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THE ADSORPTION OF URANIUM HEXAFLUORIDE, IV*

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From the point of view of the elucidation of convection-free UF_6 diffusion-adsorption processes, the knowledge of functions for the solution of non-stationary transient transport is of importance.

For the determination of the transient functions of a convection-free diffusion-adsorption operational unit, a mathematical model, taking into consideration the adsorption isotherm of Freundlich, and assuming rapid, instantaneous kinetics, has been interpreted.

The solution function is discussed, and the calculated values of the $f(C, l, t)$ function are presented for a model of given parameters.

Investigation of the processes of diffusion and adsorption (boiling) in a system free of convection

The simultaneous investigation of convection, diffusion and adsorption, the analysis of adsorption fronts have been started as early the operational units of adsorption had been introduced into the technology. In order to prove the necessity of the simultaneous investigation of convection-free diffusion and adsorption, the already known theoretical and experimental difficulties of the interpretation of adsorption fronts should be summarized. A common characteristic of the equations of adsorption fronts is their specific nature and the fact that they become inapplicable in the cases when

a) the adsorption front is not "stationary";

b) the kinetics of adsorption is a process retarded in time;

c) the adsorption equilibrium is not linear.

Let us presume that an "ideal" operational adsorption unit and an "ideal" front curve exist. In that case, this ideal adsorption front is actually deformed by the factors listed above. On investigating these anomalies of the adsorption front (which is in fact the interpretation of the real transport phenomena of adsorption proper) it appears that the technique of frontal chromatography does not afford any possibilities for the separate investigation of the single deformation effects within the same material transport process.

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Besides the theoretical problems of the adsorption fronts evolved in the convectional flow also those experimental difficulties are to be mentioned which emerge when the course of adsorption kinetics in time is actually a process not commensurable with the progress rate of the front evolving on the effect of the convectional flow. In this case it is a problem of measurement technique which line is in fact accepted as adsorption front and which is considered to be an equilibrium state. This effect manifests itself sharply on comparing the static kinetical data of the adsorbent systems of uranium hexafluoride and the gas chromatographic front curves of the same experimental systems.

It appears that the investigation of processes taking place in a system free of convection makes possible to study the effects of non-linear isotherms and of kinetics prolonged in time within the same material transport unit. The experimental equipment employed in the investigations of static diffusion proved to be directly applicable for the study of adsorption fronts free of convection.

The examined adsorbent systems of uranium hexafluoride possess non-linear isotherms and kinetics prolonged in time. For this reason, in our experiments we attempted to maintain conditions which secured the formation, in some particular cases, of an equilibrium state within the adsorption zone, facilitating, however, the prevailing of also the kinetical effect in a general case. The condition of equilibrium in the diffusion adsorption apparatus is attained by varying the concentration of adsorbate in the entering gas flow. If the condition

$$-D\left(\frac{\partial C(t)}{\partial x}\right)_{x=0} = J \leq \left(\frac{\partial n}{\partial t}\right)_{C} \tag{1}$$

is met, the diffusion front is of a quasi equilibrium nature because the condition

$$\left(\frac{\partial C(t)}{\partial x}\right)_{x} < \left(\frac{\partial C(t)}{\partial x}\right)_{x=0}$$

is fulfilled for all the points of this front.

The equation describing the process of adsorption diffusion, on applying the general simplifying presumptions introduced already earlier, reads as follows:

$$\xi \frac{\partial C}{\partial t} = D\xi \frac{\partial^2 C}{\partial x^2} - \gamma \frac{\partial n}{\partial t} \tag{2}$$

In the case of linear isotherms and equilibrium, the solution of Eq. (2) is

$$\xi \frac{\partial C}{\partial t} = D\xi \frac{\partial^2 C}{\partial x^2} - \gamma \frac{\partial n}{\partial c} \frac{\partial C}{\partial t} \tag{3}$$

where the term $\left(\frac{\partial n}{\partial c}\right)_e = H$ follows from the condition of adsorption equilibrium.

On converting Eq. (3), we obtain a correlation resembling Fick's second equation

$$(\xi + \gamma H)\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} \tag{4}$$

or, on introducing the symbol $D' = \frac{D\xi}{(\xi + \gamma H)}$

$$\frac{\partial C}{\partial t} = D'\frac{\partial^2 C}{\partial x^2} \tag{5}$$

The initial and limit conditions are:

$$\begin{array}{llll} C = C_0 & \text{if } x = 0 & \text{and} & t \geq 0 \\ C = C_\infty & \text{if } x = L & \text{and} & t \geq 0 \\ C = \varrho(x) & \text{if } 0 \leq x \leq L & \text{and} & t = 0 \end{array} \tag{6}$$

The solution of Eq. (4) with the conditions (6) is the following:

$$C = C_0 + (C_\infty - C_0)\frac{x}{L} + \frac{2}{\pi}\sum_1^\infty \frac{C_\infty \cos n\pi - C_0}{n}\sin\frac{n\pi x}{L}$$

$$e^{-\frac{Dn^2\pi^2}{L^2}t} + \frac{2}{L}\sum_1^\infty \sin\frac{n\pi x}{L}\, e^{-\frac{Dn^2\pi^2}{L^2}t} \cdot \int_0^L f'(x)\sin\frac{n\pi x'}{L}\,dx' \tag{7}$$

Now let us examine the effect of the non-linear isotherm, on presuming an adsorption equilibrium for the diffusion process.

On presuming an adsorption equilibrium and an isotherm equation of Freundlich type, Eq. (2) can be rewritten:

$$\left(\xi + \gamma\frac{\partial n}{\partial C}\right)\frac{\partial C}{\partial t} = \sqrt{\xi}\, D\frac{\partial^2 C}{\partial x^2} \tag{8}$$

where

$$\left(\frac{\partial n}{\partial C}\right)_e = \bar{k}mC^{m-1} \tag{9}$$

Now let us find the solution of the equation

$$(\xi + \gamma\bar{k}mC^{m-1})\frac{\partial C}{\partial t} = \sqrt{\xi}\, D\frac{\partial^2 C}{\partial x^2} \tag{10}$$

with the following initial and limit conditions:

$$\begin{array}{llll} C = C_0 & \text{if} \quad x = 0 & \text{and} & t \geq 0 \\ C = 0 & \text{if} \quad x = L & \text{and} & t \geq 0 \\ C = \varrho(\mathrm{x}) & \text{if } 0 < x < L & \text{and} & t = 0 \end{array} \tag{11}$$

where

$$\begin{array}{ll} \varrho(x) = C_0 & \text{if} \quad x = 0 \\ \varrho(x) = 0 & \text{if } 0 < x \leq L \end{array}$$

