloxetane.

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BEITRÄGE ZUR ANALYTIK DER 1,2-GLYKOLE UND POLYOXYVERBINDUNGEN, IX

BESTIMMUNG VON METHYL-β-D-ARABINOPYRANOSID, BENZYL-β-D-ARABINOPYRANOSID SOWIE METHYL-α-D-GLUCOPYRANOSID ÜBER DEN BEI DER OXYDATION MIT PERJODAT GEBILDETEN DIALDEHYD

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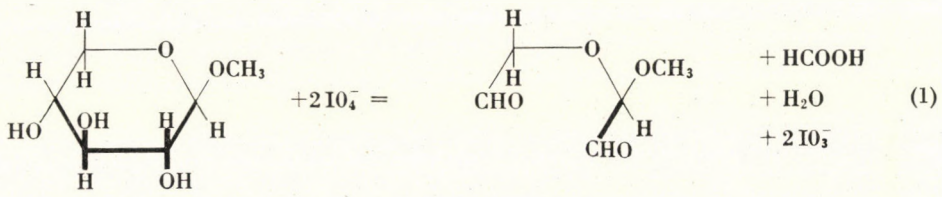
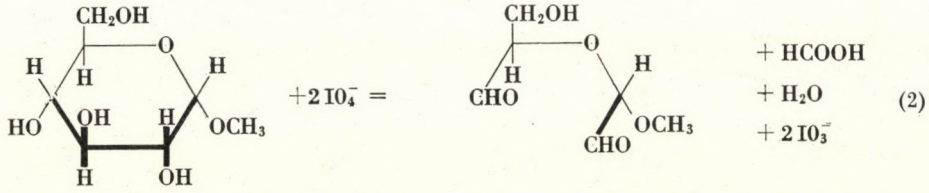
Die Oxydation der Methylhexoside und Methylpentoside mit Perjodat wurde zuerst von JACKSON und HUDSON [1, 2] untersucht. Diese Untersuchungen dienten zur Feststellung der Gliederzahl des Ringes bzw. der räumlichen Stellung der glykosidischen Hydroxylgruppe. COURTOIS und VALENTINO [3] stellten fest, daß die Acetalbindungen durch Perjodsäure nicht gespalten werden. Die Methylpentoside und Methylhexoside reagieren eindeutig mit 2 Molekülen Perjodat. Bei der Oxydation entstehen 1 Molekül Ameisensäure sowie ein Dialdehyd. Die Oxydation von Methylarabinosid und Methylglucosid wird durch die folgenden Gleichungen gekennzeichnet:



(1)

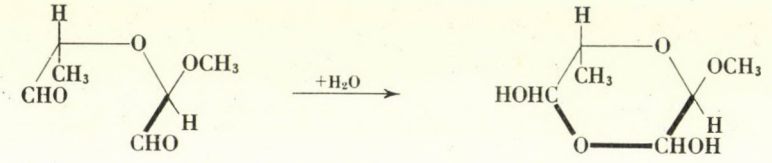


(2)

Die Bestimmung der bei der Oxydation gebildeten Ameisensäure wurde von mehreren Autoren zur Bestimmung von Pentosiden und Hexosiden benützt [4—7].

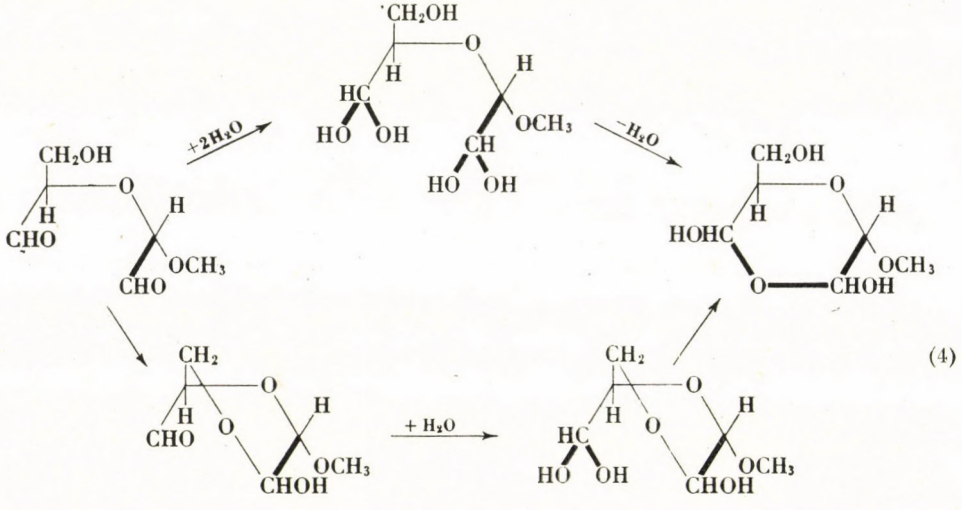
Die Struktur der Dialdehyde wurde von zahlreichen Forschern untersucht. Das *p*-Nitrophenylhydrazon des mit Perjodat oxydierten Methyl-α-D-glucosids wurde isoliert [9—11]. Wie der Stickstoffgehalt des Produktes erkennen läßt, reagiert das oxydierte Glucosid mit 1 Molekül *p*-Nitrophenylhidrazin.

Auf Grund der infrarotspektroskopischen Untersuchungen liegen die Aldehydgruppen der isolierten Dialdehyde in cyclischer Hemialdal- oder Acetalbindung vor [9—15]. Um die Hemialdalbindung zu bestätigen, wurde das Oxydationsprodukt vom Methyl-4-6-O-benzylidenglucopyranosid [10, 13, 14] und Methyl-L-rhamnopyranosid [12] untersucht. (Die cyclische Acetalbindung kann in diesen Fällen nicht in Frage kommen!) Die Anwesenheit der Carbonylgruppe konnte IR-spektroskopisch in keinem Fall bestätigt werden, beim oxydierten Rhamnopyranosid war aber die Gegenwart der Hydroxylgruppen nachzuweisen. Die Erfahrungen werden beim oxydierten Rhamnopyranosid mit der folgenden Ringschlußreaktion gedeutet:



(3)

Auf Grund dieser Erfahrungen wurde angenommen, daß der Ringschluß zwischen den beiden hydratisierten Oxogruppen eintritt, die Bildung des Acetals zwischen der freien Hydroxymethyl-Gruppe und der Oxogruppe kann nur intermediär sein. Die Aldehydgruppen des mit Perjodat oxydierten α- und β-Methyl-D-glucopyranosids wurden von GUERNET und Mitarbeitern in wäßriger Lösung mit der Hypojodit-Methode [16, 17] bestimmt. In beiden Fällen erhielten sie anstatt der berechneten 2 Moleküle Aldehyd nur 0,01 Mol; dieser niedrige Wert ließ auf eine geringe chemische Reaktionsfähigkeit der Aldehydgruppe schließen.



(4)

In unseren früheren Mitteilungen [18, 19] wurde die Oxydation der Disaccharide mit Perjodat vom Gesichtspunkte der Aldehydbestimmung untersucht.

Das bei der Oxydation der Melibiose [18] gebildete Produkt enthält drei Aldehydgruppen, von denen GUERNET und Mitarbeiter [15] nur eine bestimmen konnten. Nach unseren Untersuchungsergebnissen können alle drei Aldehydgruppen der mit Perjodat oxydierten Melibiose mit dem »Bisulfit-Cyanid«-Verfahren mit analytischer Genauigkeit bestimmt werden.

Auf Grund der obigen Ausführungen ist es — unserer Meinung nach auch über analytische Gesichtspunkte hinausgehend — begründet, die Bisulfitaddition der bei der Oxydation der Methylglucoside mit Perjodat gebildeten Dialdehyde näher zu untersuchen. Im Besitze der zahlreichen Literaturangaben könnte nämlich eventuell angenommen werden, daß die Reaktionsfähigkeit der bei der Oxydation der Glykosidderivate mit Perjodat gebildeten Polyaldehyde, den im allgemeinen verwendeten Aldehydreagenzien gegenüber, infolge der Hemialdalbindungen in hohem Maße abnimmt. Unsere nachstehend beschriebenen Untersuchungen deuten sehr entschieden darauf hin, daß solche Annahmen unrichtig sind. Unseres Erachtens sind diese Aldehyde außerordentlich aktiv, und daß ein Dialdehyd z. B. nur mit 1 Mol *p*-Nitrophenylhydrazin reagiert, folgt aus den mit gesteigerter und nicht mit verringerter Reaktionsbereitschaft verbundenen günstigen räumlichen Stellungen.

Die Oxydation vom Methylarabinopyranosid, Benzylarabinopyranosid sowie Methylglucopyranosid wurde in perjodsauren ($p_H \approx 1$), essigsauren ($p_H \approx 4$) und bicarbonatalkalischen ($p_H \approx 8$) Lösungen untersucht. Bei der Oxydation wurde das Glucosid in jedem Fall in einem Molverhältnis von 6 : 1 mit Perjodat in Reaktion gebracht.

Tabelle I

Oxydation von β-Methylarabinopyranosid mit Perjodat

Oxidationszeit	Oxydationen beim p_H-Wert der Perjodsäure			Oxydation in gepufferter essigsaurer Lösung		Oxydation in mit $NaHCO_3$ gepufferter Lösung	
	Mol Perjodat/Mol Arabinosid	Mol Ameisensäure/Mol Arabinosid	Mol Aldehyd/Mol Arabinosid	Mol Perjodat/Mol Arabinosid	Mol Aldehyd/Mol Arabinosid	Mol Perjodat/Mol Arabinosid	Mol Aldehyd/Mol Arabinosid
5 Min.	1,84	0,72	—	1,84	—	1,27	—
30 Min.	2,00	0,96	1,94	1,96	1,94	2,02	1,95
60 Min.	2,00	0,96	1,94	1,98	1,94	2,11	1,96
90 Min.	—	0,96	—	—	—	—	—
120 Min.	2,01	0,96	1,94	1,96	1,95	—	1,96
240 Min.	1,98	0,96	—	1,96	—	2,14	1,92
24 St dn.	2,02	0,96	1,94	2,03	1,94	2,34	1,78

In unseren orientierenden Untersuchungen wurde die Menge der bei der Oxydation verbrauchten Perjodsäure und der während der Reaktion gebildeten Ameisensäure bzw. Aldehyde als Funktion der Zeit bestimmt. — Die Versuchsergebnisse sind in den Tabellen I, II und III zusammengestellt.

Tabelle II

Oxydation von β-Benzylarabinopyranosid mit Perjodat

Oxydationszeit	Oxydationen beim pH-Wert der Perjodsäure			Oxydation in gepufferter essigsaurer Lösung		Oxydationen in mit $NaHCO_3$ gepufferter Lösung	
	Mol Perjodat/Mol Arabinosid	Mol Ameisensäure/Mol Arabinosid	Mol Aldehyd/Mol Arabinosid	Mol Perjodat/Mol Arabinosid	Mol Aldehyd/Mol Arabinosid	Mol Perjodat/Mol Arabinosid	Mol Aldehyd/Mol Arabinosid
5 Min.	1,90	0,60	—	1,77	—	1,88	—
30 Min.	1,99	0,92	1,92	1,92	1,94	2,00	1,94
60 Min.	1,99	1,00	1,94	1,97	1,96	2,01	1,94
90 Min.	—	1,00	—	—	—	—	—
120 Min.	1,99	1,01	1,94	1,99	1,95	2,03	1,94
240 Min.	—	—	—	—	—	2,10	1,94
24 Stdn	2,03	1,00	1,94	2,03	1,94	2,32	1,87

Tabelle III

Oxydation von α-Metylglucopyranosid mit Perjodat

Oxydationszeit	Oxydationen beim pH-Wert der Perjodsäure			Oxydation in gepufferter essigsaurer Lösung		Oxydationen in mit $NaHCO_3$ gepufferter Lösung	
	Mol Perjodat/Mol Arabinosid	Mol Ameisensäure/Mol Arabinosid	Mol Aldehyd/Mol Arabinosid	Mol Perjodat/Mol Arabinosid	Mol Aldehyd/Mol Arabinosid	Mol Perjodat/Mol Arabinosid	Mol Aldehyd/Mol Arabinosid
5 Min.	0,46	0,09	—	0,79	—	0,26	0,45
30 Min.	1,27	0,47	1,87	1,57	1,88	1,16	1,42
60 Min.	1,66	0,69	1,85	1,78	1,87	—	1,62
90 Min.	1,76	0,78	1,88	1,81	1,87	1,79	1,65
120 Min.	1,97	0,81	1,88	1,93	1,88	1,98	—
240 Min.	2,03	0,89	1,87	2,01	1,87	2,41	1,70
360 Min.	2,03	—	—	2,03	1,87	2,99	1,77
24 Stdn	2,03	0,96	1,87	2,05	1,88	—	1,42

In saurer Lösung lassen die Molzahlen des verbrauchten Perjodats und der gebildeten Ameisensäure bzw. der Aldehyde auf eine eindeutige Reaktion schließen. Die Dialdehyde können als die stabilen Endprodukte der Oxydation

betrachtet werden. Auf Grund der Erfahrungen der bei $p_H \approx 8$ durchgeführten Oxydationen kann festgestellt werden, daß auch die Oxydation der Dialdehyde bei allen drei Glycosiden eintritt, bei den Arabinosiden aber in viel geringerem Maße, als beim Glucosid.

Schon in unseren beiden früheren Mitteilungen haben wir darauf hingewiesen, daß die Acetalbindungen in den vorübergehend gebildeten Polyaldehyden sehr stabil sind, und in jedem Fall ist die α-Wasserstoff-Oxydation als die Anfangsphase der weiteren Oxydationsvorgänge zu betrachten. In der Literatur wurde eine α-Wasserstoff-Oxydation bisher nur bei solchen Sacchariden angenommen, bei denen sich vorübergehend ein Tartronaldehyd-Derivat bildet (siehe Mitteilung VIII). Im Zusammenhang mit der Oxydation der Melibiose haben wir darauf hingewiesen, daß auch die α-Wasserstoff-Oxydation des mit dem Glyoxal in Acetalbindung vorliegenden Glycerinaldehyd-Teiles in einer Lösung von $p_H \approx 8$ eintritt. Eine solche Oxydation von meßbarer Geschwindigkeit spielt sich auch bei dem aus Methylglucosid gebildeten Dialdehyd ab, der gleichfalls einen Glycerinaldehyd-Teil enthält. Der aus Methyl- bzw. Benzylarabinosid gebildete Dialdehyd kann auch in einer Lösung von $p_H \approx 8$ als ein verhältnismäßig stabiles Produkt betrachtet werden. Unserer Annahme nach war diese Stabilität im Vergleich mit dem früher erwähnten Dialdehyd bzw. den Polyaldehyden auch zu erwarten, da ein gelockerter Wasserstoff, wie er in den den Tartrondialdehyd- bzw. Glycerinaldehyd-Teil enthaltenden Polyaldehyden vorliegt, in diesen Verbindungen gar nicht vorkommt. Die bei der langdauernden Reaktion (24 Stunden) zu beobashtende sehr geringe Oxydation ist — unserer Meinung nach — gleichfalls eine Folge der als Anfangsphase ablaufenden α-Wasserstoff-Oxydation (siehe Gleichung 6). Auf Grund dieser Erfahrung und der aus dieser entwickelten Anschauung konnte ein einheitliches Bild bezüglich des Mechanismus der zweiten, bisher noch nicht erklärten Phase der Oxydation der Saccharide mit Perjodat, d. h. der Oxydation der Polyaldehyde ausgestaltet werden. Demnach kann die Reihenfolge der Reaktionsfähigkeit der in der α-Wasserstoff-Oxydation als Anfangsphase reagierenden Gruppen wie folgt aufgestellt werden:

$$\begin{array}{c} \text{CHO} \\ | \\ -\text{CH} \\ | \\ \text{CHO} \end{array} \gg \begin{array}{c} \text{CHO} \\ | \\ -\text{CH} \\ | \\ \text{CH}_2\text{OH} \end{array} \gg \begin{array}{c} \text{CHO} \\ | \\ -\text{CH} \\ | \\ \text{H} \end{array} \qquad (5)$$

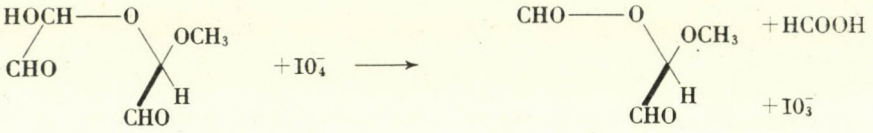
Durch Vergleich der Untersuchungsergebnisse kann festgestellt werden, daß der Unterschied zwischen den Reaktionsfähigkeiten dieser Gruppen sehr groß ist. In Fällen, in denen sich diese Gruppen bei der Oxydation mit Perjodat als Glyoxalacetale bilden, beginnt die Reaktion der Polyaldehyde mit Perjodat immer mit der α-Wasserstoff-Oxydation der nach der obigen Reihenfolge aktiveren Gruppe, und die nachfolgenden Oxydations- und mit der Esterhydro-

lyse verbundenen Vorgänge gehen in jedem Fall, nach dem Prinzip des stufenweisen Abbaus, aus dieser Gruppe ausgehend vor sich.

Im Falle des oxydierten Methylarabinosids kann der Oxydationsprozeß mit den folgenden Gleichungen beschrieben werden:



(6)

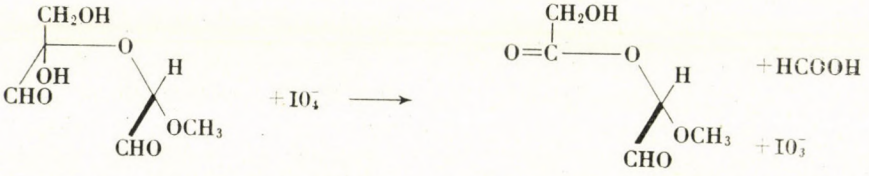


(7)

Der α-Wasserstoff-Oxydation des Methylglucosids (Gleichung 8) folgen zwei parallel verlaufende Reaktionen nach (Gleichungen 9 und 10).



(8)



(9)



(10)

Die Geschwindigkeit der α-Glykol-Oxydation (Gleichung 10) ist über $p_H \approx 7$ um so viel geringer als die der α-Oxo-Hydroxy-Oxydation (Gleichung 9), daß man praktisch nur mit dem letzteren Vorgang zu rechnen hat.

In den α-Oxo-Hydroxy-Oxydationen bilden sich Ester. Die Hydrolyse der letzteren verläuft in alkalischer Lösung sehr schnell, demzufolge tritt auch die Spaltung des Glyoxals mit Perjodat schnell ein.

Bezüglich der Methylglucoside kann, vom analytischen Gesichtspunkt aus gesehen, bloß die Möglichkeit der Bestimmung der Dialdehyde als bedeutungsvoll betrachtet werden.

Bei den Arabinopyranosiden bilden beide Aldehydgruppen des bei den sauren Oxydationen entstandenen Dialdehyds schnell und eindeutig ein stabiles Aldehydbisulfit. Bei einstündiger Oxydation mit nachfolgender 30—60 Min. dauernder Reaktion mit Bisulfit können beide Arabinoside analytischer genau mit dem »Bisulfit-Cyanid«-Verfahren bestimmt werden. Die Meßergebnisse sind in den Tabellen IV und V gezeigt.

Die Bestimmung des α-Methylglucosids über Dialdehyd ergibt niedrige Resultate (Tabelle VI).

Tabelle IV

Bestimmung von β-Methylarabinopyranosid über den bei der Oxydation mit Perjodat gebildeten Dialdehyd

Einwaage Methyl-Arabinosid g/100,00 ml	Eingemessene Lösung ml	Verbrauchte 0,1 n Jodlösung ml		Gef. Methylarabinosid	
		einzeln	Durchschnitt	mg	%
0,4108	10,00	9,70 9,72 9,74	9,73	39,93	97,2
	4,98	4,85 4,86 4,85	4,85	19,90	97,3
	2,00	1,94 1,96 1,95	1,95	8,00	97,4

Die aus verschiedenen Einwaagen erhaltenen Resultate sind in sauren Lösungen und nach Oxydationszeiten von 30 Min. bis 24 Stdn. gleich niedrig. Auch 93,5—94%ige Werte (1,87—1,18 Mole) können erst mit doppelter Bisulfitmenge vorgenommener, 2 Stunden dauernder Reaktion erreicht werden. Die unter solchen Bedingungen erhaltene Sulfitaddition bedeutet den Höchstwert, der weder durch weitere Verlängerung der Wartezeit noch durch Erhöhung des Sulfitüberschusses gesteigert werden konnte (Tabelle VII).

Die in der Bisulfitaddition der aus den Arabinopyranosiden und Glucopyranosid gebildeten Dialdehyde beobachteten bedeutenden Abweichungen können mit der Bildung des cyclischen Acetals erklärt werden. Bei den oxy-

Tabelle V

Bestimmung von β-Benzylarabinopyranosid über den bei der Oxydation mit Perjodat gebildeten Dialdehyd

Einw. Benzyl-Arabinosid g/100,00 ml	Eingemessene Lösung ml	Verbrauchte 0,1 *n* Jodlösung ml		Gef. Benzylarabinosid	
		einzeln	Durchschn.	mg	%
		9,75			
	10,00	9,77	9,75	58,56	79,4
		9,75			
		4,87			
0,6012	4,98	4,88	4,88	29,31	97,9
		4,88			
		1,95			
	2,00	1,96	1,95	11,71	97,4
		1,95			

Tabelle VI

Bestimmung von α-Methylglucopyranosid über den bei der Oxydation mit Perjodat gebildeten Dialdehyd

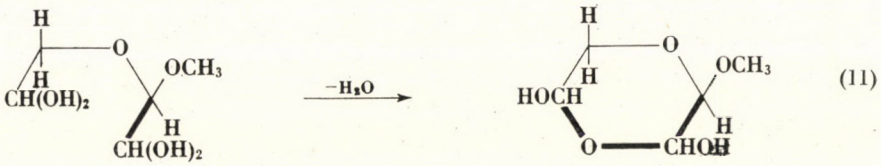
Einw. Methylglucosid g/500,00 ml	Eingemessene Lösung ml	Verbrauchte 0,1 *n* Jodlösung ml		Gef. Methylglucosid	
		einzeln	Durchschn.	mg	%
		9,16			
	9,99	9,16	9,17	44,12	93,9
		9,20			
		4,57			
2,3814	4,98	4,59	4,58	22,23	93,8
		4,59			
		1,85			
	2,00	1,84	1,84	8,93	93,8
		1,83			

Tabelle VII

Untersuchung der Bisulfitaddition des bei der Oxydation von α-Methylglucosid mit Perjodat gebildeten Aldehyds in mit Natriumacetathaltiger Essigsäure gepufferter Lösung

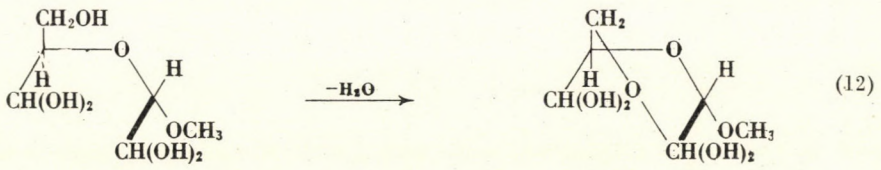
Zeit der Oxydation mit Perjodat	Wartezeit mit 200%igem Sulfitüberschuß bei Zimmertemperatur		Wartezeit mit 500%igem Sulfitüberschuß		
			bei Zimmertemperatur		bei 5 °C
	60 Min.	120 Min.	120 Min.	24 St.	120 Min.
30 Min.	1,75	1,80	1,87	—	1,82
60 Min.	1,74	—	1,85	—	1,88
90 Min.	1,76	1,79	1,88	—	1,87
120 Min.	1,79	1,79	1,88	1,87	1,87
150 Min.	1,77	—	1,87	—	—
180 Min.	1,79	1,76	—	—	1,88
240 Min.	1,76	1,80	1,87	—	1,88
24 St.	—	—	1,88	1,88	1,88

dierten Arabinopyranosiden ist nur die Hemialdalbildung möglich, da das Molekül keine primäre alkoholische Hydroxylgruppe enthält.



(11)

Beim Glucopyranosid kann ein Ringschluß außer der Hemialdalbindung auch durch Acetalbildung zustande kommen. Unserer Meinung nach ist diese Bindung stabiler, als die Hemialdalbindung.



(12)

Es sei bemerkt, daß unsere späteren Untersuchungen (siehe X. Mitteilung — Oxydation von Trehalose, Saccharose, Raffinose) noch mehr darauf hinweisen, daß die Carbonylgruppen der Polyaldehyde mit dem Bisulfit nur dann nicht reagieren, wenn die der auf Acetalbildung beruhende Cyclisierung besteht.

Nach den auf die Hydrolyse dieser Dialdehyde bezüglichen Untersuchungen (1 Stunde in 1 *n* salzsaurer Lösung bei 100 °C) erhöhte sich die Aldehyd-

zahl beim Methylarabinosid auf 2,1 Mol, beim Methylglucosid blieb sie unverändert (1,88 Mol).

Trotz des etwa 6%igen negativen Fehlers halten wir die Bestimmung des Dialdehyds für eine analytisch benützbare Methode auch im Fall von Methylglucosid. Das auf der Ameisensäure-Bestimmung beruhende Verfahren ergibt, wie aus der Tabelle III ersichtlich ist, selbst nach 24 Stunden dauernder Oxydation noch einen 4%igen negativen Fehler, liefert jedoch immer monoton steigende Resultate. Allein die Bestimmung des Perjodatüberschusses scheint eine analytisch befriedigend genaue Methode zu sein, bezüglich der qualitativen Beurteilung halten wir es für wichtig, diese Messergebnisse mit den korrigierten Aldehyd-Ergebnissen zu vergleichen.