Let us introduce the symbol

$$\frac{\gamma \bar{k}}{\xi} = A \tag{12}$$

and let us consider variable C as the sum of two functions when

$$C = w(x; t) + p(x) \tag{13}$$

Eq. (10) reads on taking into account Eqs (12) and (13) as follows:

$$\frac{\partial}{\partial t}\big(w(x;t) + p(x)\big) + A \frac{\partial}{\partial t}\big(w(x;t) + p(x)\big)^m = D \frac{\partial^2 C}{\partial x^2} \tag{14}$$

Let us convert Eq. (14), omitting the symbols used for denoting the independent variables:

$$\frac{\partial}{\partial t}(w+p) + Ap^m \frac{\partial}{\partial t}\left(1 + \frac{w}{p}\right)^m = D \frac{\partial^2 C}{\partial x^2} \tag{15}$$

Let us employ the binomial approximation for the explication of the sum of exponentials:

$$\frac{\partial}{\partial t}(w + p) + Ap^m \frac{\partial}{\partial t}\left(1 + m \frac{w}{p}\right) = D \frac{\partial^2 C}{\partial x^2} \tag{16}$$

The condition for that is

$$\left|\frac{w}{p}\right| \ll 1 \tag{17}$$

Deriving from (16) we may write

$$\frac{\partial w}{\partial t} + Amp^{m-1} \frac{\partial w}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \tag{18}$$

i.e.

$$(1 - mAp^{m-1}) \frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \tag{19}$$

Now let us define the function $p(x)$, taking into account unequality (17)

$$p(x) = C_0 \left(1 - \frac{x}{L}\right) \tag{20}$$

In this case, Eq. (19) can be converted into the form

$$\left[1 + mAC_0^{m-1}\left(1 - \frac{x}{L}\right)^{m-1}\right] \frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \tag{21}$$

Correlation (21) is actually the linearized form of the nonlinear Eq. (10), obtained by binomial approximation.

Let us introduce the designations:

$$Y = 1 + mAC_0^{m-1}$$

and

$$X = -\frac{m(m-1)\,AC_0^{m-1}}{L} \tag{22}$$

Then, instead of Eq. (21), we may write at a fair approximation that

$$(Y + Xx) \frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \tag{23}$$

Let us solve Eq. (23) by the Fourier method; then

$$C = f(x)\, g(t) \tag{24}$$

Resubstituting condition (24) into Eq. (23) we obtain

$$\frac{g'(t)}{g(t)} = D \frac{f''(x)}{f(x)} \frac{1}{Y + Xx} = -K^* \tag{25}$$

where $-K^*$ is the own value (the negative sign being the condition of decrease in time).

Since, from (25)

$$g(t) = Ke^{-K^*t}$$

and

$$f''(x) = (Y + Xx) \frac{K^*}{D} f(x) \tag{26}$$

the general solution is

$$C = \sum_{i-1}^{\infty} E_i f_i(x) e^{-K_i^* t}$$

and

$$f_i(x) = f(x; K_i^*) \tag{27}$$

Let us solve this equation under homogeneous conditions, introducing the new variable $\varepsilon = Y + Xx$. From Eq. (26), it follows because $f'(x) = X^2 f'(\varepsilon)$ [1]:

$$f(\varepsilon) = \sqrt{\varepsilon}\, A_{1/3}\left(\frac{\frac{2}{X}\sqrt{\frac{K_i^*}{D}}}{3}\,\varepsilon^{3/2}\right) \tag{28}$$

where [2, 3]:

$$A_{1/3}(x) = K_1 J_{1/3}(x) + K_2 N_{1/3}(x) \tag{29}$$

The values K_1 and K_2 are to be determined from the initial and limit conditions. Since the homogeneous conditions are

$$\begin{aligned} &C(0;\ t) = 0 \qquad \text{or } \varepsilon = Y; f(Y) = 0 \\ &C(L; 0) = 0 \qquad \text{or } \varepsilon = (Y + XL);\ f(X + XL) = 0. \end{aligned} \tag{30}$$

We may write that

$$K_1 J_{1/3}\left(\frac{2}{3X}\sqrt{\frac{K_i^*}{D}}\,Y^{3/2}\right) + K_2 N_{1/3}\left(\frac{2}{3X}\sqrt{\frac{K_i^*}{D}}\,Y^{3/2}\right) = 0 \tag{31}$$

and

$$K_1 J_{1/3}\left(\frac{2}{3X}\sqrt{\frac{K_i^*}{D}}\,(Y + XL)^{3/2}\right) + K_2 N_{1/3}\left(\frac{2}{3X}\sqrt{\frac{K_i^*}{D}}\,(Y + XL)^{3/2}\right) = 0.$$

Denoting function $J_{1/3}N_{1/3}$ by U, and converting Eqs (31), we obtain:

$$U\left(\frac{2}{3X}\sqrt{\frac{K_i^*}{D}}\,Y^{3/2}\right) = U\left(\frac{2}{3X}\sqrt{\frac{K_i^*}{D}}\,(Y + Xx)^{3/2}\right) \tag{32}$$

However, in the course of the function analysis of U we have proved that the function $J_{1/3}N_{1/3}$ is "quasi" periodical [4], from this it follows that

$$\left(\frac{2}{3X}\sqrt{\frac{K_i^*}{D}}\,Y^{2/3}\right) = \left[\frac{2}{3X}\sqrt{\frac{K_i^*}{D}}\,(Y + XL)^{2/3}\right] np \tag{33}$$

where $n = 1, 2, 3 \ldots$ and p is the period of the function.

From that, the own values are

$$K_i^* = D\left[\frac{3X}{2}\,\frac{np}{(Y + XL)^{3/2} - Y^{3/2}}\right]^2 \tag{34}$$

Let us presume that $\sqrt{K_i^*} = \lambda_n$ and let us take into account that $K_2 = -K_1 U_n(Y)$. Then the homogeneous solution function will be

$$f\lambda_n; x = \sqrt{x}\left\{K_1 J_{1/3}\left(\frac{2}{3X}\sqrt{\frac{K_i^*}{D}}\,X^{3/2}\right) - K_1 U_n(Y) N_{1/3}\cdot\left(\frac{2}{3X}\sqrt{\frac{K_i^*}{D}}\,X^{3/2}\right)\right\} \tag{35}$$

Let us find now the solution under the initial and limit conditions (11). It must be noted that if $t \to \infty$ then $\frac{\partial C}{\partial t} \to 0$, therefore the function $C(x;\infty)$ is the solution of the equation. The concentration function is being formed from the sum of two functions [5]:

$$C = \eta_1 + \eta_2 \tag{36}$$

Let us presume that

$\eta_1 = 0$ if $x = 0$ and $X = L$ and $t > 0$

$\eta_1 = \varrho_{(x)}$ if $0 \leq x \leq L$ and $t = 0$

(the definition of η_1 follows from the homogeneous conditions), and

$\eta_2 = 0$ if $0 \leq x \leq L$ and $t = 0$

$\eta_2 = C_0$ if $x = 0$ and $t \geq 0$

$\eta_2 = 0$ if $x = L$ and $t \geq 0$

Thus, η_2 is a solution which meets the conditions

$$C_0\left(1 - \frac{x}{L}\right)$$

and

$$C(x\,;0) = -C_0\left(1 - \frac{x}{L}\right);\ C(0\,;t) = C(L\,;t) = 0.$$

Let us utilize the conditions of orthogonality of the function in determining η_1 and η_2. The condition of orthogonality is

$$\int\limits_{Y}^{Y+XL} x f(\lambda_n\,;x)\, f(\lambda_n\,;x)\, dx = 0 \tag{37}$$

At the point $C(\varepsilon\,;0)$ the solution function (27) is

$$C(\varepsilon\,;0) = \Sigma\, E_i f(\lambda_i\,;\varepsilon).$$

Let us multiply both sides of the equation by $f(\lambda_i\,;\,\varepsilon)$, then

$$\int\limits_{Y}^{Y+XL} \varepsilon C(\varepsilon;0) f(\lambda_i\varepsilon)\, d\varepsilon = E_i \int\limits_{Y}^{Y+XL} f^2(\lambda_i\varepsilon) d\varepsilon \tag{38}$$

From that:

$$E_i = \frac{\int\limits_{Y}^{Y+XL} \varepsilon \overline{\varrho}(\varepsilon) f(\lambda_i\varepsilon) d\varepsilon}{\int\limits_{Y}^{Y+XL} \varepsilon f^2(\lambda_i\varepsilon) d\varepsilon} \tag{39}$$

while

$$\eta_2 = C_0\left(1 - \frac{\varepsilon - Y}{XL}\right) + \sum_{i-1}^{\infty} F_i f(\lambda_i\varepsilon) \tag{40}$$

Similarly to the above described way [5]:

$$F_i = \frac{\int\limits_{Y}^{Y+XL} \left(1 - \frac{\varepsilon - Y}{XL}\right) f(\lambda_i\varepsilon)\, d\varepsilon}{\int\limits_{Y}^{Y+XL} \varepsilon f^2(\lambda_i\varepsilon) d\varepsilon} \tag{41}$$

Let us denote the sum of $F_i + E_i$ by G_i. The general solution is

$$C(\varepsilon;t) = C_0\left(1 - \frac{\varepsilon - Y}{XL}\right) + \sum_{1}^{\infty} G_i f(\lambda_i\varepsilon) e^{-K_i^* t} \qquad a)$$

and

$$G_i = \frac{\int\limits_{Y}^{Y+XL} \left[\overline{\varrho}(\varepsilon) - C_0\left(1 - \frac{\varepsilon - Y}{XL}\right)\right] f(\lambda_i\varepsilon) d\varepsilon}{\int\limits_{Y}^{Y+XL} \varepsilon f^2(\lambda_i\varepsilon) d\varepsilon} \qquad b) \tag{42a}$$

where

$$\overline{\varrho}(\varepsilon) = C_0 \quad \text{if} \quad Y \leq \varepsilon \leq Y + \frac{XL}{N}$$

$$\overline{\varrho}(\varepsilon) = 0 \quad \text{if} \quad Y + \frac{XL}{N} < \varepsilon < Y + XL \tag{42b}$$

the function $f(\lambda_i\varepsilon)$ reads as follows:

$$f(\lambda_i\varepsilon) = \sqrt{\varepsilon}\left[J_{1/3}\left(\frac{2}{3X}\sqrt{\frac{K_i^*}{D}}\,\varepsilon^{3/2}\right) - U_n(Y) N_{1/3} \cdot \left(\sqrt{\frac{K_i^*}{D}}\,\varepsilon^{3/2}\,\frac{2}{3X}\right)\right] \tag{42c}$$

and

$$U_n(Y) = \frac{J_{1/3}\left(\frac{2}{3X}\sqrt{\frac{K_i^*}{D}}\,Y^{3/2}\right)}{N_{1/3}\left(\frac{2}{3X}\sqrt{\frac{K_i^*}{D}}\,Y^{3/2}\right)} \tag{42d}$$

Eqs (42a, b, c, d) describe the combined processes of adsorption and diffusion.

In a general case: $C(L\,;t) = 0$. Let us denote the equilibrium concentration by C_∞, in that case the substitution

$$C' = C - C_\infty$$

is to be carried out in the solution function.

Consequently, the initial and limit conditions will be

$$\begin{aligned} C'(x\,;0) &= \varrho(x) - C_\infty \\ C'(0\,;t) &= C_0 - C_\infty \\ C'(L\,;t) &= 0 \\ C'(x;\infty) &= C_0\left(1 - \frac{x}{L}\right) - C_\infty \end{aligned} \tag{43}$$

The value C_∞ is apparently the function of the space velocity of flowing gas at $x = L$. In the course of the experiment, the equilibrium concentration C_∞ can be designed according to the following considerations.

The concentration C_∞ is being formed at the outflow side of the packed column when the material transport becomes stationary. The material flow of the column can be described as follows:

$$J_1 = D\,\frac{C_0 - C_\infty}{L} \tag{44}$$

The condition of stationarity at the outflow side of the packed column means at the same time that an equilibrium exists between the diffusion flow and the convection flow of the inert gas, *i.e.*

$$GC_\infty = D\,\frac{C_0 - C_\infty}{L} \tag{45}$$

and from that

$$C_\infty = \frac{D}{L}\,\frac{C_0}{G + \frac{D}{L}} \tag{46}$$

In the following considerations we shall deal with the calculation technical problems of a diffusion adsorption model.