Beschreibung der Verfahren

Bestimmung von β-Methylarabinosid, β-Benzylarabinosid und α-Methylglucosid über den bei der Oxydation mit Perjodat gebildeten Dialdehyd.

Reagenzien:

0,1 *n* Jodlösung
5%ige Jodlösung
0,3 molare Perjodsäure-Lösung
1,5 molare Natriumsulfit-Lösung
20%ige Natriumhydroxyd-Lösung
20%ige Salzsäure
10%ige Essigsäure
1%ige Stärkelösung (mit 0,1%iger Salycilsäure abgebaut bzw. konserviert)
0,1%ige äthanolische Methylrotlösung
Kaliumcyanid (fest)
Pentan

0,35—0,45 g β-Methylarabinosid, 0,55—0,65 g β-Benzylarabinosid bzw. 0,4—0,5 g α-Methylglucosid werden analytisch genau eingewogen und in destilliertem Wasser gelöst. Die Lösung wird in einen 100-ml-Meßkolben gespült, dann wird das Lösungsvolumen bis zur Marke ergänzt. 10,00 ml der so vorbereiteten Stammlösung werden in einen 100 ml, mit Glasstopfen versehenen Erlenmeyer-Kolben pipettiert und mit 5 ml Perjodsäure versetzt. (Bei Verwendung von Natriumperjodat wird die Lösung mit 1 ml Essigsäure angesäuert.) Nach 1 Stunde wird Natriumsulfitlösung — aus einer eingeteilten 10-ml-Pipette so lange in die Probelösung getropft, bis die am Anfang ausgeschiedene Farbe des Jods verschwindet, danach wird noch 1 ml Natriumsulfitlösung zugegeben (beim α-Methylglucosid werden 2 ml Na_2SO_3-Lösung zugegeben). Nun wird die Lösung in Gegenwart von 1—2 Tropfen Methylrot-Indikator mit Natronlauge neutralisiert, dann mit 2 ml Essigsäure wieder angesäuert. Der Kolben wird verschlossen und geschüttelt, um auch das am Schliff haftende Perjodat und Jodat zu reduzieren. Die eventuell warm gewordene Lösung wird mit Wasser abgekühlt und dann mit 5 ml Pentan überschichtet.

Nach 1 Stunde Wartezeit wird der Sulfitüberschuß in Gegenwart von 10 Tropfen Stärkelösung, als Indikator mit Jodlösung oxydiert. Anfangs wird mit 5%iger, schließlich mit 0,1 *n* Jodlösung gearbeitet. Nach Erreichung der blauen Farbe wird der Kolben verschlossen, energisch geschüttelt, wobei der Stopfen von Zeit zu Zeit zu lockern ist, um auch das am Schliff haftende Sulfit zu reduzieren und wenn nötig, wird die Farbe der Lösung mit 0,1 *n* Jodlösung auf hellblau eingestellt.

Nach Entfernung des Sulfitüberschusses wird die Probe mit 4 ml Natronlauge alkalisch gemacht, dann werden 0,2—0,3 g festes Kaliumcyanid in den Kolben gegeben. Die Lösung wird vorsichtig vermischt, mit Salzsäure aus einer eingeteilten 10-ml-Pipette neutralisiert, dann mit weiteren 1,5—2 ml Salzsäure angesäuert. Nun wird unter vorsichtigem Schütteln mit 0,1 *n* Jodlösung titriert. Am Anfang wird die Meßlösung in größeren Portionen zugegeben, nach Erreichung der blauen Farbe wird der Kolben verschlossen, geschüttelt, und wenn nötig, werden noch 1—2 Tropfen Meßlösung bis zur Erreichung der blauen Farbe zugetropft.

In der Bestimmung ist das Äquivalentgewicht der Pentoside und des Hexosids: Molekulargewicht/4.

1 ml 0,1 *n* Jodlösung entspricht 4,104 mg Methylarabinosid ($C_6H_{12}O_5$), 6,006 mg Benzylarabinosid ($C_{12}H_{16}O_5$) bzw. 4,855 mg, Methylglucosid ($C_7H_{14}O_6$).

ZUSAMMENFASSUNG

Bei der Oxydation von β-Methyl- und β-Benzylarabinosid sowie α-Methylglucosid mit Perjodat in saurer Lösung entsteht ein Dialdehyd, der mit 2 Molekülen Bisulfit ein stabiles Aldehydbisulfit liefert. Zur indirekten Bestimmung der beiden obigen Pentoside und des Hexosids wird das von den Verfassern schon früher empfohlene jodometrische »Bisulfit-Cyanid«-Verfahren verwendet. Die in Lösung von $p_H \approx 8$ eintretende Oxydation der in sauren ($p_H \approx \approx 1$—4) Lösungen stabilen Polyaldehyde mit Perjodat wird von den Verfassern auf Grund einer einheitlichen Anschauung erklärt. Im Zusammenhang damit werden einige Arten der α-Wasserstoff-Oxydation beschrieben, über die in der Literatur bisher noch nicht berichtet worden ist.

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BEITRÄGE ZUR ANALYTIK DER 1,2-GLYKOLE UND POLYOXYVERBINDUNGEN, X

BESTIMMUNG VON TREHALOSE, SACCHAROSE UND RAFFINOSE ÜBER DEN BEI DER OXYDATION MIT PERJODAT GEBILDETEN POLYALDEHYD

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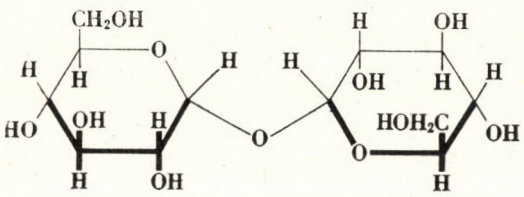
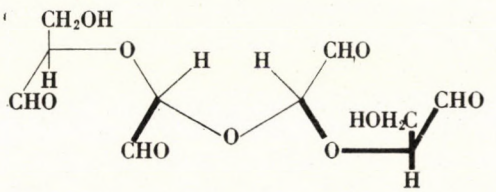
Eingegangen am 21. März, 1967

Bei der Oxydation der nicht reduzierenden Disaccharide, Trehalose und Saccharose sowie des Trisaccharids Raffinose, mit Perjodat, bilden sich vorübergehend Polyaldehyde.





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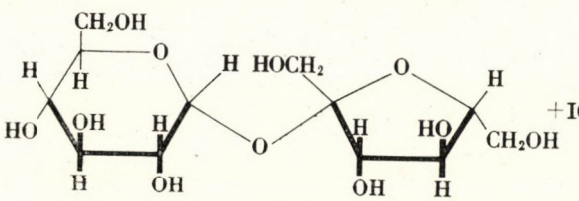

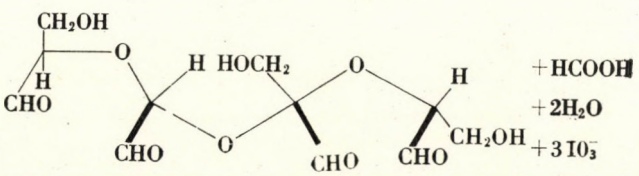

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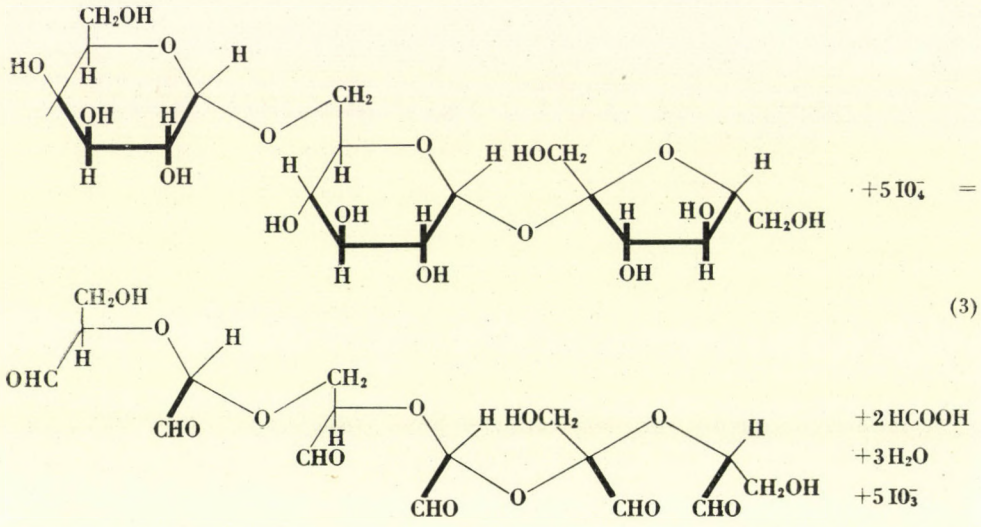
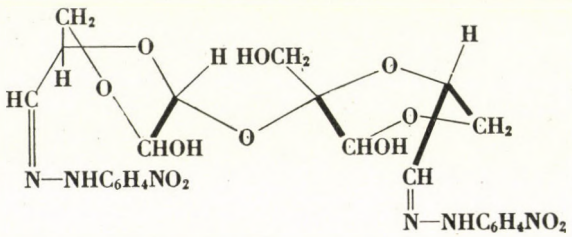


(3)

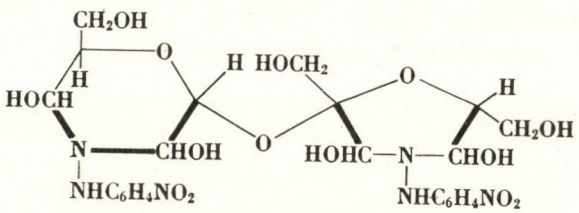
Von FLEURY, COURTOIS und Mitarbeitern [1—5] wurden die Carbonylgruppen, in Gegenwart von Strontiumcarbonat, mit Brom zu Carboxylgruppen oxydiert und die entsprechenden Carbonsäuren nach der Hydrolyse papierchromatographisch identifiziert.

Nach den Untersuchungen der genannten Autoren [4] reagiert der aus der Saccharose gebildete Tetraaldehyd nur mit 2 Molekülen *p*-Nitro-Phenylhydrazin. Ihrer Ansicht nach stehen die beiden Aldehydgruppen des Tetraaldehyds in Acetalbindung mit den entsprechenden primären alkoholischen Hydroxylgruppen. Für das *p*-Nitro-Phenylhydrazon des cyclischen Aldehyds wurde nachstehende Formel angegeben:



(4)

BARRY und MITCHELL [6] beschrieben das Phenylhydrazon des aus der Saccharose gebildeten Tetraaldehyds mit einer den Hemialdalen entsprechenden Struktur:



(5)

AKIYA, OKUI und SUZUKI [7] untersuchten die *p*-Nitro-Phenylhydrazone der aus Trehalose und Raffinose gebildeten Polyaldehyde. Sie stellten fest, daß der Polyaldehyd bei der Trehalose mit 2, anstatt 4 Molekülen *p*-Nitro-Phenylhydrazin und bei der Raffinose mit 3, anstatt 6 Molekülen reagiert. Bezüglich der Struktur des *p*-Nitro-Phenylhydrazons akzeptierten sie das Prinzip nach BARRY und MITCHELL.

Nach MESTER und MÓCZÁR [8] kann das bis-Phenylhydrazon des bei der Oxydation der Saccharose gebildeten Aldehyds mit Benzyl-Diazoniumchlorid in bis-Phenylformazan übergeführt werden. Diese Erfahrung widerlegt eindeutig die Hemialdalstruktur des Phenylhydrazons und deutet auf eine cyclische Acetalstruktur hin.

Ähnlich wie bei unseren früheren Untersuchungen haben wir auch die Trehalose, Saccharose und Raffinose in perjodsaurer ($p_H \approx 1$), in gepufferter essigsaurer ($p_H \approx 4$) bzw. in bicarbonatalkalischer ($p_H \approx 8$) Lösung oxydiert. Das Molverhältnis von Kohlenhydrat : Perjodat war bei den Disacchariden 1 : 12 und bei der Raffinose 1 : 18. In unseren orientierenden Untersuchungen bestimmten wir die Menge des bei der Oxydation verbrauchten Perjodats, der während der Reaktion gebildeten Ameisensäure bzw. des gebildeten Aldehyds, als Funktion der Zeit. Die Ergebnisse sind in den Tabellen I, II und III gezeigt.

Tabelle I

Oxydation der Trehalose mit Perjodat

Oxydationszeit	Bei p_H von Perjodsäure			In gepufferter essigsaurer Lösung	
	Mol Perjodat/ Mol Trehalose	Mol Aldehyd/ Mol Trehalose	Mol Säure/ Mol Trehalose	Mol Perjodat/ Mol Trehalose	Mol Aldehyd/ Mol Trehalose
5 Min.	0,85	0,85	—	1,37	1,49
10 Min.	1,49	1,89	0,31	2,09	2,50
20 Min.	2,09	2,80	0,64	2,74	3,06
40 Min.	2,96	3,14	1,06	3,10	3,12
60 Min.	3,30	3,20	1,23	3,26	3,14
90 Min.	3,58	3,14	1,48	3,46	3,14
120 Min.	3,82	3,16	1,57	3,58	3,14
240 Min.	4,16	3,17	1,72	4,18	3,06
24 St.	4,18	3,04	1,82	4,22	2,96

Die in saurer Lösung gebildeten Polyaldehyde können bei allen drei Kohlenhydraten als stabile Endprodukte der Oxydation betrachtet werden. — Diese Feststellung wurde durch die erhaltenen Aldehydmolzahlen des verbrauchten Perjodats sowie der bei der Reaktion gebildeten Polyaldehyde übereinstimmend unterstützt.

Tabelle II

Oxydation der Saccharose mit Perjodat

Oxydationszeit	Beim p_H von Perjodsäure			In gepufferter essigsaurer Lösung		In $NaHCO_3$-haltiger Lösung	
	Mol Perjodat/Mol Saccharose	Mol Aldehyd/Mol Saccharose	Mol Säure/Mol Saccharose	Mol Perjodat/Mol Saccharose	Mol Aldehyd/Mol Saccharose	Mol Perjodat/Mol Saccharose	Mol Aldehyd/Mol Saccharose
5 Min.	1,27	0,95	0,25	1,91	1,57	0,63	0,74
10 Min.	1,87	1,47	0,34	2,22	1,93	0,99	0,99
20 Min.	2,42	1,65	0,49	2,58	1,94	1,34	1,32
40 Min.	2,74	2,01	0,57	2,78	2,03	1,78	1,58
60 Min.	2,94	2,04	0,69	2,82	2,02	1,95	1,68
90 Min.	2,94	2,06	0,74	3,02	2,06	2,29	1,84
120 Min.	2,98	2,06	0,81	3,02	2,05	2,77	1,86
240 Min.	3,14	2,06	0,89	3,04	2,03	2,04	1,95
24 St.	3,14	2,03	0,99	3,14	2,03	4,78	1,68
48 St.	—	—	—	—	—	4,78	1,68

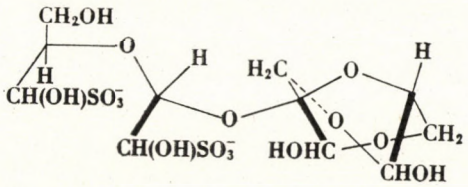
Tabelle III

Oxydation der Raffinose mit Perjodat

Oxydationszeit	Beim p_H von Perjodsäure			In gepufferter essigsaurer Lösung		In $NaHCO_3$-haltiger Lösung	
	Mol Perjodat/Mol Raffinose	Mol Aldehyd/Mol Raffinose	Mol Säure/Mol Raffinose	Mol Perjodat/Mol Raffinose	Mol Aldehyd/Mol Raffinose	Mol Perjodat/Mol Raffinose	Mol Aldehyd/Mol Raffinose
5 Min.	2,33	2,30	0,35	2,93	3,04	0,66	—
10 Min.	2,63	2,88	0,57	3,47	3,53	1,45	1,46
20 Min.	3,71	3,32	0,98	4,01	3,86	2,14	2,18
40 Min.	4,24	3,68	1,23	4,36	3,98	3,18	2,45
60 Min.	4,48	3,77	1,41	4,48	4,03	3,72	3,26
90 Min.	4,93	3,84	1,57	4,72	3,89	4,13	3,41
120 Min.	5,02	3,84	1,64	4,96	3,90	4,83	3,41
240 Min.	5,26	3,89	1,79	5,05	3,89	5,84	3,56
24 St.	5,26	3,92	1,89	5,26	3,89	9,57	3,14
48 St.	—	—	—	—	—	10,00	3,08

Der aus der Saccharose gebildete Tetraaldehyd additioniert eindeutig 2 Moleküle Bisulfit. Diese Beobachtung steht in vollem Einklang mit der cyclischen, zwei freie Aldehydgruppen enthaltenden Struktur, kann aber mit der Hemialdalstruktur nicht erklärt werden.

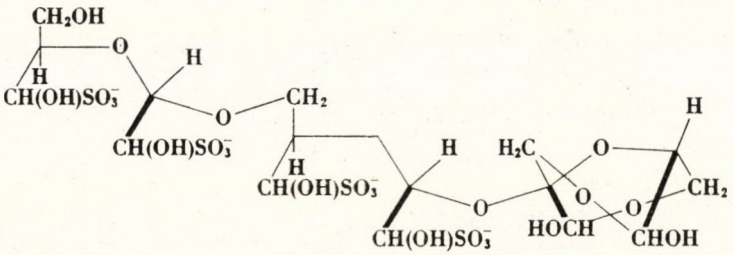
Unserer Meinung nach muß die cyclische, von FLEURY und COURTOIS angenommene Acetalstruktur auf Grund der ausführlichen Analyse unserer bisher im Zusammenhange mit den Sacchariden erhaltenen Angaben revidiert werden. Unserer Auffassung nach enthält der oxydierte Glucoseteil beide freie Aldehydgruppen und die Aldehydgruppen des oxydierten Fructoseteils bilden mit den beiden hier anwesenden primären alkoholischen Hydroxylgruppen ein bicyclisches Acetal.



(6)

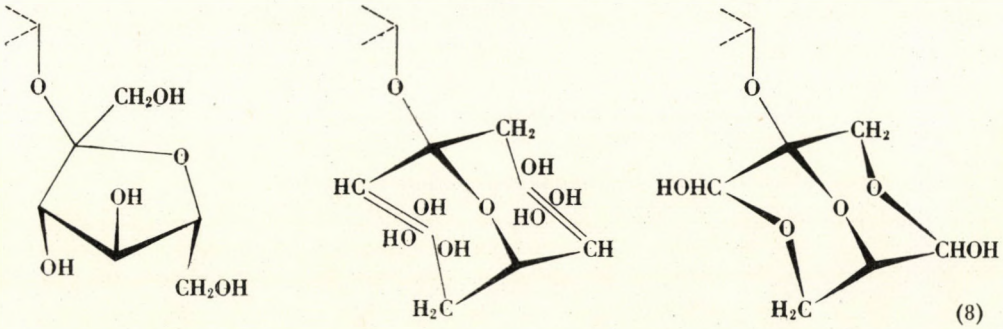
Diese Annahme wird durch mehrere Erfahrungen bestätigt. Der oxydierte Glucose- bzw. Galactoseteil additioniert sowohl beim Methylglucosid [9] als auch bei der Melibiose [10] 2 Moleküle Bisulfit.

Die Raffinose enthält Struktureinheiten, die sowohl für die Saccharose als auch für die Melibiose charakteristisch sind, und sie liefert bei der Oxydation einen Hexaaldehyd (Gleichung 3.). Dieser Hexaaldehyd additioniert, im Gegensatz zur Kondensation [7] von 3 Molekülen *p*-Nitrophenylhydrazin, 4 Moleküle Bisulfit. Diese Tatsache deutet gleichfalls, in Übereinstimmung mit den früheren Erfahrungen, auf die Acetalbindung beider Aldehydgruppen des oxydierten Fructoseteiles hin.



(7)

Die Oxydations- und Ringschlußverhältnisse, beim Fructofuranosid-Teil der Saccharose und Raffinose veranschaulichen die nachstehenden Formeln.



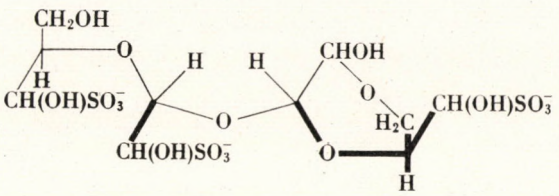
(8)

Den eindeutigsten Beweis für die Existenz des doppelten Dioxanringes könnte die Untersuchung der Oxydation des Methyl-fruktofuranosids mit Perjodat liefern. Diese Verbindung stand uns aber bisher nicht zur Verfügung; der Annahme nach kann das bei ihrer Oxydation gebildete Produkt mit Bisulfit nicht reagieren.

Die Bisulfitaddition der Oxydationsprodukte von Methyglucosid, Melibiose, Saccharose und Raffinose weist auf die Reaktionsfähigkeit beider Aldehydgruppen des oxydierten Glucose- und Galactose-Teils hin. Durch Vergleich der Additionsbereitschaft der aus Methylglucosid und Methylrabinosid gebildeten Dialdehyde ergab sich [9], daß die additionierte Bisulfitmenge beim Methylglucosid, wo eine cyclische Acetalbildung prinzipiell möglich ist, um 6% niedrieger war, als die theoretische. Dies konnte im Fall von oxydiertem Methylarabinosid nicht beobachtet werden, was sich damit erklären läßt, daß hier keine Möglichkeit zur Bildung eines cyclischen Acetals besteht. Die oxydierte Melibiose kann ein cyclisches Acetal prinzipiell bilden, nach unseren Bestimmungen additioniert sie aber trotzdem 3 Moleküle Bisulfit.

Die auf die Bisulfitaddition der oxydierten Glucose-Teile bezügliche einheitliche Anschauung wird jedoch durch jene Erfahrung gestört, daß die oxydierte Trehalose, die aus zwei oxydierten Glucose-Teilen gebildet wird, nicht 4, sondern nur etwas mehr als 3 Moleküle Bisulfit additioniert (Tabelle I). Die mit dem »Bisulfit-Cyanid«-Verfahren bestimmte Aldehydzahl ist, unseren Untersuchungen nach, ein sehr konstanter Wert, der sich auch bei verschiedenen Bisulfitüberschüssen und Reaktionszeiten nicht ändert.

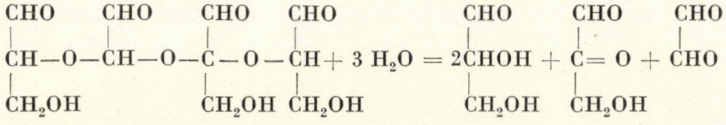
Die eingehende Analyse der sich bei den von uns beobachteten Bisulfitadditionen sowie in den Bildungsreaktionen der Phenylhydrazone zeigenden scheinbaren Wiedersprüche liefert — unserer Meinung nach — wertvolle Beiträge zur Beurteilung der Reaktionsbereitschaft und der Reaktionen von Polyaldehyden. Auch in unserer früheren Mitteilung [9] wurde schon betont, daß die Aldehydgruppen dieser Polyaldehyde sehr aktiv sind, und daher kommt es vor, daß sie im Grundzustand in Form eines cyclischen Acetals, Hemialdals bzw. Oxohydrats vorliegen. Aus den mit der gesteigerten Reaktionsfähigkeit verbundenen günstigen räumlichen Stellungen folgt auch, daß in manchen Fällen, wenn sich keine Hydroxymethylgruppe in günstiger räumlicher Stellung in der Nähe der Aldehydgruppe befindet, ein Phenylhydrazon mit Hemialdalstruktur entsteht [11]. Es ist auch einzusehen, daß jede nachfolgende Aldehydgruppe bei der sukzessiven Bisulfitaddition des Polyaldehyds Bisulfit mit verminderter Reaktionsfähigkeit additioniert. Auf Grund dieser Anschauung kann die Reaktion des bei der Oxydation der Trehalose gebildeten Tetraaldehyds mit 3 Molekülen Bisulfit auf folgende Weise gedeutet werden:



(9)

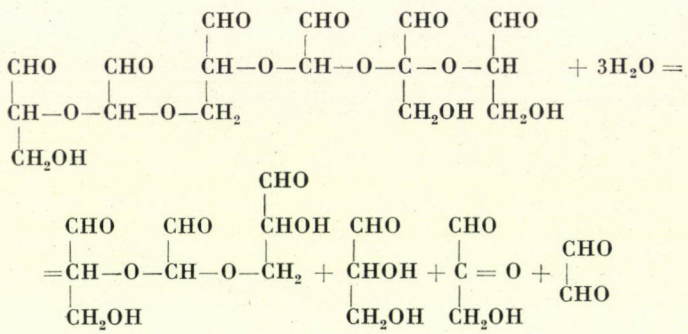
Unsere Erfahrungen bezüglich der Bisulfitaddition liefern keine Aufschlüsse über die tatsächlichen Gleichgewichtsverhältnisse der Grundfigurationen (Oxohydrat, Hemialdal, cyclisches Acetal) der Polyaldehyde, da die Gleichgewichte auf Einwirkung des Bisulfits gestört werden, und infolge der Bildung einer neuen Gruppe (α-Hydroxysulfonat) kann auch die relative Stabilität der anderen Grundkonfigurationen eine Änderung erfahren. Auf Grund des additionierten Bisulfits und der Verhältnisse aller in Betracht kommenden Aldehydgruppen des Polyaldehyds kann jedoch eindeutig bestätigt werden, daß nur die Bildung des cyclischen Acetals mit der Aldehydbisulfit-Bildung konkurrenzfähig ist. Vom analytischen Gesichtspunkt ist jene Erfahrung von entscheidender Bedeutung, daß die Bisulfitaddition in den meisten Fällen »quantiert« ist, d. h. das Molverhältnis des gebundenen Bisulfits und Polyaldehyds in entsprechendem Maße ganzzahlig ist.