Let us investigate the changes in the concentration of diffusion and adsorption taking place in a packed column, plotted against time and local coordinate.

The parameters of the column are:

$L = 5;$ $\xi = 0.6$ and $\gamma = 0.9$

while the constants of the Freundlich equation:

$\bar{k} = 10^2;\ m = 0.8;\ D = 0.7;\ C_0 = 1;\ C_\infty = 0.$

Let us now calculate the combined constants required for the solution:

$$A = \frac{\gamma \bar{k}}{\xi} = 150$$

$$Y = 1 + C_0^{m-1} mA = 121$$

$$X = - AC_0^{m-1} \frac{m(m-1)}{L} = 4.80$$

$$XL = 24$$

Let us determine first the own values:

$$K_i^* = \lambda_i^2 = D \left[\frac{2}{3} X \frac{np}{(Y + XL)^{3/2} - Y^{3/2}} \right]^2 \tag{34}$$

The values obtained from Eq. (34) are listed in Table I

Table I

i	K_i^*	λ_i
1	0.001740	0.0417
2	0.006960	0.0834
3	0.01566	0.1251
4	0.02784	0.1660

Let us now determine the values G_i using Eq. (42b):

$$G_i = \frac{\int\limits_{Y}^{Y+XL} \varepsilon \left[\bar{\varrho}(\varepsilon) - C_0 \left(1 - \frac{\varepsilon - U}{xL} \right) \right] f(\lambda_i \varepsilon)\, d\varepsilon}{\int\limits_{Y}^{Y+XL} \varepsilon f^2(\lambda_i \varepsilon) d\varepsilon} \tag{42b}$$

Let us determine the integral by an approximation technique, taking into account that the function is equal to zero at Y and $Y + XL$ (the use of the Simpson formula in a general case is made rather cumbersome by the fact that the function is periodical and thus it is more practical to apply graphical integration).

On applying approximation, the simple correlation

$$G_i \sim -\frac{1}{2}\frac{1}{f_i\left(Y + \frac{XL}{2}\right)}$$

is obtained for G_i

where the function $f_i\left(Y + \frac{XL}{2}\right)$ is numerically from Eq. (42c):

$$f_1(135.5) = \sqrt{135.5}\, J_{1/3}\left(0.1149\sqrt{\frac{0.00174}{0.7}}(135.5)^{3/2}\right) -$$

$$-\frac{J_{1/3}(7.650)}{N_{1/3}(7.650)} N_{1/3}\left(0.1149\sqrt{\frac{0.00174}{0.7}}(135.5)^{3/2}\right)$$

and from this

$$f_1(135.5) = -68.151$$

On substituting the own values (eigenvalues):

$$f_2\,(135.5) = -0.6713$$

$$f_3\,(135.5) = +0.7606$$

$$f_4\,(135.5) = -0.9711$$

Note: The Bessel functions of the order of 1/3 are to be found in tables. In the case of a great argumentum, the function values are determined on the basis of the following correlations (4):

$$J_{1/3}(z) \sim \sqrt{\frac{2}{z\pi}}\cos(z - 1.309)$$

$$N_{1/3}(z) \sim \sqrt{\frac{2}{z\pi}}\sin(z - 1.309)$$

On resubstitution, the G_i values are

$G_1 = +0.00733$

$G_2 = \quad 0.745$

$$G_3 = -0.641$$
$$G_4 = 0.515$$

The functions $f(\lambda i \varepsilon)$ are calculated on the basis of the correlation (42c), using already fixed longitudinal coordinates, and investigating the changes of concentration versus time, at the values $x = 1, 2, 3, 4$. In the case of $x = 0$ and $x = L = 5$, the solution is determined on taking into account the initial and limit conditions.

If $x = 1$ $\qquad \varepsilon = 126.8$

$$f_1(126.8) = \sqrt{126.8}\,[J_{1/3}\,(0.005748 \cdot 126.8^{3/2}) - U_1\,(Y)\; N_{1/3}\,(0.005748 \cdot 126.8^{3/2})].$$

The solution is

$$f_1\,(126.8) = -39.51$$

and similarly,

$$f_2(126.8) = -1.6216$$
$$f_3(126.8) = +1.8313$$
$$f_4(126.8) = -0.3868$$

while the product $f_i G_i$ is

$$\begin{array}{rl} i = 1 & -0.2898 \\ 2 & -1.202 \\ 3 & -1.190 \\ 4 & -0.1993 \end{array}$$

In the knowledge of the product $f_i G_i$, it is already rather easy to calculate the function values for $C(1\,;\,t)$ on the basis of the correlation (42a) (*cf.* Table II).

Table II

$x = 1$

t	$C(l;\,t)$
150	0
200	0.0367
225	0.2347
250	0.2700
300	0.4758
400	0.5847
500	0.6404
700	0.7148
1000	0.7490

In the case of $x = 2$, 3 and 4, the calculation is quite analogous to the preceding one. The concentration functions are given in Table III.

Table III

$x = 2$

t	$C(2;t)$
200	0
250	0.0943
300	0.1833
350	0.2510
400	0.3090
600	0.4308
800	0.4971

$x = 3$

t	$C(3;t)$
300	0.1079
400	0.1580
500	0.1963
700	0.2561
800	0.2798
1000	0.3144
1500	0.3645

$x = 4$

t	$C(4;t)$
300	0
400	0.0130
500	0.0440
800	0.1090
1000	0.1353
1500	0.1735

The $C(t)$ concentration curves calculated for the condition $x =$ const. are plotted in Fig. 1.

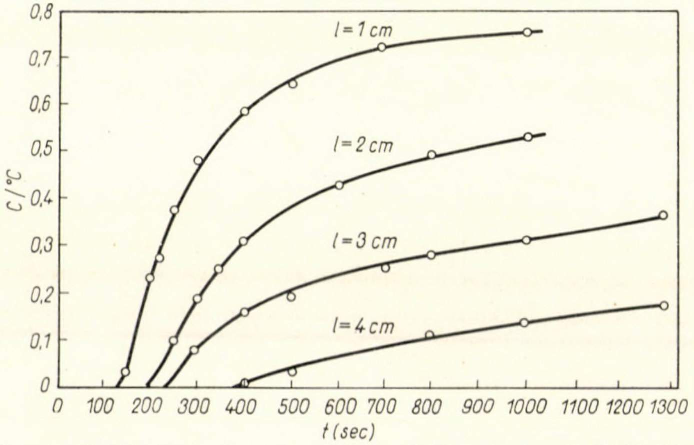

Fig. 1. Curves of diffusion adsorption fronts of the column packed with adsorbent

Also the functions $t = \text{const.}\ C(x)$ have been plotted on the basis of the curves of adsorption fronts. The functions of the distribution of concentration in the columns packed with adsorbent, plotted against various times (t) are shown in Fig. 2.

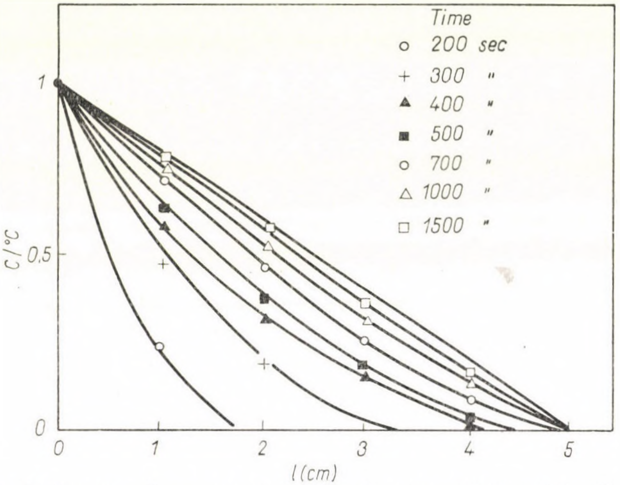

Fig. 2. Curves of concentration distribution calculated by Eq. (42)

Also a particular feature of the solution function is to be mentioned here. The term containing the infinite series does not approximate monotonously the conditions $C(t) = 0$ when only a finite number of series members are taken into account. After dissecting the time axis, the function approaches it with a periodically damped run. Consequently, the function value $C(t) < 0$ follows just from the properties of the function series proper.

In this paper it was not possible to carry out the full theoretical and numerical analysis of Eqs (42). It must be noted, however, that the comparison of the informations obtained by investigating convection-free diffusion and adsorption can be carried out by the method evolved by FÁY [6], on applying certain simplifications.

List of symbols

A	$\frac{\gamma \bar{k}}{\xi}$
C; C_0; C_∞	concentration moles/cu.cm; g/cu.cm
D	diffusion constant sq.cm/sec
G	material transport volume cu.cm/sec
J	material flow mole/sec
H	equilibrium constant of linear isotherm
k; m	constants of the Freundlich equation
L	length of column cm
$\frac{\partial n}{\partial t}$	rate of absorption (boiling)

t	time
x	local coordinate
X	$\frac{m(m-1)AC_0^{m-1}}{L}$
Y	$1 + mAC_0^{m-1}$
γ	density of adsorbent g/cu.cm
ξ	free volume factor

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PAPER CHROMATOGRAPHIC DETERMINATION OF THE APPROXIMATE MOLECULAR WEIGHT AND POLYDISPERSITY OF SILICON ORGANIC POLYMERS

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A rapid paper chromatographic method, suitable for series measurements was worked out for the approximate determination of the molecular weights and molecular weight distributions of polydimethylsiloxanes.

"Narrow" fractions and polydisperse samples prepared by mixing the former were used for the measurements.

It was found that in the range $M_w = 100 \times 10^3 - 300 \times 10^3$ a solvent mixture of the composition toluene—ethyl acetate—acetone—acetic acid in the proportion 1.5 : 6 : 0.5 : 0.27 is appropriate for the separation of fractions of different molecular weights. The location of the spot on the chromatogram provides information on the mulecular weight of the substance, and the shape of the spot on its polydispersity.

The experimental conditions for eliminating the edge effect of the paper and the mutual interference of the spots were determined.

Introduction

Determination of the exact molecular weight and molecular weight distribution of polymers by the usual methods (ultracentrifuge [1, 2], light diffraction [3], osmometry [4]) is a lengthy and cumbersome task, while quite often an approximate value of the molecular weight may furnish sufficient information on the substance. This latter is the case in the study of silicon organic polymers, more specifically of dimethylsiloxane chain polymers. Thus it was intended to develop a less time and labour consuming procedure for obtaining semi-quantitative, yet sufficiently characteristic data for practical purposes. For this end an appropriate adaptation of paper chromatography seemed to be the most expedient because of its simplicity and rapidity and the low material consumption.

Experimental

The polydimethylsiloxane subjected to investigation is a highly hydrophobic non-polar polymer enabling work only by reversed phase paper chromatography. Preliminary experiments led to the choice of acetylized paper for the task in hand. For the first experiments papers acetylized in this laboratory were used, but later it could be stated that among commercial acetylized papers the progress of the solvent front is the slowest on the Macherey Nagel 263 AC type paper with which the best results were obtained.

The samples were "narrow" fractions of commercial polydimethylsiloxanes. The fractions were prepared by precipitation with ethyl acetate as the solvent and acetone as the precipitating agent. The molecular weights and polydispersities of these fractions with narrow molecular weight distributions were determined by Debye's method of light-scattering with a Brice Phoenix apparatus.* The molecular weights of the three fractions under investigation were in the range between 100×10^3 and 300×10^3. Drops of the samples in toluene solution were applied to 18×56 cm paper strips. About 2 μl of the 10% solutions was used to obtain spots of approximately 3 mm diameter, and in no case over 5 mm diameter.

Experiments were carried out to determine the optimum quantity of the sample. Using different quantities of the polymer fractions with identical molecular weights, the optimum under the prevailing circumstances was found at 2 μl of the 10% polymer solution. Larger quantities caused marked elongation and spreading of the spot while when developing smaller quantities the paper easily soaked through under the small quantity of hydrophobic substance (Fig. 1).

The runs were performed by descending chromatography in the Chropa (VEB Glaswerke, Ilmenau) paper chromatograph. Prior to the insertion of the paper the chromatographic vessel was saturated with the vapours of the solvent mixture for 12 hours, after which the preliminary saturation of the paper with the solvent mixture vapours appeared to be superfluous.