Die bei der Oxydation von Trehalose, Saccharose und Raffinose gebildeten Polyaldehyde können — im Gegensatz zu den früher untersuchten, aus den reduzierenden Disacchariden gebildeten Polyaldehyden — in siedender 1 *n* salzsaurer Lösung hydrolysiert werden. Die Acetalbindungen der Polyaldehyde der reduzierenden Disaccharide sind ausserordentlich stabil, und die Tatsache, daß diese auch durch energische Einwirkung gar nicht hydrolysiert werden können, kann mit der Elektronenanziehung durch die benachbarten Carbonylgruppen erklärt werden. Diese Steigerung der Stabilität ist auch bei den Acetalbindungen der Polyaldehyde der nicht reduzierenden Disaccharide zu erwarten. Die Saccharose kann bekanntlich außerordentlich leicht hydrolysiert werden: die Reaktion läuft in 0,01 *n* salzsaurer Lösung bei 100 °C in einigen Minuten vollkommen ab. Die totale Hydrolyse des bei der Oxydation der Saccharose gebildeten Tetraaldehyds kann nach unseren Untersuchungen durchgeführt werden, sie nimmt aber in *n* salzsaurer Lösung bei 100 °C etwa 2 Stunden in Anspruch. Nach dieser Hydrolyse können die theoretischen 5 Moleküle Aldehyd mit dem »Bisulfit-Cyanid«-Verfahren bestimmt werden:



(10)

Der Hexaaldehyd der Raffinose kann unter ähnlichen Bedingungen nach folgender Gleichung hydrolysiert werden:



(11)

Nach der Hydrolyse können die der Gleichung entsprechenden, theoretischen 7 Moleküle mit dem »Bisulfit-Cyanid«-Verfahren bestimmt werden. Der unverändert gebliebene Trialdehyd ist ein charakteristisches Produkt der direkten Oxydation der Melibiose mit Perjodat, welches — wie von uns schon früher festgestellt wurde — unter den obigen Bedingungen nicht hydrolysiert werden kann [10]. Unserer Ansicht nach beginnen die Hydrolysen mit der Spaltung der Bindungen zwischen dem Glyoxal und dem Hydroxymethylglyoxal. Diese Bindungen sind reine Geminal-Diol-Acetalbindungen, welche sich infolge der im Zusammenhang mit der Fructose erwähnten bicyclischen Acetalbindungen (siehe Formel 9) leichter hydrolysiert werden können, als andere Acetalbindungen. Erfahrungsgemäß können die intermediär gebildeten Halbacetale hydrolysiert werden, die normalen Acetale aber sind stabil. Die Hydrolyse des Tetraaldehyds der Trehalose ist unter den obigen Umständen

Tabelle IV

Bestimmung der Trehalose über den bei der Oxydation mit Perjodat gebildeten „Trialdehyd"

Einwaage Trehalose $2\,H_2O$ g/100,00 ml	Eingemessene Lösung, ml	Verbr. 0,1 *n* Jodlösung, ml		Gefunden Trehalose $2\,H_2O$	
		einzeln	Durchschn.	mg	%
		8,42			
	10,00	8,35	8,38	52,84	104,2
		8,38			
		4,30			
0,5070	5,04	4,20	4,23	26,67	104,4
		4,20			
		1,65			
	2,00	1,66	1,66	10,47	103,2
		1,68			

auch nur eine teilweise: in 2 Stunden etwa 30%-ig. Auch dies deutet darauf, daß die Geminale-Diol-Acetalbindung (im erwähnten Fall zwischen den beiden Glyoxal-Teilen) leichter hydrolysiert, da der Anteil des cyclischen Acetals kleiner ist, so gelangt die stabilisierende Wirkung der Aldehydgruppen in gesteigertem Maße zur Geltung, als bei der Saccharose und Raffinose.

Die Ergebnisse der Bestimmung von Saccharose, Raffinose und Trehalose sind in den Tabellen IV, V und VI zusammengestellt.

Tabelle V

Bestimmung der Saccharose über den bei der Oxydation mit Perjodat gebildeten „Dialdehyd"

Einwaage Saccharose g/100,00 ml	Eingemessene Lösung, ml	Verbr. 0,1 *n* Jodlösung, ml		Gefunden Sacharose	
		einzeln	Durchschn.	mg	%
		10,20			
	20,00	10,17	10,17	87,03	101,0
		10,18			
		5,14			
0,43045	10,00	5,12	5,12	43,82	101,7
		5,11			
		2,53			
	5,00	2,51	2,52	21,56	100,0
		2,52			

Tabelle VI

Bestimmung der Raffinose über den bei der Oxydation mit Perjodat gebildeten „Tetraaldehyd"

Einwaage Raffinose 5 H_2O g/100,00 ml	Eingemessene Lösung, ml	Verbrauchte 0,1 *n* Jodlösung, ml		Gefunden Raffinose. 5 H_2O	
		einzeln	Durchschn.	mg	%
		9,85			
	10,00	9,81	9,82	72,98	98,0
		9,78			
		4,90			
0,7449	4,98	4,90	4,88	36,27	97,8
		4,85			
		1,95			
	2,00	1,98	1,98	14,72	98,2
		2,00			

Beschreibung der Verfahren

Bestimmung von Trehalose, Saccharose und Raffinose über den bei der Oxydation mit Perjodat gebildeten Polyaldehyd

Reagenzien:

0,1 *n* Jodlösung
5%ige Jodlösung
0,3 molare Perjodsäure-Lösung
1,5 molare Natriumsulfit-Lösung
20%ige Natriumhydroxyd-Lösung
20%ige Salzsäure
10%ige Essigsäure
1%ige Stärkelösung als Indikator
0,2%ige alkoholische Methylrotlösung
Kaliumcyanid (fest)
Pentan

0,5—0,6 g kristalline Trehalose, 0,8—0,9 g Saccharose bzw. 0,6—0,7 g kristalline Raffinose werden analytisch genau eingewogen und in destilliertem Wasser gelöst. Die Lösung wird in einen 100-ml-Meßkolben gespült und bis zur Marke ergänzt. Aus der so vorbereiteten Stammlösung werden 10,00 ml in einen 100 ml fassenden, mit Glasstopfen versehenen Erlenmeyer-Kolben pipettiert und mit 5 ml Perjodatsäure versetzt. (Bei Verwendung von Natriumperjodat wird die Lösung mit 1 ml Essigsäure angesäuert.) Nach 1—2stündiger Wartezeit wird Natriumsulfit-Lösung mit Hilfe einer eingeteilten 10-ml-Pipette so lange in die Probelösung getropft, bis die Farbe des anfangs ausgeschiedenen Jods verschwindet, dann wird noch 1 ml Natriumsulfit-Lösung zugegeben. Hienach wird die Lösung in Gegenwart von 1—2 Tropfen Methylrot-Indikatorlösung mit Natronlauge neutralisiert und dann mit 2 ml Essigsäure angesäuert. Der Inhalt des verschlossenen Kolbens wird mehrmals geschüttelt, um auch das am Schliff haftende Perjodat zu reduzieren. Die eventuell warm gewordene Lösung wird mit Wasser abgekühlt und mit 5 ml Pentan überschichtet.

Nach einstündiger Wartezeit wird der Sulfitüberschuß in Gegenwart von 10 Tropfen Stärkelösung mit Jodlösung oxydiert. Am Anfang wird dies mit 5%iger, zum Schluß mit 0,1 *n* Jodlösung vorgenommen. Nach Erreichung der blauen Farbe wird der verschlossene Kolben energisch geschüttelt, der Stopfen wird von Zeit zu Zeit gelockert, um auch das am Schliff haftende Sulfit zu reduzieren, und wenn nötig, wird die Farbe der Lösung aus einer Bürette mit 0,1 *n* Jodlösung auf die bläuliche Anfangsfarbe eingestellt.

Nach Entfernung des Sulfitüberschusses wird die Probelösung mit 4 ml Natronlauge alkalisch gemacht, und es werden 0,2—0,3 g Kaliumcyanid in den Kolben gegeben. Die Lösung wird vorsichtig gerührt, dann nach 3 Minuten aus einer eingeteilten 10-ml-Pipette mit Salzsäure neutralisiert, und nachher mit weiteren 1,5—2 ml Salzsäure angesäuert. Nun wird ohne lebhaftes Schütteln mit 0,1 *n* Jodlösung titriert. Anfangs wird die Meßlösung in größeren Portionen zugegeben, nach dem Erreichen der blauen Farbe wird der Kolben verschlossen, geschüttelt, und wenn nötig wird durch Zugabe von weiteren 1—2 Tropfen Meßlösung bis zur bleibenden blauen Farbe titriert.

In der Bestimmung ist das Äquivalentgewicht der Trehalose: Molekulargewicht/6, das der Saccharose: Molekulargewicht/4 und das der Raffinose: Molekulargewicht/8.

1 ml 0,1 *n* Jodlösung entspricht 6,306 mg kristalliner Trehalose ($C_{12}H_{22}O_{11} \cdot 2\,H_2O$), 8,558 mg Saccharose ($C_{12}H_{22}O_{11}$) und 7,432 mg kristalliner Raffinose ($C_{18}H_{32}O_{16} \cdot 5\,H_2O$).

ZUSAMMENFASSUNG

In saurer Lösung ($p_H \approx 1$—4) bilden sich bei der Oxydation von Trehalose, Saccharose und Raffinose mit Perjodat stabile Polyaldehyde. Die Oxogruppen dieser Polyaldehyde bilden mit Bisulfit Aldehydbisulfite. Die Reaktionsfähigkeit und die Struktur dieser Polyaldehyde wird auf Grund der Bisulfitaddition gedeutet und zur Bestimmung dieser drei nicht reduzierenden Saccharide wird das von den Verfassern schon früher empfohlene »Bisulfit-Cyanid«-Verfahren benützt.

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NATURAL CHROMONES, IV

ATTEMPTS TOWARDS THE SYNTHESIS OF KHELLIN

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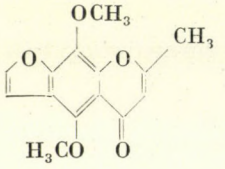
Most of the successful syntheses of the linearly disposed furochromones, such as visnagin and khellin **(I)** which are the crystalline principles of the drug *Ammi visnaga* L. [1], follow either of two routes. One [2—4] proceeds through the construction of a 2-methyl-γ-pyrone system onto a suitably substituted benzofuran, and the other [5, 6] through the elaboration of a furan at the appropriate site in the requisite chromone. Whereas the first approach has been favoured in most total syntheses, the latter one has been used in few syntheses mainly by the *Seshadri* group who conceived that such sequence follows more closely the process of biosynthesis in plants. We have also recently reported [7] a total synthesis of visnagin depending on the chromone route where the furan ring was built on a 6-formylchromone residue. We wish now to report on some experiments carried out with the ultimate objective, unfortunately not realized, of preparing khellin **(I)** from a 2-methylchromone derivative.

For the construction of the furan ring linearly onto a chromone residue, one may consider direct formylation [5] in the C-6 position followed by cyclization with the adjacent 7-phenoxyacetate grouping. An alternative and more attractive pathway [6] consists in securing an allyl group in the C-6 positon by Claisen migration from a neighbouring allyloxy group, but not by direct C-allylation which is not possible [8], followed by ozonolysis and cyclization of the resulting 6-acetaldehyde which is quite facile. It is generally appreciated in such syntheses, especially in those aiming at khellin, that the introduction of the 8-methoxy group (or a hydroxyl) should precede any attempt for the construction of the furan ring. This is because of the known [9] enhanced reactivity of the C-8 position over the C-6 position As a result, any formylation or Claisen migration from a 7-allyloxy group would most likely proceed to the vacant C-8 position which spells a potential angular constitution as opposed to the desirable linear disposition.

The material of choice in the present study was 2-methyl-5,7-dihydroxychromone **(II)** also used previously in syntheses of visnagin [6] and khellin [5]. The ready availability of this material and its importance induced us to study its preparation in some detail. For its synthesis, GULATI *et al.*

[10], depending on an original procedure by JOCHUM and KOSTANECKI [11], treated phloroacetophenone with more than 10 moles of acetic anhydride containing sodium acetate which gave mainly 2-methyl-3-acetyl-5,7-diacetoxychromone **(III)** along with some of the 5,7-dihydroxy analogue **(IV)**. In our hands, the same treatment of phloroacetophenone, however, gave no trace of **IV** but mainly **III** along with a small amount of a new compound, 2-methyl-3-acetyl-5-hydroxy-7-acetoxychromone (**V**), which was the sole product from a treatment with only 5 moles of acetic anhydride. Acetylation of both **IV** and **V** afforded **III**.



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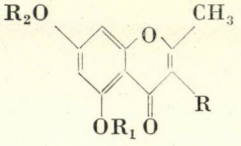
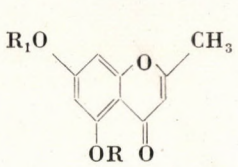


II: $R = R_1 = R_2 = H$
III: $R = R_1 = R_2 = COCH_3$
IV: $R = COCH_3$, $R_1 = R_2 = H$
V: $R = R_2 = COCH_3$, $R_1 = H$

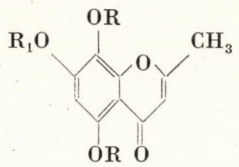
This influence of the reagent concentration in directing the reaction course appears also in the subsequent deacetylations to **II**. Thus while 5% sodium carbonate solution only effected [12] saponification of the acetoxyl groups in **III** and **V** to give **IV** from both, the use of a 10% solution of this reagent was necessary for total deacetylation in **III**, **IV** and **V** which all gave **II**. The effect of mineral acid (with **V**) was also limited to saponification (to give **IV**). We find from these transformations that the best route towards the desirable intermediate **(II)** proceeds from phloroacetophenone by treatment with 5 moles of acetic anhydride followed, directly or after the isolation of **V**, by treatment with a strong (not less than 10%) solution of sodium carbonate; this affords **II** in about 50% overall yield. It appears therefore that the formation of the C-3 acetyl is inevitable during the BAKER—VENKATARAMAN construction of the γ-pyrone system, where sodium acetate is used as a base, but the acylation of the phenolic groups and the possible complications arising therefrom may be limited by a careful control of the conditions.

Allylation of **II** gave a good yield of the C-7 ether **(VI)** in which the 5-hydroxyl group could be methylated (to give **VII**) only by intensive treatment with methyl iodide. Hydroxylation at C-8 was realized by the ELB's persulphate oxidation of **VI**, and the resulting product **(VIII)** was methylated, not without difficulty, at both hydroxyl groups to give **IX**. The same product **(IX)** also resulted, in a different sequence, by initial etherification at C-7 with benzyl chloride (to give **X**) followed by alkaline persulphate oxidation

(to give **XI**), methylation (to give **XII**) and final hydrogenolysis and direct allylation.



VI: R = H, $R_1 = CH_2 \cdot CH = CH_2$
VII: R = CH_3, $R_1 = CH_2 \cdot CH = CH_2$
X: R = H, $R_1 = CH_2 \cdot C_6H_5$



VIII: R = H, $R_1 = CH_2 \cdot CH = CH_2$
IX: R = CH_3, $R_1 = CH_2 \cdot CH = CH_2$
XI: R = H, $R_1 = CH_2 \cdot C_6H_5$
XII: R = CH_3, $R_1 = CH_2 \cdot C_6H_5$

While these experiments were in progress, the preparation of the same 2-methyl-5,8-dimethoxy-7-allyloxychromone **(IX)** was reported by ANEJA *et al.* [3] by a different route starting from 2,4-dihydroxy-3,6-dimethoxyacetophenone. As in the latter report [3], all attempts made to induce a Claisen migration in **IX** failed. These attempts included heating of the dry solid alone or in a solution of N,N-dimethylaniline and other high boiling solvents for various lengths of time, leading in all cases to intractable mixtures. It was for this reason that ANEJA *et al.* [3] abandoned this approach and followed another pathway trough the initial elaboration of the furan ring onto the parent acetophenone derivative when the Claisen migration of the allyloxy group proceeded smoothly. It is remarkable that such migration is also possible from a C-5 allyloxy group (proceeding to the vacant C-6 position) in a chromone system as made by ANEJA *et al.* [6] in their total synthesis of visnagin. We wish, finally, to mention that an attempted alkaline persulphate oxidation of **V** resulted only in decylation to give **II**.

Experimental

2-Methyl-3-acetyl-5-hydroxy-7-acetoxychromone (V)

Phloroacetophenone (36 g) together with freshly fused sodium acetate (45 g) was refluxed in acetic anhydride (120 ml) for 6 hrs. After cooling, the reaction mixture was poured into ice-water (500 g), and the resulting crude product (52 g) was treated with Norite and finally crystallized from ethanol to give **V** as colourless needles, m.p. 135—137°. The substance gave brownish-red colour with alcoholic ferric chloride solution, and yellow colour with 0.1% aqueous uranyl acetate, indicating the presence of a free 5-hydroxyl group.
$C_{14}H_{12}O_6$ (276.24). Calcd. C 60.87; H 4.38. Found C 60.96; H 4.50%.

2-Methyl-3-acetyl-5,7-diacetoxychromone (III)

(a) A mixture of dry phloroacetophenone (1 g) and fused sodium acetate (1 g) was refluxed in acetic anhydride (6 ml) for 6 hrs. The reaction mixture was poured into ice-water, and the resulting precipitate was filtered off and crystallized from ethyl alcohol to give **III** (0.7 g) as colourless plates, m.p. 130—132°.
$C_{16}H_{14}O_7$ (318.27). Calcd. C 60.38; H 4.43. Found C 60.88; H 4.63%.
From the mother liquor, compound **V** (120 mg), m.p. and mixed m.p. 135—137°, was isolated.

(b) A mixture of 2-methyl-3-acetyl-5-hydroxy-7-acetoxychromone (**V**, 100 mg) and fused sodium acetate (50 mg) was boiled under reflux in acetic anhydride (1.5 ml) for 2 hrs. The solid product (90 mg), obtained after working up as usual, was crystallized from ethyl alcohol to give **III** in colourless plates, m.p. and mixed m.p. 130—132°.

(c) A similar acetylation of compound **IV** (see below, 120 mg) afforded **III** (110 mg), m.p. and mixed m.p. 130—132°.

2-Methyl-3-acetyl-5,7-dihydroxychromone (IV)

(a) A solution of **III** (1 g) in aqueous sodium carbonate solution (5%; 10 ml) was refluxed for 3 hrs. The product (0.8 g) obtained by acidification with dilute hydrochloric acid was crystallized from aqueous ethyl alcohol to give colourless needles of **IV**, m.p. 262—264°. Its solution in alcohol gave a wine-red colour with alcoholic ferric chloride and a yellow colour with 0.1% aqueous uranyl acetate.

$C_{12}H_{10}O_5$ (234.20). Calcd. C 61.54; H 4.30. Found C 61.47; H 4.49%.

(b) The same product (**IV**) was obtained by a similar treatment of **V** (5 g) with aqueous Na_2CO_3 (5%; 35 ml) by refluxing for 3 hrs. The product (4.5 g) obtained upon acidification with dilute HCl was crystallized from aqueous ethyl alcohol to give colourless needles, m.p. and mixed m.p. 262—264°.

(c) Compound **V** (250 mg) was refluxed with a mixture of conc. HCl (3 ml) and water (3 ml) for 30 min., then diluted with 30 ml of ice-cold water. The resulting precipitate (230 mg) of **IV** was then crystallized from aqueous ethyl alcohol to give colourless needles, m.p. and mixed m.p. 262—264°.

2-Methyl-5,7-dihydroxychromone (II)

(a) A solution of **III** (1 g) in aqueous Na_2CO_3 (10%; 20 ml) was refluxed for 2 hrs. The clear solution was acidified with dilute HCl, the resulting precipitate was filtered off and crystallized from ethyl alcohol to give **II** as colourless long plates, m.p. 292—294°; lit. [10, 11] m.p. 279° and 290°.

(b) Similar treatment of **IV** (2.5 g) with aqueous Na_2CO_3 (10%; 80 ml) by boiling for 2 hrs., followed by the usual work-up and crystallization from ethyl alcohol gave **II** as colourless plates, m.p. and mixed m.p. 292—294°.

(c) Treatment of **V** (3 g) as described above afforded **II** (2 g), m.p. and mixed m.p. 292—294°.

2-Methyl-5-hydroxy-7-allyloxychromone (VI)

A mixture of 2-methyl-5,7-dihydroxychromone (**II**; 2 g), anhydrous potassium carbonate (7 g), and allyl bromide (5 ml) in dry acetone (30 ml) was refluxed for 6 hrs. The carbonate residue was filtered off while hot, and washed with hot acetone. The filtrate and washings were evaporated to dryness, and the oily residue was treated with petroleum ether (b.p. 40—60°). The solidified mass which formed (1.8 g) was crystallized from ethyl alcohol to give colourless needless of **VI**, m.p. 110—112°.

$C_{13}H_{12}O_4$ (232.23). Calcd. C 67.23; H 5.21. Found C 67.01; H 5.38%.

2-Methyl-5-methoxy-7-allyloxychromone (VII)

To a solution of the previous compound (**VI**, 2 g) in dry acetone (30 ml) there was added anhydrous potassium carbonate (7 g) followed by methyl iodide (5 ml), and the mixture was refluxed for 50 hrs. The oily residue obtained after the usual work-up solidified on treatment with *n*-hexane (20 ml) and cooling. Crystallization from benzene-*n*-hexane afforded **VII** in colourless plates, m.p. 85—87°.

$C_{14}H_{14}O_4 \cdot 1/2\ H_2O$ (255.25). Calcd. C 65.88; H 5.88. Found C 65.89; H 5.91%.

2-Methyl-5,8-dihydroxy-7-allyloxychromone (VIII)

A solution of compound **VI** (0.7 g) in a mixture of NaOH solution (4%; 17 ml) and pyridine (14 ml) maintained at 10—15°, was treated with aqueous potassium persulphate solution (2%; 70 ml) and sodium hydroxide solution (4%; 17 ml) added alternately dropwise, with

stirring, during 4 hrs. The red solution thus obtained, after standing for 24 hrs., was acidified to Congo Red with HCl and extracted with ether to remove any unchanged starting material. The clear solution was treated with sodium sulphite (0.7 g) and conc. HCl (10 ml) then warmed on a steam bath for 30 min. The cooled solution was extracted with ether and the yellow residue (120 mg) was crystallized from ethyl alcohol to give **VIII** in yellow needles, m.p. 172—174° (d.). The substance gave a green colour with alcoholic ferric chloride solution.
$C_{13}H_{12}O_5$ (248.23). Calcd. C 62.9; H 4.87. Found C 63.01; H 5.44%.

2-Methyl-5,8-dimethoxy-7-allyloxychromone (IX)

A solution of **VIII** (0.35 g), anhydrous K_2CO_3 (2 g) and methyl iodide in acetone (60 ml) was refluxed for 50 hrs. After working up in the usual manner **IX** was obtained (0.3 g). Recrystallization from methyl alcohol-*n*-hexane gave colourless long needles, m.p. 79—81°, lit. [3] m.p. 83—84°.
$C_{15}H_{16}O_5 \cdot 2\ H_2O$ (312.28). Calcd. C 57.69; H 6.41. Found C 57.99; H 6.56%.

2-Methyl-5-hydroxy-7-benzyloxychromone (X)

A mixture of compound **II** (2 g), anhydrous K_2CO_3 (5 g) and benzyl chloride (6 ml) in dry acetone (50 ml) was refluxed for 6 hrs. The crude creamish substance (1.5 g) which resulted after the usual work-up, was crystallized from ethyl alcohol to give **X** as pale yellowish plates, m.p. 136—138°. The substance gave brownish-red colour with alcoholic ferric chloride solution.
$C_{17}H_{14}O_4$ (282.28). Calcd. C 72.33; H 5.00. Found C 72.24; H 5.31%.

2-Methyl-5,8-dihydroxy-7-benzyloxychromone (XI)

Compound **X** (0.3 g) dissolved in a mixture of NaOH solution (4%; 10 ml) and pyridin (7 ml), kept at 10—15°, was treated with aqueous potassium persulphate solution (2%; 30 ml) and NaOH solution (4%; 10 ml) added alternately dropwise while stirring for 4 hrs. The red solution obtained was allowed to stand for 24 hrs., then acidified to Congo Red with HCl and extracted with ether to remove any unchanged starting material. The aqueous solution was treated with sodium sulphite and conc. HCl (7 ml), then warmed on a steam bath for 30 min. Extraction with ether gave a yellowish crude product (80 mg) which was recrystallized from ethyl alcohol to give **XI** in yellow needles, m.p. 230—232°. It gave a green ferric chloride reaction.
$C_{17}H_{14}O_5$ (298.28). Calcd. C 68.45; H 4.73. Found C 68.48; H 4.97%.

2-Methyl-5,8-dimethoxy-7-benzyloxychromone (XII)

A mixture of compound **XI** (0.4 g), anhydrous K_2CO_3 (2 g) and methyl iodide (2 ml) in acetone (50 ml) was refluxed for 50 hrs. The crude product (0.3g), obtained after the usual work-up, was recrystallized from alcohol to give **XII** in colourless plates, m.p. 174—176°.
$C_{19}H_{18}O_5$ (326.33). Calcd. C 69.92; H 5.56. Found C 70.02; H 5.62%.