It is one of the essential characteristics of the method that the hydrophobic property of polydimethylsiloxane can be advantageously utilized in the development of the chromatogram. When the dried chromatogram is moistened with water all parts of the paper not covered by the hydrophobic substance will soak through. The location of the spots is more easy to observe when a copper salt solution is used for moistening followed by an exposure of the paper to ammonia. Should the developing solution contain acetic acid the acetylized paper will be instantaneously soaked through and the spots appear more sharply. The composition of the developing solution was the following: 6.2 g of $Cu(CH_3COO)_2 \cdot H_2O$ dissolved in a mixture of 60 ml of 91% acetic acid with 440 ml of water. The sensitivity of development can be increased by spraying the paper prior to development with a slightly acidic 3% hydrogen peroxide solution which enhances the hydrophility of the paper without

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* The measurements were carried out in the Laboratory for Chemical Structure Research of the Hungarian Academy of Sciences by Mr. GY. SCHULTZ to whom the authors wish to express their sincere thanks.

affecting in any way the polydimethylsiloxane polymer thereby increasing the difference between the hydrophobities of the paper and the spot.

Selection of the appropriate solvent mixture for the runs required thorough investigation. But for the 91% acetic acid of chromatographic grade (BDH) the other solvents were of analytical grade manufactured by Reanal.

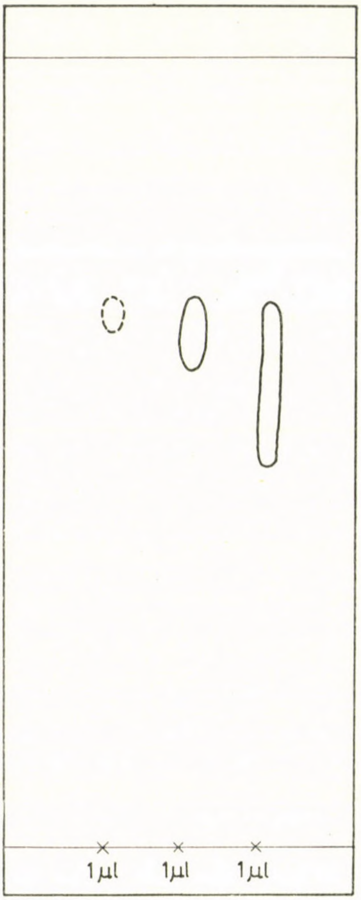

Fig. 1. Substance: $M_w = 110 \times 10^3$ fraction

The solvent mixture had to meet the solubility requirements and at the same time one of its components had to form a stationary phase on the acetylized paper. Among others the following solvents form stationary phases on acetylized paper: ethyl acetate, chloroform, trichloroethylene, chlorobenzene and benzyl chloride [5]. The tested solvent mixtures always contained one of these solvents. From the point of view of separation the solvent mixtures toluene : chlorobenzene 3 : 1 and toluene : ethyl acetate 1 : 6 were found to be satisfactory, but the reproducibility of the chromatograms did not meet the requirements. When small quantities of acetic acid were added to the solvent mixture the spots had a regular shape without tails. These observations led finally to the choice of the mixture of toluene—ethyl acetate—acetone—acetic acid in the proportion of 1.5 : 6 : 0.5 : 0.27.

Quite frequently the extreme spot corresponding to the lowest molecular weight fraction lagged behind with an R_f value other and much lower than the expected. As this fraction was always applied last near to the edge of the paper, it was assumed that its too close vicinity to the edge of the paper caused it to lag behind. The validity of this assumption was checked by applying the same fraction to different parts of the paper in such a way that the distance between the spots should be 2 cm while the distances of the first and last spot from the edges of the paper were varied. When the first *i.e.* last spot was only 1, 2 or 3 cm from the edge of the paper it kept lagging behind and that

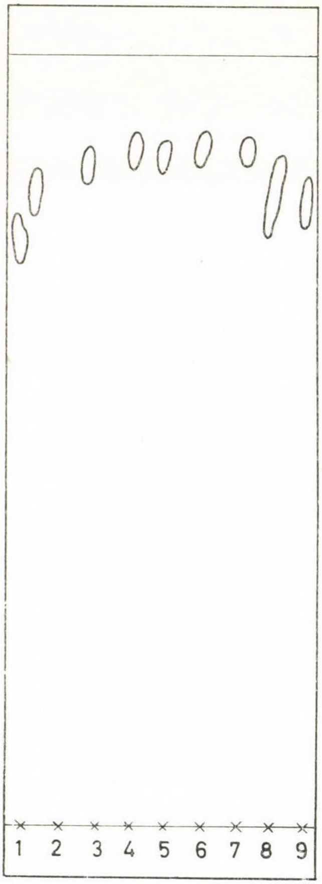

Fig. 2. Substance: $M_w = 110 \times 10^3$ fraction

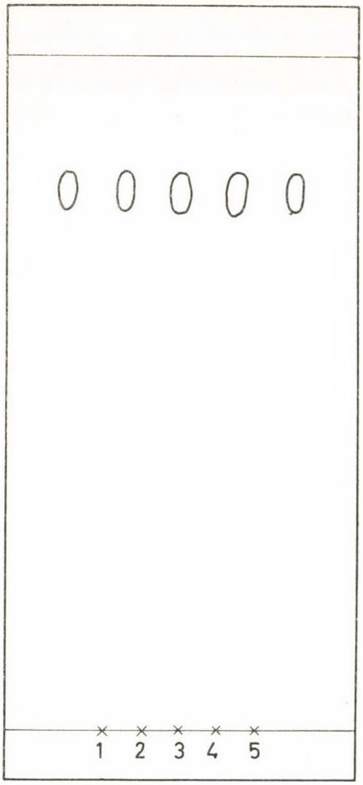

Fig. 3. Substance: $M_w = 110 \times 10^3$ fraction

the more so the closer it was to the edge of the paper, while the R_f values of the spots in the middle of the paper were identical. These findings are illustrated in Fig. 2. When the drops were applied in such a way as to have the extreme spots located 5 cm from the edges of the paper, these spots no longer lagged behind, but instead tended to shift towards the edges and to occupy positions with the greatest possible distance between them (Fig. 3).

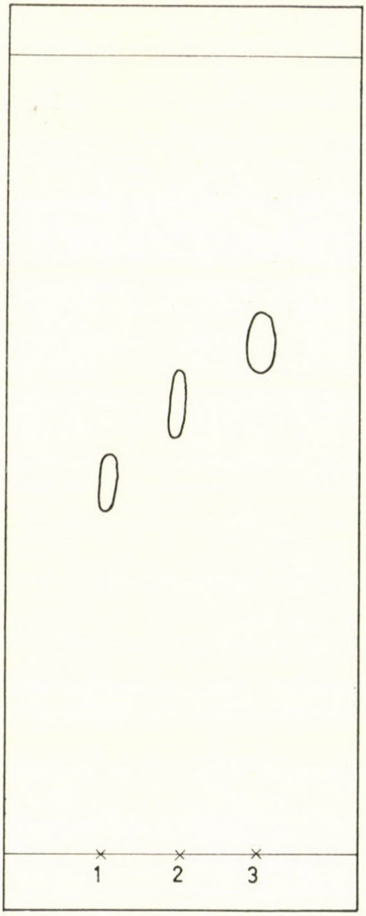

Fig. 4. 1. $M_w = 291 \times 10^3$ fraction — 2. $M_w = 215 \times 10^3$ fraction — 3. $M_w = 110 \times 10^3$ fraction

In the following experiments we tried to determine the smallest distance at which the spots do not influence each other. The same fraction was again applied to various points on the paper, but now the distance of the extreme spots from the edges was 5 cm and the distance between the other spots has been varied. It was found that when the drops were applied at least at 4 cm intervals the spots after the run were above the points of application, that is any undesirable lateral migration was eliminated.

The method could at that stage be applied to the determination of molecular weights, as shown on the examples of the $M_w = 219 \times 10^3$ 215×10^3 and 110×10^3 fractions. The chromatograms are presented in Fig. 4 indicating the location of the spots depending on the molecular weight, or, in other words, the R_f values corresponding to the different fractions decrease in the order of increasing molecular weight. Thus in the particular solvent mixture mentioned even relatively only slightly different molecular weights can still be distinguished. It is quite obvious that for other molecular weight ranges the composition of the solvent mixture must be appropriately altered; in the case of higher molecular weights more developing solvent, for smaller molecular weights more of the precipitant must be used.

Accuracy of the method

The comparison of the R_f values of 20 runs carried out under identical conditions gives some information on the reproducibility of the method. The results are summed up in Table I. It appears that there is a fairly considerable scattering between the R_f values which was attributed to differences in the properties of the papers. This effect can be minimized by referring the obtained R_f values to the R_f value of a certain fraction of known molecular weight run on the same paper. This R_f value is then an internal standard. Table I contains also the $(R_f)_{\text{rel}}$ values which refer to the $M_w = 215 \times 10^3$ fraction. The scattering of the relative values is considerably less than that of the absolute R_f values. Consequently for the determination of the molecular weight of a fraction of unknown molecular weight at least one or two fractions of identical material composition, and of known molecular weight have to be applied concomitantly as reference substances, when fairly reliable results may be expected.

As substances occurring in practice are generally polydisperse it was investigated whether the shape and elongation of the spot may offer a clue on the polydispersity of the substance applied to the paper. With this end in mind a 1 : 1 mixture of the fractions $M_w = 291 \times 10^3$ and $M_w = 110 \times 10^3$ was applied simultaneously with the same two pure fractions to the same paper. This chromatogram is presented in Fig. 5.

In accordance with expectation the spot of the mixture is located between the lower *i.e.* upper limits of the spots corresponding to the pure fractions. The degree of separation can be altered by altering the quantity of acetic acid in the mixture. With more acetic acid than given above separation will be more complete and the two components may be completely separated,

Table I

No.	$M_w = 291 \times 10^3$	$M_w = 215 \times 10^3$	$M_w = 110 \times 10^3$	$M_w = 291 \times 10^3$	$M_w = 215 \times 10^3$	$M_w = 110 \times 10^3$
	R_f			$(R_f)_{\text{rel}}$		
1	0.447	0.491	0.619	0.910	1.00	1.26
2	0.552	0.581	0.569	0.898	1.00	1.13
3	0.608	0.674	0.782	0.902	1.00	1.17
4	0.585	0.646	0.749	0.907	1.00	1.16
5	0.579	0.644	0.764	0.907	1.00	1.19
6	0.570	0.644	0.717	0.905	1.00	1.23
7	0.555	0.617	0.703	0.900	1.00	1.14
8	0.599	0.645	0.723	0.908	1.00	1.12
9	0.588	0.628	0.708	0.906	1.00	1.13
10	0.565	0.620	0.693	0.914	1.00	1.12
11	0.572	0.640	0.716	0.893	1.00	1.18
12	0.490	0.545	0.654	0.900	1.00	1.20
13	0.470	0.522	0.614	0.900	1.00	1.17
14	0.449	0.498	0.593	0.901	1.00	1.19
15	0.489	0.538	0.650	0.908	1.00	1.20
16	0.437	0.485	0.581	0.901	1.00	1.19
17	0.452	0.501	0.604	0.902	1.00	1.20
18	0.458	0.506	0.613	0.905	1.00	1.21
19	0.467	0.528	0.621	0.884	1.00	1.18
20	0.460	0.512	0.614	0.898	1.00	1.20
average:	0.518	0.573	0.669	0.902		1.18
±	0.056	0.061	0.053	0.007		0.03

while with less acetic acid separation will be more limited. However, as separation becomes more perfect the width of the molecular weight range to which the given solvent mixture is applicable will be obviously narrower. Thus for the separation of highly polydisperse samples a solvent mixture with less acetic acid should be used, while in the case of samples of lower polydispersity separation may be enhanced by using more acetic acid.

These experiments prove the applicability of paper chromatography to the determination of the approximate values of the molecular weights of polydimethylsiloxanes from the location of the spots and of the molecular weight distributions from the shape of the spots.

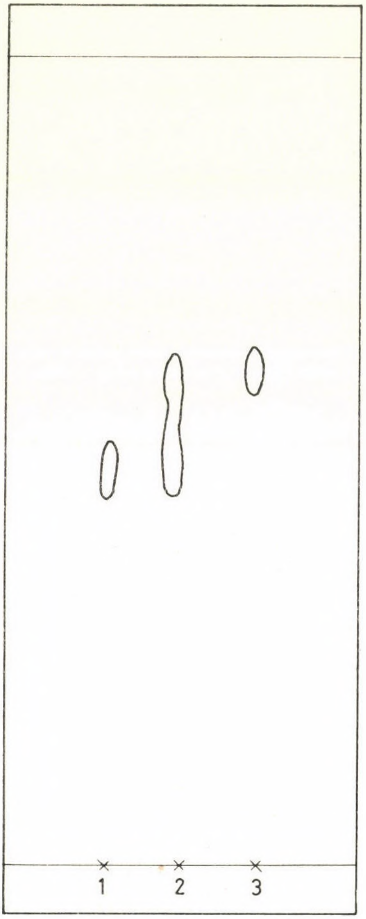

Fig. 5. 1. $M_w = 291 \times 10^3$ fraction — 2. 1 : 1 mixture of the $M_w = 291 \times 10^3$ and $M_w = 110 \times 10^3$ fractions — 3. $M_w = 110 \times 10^3$ fraction

Discussion

The main advantage of the method described above is its simplicity due to the utilization of the strongly hydrophobic nature and chemical stability of polydimethylsiloxanes. The stability of the polymers permitted *e.g.* treatment with peroxide and thereby a simple way of developing the spots. For analytical application it is unavoidable to have at our disposal at least one pure (narrow) fraction of known molecular weight which should be of the same order as that of the sample under investigation. Should such a fraction not be available the method is applicable only to the comparison of several samples, but even then because of its simplicity and rapidity it still may offer certain practical advantages (*e.g.* in works control).