Transformation of XII into IX

To a solution of compound **XII** (100 mg) in absolute ethanol (20 ml) palladized charcoal (10%; 100 mg) was added, and the mixture was treated at room temperature and atmospheric pressure with hydrogen (1.5 hrs.). The catalyst was filtered off and the filtrate evaporated to leave a colourless solid. This was directly boiled under reflux with anhydrous K_2CO_3 (0.5 g) and allyl bromide (1 ml) in dry acetone (20 ml) for 8 hrs. After the usual work-up, the product was inspected on silica gel chromatoplates. The formation of 2-methyl-5,8-dimethoxy-7-allyloxychromone (**IX**) was established by comparison with **IX** prepared in a previous experiment. The two spots had the same location (R_f 0.65) using a solvent system of xylene-acetone (20 : 5) and the same yellowish-green UV fluorescence before and after spraying with 10% aqueous NaOH.

Reaction of V with alkaline potassium persulphate

Compound **V** (1 g) was treated, in a mixture of sodium hydroxide solution and pyridine solution, with alkaline potassium persulphate as described before. After the same work-up, the crude product (0.6 g) was crystallized from ethyl alcohol and shown to be identical with 2-methyl-5,7-dihydroxychromone (**II**), m.p. and mixed m.p. 292—294°.

SUMMARY

A study of the reactions involved in the preparation of 2-methyl-5,7-dihydroxychromone from phloroacetophenone is described. In an attempt to prepare khellin, this intermediate was transformed by two methods into the 5,8-dimethoxy-7-allyloxy derivative which, however, was not amenable to Claisen rearrangement.

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ALKYLATION OF METHYLDICHLOROSILANE AND METHYLDIMETHOXYSILANE WITH BUTYLLITHIUM AND WITH BUTYLMAGNESIUM BROMIDE

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According to the observations of GILMAN and other authors, the alkyl substitution of a hydrogen atom participating in a Si-H bond can generally be successfully accomplished by means of organo lithium compounds [1, 2]. The Grignard reaction can be made in tetrahydrofuran [3, 4]; in ether it does not always take place [4, 5, 6, 7]. The alkyl substitution of a chlorine atom and methoxyl group attached to a silicon atom can be achieved in satisfactory yields by means of Grignard reagents [8] or organolithium compounds [9], though the rate of alkylation is different for the two types of compounds. During the experiments to be reported, the reactions of methyldichlorosilane and methyldimethoxysilane with butyllithium and butylmagnesium bromide were investigated with the purpose to compare the reactivities of the hydrogen, chlorine and methoxyl substituents. The quantity of the metal-organic compound was chosen to be equivalent with one or both chlorine (or methoxyl) substituents, and the degree of alkyl substitution on the silicon-hydrogen bond was examined.

The experimental results were evaluated by gas chromatographic analysis.

The methyldichlorosilane used in the experiments was prepared by the known procedure [10], and its purity checked by gas chromatography. Several authors have prepared methylhydrogenalkoxysilanes by means of transesterification [11, 12, 13]. As the hydrogen chloride evolved during the direct preparation with alcohol splits the Si—H bond, KÖRNER's patent [14] recommends the use of urea for neutralization.

The methyldimethoxysilane used in our experiments was prepared from methyldichlorosilane with methanol. To neutralize hydrochloric acid, ammonia gas was led into the mixture, as the Si—H bond reacts with ammonia only in the presence of an alkali amide catalyst [15]. The same method was used for the methanolysis of the Si—Cl bond that had remained unchanged after alkylation of the methyldichlorosilane. The aim of this operation was to avoid difficulties arising in the quantitative gas chromatographic investigation of readily hydrolyzing chlorine-containing products, and at the same time it had the ad-

vantage that the compositions of the reaction products formed both from chlorosilane and methoxysilane were evaluated in this way by the quantitative determination of the same three compounds (See Table I).

Discussion of the results

During the alkylation of methyldichlorosilane and methyldimethoxysilane, the following main reactions may take place:

$$CH_3 \cdot X_2SiH + C_4H_9M \rightarrow CH_3 \cdot C_4H_9 \cdot X \cdot SiH + MX$$

$$CH_3 \cdot X_2SiH + 2\ C_4H_9M \rightarrow CH_3(C_4H_9)_2SiH + 2\ MX$$

$$CH_3 \cdot X_2SiH + C_4H_9M \rightarrow CH_3 \cdot X_2 \cdot SiC_4H_9 + MH$$

where X = halogen (Cl) or methoxyl group,
M = lithium or bromomagnesium.

The composition of the crude reaction products was determined by gas chromatographic analysis after converting the chloro derivatives into methoxy derivatives. The quantitative data are shown in Table I.

Table I

Alkylation reactions

Quantitative data

Starting materials and molar ratios	Composition of the reaction products, %		
	$CH_3 \cdot C_4H_9(CH_3O)SiH$	$CH_3(C_4H_9)_2SiH$	$CH_3 \cdot C_4H_9(CH_3O)_2Si$
1. $2\ CH_3Cl_2SiH + C_4H_9MgBr$	62.0	34.0	4.0
2. $CH_3Cl_2SiH + 2\ C_4H_9MgBr$	6.2	93.0	0.2
3. $CH_3(CH_3O)_2SiH + C_4H_9MgBr$	54.0	26.9	19.1
4. $CH_3(CH_3O)_2SiH + 2\ C_4H_9MgBr$	7.0	91.0	2.0
5. $2\ CH_3Cl_2SiH + C_4H_9Li$	73.2	24.0	2.4
6. $CH_3Cl_2SiH + 2\ C_4H_9Li$	58.8	41.2	—
7. $CH_3(CH_3O)_2SiH + C_4H_9Li$	42.2	29.6	28.2
8. $CH_3(CH_3O)_2SiH + 2\ C_4H_9Li$	37.1	35.4	27.5

It is to be mentioned that in Reactions 1 and 5 of Table I, twice the equimolar quantity of chlorosilane was used because of its readiness to further alkylation. As it is well known, chlorosilanes readily undergo further alkylation if one of the hydrogen atoms has been replaced by an alkyl group. Methoxysilanes are less prone to further alkylation. So in Reactions 3 and 7 the reagent

was applied in the stoichiometric ratio. Finally, it should be taken into consideration that the formation of the Grignard reagent is nearly quantitative, while the formation of buthyllithium takes place in 80% yield only. Therefore, the molar ratios of the starting materials shown in rows 5, 6, 7 and 8 of Table I had to be corrected accordingly (0.8 and 1.6 moles of butyllithium, resp.).

It can be seen from Table I that when equimolar quantities of the reagents or an excess of chlorosilane is used, the main product is a monobutyl derivative; while on applying two moles of the alkylating agent, the formation of the dibutyl derivative is considerably favoured. The only exception is the system methyldimethoxysilane—butyllithium, where a change in the ratio of the starting materials produces but a small deviation in the composition of the reaction products. However, in the case of Reactions 1 and 5 of Table I, in spite of a double molar ratio of methyldichlorosilane, a considerable quantity of the dibutyl derivative has also been formed.

It is remarkable that the Grignard reagent reacts with the Si—H bond also in the presence of a Si—Cl bond (Table I, 1st row).

The experimental results show that, with one exception, in all cases both kinds of reaction proceed, thus besides the breaking of the Si—Cl or Si—OCH_3 bond, the Si—C bond can also be formed by the breaking of the Si—H bond. However, the two reactions do not take place simultaneously: no product of the possible mixed reactions (*e.g.*, alkyl substitution of the hydrogen atom in methylbutylchlorosilane or methyldibutylsilane) has been formed in detectable quantity. This is in agreement with the other experience that when double quantity of the metal-organic reagent is used, the quantity of the product substituted by alkyl group on the place of the hydrogen atom is decreased. Both observations can be explained with the readiness of the chloro- and methoxysilanes to undergo further alkylation.

Considering the readiness to alkyl substitution, the difference between hydrogen and chlorine has been found greater than between hydrogen and methoxyl substituents, with either of the two alkylating agents. However, in the first case the reaction with butyllithium resulted in a greater difference, while in the second the substitution of the hydrogen and methoxyl groups took place almost to an equal extent. This latter result was not affected significantly by an increase of the molar ratio of butyllithium. With a Grignard reagent a considerable difference has been found in the reactivities of the hydrogen and methoxy groups, and this difference became greater when the reagent was used in higher molar ratios.

The reactivity of the Si—H bond was also studied by breaking it by means of sodium hydroxide. The Si—H bond and NaOH react with hydrogen evolution. In the case of methyldimethoxysilane the reaction is very rapid, and it takes place with strong heat evolution; methylbutylmethoxysilane reacts only slowly at room temperature, while the reaction of methyldibutyl-

silane requires elevated temperatures to occur. Thus it can be stated that the reactivity of the Si—H bond decreases in the order $Me(MeO)_2SiH > MeBu(MeO)SiH > MeBu_2SiH$, and the rate of alkylation decreases in the same sequence.

Similar experimental results have been found by HETFLEIS *et al.* [22] in the alkaline solvolysis of ethoxyhydrogenalkylsilanes. Though an unambiguous explanation of these experimental results has not been suggested by the authors, it is probable that also in this case the effect of the lone electron pair of the oxygen atom acting through the empty d-electron orbital of the silicon atom is responsible.

The boiling point of methyldichlorosilane obtained by the alkylation of the Si—H bond was 147.5—148°/744 Hgmm [17]; methylbutyldimethoxysilane had b.p. 205.4°/760 Hgmm [18].

Experimental

(a) Reactions with butylmagnesium bromide

The Grignard reagent was prepared by DREGER's method [19]. Into flask A (see Fig. 1) (without filter C) 137 g (1 mole) of *n*-butyl bromide was added by drops to 24 g (1 g-atom) of magnesium in 500 ml of absolute ether. (When the reagents are water-free, the addition of odine is not necessary.) [20]

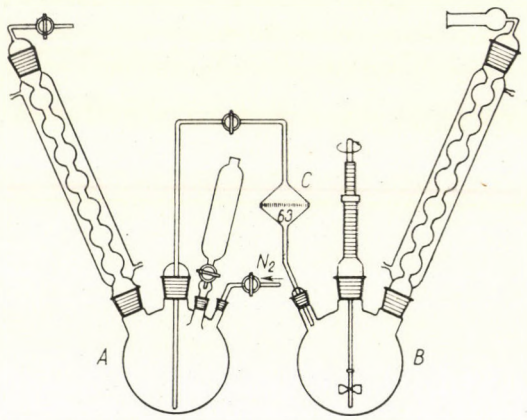

Fig. 1. Apparatus used for the alkylation reactions

The reaction mixture was refluxed until the magnesium completely dissolved (20—40 minutes). Meanwhile the chlorosilane or methoxysilane (for molar ratios see Table II) and 200 ml of absolute ether were measured into flask B. After cooling in ice-water, the Grignard reagent was added to this solution by means of applying a slight pressure of nitrogen. During the addition of the reagent and the subsequent boiling the reaction mixture was continuously stirred. The mixture was refluxed for a given period (see Table II). The mixture was filtered from the magnesium halide on a *G3* glass filter, and the ether evaporated. Then a sample was withdrawn from the residue for gas chromatographic analysis. When the product was chlorosilane, it was converted into the methoxy derivative before analysis. The products were purified by distillation with 1 : 5 reflux ratio on a 60 cm long heated column packed with Rashig rings and equipped with a column-head adjustable refluxe ratio. The properties of the materials obtained are shown in Tables II and III.

Table II

Alkylation reactions

Preparative data

Starting materials and molar ratios	Boiling time, hrs.	Product	Yield, %	B. p., °C	n_D^{20}
$CH_3Cl_2SiH + C_4H_9MgBr$	4	$CH_3 \cdot C_4H_9 \cdot Cl \cdot SiH$	53,1	127	1.4239
$CH_3Cl_2SiH + 2\ C_4H_9MgBr$	4	$CH_3(C_4H_9)_2SiH$	88.0	174	1.4242
$CH_3(CH_3O)_2SiH + C_4H_9MgBr$	6	$CH_3 \cdot C_4H_9 \cdot CH_3O \cdot SiH$	53,7	132	1.4023
$CH_3(CH_3O)_2SiH + 2\ C_4H_9MgBr$	6	$CH_3(C_4H_9)_2SiH$	84.0	174	1.4242
$CH_3Cl_2SiH + C_4H_9Li$	2	$CH_3 \cdot C_4H_9 \cdot Cl \cdot SiH$	63.8	127	1.4239
$CH_3Cl_2SiH + 2\ C_4H_9Li$	2	$CH_3(C_4H_9)_2SiH$	34.9	174	1.4242
$CH_3(CH_3O)_2SiH + C_4H_9Li$	3	$CH_3 \cdot C_4H_9 \cdot CH_3O \cdot SiH$	33.6	132	1.4023
$CH_3(CH_3O)_2SiH + 2\ C_4H_9Li$	3	$CH_3(C_4H_9)_2SiH$	30.6	174	1.4242

Table III

Physical and gas chromatographic data of the alkylated products

Symbol	Si,		d_4^{20}	Retention index, according to KOVÁTS	
	Calcd.	Found		on *SE* 30 silicone elastomer	on *Tween* 60
$CH_3 \cdot C_4H_9 \cdot Cl \cdot SiH$	20.5	20.3	0.914	—	—
$CH_3 \cdot C_4H_9 \cdot CH_3O \cdot SiH$	21.2	21.2	0.791	782	827
$CH_3(C_4H_9)_2SiH$	17.7	17.5	0.756	992	989

(b) Reactions with butyllithium

Butyllithium was prepared in flask A of the apparatus shown in Fig. 1, but instead of the nitrogen inlet pipe a stirrer was fitted into the middle neck. After rinsing flask A with dry nitrogen, 400 ml of anhydrous ether and 14.4 g (2.2 g-atoms) of freshly cut metallic lithium were added, then 137 g (1 mole) of *n*-butyl bromide dissolved in 100 ml of absolute ether was introduced dropwise through a funnel. After the reaction had started, the mixture was stirred and cooled to 0—10°, according to GILMAN's method [21]. After the addition of the butyl bromide solution had been finished, the mixture was maintained at +10° for 1—2 hours to complete the reaction. (The progress of the reaction was shown by the metallic glitter of the lithium surface.)

The stirrer was then replaced by a pressure transfer tube equipped with a *G3* glass filter (see C in Fig. 1).

In flask B, a solution was prepared from dichloro- or dimethoxysilane in 200 ml of absolute ether (for quantities, see Table II). The mixture was cooled in ice and the butyllithium solution was passed into it by means of a slight nitrogen pressure from flask A through the *G3* filter, during about 20 minutes, with continuous stirring. After boiling (for times of boiling, see Table II) the mixture was filtered from the precipitated lithium salt on a *G3* glass filter. The ether was distilled off, and a sample was taken from the residue for gas chromatographic analysis. The residue was purified using the column mentioned before. The properties of the products are listed in Tables II and III.

(c) Methanolysis of chlorosilanes

Methanol dissolved in xylene was measured into a flask equipped with a reflux condenser, stirrer and dropping funnel. A few drops of methyl red—methylene blue mixed indicator was added. The mixture was cooled to —30— —40° and stirred. The cooling did not influence the formation of methoxysilane, while the splitting of the Si—H bond was completely eliminated. The required quantity of chlorosilane was added by drops into the flask and simultaneously dry ammonia gas was passed into the solution maintaining the pH at about 4. When the addition of the chlorosilane had been completed, the ammonia current was also stopped, and the mixture was allowed to warm to room temperature during continuous stirring. If the indicator turned again red (indicating subsequent reaction) the mixture was neutralized with a further amount of ammonia. The ammonium chloride was filtered off on a *G3* glass filter. The products were purified by fractional distillation on the above-mentioned column. The dimethoxysilane prepared in this way was found to be pure after two distillations. No methanol or any other impurity was detected by gas chromatographic analysis in the product.

Methyldimethoxysilane was prepared from methylhydrogendichlorosilane (1 mole) with methanol (2.1 moles) in absolute xylene (500 ml). Yield: 41.5 g (39.2%). B.p.$_{760}$: 62° (lit. b.p. [13]: 61.1°). $n_D^{20} = 1.3631$; d_4^{20} : 0.861. Retention index on *SE 30* at 60° : 568; on *Tween* 60 : 661.

Methylbutylmethoxysilane was made from methylbutylchlorosilane (1 mole) with methanol (1.2 moles) in absolute ether (300 ml). Yield: 109 g (84.0%) after purification. B.p.$_{760}$: 132°; $n_D^{20} = 1.4023$; d_4^{20} : 0.791. Retention index on *SE 30* at 60° : 782; on *Tween* 60 : 827.

(d) Gas chromatographic analysis

The analyses were carried out with a *Carlo Erba Type Fractovap C, PAID/ff* instrument. Column: 2 m×2 mm. Packing: 3% *SE 30* silicone elastomer on *Chromosorb W* of 60—80 mesh grain size. Temperature: 60° and 68°, resp. Nitrogen was applied as the carrier gas, at 20 ml/minute flow rate. A flame ionization detector was used.

SUMMARY

The alkylation reactions of methyldichlorosilane and methyldimethoxysilane have been investigated with butyllithium and butylmagnesium bromide. The molar ratio of the metal-organic compound was chosen to be equivalent with one or both chlorine (or methoxyl) substituents. The methoxyl derivative was prepared from the corresponding chlorosilane with methanol. The reaction products were identified by gas chromatographic analysis. It has been shown that besides the replacement of the chlorine atom or methoxyl group, the substitution of the hydrogen atom also takes place. The substitution by alkyl groups of the hydrogen atoms has been found the greatest in the reaction of methyldimethoxysilane with butyllithium, and the least in the case of methyldichlorosilane and butyllithium. Mixed alkylation, *i.e.* the reaction of Si—H and Si—Cl (or Si—OCH_3) bonds within the same molecule, has not been observed. The reactivity of the Si—H bond has been found to decrease as the molecule is increasingly alkylated.

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KINETIC INVESTIGATION OF THE CLAISEN-SCHMIDT CONDENSATION OF AROMATIC KETONES AND ALDEHYDES CATALYZED BY ANION EXCHANGE RESINS

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Recently, in reactions catalyzed by bases, anion exchange resins have often been used as the catalyst. According to the literature [1], anion exchange resins were first applied for this purpose in the investigation of the mutarotation of glucose. The next work dealt with the hydratation of nitriles: GALAT [2] converted nicotinonitrile in the presence of *Amberlite IRA-400* to nicotinamide. The method was studied more thoroughly by PIERCE [3].

SCHMIDLE and MANSFIELD [4] reported on a more extended use of anion exchange resins as catalysts. These authors found that cyanohydrin formation, benzoin condensation, diacetone alcohol formation, cyanoethylation, and the formation of nitroalcohols were catalyzed by weakly and strongly basic anion exchangers.

Probably the most intensively studied reaction catalyzed by an anion exchange resin is the dimerization of aldehydes and their reactions with compounds containing active hydrogen. DURR [5] found that 2-ethyl-2-hexenal could be prepared from propionaldehyde by means of the anion exchange resin *Amberlite IR-4B*; no aldol intermediate was isolated. He also observed that the reaction could not be accomplished with the stronger basic resin *IRA-400*. Weakly basic anion exchangers, such as *Amberlite IR-4B, IR-45* and *Deacidite-G*, in the form of the base or the acetate, were also used by ASTLE and ZASLOWSKY [6] to convert aldehydes into aldols, and into substituted acroleins. The anion exchangers mentioned had no effect on acetone. Using quaternary ammonium bases *(Amberlite IRA-400, Permutit S, Dowex 1)*, the acid formed from the aldehyds by oxidation partly deactived the resin, which thus became suitable for the conversion of acetone. A more detailed study about the efficiency of the various forms of strongly basic anion exchangers by KEIHEI UENO and YASUTO YAMAGUCHI [7] showed a decrease in the order cyanide, base (OH), and chloride; acetate was found inefficient in the reaction they investigated. AUSTERWEIL and PALLAND [8, 9] pointed out the role of temperature in this reaction, and found that aldehydes and ketones were converted in the presence of quaternary polyaminostyrene resins into aldol or ketol, and at higher temperatures by dehydratation to the corresponding unsaturated derivatives.

MASTAGLI [10] was the first to report the conversion of acetaldehyde to β-hydroxybutyraldehyde and crotonaldehyde.

Anion exchange resins proved to be suitable for the substitution of the base catalyst also in reactions of the KNOEVENAGEL type. ASTLE and ZASLOWSKY [11] establishes that weakly basic resins containing amino groups *(Amberlite IR-4B, IR-45, Deacidite G* and *Duolite A-4)*, and resins marketed in the quaternary ammonium chloride form and converted before use to the strongly basic form *(Amberlite IRA-400, Dowex-1)*, efficiently catalyzed the KNOEVENAGEL condensation of aldehydes and ethyl acetoacetate, cyanoacetic acid, and ethyl malonate. BELYAEV [12] applied this method in the condensation of furfural and acetoacetic ester to obtain furfurylidene acetoacetic ester in 24% yield. With the resin he used, benzaldehyde gave the benzylidene derivative in 17% yield. CSŰRÖS *et al.* [13] successfully used the anion exchanger *Amberlite IRA-400* as catalyst in the condensation of aromatic aldehydes and phenylacetonitrile derivatives to obtain several new derivatives of α-phenylcinnamonitrile in good yields.

ASTLE and GERGEL [14] found that a weakly basic anion exchange resin *(e.g., Amberlite IR-4B* or *Dowex-3)* was the most suitable for the condensation of aldehydes and cyanoacetic acid. Ketones, with the exception of cyclohexanone, do not react under these conditions. Besides those mentioned above, other compounds containing active methylene groups can also be used in the reaction. Thus, for example, in the presence of *Deacidite 300, Amberlite IRA, Dowex 1* or *2* and *Permutite S* anion exchangers, fulvenes can be obtained from aldehydes or ketones with cyclopentadiene (or with its aliphatic or aromatic analogues, such as 1-methylcyclohexadiene or benzocyclohexadiene) [15]. PALLAND and DELEST [16] achieved the condensation of aldehydes and β-diketones; SHUNICHI YAMADA *et al.* [17] effected the reaction of formaldehyde with propiophenone, methyl ethyl ketone, and with ethyl acetamidomalonate, in the presence of resins of the quaternary ammonium hydroxide type.

TRIVERDI [18] used *Amberlite IRA-400* to prepare 3-cyano-4,6-dimethyl-2-pyridone from cyanoacetamide and acetylacetone; from salicylaldehyde with malonic ester 3-carbethoxycoumarin, with acetoacetic ester 3-acetylcoumarin, and with cyanoacetic ester diethylsalicylidene-bis-cyanoacetate were synthesized. ANDRIC [19] made a detailed study of KNOEVENAGEL condensations catalyzed by anion exchange resins.

In one group of the reactions of aldol type, nitroparaffines were used as the component containing the active methylene group. In this case again, anion exchangers proved to be efficient catalysts, in accordance with the earlier results of SCHMIDLE and MANSFIELD [4]. The reaction was studied in detail by ASTLE and ABBOTT [20] who found that the reaction of aliphatic aldehydes and of benzaldehyde with nitromethane, nitroethane or nitroisopropane could be catalyzed by both *Amberlite IRA-400* and *IR-4B* resins. Using this method,

ISAGULYANTS and SHIROKI [21] prepared trimethylol nitromethane by the reaction of paraformaldehyde with nitromethane.

Anion exchange resins are suitable also for the catalysis of MICHAEL-type additions. The method is of particular interest in cyanoethylation. ASTLE and ETHERINGTON [22] found that the reaction of primary and secondary alcohols with acrylonitrile was catalyzed by strongly basic resins *(Amberlite IRA-400, Dowex 1, Permutit S)*, however, these resins quickly became inactive on repeated use, presumably owing to a polyacrylonitrile film formed on their surface. The reaction was studied in greater detail by MASTAGLI *et al.* [23], who successfully accomplished the cyanoethylation of alcohols, phenols, ketones and formamide. The cyanoethylation of alcohols was also studied by ISAGULYANTS *et al.* [24, 25]. These authors used a strongly basic anion exchange resin Type *AV-17* for the cyanoethylation of several primary alcohols (propyl, butyl, amyl, hexyl, heptyl, octyl, isobutyl, isoamyl and β-phenylethyl alcohols). HSIA CHEN [26] studied the cyanoethylation of diols, and tried to explain the high efficiency of the reaction catalyzed by an ion exchanger. According to his interpretation, the difference between the dimensions and the functional groups of the reactants and the product results in a much stronger swelling of the resin by the reactants than by the product. Owing to this fact, the reaction opposing cyanoethylation is suppressed. ISAGULYANTS and POREDDA [27] effected the cyanoethylation of nitroparaffines (nitromethane, nitroethane and nitropropane) in the presence of strongly basic ion exchange resins. The procedure was applied for the cyanoethylation of mono- and disaccharides (glucose, mannose, xylose and cellobiose), using 0.2 to 2.0% of *Wofatit SBW* as the catalyst [28].

The Michael-addition catalyzed by anion exchangers can be achieved also with other α, β-unsaturated compounds. Thus, 2-dimethoxymethyl-3-metoxypropionitrile was prepared from 2-methoxymethylene-3-methoxypropionitrile by TURSIN *et al.* [29]. Acrolein was used first as the α, β-unsaturated component by SHUNICHI *et al.* [30]. It was reacted in the presence of *Amberlite IRA-400* with diethyl acetylaminomalonate. According to a patent [31], acrolein can be converted with acetic acid in the presence of this catalyst to give acetoxypropionaldehyde in 40% yield. TRIVERDI [32] used coumarins as the α, β-unsaturated components, and converted them with cyanoacetamide into the corresponding substituted 3,4-dihydrocoumarin-4-cyanoacetamides.

The use of anion exchange resins as catalysts was investigated in many reactions besides those discussed above. According to a French patent [33] acrylic acid can be reacted at 80—125°, and under pressure, with ethylene carbonate in the presence of a mixture of a tertiary amine, *e.g.* pyridine, and an anion exchange resin of the general formula $[CN_2N^+(CH_2CH_2OH)Me_2]X^-$, to obtain β-hydroxyethyl acrylate in 93% yield. Anion exchange resins can

also be used for the catalysis of alcoholysis. YOSHINOBU HIRASAKA and KENJI UMEMOTO [34] prepared methyl- and ethyl-D-glycopyran uronates from D-glycuronolactone with the corresponding alcohol in the presence of *Amberlite IR-4B* resin. According to a patent [35], the preparation of acids by hydrolysis or of esters by alcoholysis can be catalyzed by anion exchangers. In this way amyl alcohol can be prepared from amyl salicylate; ethyl laurate and methyl laurate are obtained from cacao-butter, *etc.* According to another patent [36], anion exchanger resins are efficient catalysts of ethynylation reactions. Acetylene and ketones can be converted in the presence of an anion exchanger in the cyanide form into alkynols, *e.g.*, dimethylketone and acetylene give 2-methyl-3-butyne-2-ol in a continuous process, in 93% yield. According to a British patent [37], polyepoxy resins can be prepared by heating polybasic acids or their anhydrides with epichlorohydrin in the presence of an ion exchange resin, such as *Dowex 1.* A French patent [38] described the preparation of 2-phenoxyethanol from phenol and ethylene oxide in benzene solution, catalyzed by a strongly basic anion exchanger *(Duolite A-50). Amberlite IRA-400* also catalyzes the reaction of primary or secondary amines and fatty acids to yield acid amides [39].

Although there are many examples for the use of anion exchange resins as catalysts, it is remarkable that relatively little work has been done to investigate the mechanism of action of the resins. Similarly, the literature contains few data on the kinetics of the reactions catalyzed by anion exchangers. The first measurements of this kind were made by HSU-PING CHEN *et al.* [40]. They investigated the alsol dimerization of acetaldehyde, and found reaction to be kinetically of first order for acetaldehyde. The activation energy of the reaction was found to be 14 and 7—10 kcal/mole with strongly basic and weakly basic anion exchanger, respectively.

BASINSKI and NAREBSKA [41, 42] investigated, under similar conditions, the dimerization of acetone and the decomposition of diacetone alcohol. The kinetics of the reaction between furfural and nitromethane were investigated in detail by USMAROV and RUSTAMOV [43]. These authors found the reaction rate under the applied condition to be independent of the rate of mixing. This finding indicates that the diffusion of the reactants to the surface and into the bulk of the resin cannot be rate determining process. The reaction was found to follow second order kinetics. They established that the exchange capacity of the resin and the rate of the catalyzed reaction increased gradually with the decreasing grain size of the resin. They found a non-linear relationship between the capacity of the ion exchanger and the reaction. From this results they came to the conclusion that only a part of the hydroxyl groups of the resin had catalytic action. The activation energy was found to be independent of the grain size. On the basis of the experiments, the authors assumed the measured rate to be identical with the rate of the chemical reaction.

Results and discussion

The object of our investigations was to study the aldol-type reaction between aromatic aldehydes and compounds containing active hydrogen, catalyzed by anion exchange resins. First, we wanted to establish in preparative experiments which of the selected compounds containing an active methylene group are suitable for the reaction to occur, and whether the product is identical with that obtained in similar reactions catalyzed by bases.

In our further work, we intended studying in detail one of the investigated reactions, to establish the kinetic order, the activation energy and other characteristics of the reaction.

Preparative experiments

In our experiments benzaldehyde was reacted in hot methanolic solution, with stirring, in the presence of the strongly basic anion exchange resin *Amberlite IRA-410*, with benzyl cyanide, acetone, acetophenone, acetylacetone, ethylacetoacetate malononitrile, diethyl malonate, and ethyl cyanoacetate. After the reaction period, the resin was removed by filtration, the filtrate was cooled, and the product, if crystalline, was isolated. If the product did no crystallize, the solvent and unchanged starting materials were removed by vacuum distillation, and the residual substance was crystallized, or purified by distillation.

The quantity of the catalyst used in the experiments was 10% of the weight of the substrate. The duration of boiling was 2, 4 or 6 hours. In another series of experiments, the quantity of the catalyst was varied (10, 20, 30 and 40%), and the reaction time was kept constant at 2 hours.

With benzyl cyanide, the expected α-phenylcinnamonitrile was formed, the best yield being 80%. Acetone, however, when taken in equimolar quantity with benzaldehyde gave dibenzylidene acetone, instead of the expected benzylidene acetone. When the molar ratio acetone : benzaldehyde was 2 : 1, the reaction resulted in benzylidene acetone in a low yield (max. 16%).

In the reactions of benzaldehyde with acetophenone, malononitrile and ethyl cyanoacetate the anion exchange resin proved to be an efficient catalyst, and the corresponding benzylidene derivatives were obtained in maximum yields of 65, 80 and 58%, respectively. In the case of the three further model compounds, acetylacetone, ethyl acetoacetate and diethyl malonate, no reaction was observed or only very small amounts of unidentified products, other than the expected ones, were formed.

The results obtained in these experiments are summarized in Table I.

Table I

The reaction of benzaldehyde and compounds containing active methylene groups, catalyzed by anion exchange resins at the boiling point of methanol

Reagent	Product	Reaction time, hr.	10% of catalist		20% of catalyst		30% of catalyst		40% of catalyst		Lit. m. p., °C
			Yield, %	M. p., °C	Yield, %	M. p., °C	Yield, %	M. p., °C	Yield, %	M. p., °C	
Benzyl cyanide	α-Phenylcinnamo-nitrile	2	56	86	61	86	70	86	80	86	88 [44]
		4	69	86							
		6	77	86							
Acetone	Dibenzal-acetone	2	9	116	11	113	13	112	16	112	
		4	12	114							112.5 [45]
		6	16	113							
Acetophenone	Benzylidene aceto-phenone	2			51	58	56	58	66	58	
		3			52	58					58 [46]
		6			55	58					
		8			56	58					
Malononitrile	Malononitrile	2	66	85	70	86	73	86	76	86	
		4	69	86							86 [47]
		6	80	86							
Ethyl cyanoacetate	Ethyl α-cyanocinna-mate	2	47	50	47	50	52	50	59	50	
		4	47	50							50 [48]
		6	48	50							

Kinetic measurements

For the purpose of reaction kinetic measurements, the condensation of aromatic aldehydes with acetophenone, or its derivatives substituted in the ring, yielding chalcones (benzylidine acetophenones) was selected. As shown by the preparative experiments, this reaction takes place in the presence of ion exchange resins to give good yields, and moreover, the kinetics of the reaction have been studied under conditions of homogeneous catalysis [49]. The primary aim of our investigations was to find out whether some physical process (diffusion of the reagents to the surface and into the bulk of the resin) or the chemical reaction was the rate determining step. In the latter case it would be possible to compare the characteristic kinetic factors (rate constant, activation energy, dependence of the reaction rate on the quantity of the catalyst) of the reaction catalyzed by an ion exchanger with the homogeneous reaction catalyzed by a base.

According to HELFERICH [50], the process catalyzed by an ion exchanger can be divided into three parts:

1. diffusion of the reactants and the products through the liquid film on the catalyst particles;
2. diffusion of the reactants into the bulk of the catalyst, and diffusion of the products into the solution;
3. chemical reaction.

The slowest of these three steps will determine the overall reaction rate.

If diffusion through the liquid film is much slower than the chemical reaction, the former will be the rate determining process, since in this case all the reactants will react immediately on reaching the surface of the catalyst particle.

If the chemical reaction is slower than the diffusion process, the sorption equilibrium of the reactants can be maintained, since the diffusion rate is sufficiently high to replenish the reactants used up in the chemical reaction. Thus, the overall reaction rate will be determined by the rate of the chemical reaction proceeding within the bulk of the catalyst resin particle.

If the diffusion within the bulk of the catalyst particles is much slower than the chemical reaction, the molecules will react before get into the interior of the catalyst. In this case, the reaction takes place only in the thin surface layer of the particle, and its rate may be determined by the diffusion through the film, or by the chemical reaction on the surface. The diffusion within the bulk of the particle may thus influence the overall reaction rate, but it cannot be the only rate determining step. Various experimental data can be explained on the basis of these considerations. Besides these extreme cases, there are intermediate cases, where the rates of the three different steps are comparable.

First, an analytical method for following the reaction had to be selected and tried experimentally. The hydroxylamine method was found to be suitable, owing to its relative simplicity and satisfactory accuracy. In this method, under suitable conditions, the aldehyde, the ketone and the chalcone formed all react with hydroxylamine hydrochloride to yield oximes, and the liberated hydrochloride can be determined.

Measurements were carried out to establish the error of the analytical method used. On the basis of seven parallel measurements, scattering due to the measuring error in the range used (8—12.5 ml of 0.1 *N* NaOH consumption) was found to be 0.07 ml. This means that the true concentration values are, with a probability of 95%, within the following limits: the value calculated from the consumption of 0.1 *N* NaOH $\pm 1.96 \cdot 10^{-4} \cdot 7 \cdot \sqrt{6}$, with the starting value as exception, for which this calculated value will be $\pm 1.96 \cdot 10^{-4} \cdot 7 \cdot \sqrt{2}$ (for details of the calculation, see Experimental).

The deviation is due to difference in the expressions used for the calculations:

1. Starting benzaldehyde concentration:

$$\frac{(V_0 - V_v)\,0.1}{2{\cdot}5}$$

2. Benzaldehyde concentration of the sample taken at the time t:

$$\frac{(V_0 - V_v)\,0.1}{2{\cdot}5} - \frac{(V_0 - V_t)\,0.1}{5} = \frac{0.1\,(2V_t - V_0 - V_v)}{10}$$

where:

V_0 = the volume of the 0.1 *N* NaOH consumed for the sample taken at $t = 0$ (ml);

V_v = the volume of the 0.1 *N* NaOH consumed in the blank test (ml);

V_t = the volume of the 0.1 *N* NaOH consumed for the sample taken at time t (ml).

Since the measuring error is caused by the combined action of many factors (error in weighing the sample, indicator error, drop error, *etc.)*, errors follow a normal distribution. The measuring of the various V values is independent in each case; the scattering of the sum and the difference of independent variables is calculated by the summation of the squares of dispersion:

$$1.\quad \frac{0.1}{10}\sqrt{(0.07)^2 + (0.07)^2} = 10^{-4}\sqrt{2}$$

$$2.\quad \frac{0.1}{10}\sqrt{(2.0.07)^2 + (0.07)^2 + (0.07)^2} = 10^{-4}\cdot 7\cdot\sqrt{6}$$

This means that the error of analysis may cause a difference of about ± 3 units in the third decimal of the concentration values. It also explains why experiments can be evaluated only up to a conversion of 75—80%, because above this value the relative error becomes very great, though the absolute

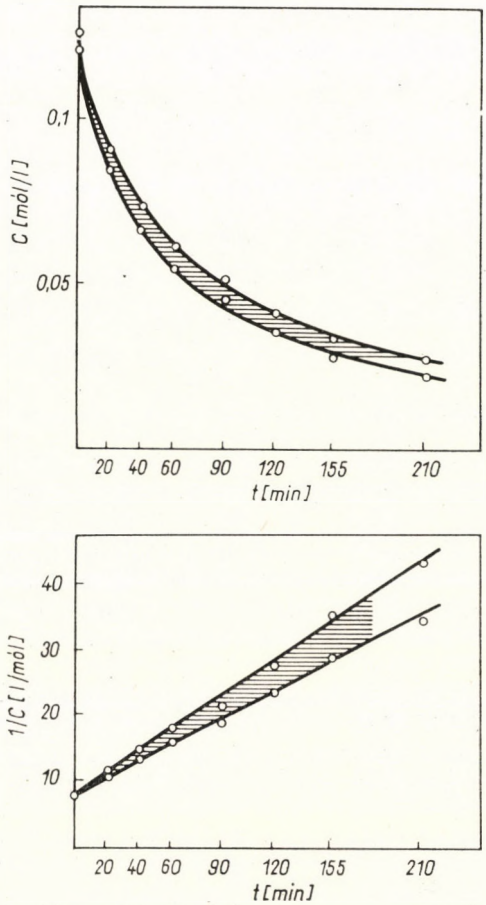

Fig. 1. The condensation of benzaldehyde and acetophenone catalyzed by an anion exchange resin

error remains constant. This is illustrated in Table II and Fig. 1 by data obtained in a concrete measurement.

In our experiments the values within the concentration limits falling into the striated area were considered. Probably, the course of the process could be followed more exactly by spectrophotometry than by the described method, since the reaction product is a coloured substance. However, in this case the presence of an uncontrollable quantity of colouring substances, extracted from the resin, may cause errors.

Table II

Condensation of benzaldehyde and acetophenone catalyzed with an anion exchanger

Reaction time, min.	C Calculated, mole/lit.	C+0.003	C −0.003	1/C, l/mole	
0	0.1230	0.1250*	0.1210*	8.0	8.27
20	0.0870	0.0900	0.0840	11.1	11.9
40	0.0700	0.0730	0.0670	13.7	14.9
60	0.0580	0.0610	0.0550	16.4	18.2
90	0.0490	0.0520	0.0460	19.25	21.75
120	0.0390	0.0420	0.0360	23.8	27.8
155	0.0314	0.0344	0.0284	29.1	35.2
210	0.0260	0.0290	0.0230	34.5	43.5

* The error made in the starting value is 0.02 instead of 0.03 (see formula above, on p. 418.

Our next task was to establish suitable experimental conditions. In our reaction the usual method of sampling homogeneous reaction mixtures is not practicable, since the drawing of samples from the solution would gradually decrease the volume, and consequently increase the specific quantity of the catalyst. This would result in a continuous increase of the reaction rate, because the latter is dependent on the concentration of the catalyst. Therefore, our only possible approach was to prepare several mixtures of an identical concentration of the reactants and the ion exchanger, and to analyse the single samples after given periods. The temperature of the samples had to be controlled, and means had to be provided for the adequate mixing of the heterogeneous reacting system. First, ampoules for injections were used, which were fastened to the end of the shaft of a vibrating agitator, submerged in an ultrathermostat and the ampoules were shaken vertically. However, it was found that agitation by this method did not impart an intensive movement to the ion-exchanger grains in the experimental mixture. Therefore, in our further work the ampoules and the test tubes with ground-glass stopper used later,* were fixed in a thermostated glass vessel, mounted on a shaking machine, as shown in Fig. 2. This arrangement was satisfactory both from the point of view of the intensive mixing of the catalyst and the reaction mixture, and the maintaining of constant temperature.

Amberlite IRA-410 and *Zerolit FF-IP* strongly basic anion exchange resins were used as the catalyst. Both resins are polystyrene bead polymers with quaternary ammonium base active groups.

* The substitution of the ampoules for test tubes with ground-glass stopper was thought to be necessary on account of the fact that an indeterminate part of the catalyst got into the neck of the ampoule during shaking, and this restricted place did not permit intensive mixing.

The reaction parameters were chosen such that the reaction should proceed to about 80% in 1.5 to 5 hours, and the change in concentration of the samples taken at different times should be sufficiently great. Otherwise, owing to the reasons already mentioned, the magnitude of the error of analysis would be comparable to that of the change taking place during the reaction, which might give rise to incorrect evaluation.

The reaction rate could be regulated by varying the concentration of the reactants and the quantity of the catalyst. Owing to the heat sensitivity of the resin, the possibility of influencing the reaction rate by the temperature was restricted.

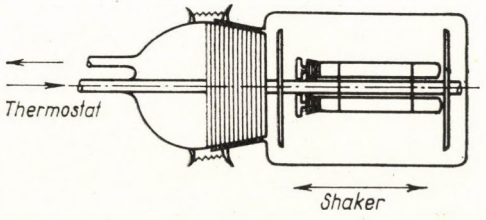

Fig. 2. Apparatus used for the experiments

The first task during our measurements was to establish whether the rate of the reaction was influenced under the given conditions by the intensity of shaking. At this time neither the kinetic order of the reaction, nor the stability characteristics of the anion exchanger (possibility of decomposition when standing in the base form and a consequent loss in catalytic activity) were known. Therefore, these measurements were carried out within a short time with small amounts of a regenerated resin from the same lot, and diagrams of the benzaldehyde concentration *vs.* time were compared. It was found that the reaction rate did not change when — starting from an initial minimum value characteristic of the machine — the shaking velocity was increased. Therefore, it is to be assumed that diffusion to the resin has no influence, that is to say, the diffusion is quicker than the chemical reaction. In our further work, measurements were carried out at medium shaking velocity.

Next, the decomposition of the anion exchange resins used was studied, to establish under which conditions the regenerated resin, *i.e.* the resin in base form, could be stored, and how long it could be used as a catalyst in our kinetic measurements.

Ion exchange resins, particularly those of polymerization type, are fairly resistant to both acids and alkalies. However, anion exchangers, owing to the lesser resistance of the basic groups, are rather sensitive to strong bases. Experience showed that during a longer standing in the OH-form, part of the base

groups may be split off, thus reducing the capacity of the resin. The unpleasant odour of the volatile amine bases split off may even be perceived.

Measurements were made to establish the allowable storage time of the active resin, *i.e.* of resin in the OH-form, without a substantial loss in capacity due to decomposition.

The determination was carried out on *Amberlite IRA-410* resin, which was stored in the base form under anhydrous ethanol.

Several capacity values are used for the characterization of ion exchange resins: the total, salt decomposing and residual capacity. The total (or neutralization) capacity is the sum of the salt decomposing and residual capacities.

The total capacity of monofunctional, strongly basic resins is partially identical with their salt decomposing capacity. Our measurements showed the residual capacity to be only 0.5 to 2% of the salt decomposing capacity, which is not considerable, because the relative error of the determination is of about this magnitude.

The decomposition of the resin was followed by measuring the salt decomposing capacity, and these measurements were supplemented in each case by the determination of the residual capacity.

This method, apparently more complicated than the determination of the neutralizing capacity, was chosen on account of its higher accuracy. Namely, in the determination of the total capacity, an exactly known volume of a standard acid solution in excess is passed through the resin column, and the excess of acid is titrated. It may occur, however, that the resin converted to the OH-form, adsorbs CO_3^{2-} ions or CO_2 from the regenerating alkali solution or the washing water, and possibly from the atmosphere, which is liberated by hydrochloric acid giving rise to air bubbles, making an exact determination difficult. Therefore, the following procedure was adopted: a column was prepared from the swelled resin, and 1 *N* NaOH solution was passed at a slow rate through the column. Next, the column was washed until it became neutral, and the NaOH having passed the column was titrated with 0.1 *N* HCl standard solution. After this, 10 ml of 0.1 *N* HCl was introduced with a pipette into the column. When the acid had dripped down, the column was again washed until it became neutral; the excess of acid which passed the column was titrated, and the residual capacity calculated from this value.

The change in capacity was followed in two series of experiments; the values obtained are summarized in Table III and shown in Fig. 3.
On the basis of these measurements the conclusion may be drawn that — stored at room temperature under absolute alcohol — the resin may be used for 15—20 days after activation, without a substantial loss of capacity.

Simultaneously with the determination of the capacity, reaction rate measurements were also carried out with the resin after various times of

standing. These experiments showed that within the period of 15—20 days the reaction rate constant did not change within the limits of experimental error.

Therefore, in our further work, individual measuring series were always carried out with the same resin within two weeks of the regeneration.

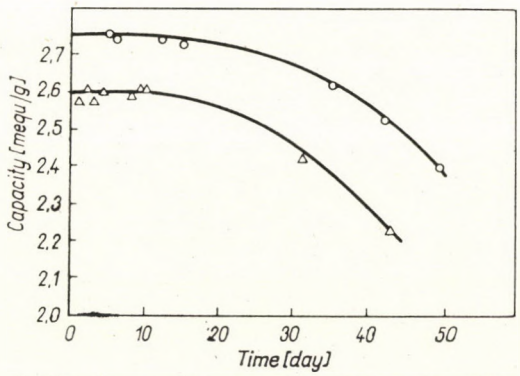

Fig. 3. The change of the capacity of the resin with time

As it has been mentioned, the role of diffusion was eliminated by shaking with adequate intensity. It was to be expected, therefore, that the measured reaction rate represented the rate of the chemical reaction. This was also substantiated by the observation that the rate of the reaction increased when equivalent but increasing quantities of benzaldehyde and acetophenone were taken (Fig. 4).

Table III

Change of capacity of the ion exchange resin with time

I		II	
Time (day)	Capacity (meq./g)	Time (day)	Capacity (meq./g)
1	2.57	5	2.75
2	2.60	6	2.74
3	2.57	12	2.74
4	2.59	15	2.72
8	2.59	35	2.62
9	2.60	42	2.52
10	2.60	49	2.40
31	2.42		
43	2.23		

Since COOMBS and EVANS [49] found the reaction to follow second order kinetics in a homogeneous system, we wanted to find out whether the same is true if the reaction is catalyzed by an ion-exchanger. It is known that, if the initial concentration of the reactants is identical, a reaction of second order

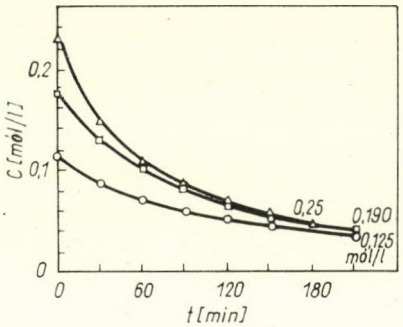

Fig. 4. Effect of the change in the concentration of the compound on the rate of the reaction at 35 °C between benzaldehyde and acetophenone yielding chalcone. Catalyst: *Amberlite IRA-410* equivalent to 0.07 mole/lit. of $[OH^-]$

should be represented by a straight line when the reciprocal of the concentration is plotted *vs.* time. As it can be seen in Fig. 5, this linearity was, indeed, established in the case we investigated, so second order kinetics may be assumed.

The rate constant of the reaction was calculated from the slope of the straight line. The values for different initial concentrations are listed in Table IV.

According to Table IV, the value of the rate constant is independent of the concentration of the reacting compounds within the limits of experimental errors. This fact also shows that the kinetic order of the reaction has been determined correctly. However, final proof will be obtained only if the rate constant

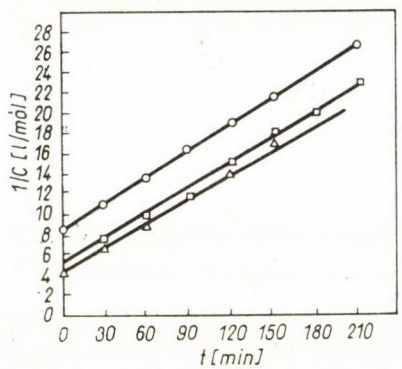

Fig. 5. Determination of the kinetic order and the rate constant of the condensation of benzaldehyde and acetophenone (calculated from Fig. 4)

Table IV

Rate constants of the reaction of benzaldehyde and acetophenone at 35 °C yielding chalcone, in the case of different starting concentrations

Catalyst: *Amberlite IRA-410* resin, equivalent to 0.07 mole/lit. of [OH^-]

Starting aldehyde = ketone concentration, mole/lit.	Rate constant, k_2 1/mole, min. 10^2
0.125	8.50
0.190	8.30
0.250	8.24

remains unchanged when the initial concentrations of the starting materials are varied independently from one another. In this case log A/B is to be plotted instead of 1/c as a function of time (where $A = A_0 - x$ and $B = B_0 - x$ are the actual concentrations of the aldehyde and ketone, respectively).

The rate constants calculated in this way are shown in Table V.

Table V

Rate constants of the reaction of benzaldehyde and acetophenone at 35 °C yielding chalcone in the case of different starting concentrations

Catalyst: *Amberlite IRA-410* equivalent to 0.07 mole/lit. of [OH]

Starting concentration, mole/lit.		Rate constant, k_2 1/mole.min.10^2
aldehyde	ketone	
0.125	0.25	8.14
0.25	0.125	8.21

Table V shows that the value of the rate constant is practically independent of the initial benzaldehyde and acetophenone concentrations, and therefore the reaction proceeds also in the presence of an ion-exchanger according to kinetics of second order. This proves at the same time that the rate determining step is the chemical reaction.

The next step in our investigations was to study the dependence of the reaction rate constant on the quantity of the catalyst. It is known that the rate constant measured in catalytic reactions is only an apparent value, since it depends on the concentration of the catalyst; therefore, $k_2 = k_2' \cdot [K]^n$, where k_2', is the true rate constant, $[K]$ is the concentration of the catalyst, and n is a number indicative of the reaction mechanism, and is frequently equal to unity. In the latter case, the rate constant is a linear function of the concentration of the catalyst.

The results of experiments, carried out at different catalyst concentrations are shown in Figs 6 and 7.

It may be seen from Fig. 8. and Table VI that the rate constant is a non-linear function of the concentration of the catalyst.

The relationship between the rate constant and the catalyst is plotted in Fig. 8.

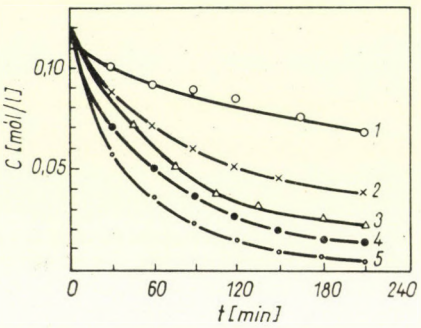

Fig. 6. Influence of the quantity of the catalyst on the rate of the reaction between benzaldehyde and acetophenone at 35 °C, catalyzed by an ion exchanger. C_0, aldehyde, ketone = 0.125 mole/lit. Catalyst: *Amberlite IRA-410*

On the basis of the measured data, the relationship seems to be linear. However, considering the fact that no reaction takes place at a catalyst concentration of zero, k_2 must also be zero (dotted line). As it has been shown,

$$k_2 = k_2' [K]^n$$

whence

$$\log k_2 = \log k_2' + n \log [K],$$

Table VI

Dependence of the rate constant on the concentration of the catalyst in the reaction of benzaldehyde and acetophenone at 35 °C, catalyzed with Amberlite IRA-410 ion exchange resin.

C_0, aldehyde, ketone = 0.125 mole/lit.

Quantity of the catalyst, g/sample	$[OH^-]$ mole/lit.	k^2 1/mole.min.10^2	$k_2' = k^2/g$ 1/mole. min. g. 10^2
0.10	0.035	2.8	2.80
0.20	0.070	8.66	4.33
0.25	0.089	16.40	6.56
0.30	0.011	20.10	6.70
0.40	0.140	30.60	7.65

thus, the logarithm of the measured rate constant plotted against the logarithm of the catalyst concentration must give a straight line, the slope of which is equal to the exponent n. This relation is plotted in Fig. 9, giving a value of 1.7 for tg α. From this, the equation representing the overall reaction rate (w) is:

$$w = k_2' [K]^{1.7} \text{ [aldehyde] [ketone]}$$

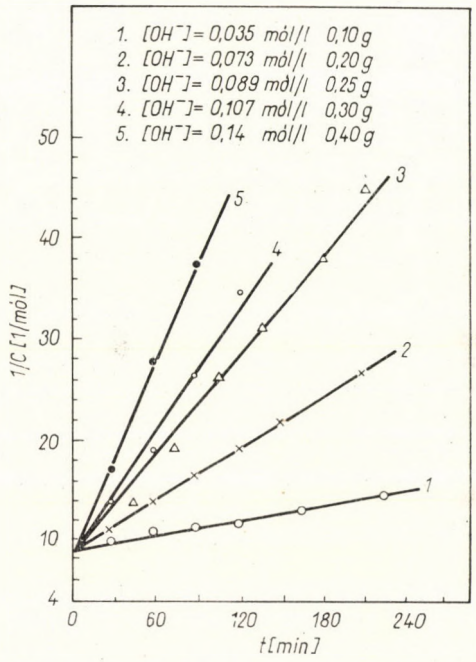

Fig. 7. Dependence of the rate constant on the concentration of the *Amberlite IRA-410* catalyst in the reaction of benzaldehyde and acetophenone (calculated from Fig. 6)

COOMBS and EVANS [49] found the rate constant of the reaction in homogeneous medium to be proportional to the hydroxyl ion concentration. The exponent of 1.7 found for catalysis with the ion-exchanger is indicative of the different character of the reactions with the two kinds of catalysts. The more complicated dependence of the rate constant of the reaction on the concentration of the catalyst is presumably the result of complex adsorption and desorption processes, which requires further experimental work for elucidation.

Our next task was the determination of the activation energy of the reaction. For this purpose, the reaction rate was measured at three temperatures, 25, 35 and 45°, and the rate constants were calculated. The results are shown in Figs 10 and 11, and in Table VII.

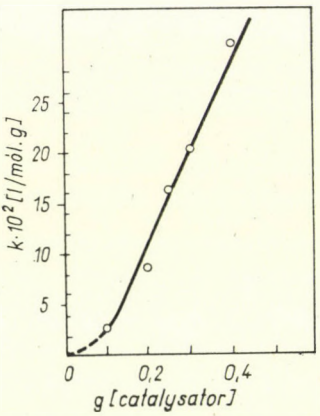

Fig. 8. Relationship between the rate constant k_2 and the catalyst concentration in the reaction of benzaldehyde and acetophenone (calculated from Table VI)

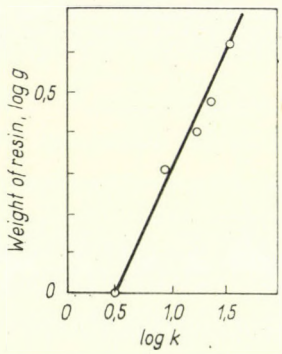

Fig. 9. Dependence of the rate constant on the concentration of the catalyst in the condensation of benzaldehyde and acetophenone, catalyzed by *Amberlite IRA-410*

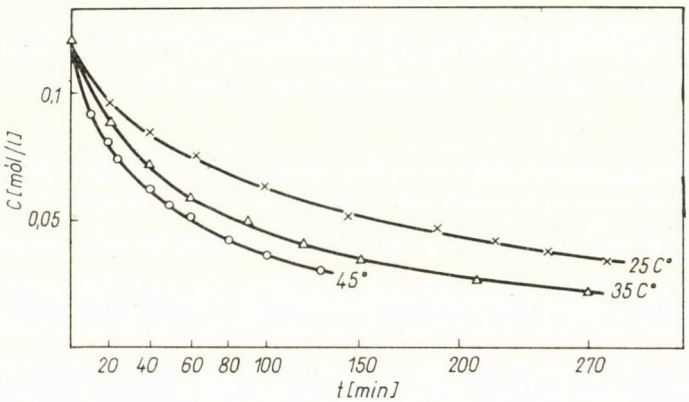

Fig. 10. The condensation of benzaldehyde and acetophenone, catalyzed by *Amberlite IRA-410*, at various temperatures. C_0, aldehyde, ketone = 0.125 mole/lit. Catalyst: resin equivalent to 0.04 mole/lit. of $[OH^-]$

Table VII

Condensation of benzaldehyde and acetophenone catalyzed by Amberlite IRE-410 at various temperatures. C_0 aldehyde, ketone = 0.125 mole/lit.; catalyst resin equivalent to 0.04 mole/lit. of $[OH^-]$

t, °C	T, °K	$\frac{10^3}{T}$ (°K)$^{-1}$	k (1/mole. min)	$\bar{k}$	lg $\bar{k}$ + 2
25	298	3.356	$7.42 \cdot 10^{-2}$		
			$7.44 \cdot 10^{-2}$	$7.42 \cdot 10^{-2}$	0.8710
35	308	3.246	$13.4 \cdot 10^{-2}$		
			$14.1 \cdot 10^{-2}$	$13.7 \cdot 10^{-2}$	1.1367
45	318	3.145	$20.2 \cdot 10^{-2}$		
			$18.4 \cdot 10^{-2}$	$19.3 \cdot 10^{-2}$	1.2856

From the rate constants determined for various temperatures, the activation energy can be calculated by the Arrhenius equation:

$$= \frac{\Delta H^*}{RT} + B,$$

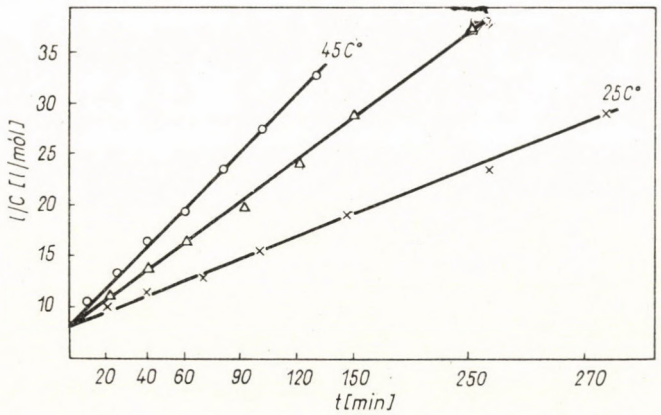

Fig. 11. Dependence of the rate constant on the temperature (from Fig. 10)

where R is the universal gas constant (1.987 cal/mole). Plotting lg k as a function of $1/T$, from the slope of the resulting straight line the activation energy can be found (Fig. 12).

Determined graphically, a value of 9.0 kcal/mole was obtained for the activation energy. The data of the reactions catalyzed with an ion-exchanger and with sodium methoxide in homogeneous solution [49], respectively, are compared in Table VIII.

Considering that in catalysis with an ion-exchanger the change of the reaction rate with the catalyst concentration is not directly proportional but

Table VIII

Comparison of the rate constants and activation energies obtained in catalysis with an ion-exchanger resin and in homogeneous catalysis with a base

	Catalysis with ion-exchanger $[OH^-] = 0.04$ mole/lit.	Homogeneous catalysis with base [49] $[OH^-] = 0.02$ mole/lit.
k 25 °C	$7.43 \cdot 10^{-2}$	$5.1 \cdot 10^{-2}$
k 45 °C	$19.3 \cdot 10^{-2}$	$14.5 \cdot 10^{-2}$
H* (kcal/mole)	9.0	9.8

almost quadratic, the reaction proceeds substantially slower than in homogeneous catalysis with a base. This can be ascribed to the complexity of heterogeneous catalysis.

In our further work, experiments were carried out to study the possible influence of the particle size of the resin catalyst on the reaction rate. Polymerization resins are beads of about 1—0.075 mm diameter. The total capac-

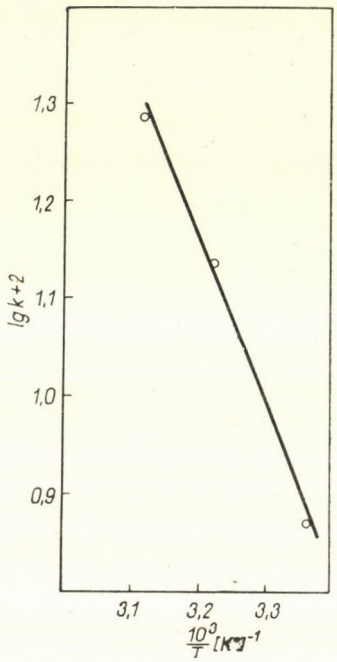

Fig. 12. Calculation of the activation energy in the condensation of benzaldehyde and acetophenone catalyzed by an anion exchanger (see Table VII)

ity (meq./g) is independent of the particle size, and does not influence the fine-structure, that is to say the pore size. The catalytic process is not restricted to the surface, but proceeds to a high extent in the capillaries. If the pore size is such that the reagents can reach the active centres unhindered, it is to be expected that the reaction rate will be independent of the particle size.

For these measurements, *Zerolit FF-IP* anion exchange resin was used. Keeping the temperature, the OH^- concentration and the degree of cross-linking constant, the particle size was varied in these experiments. In accordance with the particle size limits mentioned above, measurements were undertaken with 14—52 mesh and $<$ 200 mesh resins. The results verified our assumption (see Table IX).

In the next measuring series the effect of the degree of cross-linking on the reaction rate was studied. The degree of cross-linking of a resin is deter-

mined by the ratio of the mono- and bifunctional components in the copolymer, that is to say, by the ratio of styrene to divinyl benzene. The swelling ability and the pore dimensions of the resin are determined by this factor. The number of active centres and pore dimensions decrease with the increasing degree of cross-linking. If the capillaries become so constricted that the OH^- ions in the pores become inaccessible for the bulky organic molecules, a slowing down of the reaction is to be expected, since it amounts to a decrease of the alkali concentration.

Table IX

Effect of the particle size on the reaction rate in the condensation of benzaldehyde and acetophenone, catalyzed by Zerolit FF-IR anion exchange resin

$[OH^-] = 0.03$ mole/l; degree of cross-linking 3—5%; temperature 25 °C

	Particle size	
	14—52 mesh	< 200 mesh
Rate constant	0.102	0.099
k (l/mole · min)	0.108	0.102
$\bar{k}$	0.106	0.100

In the experiments carried out with *Zerolit FF-IP*, the particle size, the OH^- concentration and the temperature were kept constant. The results are summarized in Table X. The reaction rate decreases with a higher degree of cross-linking, in accordance with the assumption made above.

Finally, the effect of various substituents in the substrate on the reaction rate constant was investigated, by reacting benzaldehyde with acetophenone derivatives substituted in the nucleus. In this case also the hydroxylamine method was used for the determination of the concentration, and only the conditions of the determination were altered so that oxime formation should be complete with the substituted compounds. The reactions with the derivatives of acetophenone, substituted in para or meta position, were carried out under identical conditions, using the same quantity of anion exchange resin. The results obtained are presented in Fig. 13.

Fig. 13 shows that in case the of *p*- and *m*-bromoacetophenone the reaction rate was too high with the initial catalyst concentration. Therefore some of the measurements were carried out also at a lower catalyst concentration. The results are shown in Table XI.

It may be seen that the value of the rate constant is reduced by a methoxy substituent, and increased by bromine or fluorine substitution.

When interpreting the effect of substituents on the reaction rate, consideration must be given to the fact that the condensation of benzaldehyde with acetophenone is a complex reaction involving three consecutive steps:

Table X

Dependence of the rate constant on the degree of cross-linking of the resin in the condensation of benzaldehyde and acetophenone catalyzed by Zerolit FF-IR;
$[OH^-]$ = size: 52—100 mesh
Temperature: 25 °C

	Degree of cross-linking	
	3—5%	7—9%
Rate constant	0.091	0.068
k (1/mole · min)	0.085	0.065
$\bar{k}$	0.088	0.067

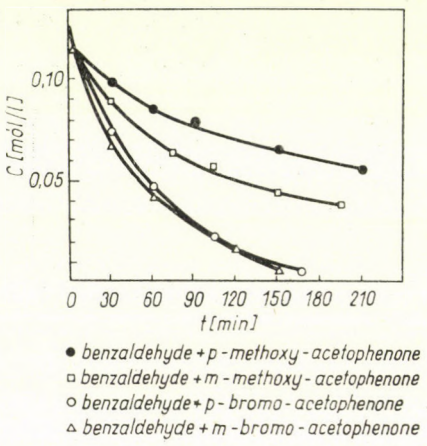

Fig. 13. The reaction of benzaldehyde and substituted acetophenone derivatives at 35 °C catalyzed by *Amberlite IRA-410* C_0, aldehyde, ketone = 0.125 mole/lit. Catalyst: resin equivalent to 0.07 mole/lit. of $[OH^-]$

Table XI

The reaction of benzaldehyde with substituted acetophenone derivatives at 35 °C, catalyzed by Amberlite IRA-410. C_0 aldehyde, ketone = 0.125 mole/lit.

	$[OH^-]$, mole/lit.	Rate constant, k (1/mole.min). 10^2
Acetophenone	0.035	2.80
	0.07	8.66
p-Methoxyacetophenone	0,07	5.0
m-Methoxyacetophenone	0,07	8.05
p-Bromoacetophenone	0.035	8.4
	0.07	22.0
m-Bromoacetophenone	0.07	24.6
p-Fluoroacetophenone	0.035	6.65

1. The action of the basic catalyst causes a proton to split off from the active methylene group of acetophenone:

$$C_6H_5COCH_3 + OH^- \underset{k_2}{\overset{k_1}{\rightleftharpoons}} C_6H_5COCH_2^- + H_2O$$

2. This is followed by the addition of the carbanion on benzaldehyde:

$$C_6H_5COCH_2^- + C_6H_5CHO + H_2O \xrightarrow{k_3} C_6H_5COCH_2CHOHC_6H_5 + OH^-$$

3. The final step is water elimination:

$$C_6H_5COCH_2CHOCH_6H_5 \rightarrow C_6H_5COCH = CHC_6H_5 + H_2O$$

The second order kinetics of the reaction shows the condensation step to be the slower, and consequently the rate determining step. The overall velocity is:

$$w = \frac{k_1 - k_3}{k_2} [\text{benzaldehyde}] [\text{acetophenone}] \cdot [\text{OH}] \qquad (1)$$

or, after a slight modification:

$$w = K_A \cdot k_3 [\text{aldehyde}] [\text{ketone}] \cdot [\text{OH}] \qquad (2)$$

where K_A is the acid dissociation constant of acetophenone, while the value of k_3 is dependent on the degree of the nucleophilic character of the conjugated carbanion; this is the less, the stronger the acid from which the carbanion is derived; *i.e.*, the higher is the value of K_A, the smaller is k_3.

Owing to this, the reaction rate is not an unequivocal function of the value of K_A, as would be expected on the basis of Eq. (2). The effect of the substituent on the value of K_A cannot be predicted.

It follows that though the effect of the substituent on the rate constant can be measured, the kinetic measurements do not reveal to what degree the values of K_A and k_3 are influenced by the substituent.

The experiments with substituted acetophenone derivatives furnished further evidence substantiating the assumption that the measured rate constant represents the velocity of the chemical reaction.

Experimental

Benzaldehyde, freed of perbenzoic acid and stored under nitrogen atmosphere, and acetophenone, purified by fraction, and its derivatives were used in the measurement.

Preparation of the catalyst and determination of its capacity

The conversion of the resins *Amberlite IRA-410* and *Zerolit FF-IR*, used as catalysts, into the base form was effected as described in the literature [50].

The quantity of resin required for the determination of the capacity was always prepared the previous day. It was washed with anhydrous ethanol, filtered off with suction at a water pump, and stored overnight in a vaccum desiccator over $CaCl_2$ (for about 15—16 hrs). From the resin prepared in this way, 3 g was allowed to swell for 1 hr. in distilled water. Then a column was prepared from the resin, and first 200 ml of 1 *N* NaOH solution, then 50 ml of distilled water were passed at a slow rate (3 ml/min) through it. The two solutions were combined, the volume made up to 250 ml, and 50 ml portions of this solution were titrated with 0.1 *N* HCl standard solution, in the presence of methyl red indicator.

Next, 10 ml of 0.1 *N* HCl standard solution was introduced with a pipette on the column, and passed through it at the same rate as before. The column was washed distilled water until it became neutral, and the excess of hydrochloric acid was titrated with 0.1 *N* NaOH standard solution, using methyl red indicator.

Measuring techniques used in the kinetic investigations

From the resin, regenerated and prepared as described above, the required quantities were measured on an analytical balance into test tubes with ground-glass stopper. From previously prepared stock solutions of benzaldehyde and acetophenone in anhydrous ethanol, appropriate quantities (totalling 7 ml and in some of the experiments 8 ml) were added with a pipette to the contents of the test tubes. (In the experiments with the resin *Zerolite FF-IP*, 8 ml were taken, because the reaction mixture had to be filtered before the ketone determination to remove any suspended catalyst particles.) The test tubes were stoppered immediately, placed into the thermostated glass vessel, fixed on the shaking machine, and shaken. At various times a sample was taken from each tube, and the benzaldehyde concentration was determined as follows: With a pipette, a 5-ml sample was withdrawn from the reaction mixture, 15 ml of 0.5 *M* hydroxylamine hydrochloride solution in 90% ethanol was added, and the mixture was refluxed for 40 min. After cooling, the solution was titrated with 0.1 *N* NaOH solution in the presence of bromophenol blue indicator solution (2 drops of a 0.1% aqueous solution) until the colour became the same as that of a blank test.

Blank test: 5 ml of anhydrous ethanol was refluxed with 15 ml of 0.5 *M* hydroxylamine hydrochloride solution for 40 min. After cooling, the solution was diluted with 10—12 ml of distilled water, and titrated in the presence of bromophenol blue indicator solution with 0.1 *N* NaOH standard solution to the transition colour.

Calculation:

$$B_t = B_0 - \frac{(V_0 - V_t)\,0.1}{5} \text{ (mole/litre)}$$

where:

B_0 = initial concentration of benzaldehyde (mole/litre)

B_t = benzaldehyde concentration of the sample taken at time t (mole/litre)

V_0 and V_t = the volume of the 0.1 *N* NaOH solution, consumed by the sample taken at $t = 0$ and at time t, resp. (ml).

Determination of the error of the analytical method

Stock solutions:

benzaldehyde	0.3975 g	0.075 mole/litre
acetophenone	0.4500 g	0.075 mole/litre
chalcone	0.7800 g	0.075 mole/litre

In a 50-ml flask 5-ml portions of the solution in abs. ethanol were titrated with 0.1 *N* NaOH standard solution, in the presence of bromophenol blue indicator.

The volumes required (m_i) in seven titrations ($n = 7$), the deviation from the mean value ($M - m_i = E_i$), and the square of the deviations (E_i^2) are listed in Table XII.

Table XII

Calculation of error in the determination of benzaldehyde, acetophenone and chalcone by the hydroxylamine hydrochloride method

n	m_i	$M-m_i=E_i$	E_i^2
1	10.88	—0.04	0.0016
2	10.98	+0.06	0.0036
3	10.80	—0.12	0.0144
4	10.95	+0.03	0.0009
5	10.95	+0.03	0.0009
6	10.90	—0.02	0.0004
7	11.0	+0.08	0.0064
	$M=10.92$		$\Sigma E_i^2=0.0282$

The mean error of an individual measurement is:

$$\delta = \pm \sqrt{\frac{E_i^2}{n-1}} = \pm \sqrt{\frac{0.0282}{6}} = \pm \sqrt{0.0047} = \pm 0{,}07 \text{ (ml)}.$$

We wish to thank Mrs. L. KŐFALVI for her valuable technical assistance in a part of the experimental work.

SUMMARY

The Claisen–Schmidt condensation of benzaldehyde and acetophenone in ethanol, catalyzed by the anion exchange resins *Amberlite IRA-410* and *Zerolit FF-IR* (OH^--form) yielding chalcone has been studied, and kinetic measurements were made. The results of these investigations show that under the experimental conditions applied the rate of the reaction is no longer influenced by diffusion, thus the measured reaction rate represents the rate of the chemical reaction. The reaction is kinetically of second order; the relation between the concentration of the catalyst and the rate constant is nonlinear. In the rate equation, the exponent of the catalyst concentration is 1.7.

The activation energy of the reaction was found to be almost identical with that obtained for homogeneous catalysis. It has been shown that the particle size of the ion exchange resin does not influence substantially the reaction rate, while the degree of cross-linking has a marked effect: with resins of a higher degree of cross-linking the reaction is slower at the same hydroxyl ion concentration. Substitution in the acetophenone component affects the rate of the reaction, and this further substantiates the assumption that the measured rate represents the rate of the chemical reaction.

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CONSTRUCTIONAL OPTIMIZATION OF GRID-TRAY DISTILLATION COLUMNS

MINIMUM COLUMN WEIGHT FOR GIVEN OPERATION AND SEPARATION CONDITIONS

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1. Outline of the task

A very important point in the design of distillation columns is the correct choice of dimensions that lead to the most economical construction. There are several ways to consider this point, and the factors to be kept at their lowest or highest figures are to be selected accordingly. The various definitions of economical optimum involve various functions that embody different aims and attempt to correlate different variables [1, 2, 3, 4].

The task in its most general terms refers to constructional, statical, and operational features, to product quality and quantity as the variables, in some function of which the minimum overall production cost is to be established so that both investment and operational costs are considered. This means complete optimization. As a first step on the way towards this final goal, we shall discuss constructional optimization problems, when optimum is represented by the minimum weigh of a column suitable to effect a given separation under given operating conditions. This is a frequent case when expensive stainless steel or some other similar material of construction must be used in a column of large diameter with a high number of trays. In a case like this the capital investment costs of the column alone have an important influence on the economics of the process. Besides this, very often a partial optimization may approximately meet the demand for complete optimization [1].

With grid-trays the task is comparatively simple, since the number of geometric variables is small; the solution of this problem may furnish useful hints utilizable in the design of other column construction.

2. Basic correlations and initial considerations

The degree of separation, or the efficiency, of a grid-tray column is a function of vapour velocity, free area of trays, tray spacing, reflux ratio, pressure, and to a lesser degree, of the composition of the mixture to be handled. If the parameters just mentioned are constants, the slit width is of no practical

significance [6]. Other things being equal, maximum efficiency is a function of vapour velocity. In what follows, we shall regard this maximum efficiency and the corresponding optimum vapour velocity as our starting point. For the determination of optimum vapour velocity the following relation is used [5]:

$$w = 6.9F\left(\frac{L}{G}\right)^{-0.34}\sqrt{\frac{1.2}{\gamma}}. \tag{1}$$

The efficiencies corresponding to the vapour velocities thus calculated are obtained from the expression [7, 8, 9]:

$$\eta = 0.53\,Fr^{-0.3}\left(\frac{L}{G}\right)^{r}\left(\frac{p}{p_0}\right)^{-0.21}. \tag{2}$$

Let a grid-tray column, in continuous operation at atmospheric pressure for a separation task, be considered when the initial mixture and point of feed are fixed, product concentrations, reflux ratio, thermal conditions of the material streams and with these the theoretical number of plates are given, and further, when the quantity per hour of one of the products, *e.g.* of the distillate or of the feed, is also pre-determined. The question is, what free area and spacing of trays should be chosen?

It follows from the correlations mentioned before that a minimum weight column of optimum construction can be designed to suit the task. The following facts should be considered: an increase of the free area of trays, on the one hand, will allow higher throughputs and thus the reduction of cross section, but on the other hand, it will reduce the efficiency and thus necessitate the use of more (actual) trays, *i.e.* the construction of a higher column. Under given conditions, the two opposite effects may define a minimum weight of the column at a certain free area of trays. Increase of F at small diameters and wide spacing of the trays can cause an increase in the column weight because in such an instance the wall of the column assumes a greater role. In the case of high capacities and correspondingly great diameters, an increase of the free area of trays can bring about a decrease of the total column weight, since the weight of trays represents the relatively greater part. Similar considerations hold in connexion with tray spacing.

3. Functions

The foregoing can be expressed quantitatively. (In the weight equations, the dimensional conversion factors are not given. According to their sense, the variables can be written in any system of units, keeping in mind that was used is $\left[\frac{\mathrm{m}}{\mathrm{s}}\right]$, and V is $\left[\frac{\mathrm{m}^3}{\mathrm{s}}\right]$.)

We define a value A characteristic of the operating conditions as follows:

$$A = \frac{V}{6.9}\sqrt{\frac{\gamma}{1.2}}\left(\frac{L}{G}\right)^{0.34}[\mathrm{m}^2]\,. \tag{3}$$

Using this, Eq. (1) becomes:

$$w = \frac{FV}{A}\,. \tag{4}$$

The cross section, or the diameter, of the column can be expressed by the volume rate of the ascending stream of vapour and by the vapour velocity:

$$\frac{D^2\pi}{4} = \frac{V}{w} = \frac{A}{F} \tag{5}$$

$$D = \frac{2}{\sqrt{\pi}} A^{0.5} F^{-0.5}\,. \tag{5a}$$

The total weight of the column comprises the weight of the trays and the weight of the column wall:

$$G = G_t + G_k \tag{6}$$

and these can be calculated from geometrical data.

The thickness e of a tray and the specific gravity γ_a of the material of construction are known, thus:

$$G_{1t} = \frac{D^2\pi}{4}(1 - F)\,e\gamma_a\,, \tag{7}$$

and the total weight of the trays is:

$$G_t = \frac{n}{\eta}\frac{D^2\pi}{4}(1 - F)e\gamma_a\,. \tag{8}$$

Using (2), (1) and (5), we get:

$$G_t = n\frac{1}{0.53}g^{-0.3}\left(\frac{L}{G}\right)^{-r}H^{-0.3}\left[6.9\sqrt{\frac{1.2}{\gamma}}\left(\frac{L}{G}\right)^{-0.34}\right]^{0.6}\cdot$$

$$\cdot F^{0.6}AF^{-1}(1 - F)e\,\gamma_a\,. \tag{9}$$

The constants and the fixed quantities can be gathered into one constant:

$$k = n\frac{1}{0.53}g^{-0.3}\left(\frac{L}{G}\right)^{-r}\left[6.9\sqrt{\frac{1.2}{\gamma}}\left(\frac{L}{G}\right)^{-0.34}\right]^{0.6}e\gamma_a \tag{10}$$

then

$$G_t = k\, H^{-0.3}\ F^{-0.4}\ (1-F)A\,. \tag{11}$$

The quantity proportional to the weight of the trays is:

$$G'_t = \frac{G_t}{k} = H^{-0.3}\, F^{-0.4}\,(1-F)\,A\,. \tag{12}$$

Let us now consider the calculation of the weight of the column wall. To each tray belongs an annular section of height H of the column wall. The ratio of tray thickness to wall thickness is denoted by s (this takes into account also flange weights which amount to a few per cents). Thus, wall thickness is $s{\cdot}e$.

The weight of one annular column wall section is:

$$G_{1k} = (D + se)\pi\, se\, H\, \gamma_a \approx n\, D\, \pi\, se\, H\, \gamma_a\,. \tag{13}$$

The total weight of the column wall will be:

$$G_k = \frac{n}{\eta} D\pi\, se\, H\gamma_a = n\,\frac{1}{0.53}\, g^{-0.3}\left(\frac{L}{G}\right)^{-r} H^{0.3}\left[6.9\sqrt{\frac{1.2}{\gamma}}\left(\frac{L}{G}\right)^{-0.34}\right]^{0.6} \cdot$$

$$\cdot\, F^{0.62}\, 2\sqrt{\pi}\, A^{0.5}\, F^{-0.5}\, se\, H\gamma_a\,. \tag{14}$$

With the denotations used before

$$G_k = k\, 2\sqrt{\pi}\ H^{0.7}\, F^{0.1}\, A^{0.5}\, s \tag{15}$$

$$G'_k = \frac{G_k}{k} = 2\sqrt{\pi}\, H^{0.7}\, F^{0.1}\, A^{0.5}\, s\,. \tag{16}$$

The value proportional to the column weight is:

$$G' = \frac{G}{k} = G'_t + G'_k \tag{17}$$

$$G' = H^{-0.3}\, F^{-0.4}\,(1-F)\,A + 2\sqrt{\pi}\, H^{0.7}\, F^{0.1}\, A^{0.5}\, s\,. \tag{18}$$

It is to be seen that in two terms of the right hand side, of Eq. (18), H and F have exponents of opposite sign and also a factor $(1-F)$ is present. In consequence of this, and in comformity with that has been said before, under certain conditions the column weight has a minimum value in function of these two magnitudes.

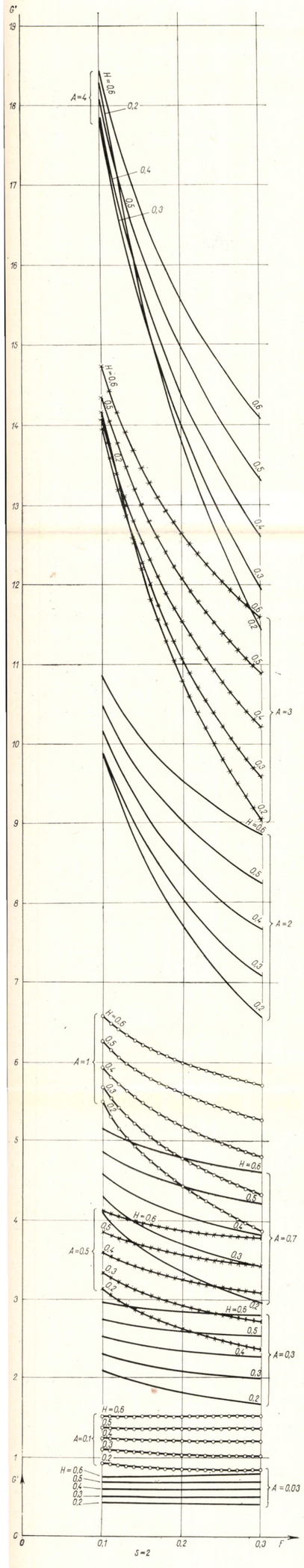

Fig. 1

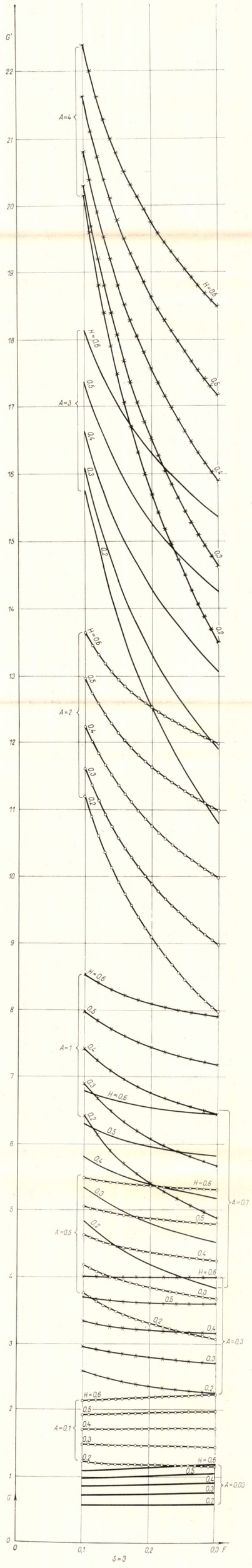

Fig. 2

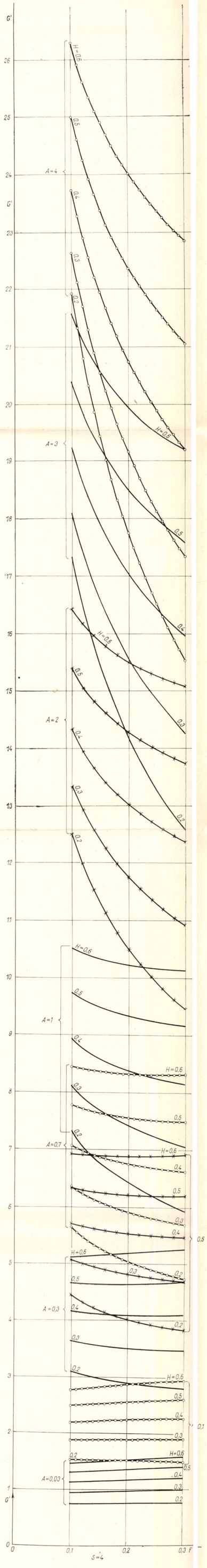

Fig. 3

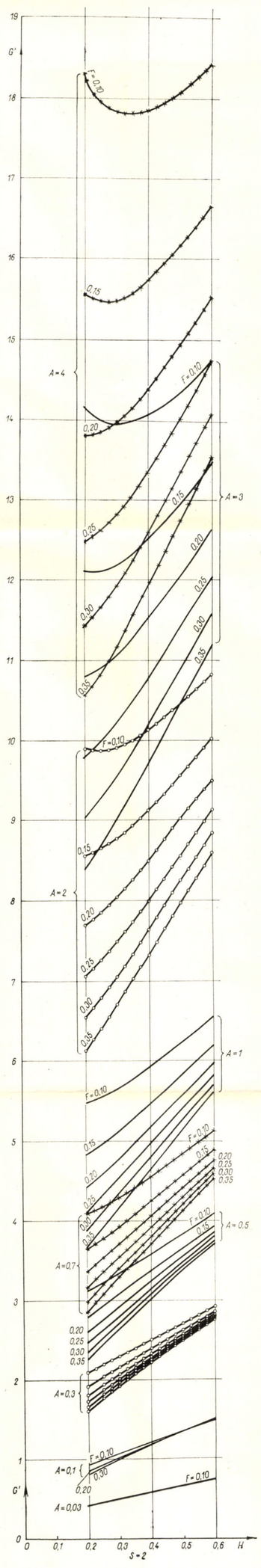

Fig. 4

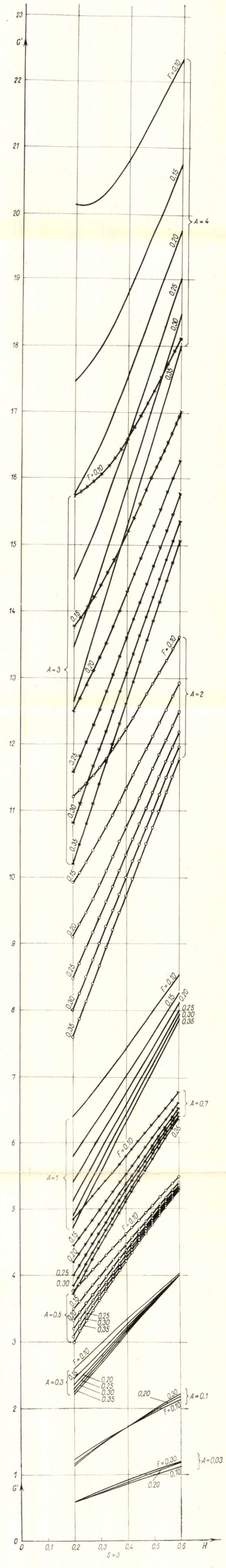

Fig. 5

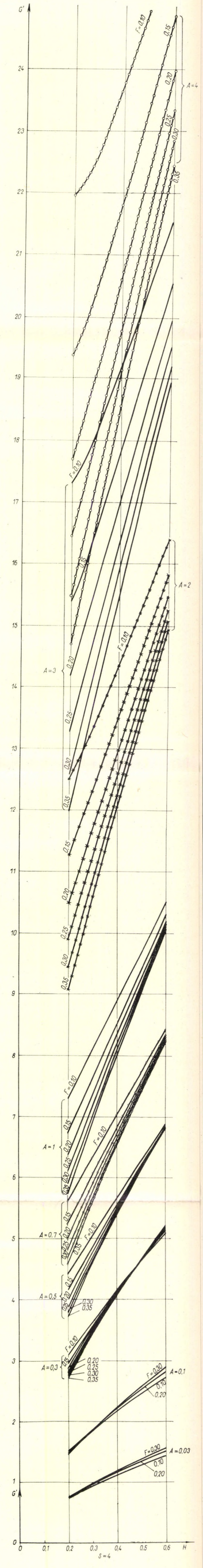

Fig. 6

The minima can be calculated by differentiation:

$$\left(\frac{\partial G'}{\partial H}\right)_F = -0.3\,A\,H^{-1.3}\,F^{-0.4}(1-F) + 1.4\sqrt{\pi}\,A^{0.5}\,H^{-0.3}\,F^{0.1}\,s = 0 \qquad (19)$$

hence

$$H = 0.121\,\frac{A^{0.5}(1-F)}{F^{0.5}\,s} \qquad (20)$$

$$\left(\frac{\partial G'}{\partial F}\right)_H = -0.4A\,H^{-0.3}\,F^{-1.4} - 0.6A\,H^{-0.3}\,F^{-0.4} + 0.2\sqrt{\pi}\,A^{0.5}\cdot$$

$$\cdot H^{0.7}\,F^{-0.9}\,s = 0\,. \qquad (21)$$

$$F - \frac{\sqrt{\pi}\,Hs}{3\sqrt{A}}\sqrt{F} + \frac{2}{3} = 0. \qquad (22)$$

This equation can be solved by the substitution of $\sqrt{F} = n$ as a quadratic one.

Figs 1, 2, 3, 4, 5 and 6 show the changes of the value of G', which is proportional to the total column weight, according to Eq. (18). The diagrams show the multivariable correlation functions in the domain of practical importance, when $H = 0.2$ to 0.6 metre and $F = 0.10$ to $0.35\ \frac{\mathrm{m}^2}{\mathrm{m}^2}$. The spacing and free area of trays are shown on the horizontal axis, the other data as parameters. The value of A characteristic of the operating conditions is proportional to the column capacity, and when A increases also the diameter of the column becomes greater.

According to the diagrams (Figs 1, 2, 3) an increase of the free area of trays is conducive to significant reductions of weight only when A has higher values, and this is explained by the fact that with greater column diameters corresponding to such higher values of A the weight of trays relative to the weight of the column increases. When throughputs are small, the material requirement is practically independent of the free area of trays, there is even a weight minimum in its function.

Generally it is advisable to adopt a close spacing of trays (cf., Figs 4, 5, and 6), and this at a first consideration, seems obvious enough. It is well, however, to point out that at high throughput figures the material requirement of the column shows a minimum in function of the tray-spacing, especially when column wall thickness s is low in comparison to tray thickness. The explanation for this is given therein that when the column diameter is large, the material requirement for the trays is the predominating factor, since this grows at the second power while the material requirement for the column wall structure grows linearly; further, the wider spacing of trays has a twofold effect: an

increase in efficiency, thus the number of actual trays may become less with a concomitant reduction of weight, but, at the same time, the material requirement for the column wall increases, and due to this the column weight will become greater. When the diameter is small, the latter factor is the more important one.

An analysis of data presented in the Figures is useful also in cases when no minimum value can be found in the function of a parameter. Even so, the effect exerted by the several factors upon the column weight can be estimated, *e.g.* that it is not worth while to choose an extreme value for a parameter, and this lends elasticity to design work. Such is the situation with the curves of column weights *vs.* free area of trays; the flat shape of these curves allows a choice of the free area to fall between 15 and 25%, without detriment to economics, and according to other points of view, such as standard specifications, technology, etc.

The curves presented are of general validity, they refer to any system and to a rather extended domain of throughput and reflux values. All these parameters are included in the generalized values A and k.

Of course, the correlations presented are valid only when, and in so far as, the fundamental relations (1) and (2) are correct. We think, however, that even after further precision of the constants and exponents the conclusions drawn here in respect of optimization according to weight will tend in the same direction, and changes in the numerical values will leave the character of the correlations unchanged. Even if formulas with differing contents and forms will be applied, conclusions similar to ours will be found valid.

Finally, we may mention that, in certain cases, especially when no sharp maximum is to be found on an efficiency *vs.* vapour velocity curve, it is advisable to choose a vapour velocity higher than indicated by Eq. (1). This may often result in an increased capacity that outweights small reductions in efficiency. Accordingly, the vapour velocity assignable to maximum efficiency may be regarded as the lower limit of the optimum range of throughput.

Economics, in respect of both operating costs and initial investment, of a given separation job to be handled by distillation depend, in addition to the design and construction parameters mentioned before, on the reflux ratio and the corresponding theoretical number of plates. These factors are included in the constructional optimization constants A and k which thus cease to remain constants. New variables may be taken into account in various ways, *e.g.* by incorporating them in our preceding equations. In this case to be able to write a general mathematical expression of closed form, the exact correlation between the number of theoretical plates and reflux ratio, which, essentially, is equivalent to the $\left(\frac{L}{G}\right)$ ratio, must be known. This problem seems to be amenable to solution with the help of a computer.

Symbols

A a quantity comprising throughput and operation conditions (see explanation in text in connexion with calculations of the column weight), m^2

D internal diameter of the column, m

e thickness of grid tray, mm

F free area of trays, in relation to the entire cross section area of the column, $\frac{m^2}{m^2}$, %

$Fr = \frac{w^2}{Hg}$ Froude number

g gravitational acceleration, $\frac{m}{sec^2}$

G column weight, kp

G' magnitude proportional to the total column weight

G_k weight of column walls, kp

G'_k magnitude proportional to the total weight of column wall

G_t weight of trays, kp

G'_t magnitude proportional to the total weight of trays

H distance between trays, m

k constant comprising throughput and operation conditions (see explanation in text in connexion with calculations of the column weight)

$\frac{L}{G}$ mass velocity ratio of liquid to vapour within the column, $\frac{kg \cdot h^{-1}}{kg \cdot h^{-1}}$

n theoretical number of plates

p pressure in the column, Torr

p_0 atmospheric pressure, Torr

r empirical exponent

s ratio of column wall thickness to plate thickness, $\frac{mm}{mm}$

$s \cdot e$ column wall thickness, mm

V ascending mass of vapour, $\frac{m^3}{s}$

w optimum vapour velocity in the grid tray column, referred to empty column diameter, $\frac{m}{sec}$

γ_a specific gravity of the material of construction used for the column, $\frac{kp}{m^3}$

η efficiency of the column

γ specific gravity of the vapour, $\frac{kp}{m^3}$

SUMMARY

The dependence of the weight of grid-tray distillation columns on the tray spacing, the free cross section, the thickness of the jacket and the loading was investigated under the given conditions of separation and operation. In the derivation of this function, the maximum efficiency and the corresponding vapour velocity were considered as basis. It was established that, under certain conditions, the weight of the column presents a minimum in function of the free cross section and of the tray spacing. Results obtained are discussed in detail, illustrated by diagrams and interpreted.

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H. G. Henning, W. Jugelt, G. Sauer: *Praktische Chemie für Mediziner* VEB Verlag Volk und Gesundheit. Berlin, 1966. 464 S.

Das Werk ist als Einführung für Medizinstudenten gedacht, die künftig auf Grenzgebieten der Chemie arbeiten werden. Diesen Gesichtspunkt vor Augen haltend, wurde ihr Praktikum in den nachstehenden fünf Kapiteln zusammengestellt:

I. *Einführung in die chemische Laboratoriumstechnik*

Hier werden die in den Labors einzuhaltenden, grundlegenden Vorsichtsmaßregeln, das Wägen, das Biegen von Geräteglas, Korkbohren, die Filtergefäße usw. beschrieben.

II. *Elemente und Verbindungen*

Das Kapitel bespricht die Gruppen des periodischen Systems sowie die häufigeren Reaktionen ihrer Elemente. Es bringt Beispiele und erläutert diese auf der Grundlage der Elektronenkonfigurationen.

III. *Physikalisch-chemische Grundlagen*

Dieses Kapitel macht die Hörer mit den Gesetzen der Stöchiometrie bekannt und bringt auch mit Beispielen illustrierte Berechnungen.

Sehr anschaulich ist die Erklärung der Katalyse der chemischen Reaktionen. Schade, daß sie nur kurz behandelt wird, da die Erklärung der Wirkungsweise von Biokatalysatoren für den sich mit dem lebenden Organismus beschäftigenden Arzt und Biologen zum Verständnis der Reaktionen »in vivo« überaus wichtig ist; dieser Teil des Kapitels hätte auf Kosten des der elektrischen Dissoziation gewidmeten Volumens erweitert werden können.

IV. *Funktionelle Gruppen organischer Verbindungen*

Das Kapitel gibt eine mit Beispielen illustrierte Übersicht der Chemie der Kohlenstoffverbindungen, auf Grund des Zusammenhanges zwischen Bindungsarten, Elektronenkonfiguration und Reaktionsfähigkeit.

V. *Analytische Methoden*

Es werden die in den biologischen ärztlichen Laboratorien verwendeten analytischen Methoden behandelt. Schade, daß die auch in den ärztlichen Laboratorien immer ausgedehnter eingesetzten UV-Spektrophotometer — im Zusammenhang mit der Besprechung der Grundlagen der Photometrie — nicht eingehender beschrieben wurden. Es wäre zweckmäßig gewesen, auch die Analyse der funktionellen Gruppen kurz zu streifen.

In seiner Gesamtheit wird dieses praktische Werk in der Ausbildung der künftig auf den Grenzgebieten der Chemie arbeitenden Ärzte und Biologen sehr erfolgreiche Dienste leisten.

Das Buch ist auch in seiner äußeren Form, drucktechnisch ausgezeichnet und sehr übersichtlich.

K. Hideg

WALTER B. MORS and CARLOS T. RIZZINI: *Useful Plants of Brazil.* Holden-Day Inc., San Francisco, London, Amsterdam, 1966.

This book is a valuable and interesting lexicographic presentation of the useful plants of the Brazilian flora. Usefulness is here considered in almost its entire range, from medically utilizable plants to those employed in carpentry and cabinet making, excluding only those that furnish food or fodder.

Over 160 pages, in 16 chapters, the grouping according to this point of view includes plants that yield 1. latex, 2. coffee, 3. oils, 4. waxes, 5. trunk exudates, 6. tannin, 7. dyes, 8. aromatic oils, 9. spices, 10. medicinal substances, 11. toxic substances, 12. fibres, 13. timber, 14. cork, 15. cellulose and paper, 16. miscellaneous other products.

No chemical formulas are given, not even in discussions concerning drugs. Data, however, are presented about the reserpine content of the various Rauwolfia species; further about the size of plants. In the introductory part, data about the lives of botanists whose names figure in abbreviated form as discoverers of plants, are very instructive. The bio-climatological division of Brazil, shown also by maps, conveys much useful information.

The suitably selected bibliography will be appreciated by all who wish to become better acquainted with the topics dealt with in this book, and its beautiful presentation, together with the illustrations, certainly helps it to effect its purpose.

P. BITE

I. PROSZT, V. CIELESZKY, K. GYŐRBIRÓ: *Polarographie.* Akadémiai Kiadó (Akademie-Verlag) Budapest, 1967.

Die Polarographie erwarb sich in den vergangenen vierzig Jahren unter den elektrochemischen Methoden in der Analytischen Chemie eine Vorrangstellung. Da sowohl ihre theoretische Bedeutung wie ihre praktischen Vorteile gleichermaßen sehr groß sind, wurde das Interesse für die Polarographie in Fachkreisen ganz allgemein. Deshalb ist die Übersetzung des Buches von PROSZT und Mitarbeitern nach dem Erscheinen der ungarischen Ausgabe von großer Bedeutung. Das Buch trägt nämlich die wichtigen Gebiete der Polarographie mit einem für den Leser sehr glücklichen didaktischen Geschick vor. Dadurch wird es für die Interessenten möglich, sich von den entsprechenden elektrochemischen Grundlagen ausgehend sowohl in die Theorie der Polarographie als auch in ihre praktische Anwendung einzuarbeiten.

Das Buch besteht aus drei Hauptteilen. Der erste enthält die allgemeinen theoretischen Grundlagen, u.zw. vor allem das Gebiet der sog. klassischen Polarographie, wo die Theorie der verschiedenen polarographischen Stromarten eingehend besprochen wird. Die Meßeinrichtungen und Meßzellen werden erörtert und in einem kurzen Kapitel die neuen polarographischen Meßverfahren beschrieben. Dieses dient im Gegensatz zu den anderen Kapiteln des theoretischen Teiles lediglich der Orientierung.

Der zweite Teil des Buches beschäftigt sich mit der anorganischen Polarographie. Er bietet auf einem Umfang von etwa 110 Seiten ein sehr gutes praktisches Hilfsmittel für die mit der anorganischen Polarographie arbeitenden Fachleute, da in ihm das polarographische Verhalten der einzelnen aufgezählten Elemente auf Grundlage der Originalliteratur eingehend beschrieben wird. Die Bedeutung des die praktischen Vorschriften enthaltenden Teiles (ca 20 Seiten) soll besonders betont werden. Diese Vorschriften beziehen sich vor allem auf die Analyse verschiedener Legierungen.

Im dritten Teil des Buches werden die Probleme der organischen Polarographie behandelt. Dieses Gebiet entwickelt sich gegenwärtig in solchem Maße, daß die Verfasser wegen des begrenzten Umfanges hier nur einen Überblick bieten konnten. Diese Aufgabe haben sie tadellos gelöst. Der Leser bekommt eine sehr gute Vorstellung von der Anwendung der Polarographie bei der theoretischen Untersuchung organischer Verbindungen. Die Zusammenhänge zwischen den strukturellen und polarographischen Eigentümlichkeiten werden dargestellt. Im Abschnitt über die praktische organische Polarographie schließlich wird dem Leser eine gute Orientierung über die Möglichkeiten der polarographischen Bestimmung der verschiedenen organischen Verbindungen gestattet. Am Ende des Buches ist eine Tabelle von häufig verwendeten Puffern zu finden.

Das Werk »Polarographie« von PROSZT und Mitarbeitern ist geeignet, die zunehmende Verbreitung des Verfahrens weiter zu fördern.

E. PUNGOR

W. SIMON, and T. CLERC: *Strukturaufklärung organischer Verbindungen mit spektroskopischen Methoden.* Akademische Verlagsgesellschaft, Frankfurt am Main, 1967.

A. J. BAKER, T. CAIRNS, G. ELINGTON, and F. PRESTON: *More Spectroscopic Problems in Organic Chemistry.* Heyden and Son, London, 1967.

These two books, of similar aim and character, have been published recently. As both are based on university lectures and practical classes, their aim is primarily didactic: to present examples suitable for the acquisition of practical knowledge in the use of up-to-date methods for the study of chemical structures, such as ultraviolet, infrared and nuclear magnetic resonance spectroscopy, and mass spectrometry, which are perhaps the most successful of the physico-chemical techniques. The subject-matter of the book has increasing importance, since after the instruments for UV and IR spectroscopy, also those for NMR and mass spectrometry have started to enter the everyday practice of chemists. Today quite a lot of experimentally ascertained data can be used in the simultaneous evaluation of the results of the four methods, in addition to the correlation tables which can be applied separately for each method. The work of SIMON and CLERK is a realization of this new aspect when, following the initiative of Silverstein and Bassler, it gives new tables of correlations, though, clearly on the presumption that they are known, it does not treat the underlying theories. In these tables UV, IR, NMR, and these deal with the relations between the spectra and the characteristics of fine structure. There is an additional booklet with 50 practical examples that shows how to apply these tables, and thus helps the reader to become proficient in their use.

The book is a very good initiation, and as a serviceable tool in up-to-data research work, it is bound before long to become a much consulted handbook.

The other work, that of BAKER *et. al.*, in accordance with its somewhat more moderate objective, gives sixty examples with accurate statement of the experimental conditions. This, together with the careful selection of data referring to many of the most common functional groups and structural features, *e.g.* substituted benzene rings, unsaturation, carbonyl, hydroxyl, amino, nitro, sulpho groups, and heterocycles, to name but a few, render the book suitable for use also as a collection of spectra. This purpose could have been still better served by giving a simple index to list the different examples in which the various structural characteristics could be found *(e.g.*, item 13 for terminal triple bond, item 47 for 1, 2, 3, 5-tetrasubstituted benzene ring, *etc.)*. A minor defect is that though this book is the fourth in a series, the data given in the preceding volumes (especially in Vol. 2) are not always sufficient for working out the examples, thus an additional search in the literature is necessary. This may have its advantages from a didactic point of view, but may cause difficulties when this additional literature is not available.

Apart from these slight defects which are, perhaps, irrelevant as far as the purpose of the book is concerned, this collection provides opportunities for stimulating mental exercise by the problems presented. In addition to the satisfaction obtained by correctly solving the examples, the reader will also acquire readiness and ease in the handling of spectrometric problems.

GY. DEÁK

SUBRAMANIA RANGANAHAN: *Fascinating Problems in Organic Reaction Mechanisms.* Holden-Day Inc., San Francisko, London, Amsterdam, 1967, 88 pp.

Chemists engaged in preparative organic chemistry often encounter in their everyday practice rearrangement reactions, which, contrary to all expectation, yield products of most remarkable structure. For some of these rearrangements, the underlying processes have already been explained from the theoretical aspect, however, the mechanism of many of these conversions has still to be elucidated. In such cases, the elucidation of the reaction process can be attempted in knowledge of the end product, the structures of the starting materials and the reaction conditions.

The Author, who with the writing of this book undertook a very interesting and, of its kind a rather pioneer task, selects from recent literature rearrangement reactions which take such "suprising" course. With a total of 243 problems, the Author spurs the reader on to have

a try at working out the reaction mechanism for himself. In every case, cited literature may be consulted. However, even the original publications are based more or less on assumptions, so that intellects well versed in the field of reaction mechanism, will often find these assumptions defective or sometimes even unfounded, which will prompt the reader to propose a new, more plausible mechanism.

The deeper study of the problems is an excellent intellectual game for organic chemists; in consideration of the practical importance of the examples, it contributes to a widening knowledge, and is instrumental in developing the way of thinking in this particular field.

Cs. SZÁNTAY

A. N. NESMEYANOV and R. A. SOKOLIK: *Methods of Elemento-Organic Chemistry, Vol. 1: The Organic Compounds of Boron, Aluminium, Gallium, Indium and Thallium.* North-Holland, Amsterdam, 1967, 628 pp., 40 fig. and several tables.

Students of metallo-organic (or elemento-organic) chemistry all over the world are well acquainted with the immense work carried out by the NESMEYANOV school in this field, and with their series of monographs published in Russian in the last two decades on this topic. Out of the series comprising the methods of elemento-organic chemistry, the work dealing with the chemistry of the elements of Group III/a is now presented in English, in a revised and enlarged edition, based on the Moscow edition of 1964.

The subject-matter gives a critical coverage to the most important results published in literature up to 1962—63. Though concise, the book is written in a very lucid style, and the subject is well arranged. In the construction of the chapters a uniform and readily applicable method is followed. A modern structural-chemical view pervades the whole work, forming its very backbone. Compounds and their characteristic reactions are discussed troughout the whole book on the basis of a consistent system of bond theory. Nevertheless, this does not render the book too theoretical, and it remains true to its title and to the preparative chemical character. This must be emphasized, as one of the special merits of the book. The work proves that descriptive chemistry, giving a detailed account of methods of synthesis and an almost complete summary of characteristic reactions, need not stay on a descriptive-phenomenological level, but can be modern in its concept. In the description of syntheses and characteristic reactions, fundamental features and underlying principles are always accentuated to a well-balanced degree, so that the following detailed description can be readily built on this foundation. Theoretical summaries preceding each chapter are short, but reflect the essentials. Thus, *e.g.*, the introductory part on organoaluminium compounds comprises only 7—8 pages, still it emphasizes with a proper sense of criticism which is important and new in the field of synthesis and bond theory. In this respect it deserves special mention that the book gives the first really complete summary of the reactions of organoaluminium compounds, and calls attention to the fact that this family of compounds opened up new paths of syntheses. It gives an idea of the intensive development in this respect that we are witnessing at present.

The concise review of organic boron complexes and polyhedral borane and carborane chemistry, is unique of its kind. Naturally, chapters on boron chemistry have the strongest competition in literature, to mention only the excellent monographes of STEINBERG and GERRAD. However, the book of NESMEYANOV and SOKOLIK, owing to its method and concept, holds its ground against these, in general, more detailed works. It should be mentioned in this respect that monographs on metallo-organic chemistry, published up to 1962 have been carefully considered — as pointed out in the preface by the authors.

Among the merits of the book are the concise analytical chapters, which give, in a form that can be used also by chemists engaged in preparative work, the most important methods of testing and determination of these compounds.

The difficult problem of rendering the book a valuable source of bibliography without having to sacrifice essentials or conspicuity, has been successfully solved; works which are not of primary importance or those of predominantly theoretical character are mentioned only in a few works or half a sentence, so as not to divert the attention of the reader from the main theme. Those, however, who wish to deepen their knowledge on the subject, will easily find the original work.

Perhaps the only criticism that can be made in connection with the book is the fact that both in the evaluation of the syntheses and in the discussion of the various bond-theoretical statements the approach could be more polemic. This would give more assurance to the reader in finding his way in the multitude of rapidly accumulating information.

T. SZÉKELY

Reinstoffprobleme, Band I. Reinstoffdarstellung Tagungsbericht, 2. Internationales Symposium »Reinststoffe in Wissenschaft und Technik« (Herausgegeben von E. REXER) Akademie-Verlag, Berlin, 1966, 600 S. mit 246 Abb. und 62 Tab.

Der Akademie-Verlag plant die Vorträge des in September 1965 in Dresden stattgefundenen Internationalen Symposiums in drei Bänden herauszugeben. Der erste Band, der sich mit dem Problemen der Reinststoffdarstellung befaßt, enthält drei plenare und 42 weitere Vorträge. Der russische Text des mehrsprachigen (deutsch, russisch, englisch, französisch) Buches ist auch in die deutsche Sprache übersetzt worden.

Der erste Teil des Buches behandelt die zur Darstellung der Reinststoffe verwendeten chemischen Methoden. Hier werden vor allem kinetische, technologische und thermodynamische Probleme in Verbindung mit der Darstellung von Halbleiter-Germanium und -Silizium besprochen, wie z. B. Rektifikationsprobleme der Chlorsilane bzw. des Germaniumtetrachlorids, technologische Fragen der Trichlorsilan-Reduktion, Gleichgewichtsuntersuchungen bei aus Chlorosilanen und anderen Halogeniden bestehenden Systemen, kinetische Untersuchung der Darstellung von Germanium-Einkristallen usw.

Zahlreiche Vorträge behandeln die Methoden der elektrolytischen Herstellung hochreiner Metalle (Ag, Cd, Zn, Mn, Al, Fe) und Metall-Einkristalle (Pb, Cd, Zn, Sn, Bi, Cs).

Dieser Abschnitt bringt auch mehrere Beispiele der mit Umkristallisation kombinierten Methoden, zur Darstellung hochreiner und zur Züchtung von Einkristallen geeigneter Alkalimetallhalogenide. Besonders interessant unter diesen Arbeiten sind die im *Institut für Anorganische Chemie* in Novosibirsk durchgeführten Untersuchungen über die Löslichkeit der Fluoride in wasserfreiem Fluorwasserstoff, die zu einer neuen Reinigungsmethode in der Darstellung von Halbleitern geführt und außerdem bisher fehlender Daten über die Lösungsmitteleigenschaften des Fluorwasserstoffs geliefert haben. Unter den Vorträgen enthalten einige auch Beispiele über die Heranziehung der Extraktion und des Ionenaustausches in der Darstellung von Reinststoffen.

Im zweiten Teil des Buches werden die Methoden der Entgasung, Vakuumdestillation und der Reinigung durch Zonenschmelzen behandelt, bei deren praktischer Ausführung besonders die Verwendung des Elektronenstrahls eine wichtige Rolle spielt. Dementsprechend dürfte in diesem Abschnitt der plenare Vortrag von R. BAKISH mit dem größten Interesse rechnen, der sich eingehend mit der gegenwärtigen Verwendung des Elektronenstrahls in Wissenschaft und Industrie befaßt und auch auf die zukünftigen Entwicklungsrichtungen der Elektronenstrahl-Technologie hinweist.

Das Buch ist vor allem den sich mit Strukturproblemen und strukturempfindlichen Eigenschaften befassenden Forschern sowie den in der Erzeugung von Halbleitern oder optische Verwendung findenden Einkristallen betätigten Ingenieuren zu empfehlen, doch wird es sicher auch für in anderen Gebieten der anorganischen Chemie arbeitende Fachleuten eine nützliche Lektüre sein.

B. CSÁKVÁRI

Reinststoffanalytik. 2. Internationales Symposium »Reinststoffe in Wissenschaft und Technik« Dresden. Akademie-Verlag, Berlin, 1966, 707 S.

An dem in Dresden im Jahre 1965 veranstalteten Symposium wurden 147 Vorträge über die aktuellen Probleme auf den verschiedenen Gebieten der hochreinen Stoffe gehalten. Die Vorträge veröffentlichte der Akademie-Verlag in drei Bänden:

I. Reinststoffdarstellung
II. Reinststoffanalytik
III. Realstruktur und Eigenschaften von Reinststoffen

Im zweiten Band wird die Analytik der Reinststoffe behandelt. Der Band enthält die über dieses Thema gehaltenen Plenar- und sonstigen Vorträge sowie die wichtigsten Diskussionen in der jeweiligen Vortragsprache. Außerdem wurde als Einführung jedem Vortrag eine kurze Zusammenfassung in englischer, russischer und deutscher Sprache zugefügt.

Als Einführung befasst sich A. SPECKER (Dortmund) in der Einführung in seinem Plenarvortrag über die Möglichkeiten und Probleme der Bestimmung der in den Reinststoffen befindlichen Spurenverunreinigungen. Er unterstreicht, daß diese Aufgaben ausschließlich mit physikalisch-chemischen Methoden gelöst werden können, daher ist die Analytik der

Reinststoffe sowohl bezüglich der Zahl der Laboratorien als auch hinsichtlich des Personals und der notwendigen Instrumente sehr aufwendig. Die durch die Produktion aufgeworfenen analytischen Probleme können aber nur auf diese Weise gelöst werden.

Die Vorträge erfaßten die folgenden Themenkreise: Verwendung der Methode der mathematischen Statistik in der Spurenanalyse, Spektralanalyse, Massenspektroskopie, Aktivierungsanalyse, photometrische, kinetische und elektrochemische Analysenverfahren, Gasbestimmung in Metallen. In diesen Themakreisen wurden einerseits die theoretischen Grundlagen der einzelnen Methoden, die Anwendungsmöglichkeiten in der Spurenanalyse mit besonderer Rücksicht auf die Grenzen der Nachweisbarkeit; andererseits die Weiterentwicklung der betreffenden Instrumente und technischen Kunstgriffe sowie die zur Bestimmung der Spurenelemente ausgearbeiteten Methoden besprochen..

Mit Rücksicht darauf, daß die Ausarbeitung der Analytik der Reinststoffe vom Gesichtspunkte der fernmeldetechnischen Industrie, der Herstellung von reinsten Reagenzien, des Reaktorenbetriebes usw., auch in Ungarn immer dringlicher wird, werden praktische Analytiker diesen Band sehr vorteilhaft verwerten können. Er gibt eine gute Übersicht über die Leistungsfähigkeit der Methoden, und die bereits ausgearbeiteten analytischen Verfahren können in der Lösung konkreter Aufgaben wertvolle Hilfe leisten.

É. BÁNYAI

J. DERKOSCH: *Absorptionsspektralanalyse im ultravioletten, sichtbaren und infraroten Gebiet.* Methoden der Analyse in der Chemie, Band 5. Akademische Verlagsgesellschaft Frankfurt am Main, 1962, 141 Abb., 38 Tab. im Text, 3 Tab. und 25 Lösungsmittel-Spektren im Anhang.

Die ultraviolette, sichtbare und infrarote Spektroskopie, die anfangs vorwiegend bei Arbeiten von rein theoretischem Charakter Verwendung fand, wurde in den letzten Jahrzehnten eine der wichtigsten Untersuchungmethoden der sich mit praktischen Fragen beschäftigenden Forscher und Betriebsingenieure. Außer den für Fachleute dieser Wissenschaft geschriebenen grundlegenden Arbeiten war daher ein Buch, das Analytiker, in verschiedenen Gebieten arbeitende Chemiker, Physiker, Ärzte, Biologen und andere Naturwissenschaftler anspricht, für die die Absorptions-Spektralanalyse bloß ein Mittel zum Zweck ist, dringend notwendig. Dieses Ziel vor Augen haltend, behandelt der Author theoretische Zusammenhänge nur bis zur unbedingt notwendigen Tiefe, und legt vielmehr besonderes Gewicht auf die verschiedenen Anwendungsgebiete und Arbeitsmethoden, unter Angabe der einschlägigen Literatur. Das Studium des Buches macht es dem Leser möglich, die zur Lösung des gegebenen Problems optimale Methode auszuwählen, so daß der Autor auch jenen eine bedeutende Hilfe leistet, die sich nur mit Teilgebieten innerhalb des Themas beschäftigen wollen.

Das Buch gliedert sich in acht Abschnitte. Die ersten vier behandeln die wichtigsten allgemeinen theoretischen und praktischen Fragen, wie z. B. das LAMBERT—BOUGNER—BEERsche Gesetz, die Aufnahme und graphische Darstellung der Spektren, Lichtquellen und Detektoren, die wichtigsten Typen der auf den Markt gebrachten Geräte, die Aufnahme der Reflexionsspektren sowie das Arbeiten mit polarisiertem Licht. Die zusammenfassenden, übersichtlichen Tabellen in diesen Abschnitten — in denen z. B. die Typen, charakteristischen Daten und Verwendbarkeitsbereiche von Prismen, Zellen und Spektrophotometern zusammengefaßt werden — gestalten die Ausführungen noch anschaulicher.

Der fünfte Abschnitt beschäftigt sich mit der qualitativen analitischen Verwendung der Absorptionsspektren, wobei zuerst das infrarote und dann das ultraviolette Gebiet behandelt wird. Die theoretischen Grundlagen der Entstehung des Infrarotspektrums, die Molekularsymmetrie, Rotationsstruktur und der Isotopeneffekt werden besprochen. Ein besonderes Kapitel behandelt — mit Hilfe vieler, gut übersichtlicher Tabellen—die charakteristischen Infratot-Frequenzen.

Die Theorie der Elektronenspektren, der Zusammenhang zwischen den Spektren und der chemischen Struktur, und schließlich der Einfluß der Umgebung wird im nächsten Kapitel besprochen.

In den Abschnitten über die Verwendung der Absorptionsspektren in der quantitativen Analyse wird die Aneignung der Methoden mit Hilfe von Beispielen zur Analyse von organischen bzw. anorganischen Verbindungen erleichtert.

Der letzte und vom Gesichtspunkt des Praktikers besonders wichtige Abschnitt des Buches ist eine Aufzählung der Spektrensammlungen, Monographien sowie grundlegender und

spezieller Werke. Für Fachleute, die sich auf diesem Gebiet betätigen wollen oder Kenntnisse aus diesem Gebiet zu ihrer Arbeit benötigen, ist diese Zusammenstellung der Literatur von überaus großem Wert.

Der Anhang erspart dem Praktiker viel Arbeit; er enthält nämlich die Spektren der wichtigsten Lösungsmittel sowie die Umbrechungstabellen Wellenzahl-Wellenlänge und Transmission-Extinktion.

Das Werk bringt fast 600 Literaturangaben (Bücher, Artikel und Kataloge).

Das auf einem hohen fachlichen Niveau, in leicht verständlichem Stil geschriebene Werk wird für die andauernd wachsende Zahl jener Fachleute, die auf diesem Gebiet in Routine- oder Forschungslaboratorien arbeiten, eine nützliche Lektüre sein.

L. ERDEY

Modern Packaging Films. Ed. by S. H. PINNER. Butterworths, London, 1967. 249 pp., 55 s.

The book deals with one of the most important application areas of plastic films: with their usage in the packaging industry. Regenerated cellulose film has been made for this purpose since 1924, but a wide-spread use of polymer packaging materials began only after the Second World War. At this time a number of new synthetic products (polythene, polypropylene, polystyrene, PVC) suitable for the production of thin films appeared on the market in large quantities.

This is perhaps the first authoritative book giving a balanced account of the production techniques, properties and application possibilities of the principal modern packaging films. It is intended mainly for people concerned with the problems of tailor-making, converting, machining and end-use promotion of packaging films, that is to people of packaging practice.

Consequently it pays minor attention to the chemical aspects of plastic materials. But packaging is a rather difficult problem of the chemical industry, too, therefore it may be of interest for the industrial chemists.

After a brief introduction, the book starts with an account of the early origins and progression of packaging films. Successive chapters deal with the production methods, advantages disavantages, and application areas for polyethylene, polypropylene, polystyrene and polyvinyl chloride films which, next to cellulose, are the most important packaging films. The so-called shrink wrapping films, also of great importance in modern packaging, are grouped together for comparison in one Chapter. In another Chapter the special problems of the testing and analysis of thin polymer films are dealt with comprehensively. A separate Chapter is devoted to the problems of printing and adhesion of packaging film, but unfortunately, only in general terms. There is a very interesting Chapter dealing with a completely new technique of cold-seal pattern printing of polypropylene and similar films. The penultimate Chapter reviews the work in progress of adapting automatic packaging machines to modern packaging films. Finally, the book gives a cautious assessment of the future growth potential for packaging films in general.

The book is arranged systematically and logically; it is compact and therefore practical, but it may leave some readers dissatisfied who look for more detailed information. The abundant references help to make up for this deficiency.

V. TAKÁCS

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ACTA CHIMICA

ТОМ 55 — ВЫП. 4

РЕЗЮМЕ

Изучение химических превращений диолов и органических окисей XIII. Получение 2,2-диалкил- и арил-замещенных оксетанов

М. БАРТОК

Рассматриваются синтезы гомологов 2,2-диалкил- и арил-замещенных оксетанов. 1,3-Хлоргидрины, содержащие в соответствующем положении первичный атом хлора, под влиянием гидроокиси калия превращались (с выходом 80%) в следующие оксетаны: 2,2-диметил-, 2,2-диэтил-, до сих пор неописанный 2-метил-2-*н*-пропил-, 2-метил-2-изопропил- и 2-метил-2-фенил-оксетаны. Образование оксетанов происходит по S_Ni механизму. Приводится несколько новых примеров участия (O^- — 4) соседних групп, которые иллюстрируются синтезами упомянутых эфиров. Хлористый 3,3-дифенил-3-гидрокси-пропил вышеупомянутым путем не дает 2,2-дифенил-оксетан, а изомерный с ним β-фенилпропиофенон.

Данные к аналитике 1,2-гликолей и полиокси-соединений, IX. Определение метил-β—D-арабинопиранозида, бензил-β—D-арабинопиранозида, а также метил-α—D-глюкопиранозида через диальдегиды, образующиеся при перйодатном окислении

И. МОЛНАР-ПЕРЛ и Л. МАРОШ

При перйодатном окислении β-метил- и β-бензил-арабинозида, а также β-метил-глюкозида в кислом растворе (pH $\approx$ 1 — 4) образуется диальдегид, который при взаимодействии с 2 молями сернистой кислоты образует стабильный альдегид-бисульфит. Для анализа этих двух пентозидов и гексозида использовался разработанный ранее авторами бисульфит-цианидный йодометрический метод. Перйодатное окисление при pH $\approx$ 8 полиальдегидов, стабильных в кислых растворах с pH $\approx$ 1 — 4, интерпретируется по единым гипотезам и в связи с этим указываются некоторые случаи окисления α-водорода, неизвестные до сих пор в литературе.

Данные к аналитике химии 1,2-гликолей и полиокси-соединений, X. Определение трегалозы, сахарозы и рафинозы через полиальдегид, образующийся при перйодатном окислении

И. МОЛНАР-ПЕРЛ и Л. МАРОШ

При перйодатном окислении трегалозы, сахарозы и рафинозы в кислом растворе (pH $\approx$ 1 — 4) образуется стабильный полиальдегид. Оксо-группы полиальдегида дают с сернистой кислотой альдегид-бисульфиты. Реакционная способность и структура этих

полиальдегидов интерпретируется на основе реакции присоединения сернистой кислоты. Для анализа этих трех невосстанавливающих сахаридов использовался уже ранее разработанный авторами сернистокислый-цианидный метод.

Природные хромоны, IV. Попытки синтеза келлина

М. М. БАДАВИ и М. Б. Е. ФАЙЕЗ

Изучаются реакции, включающихся в получение 2-метил-5,7-дигидроксихромона из флорацетофенона. При попытках получения келлина этот промежуточный продукт был превращен двумя методами в 5,8-диметокси-7-аллилокси-производное, которое, однако, не подвергалось перегруппировке Клэйзена.

Алкилирование метил-дихлорсилана и метил-диметоксисилана с помощью бутиллития и бромистого бутилмагния

И. ФЁЛЬДЕШИ, Д. ФРИТЦ, Г. КРАЙС и Т. СЕКЕЙ

Изучалось алкилирование метил-дихлорсилана и метил-диметоксисилана с помощью бутиллития и бромистого бутилмагния. Молярное отношение металлоорганического соединения к силану выбиралось таким образом, чтобы оно соответствовалось одному или двум заместителям (хлор- или метокси-). Метоксипроизводное приготовлялось из соответствующего хлорсилана обработкой метанолом. Продукты реакции идентифицировались с помощью газовой хроматографии. Было показано, что наряду с замещением хлора и метоксигруппы происходит также замещение и водорода. Самая высокая степень замещения водорода на алкил была найдена при взаимодействии бутиллития с метил-диметоксисиланом и самая низкая — бутиллития с метил-дихлорсиланом. Смешанное алкилирование, а именно реакции связей Si—H и Si—Cl (или Si—OCH_3) в одной и той же молекуле не наблюдалось. Было найдено, что реакционная способность связи Si—H уменьшается с увеличением степени алкилирования молекулы.

Исследование конденсации типа Клэйзена—Шмидта для ароматических альдегидов и кетонов, катализированной анионообменником

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Изучалась конденсация Клэйзена—Шмидта бензальдегида и ацетофенона, в абсолютном спирте, катализированная анионообменными смолами типа Амберлит IRA-410 и Зеролит FF-IR (в OH^- форме), приводящая к образованию калкона, и проводились обширные кинетические измерения. Было установлено, что при наших экспериментальных условиях диффузия не оказывает влияния на скорость реакции, и измеряемая скорость является скоростью химической реакции. Кинетически реакция имеет второй порядок, зависимость между концентрацией катализатора и константой скорости является нелинейной, и показатель степени по концентрации катализатора в уравнении скорости равен 1,7.

Была определена энергия активации реакции, которая находится в хорошем согласии с величиной, полученной при гомогенном катализе. Было установлено также, что размер зерен ионообменных смол не оказывает значительное влияние на скорость реакции, в то время как с увеличением количества сшивочных связей при одном и том же содержании OH^- реакция замедляется. Замещение в субстрате влияет на скорость реакции, что опять-таки подтверждает то, что измеряемая скорость реакции является скоростью химической реакции.

Конструктивная оптималиэация ректификационных колонн с провальными решетчатыми тарелками. Минимальный вес колонны при заданных разделительных и рабочих условиях

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Изучался вес ректификационных колонн с провальными решетчатыми тарелками при заданных разделительных и рабочих условиях в зависимости от расстояния между тарелками, свободного сечения, толщины кожуха и нагрузки. При постановке этой целевой функции взяли за основу максимальный к. п. д. и соответствующую ему скорость пара. Было установлено, что при определенных условиях вес колонны имеет минимум в зависимости от свободного сечения и расстояния между тарелками. Дается подробная интерпретация, графическое изображение и оценка полученных результатов.

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