We should like to mention finally that this method is obviously adaptable to the determination of the molecular weights of a lot of other polymers too, but an appropriate method of development corresponding to the nature of the substance has to be found.

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ÜBER DIE HYDRATE DES ALUMINIUMSULFATS

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Das gewöhnliche (höchste) Hydrat des Aluminiumsulfats enthält 17 Molekel Kristallwasser. Es ist triklin, $a = 7{,}420 \pm 0{,}004$ Å, $b = 26{,}900 \pm 0{,}04$ Å, $c = 6{,}105 \pm 0{,}004$Å, $\alpha = 90{,}00 \pm 0{,}03°$, $\beta = 97{,}30 \pm 0{,}13°$, $\gamma = 91{,}80 \pm 0{,}07°$; $Z = 2$, $d_x = 1{,}782\ \mathrm{g \cdot cm^{-3}}$, $d_{gem} = 1{,}771\ \mathrm{g \cdot cm^{-3}}$. Durch Dehydratisierung kann man aus dem 17-Hydrat das 14-Hydrat und das 12-Hydrat herstellen, die durch ihre Diffratogramme charakterisiert sind; ersteres ist rhombisch indizierbar. Ein 16-Hydrat konnte nicht dargestellt werden, das dieser Zusammensetzung entsprechende Produkt enthielt hauptsächlich die Linien des 17-Hydrats, daneben einige des 14-Hydrats. Bei der Dehydratisierung zeigt sich ein scharfer Knick in dem TG bei einem dem 3-Hydrat entsprechendem Wassergehalt, ein solches Produkt gibt aber ein amorphes Diffraktogramm. Das Derivatogramm des 17-Hydrats wird mitgeteilt.

Obzwar Aluminiumsulfat bzw. dessen Hydrate schon seit altersher bekannt sind und in der Industrie ausgedehnt verwendet werden (z.B. betrug die Produktion in den USA schon 1929 350 000 t), sind die Eigenschaften und die Zusammensetzung der Aluminiumsulfat-Hydrate überhaupt noch nicht sicher bekannt. Die äußerst breite Literatur, welche bis 1924 im Buch von Mellor [1], danach in den Handbüchern von Gmelin [2] und Pascal [3] zusammengefaßt ist, enthält eine Menge widerspruchsvoller und fast durchweg unbefriedigender Angaben. Daher schien es wünschenswert, diese Frage mit neueren Methoden, d.h. mit dem Derivatograph und mit der Röntgendiffraktion anzugreifen.

In der Industrie benützt man zweierlei Aluminiumsulfat-Sorten; die eine enthält 14,3—14,5% Al_2O_3 (also bedeutend weniger als das sog. 18-Hydrat mit 15,13% Al_2O_3); die andere, das sog. konzentrierte Aluminiumsulfat dagegen 17—18% Al_2O_3, was etwa 12—14 Mol Kristallwasser pro $Al_2(SO_4)_3$ entspricht (Neumann [4]). Mit der Entwicklung der Papierindustrie, der Ausdehnung der Wassereinigung usw. wird die Wichtigkeit des Aluminiumsulfats ständig erhöht.

Bisherige Arbeiten

Es wurde eine Anzahl von Aluminiumsulfat-Hydraten beschrieben. Im folgenden behandeln wir nur die Hydrate des normalen Aluminiumsulfats $Al_2(SO_4)_3$, die der sauren und basischen Aluminiumsulfate also nicht.

Nach METZGER [5] kann man Kristalle des 27-Hydrats durch Verreiben von Kristallen des 16-Hydrats mit Wasser unter 9,5 °C herstellen; dieses 27-Hydrat ist nach RAMMELSBERG [6] rhomboedrisch. An Luft verlieren seine Kristalle Wasser, im geschlossenen Gefäß sind sie aber beständig, sogar bei Erhitzung. Diese sehr alten Arbeiten sollten wiederholt werden.

Das bei gewöhnlicher Temperatur stabile Hydrat kommt in der Natur als das Mineral Alunogen vor; es wurde durch HLAWATSCH [7] und GORDON [8] kristallographisch untersucht. Die Messungen des letzteren Autors zeigen, daß die sehr seltenen, meßbaren Kristalle triklin sind mit dem Achsenverhältnis $a : b : c = 0{,}8355 : 1 : 0{,}6752$ und mit den Winkeln $\alpha = 89°58'$, $\beta = 97°26'$, $\gamma = 91°52'$. Sie sind optisch zweiachsig positiv; der mittlere Berechnungsindex ist 1,479 und ändert sich mit dem Wassergehalt. Nach der Analyse enthält der Alunogen von Francisco DA VERGARA (Chile) 46,10% H_2O (berechnet für das 16-Hydrat 45,7%) [8]; die Dichte ist 1,77 $g \cdot cm^{-3}$. — Eine andere Analyse von JIRKOVSKY [9] am Mineral von Valchov, Tschechoslowakei, ergibt fast genau den dem 16-Hydrat entsprechenden Wert.

Nach einer alten Arbeit von MARGUERITE-DELACHARLONNY [10] soll das gewöhnliche künstliche Salz ein 16-Hydrat mit rhombischer Kristallsymmetrie sein. SMITH und WALSH [11] fanden in einer sehr gründlichen Untersuchung, daß das bei Zimmertemperatur stabile Hydrat 17 Mole Wasser enthält; nach ihnen ist aber auch ein 16-Hydrat möglich und die beiden wären ineinander löslich. Das würde bedeuten, daß das Gitter des 17-Hydrats bis ein Mol Wasser pro Formeleinheit verlieren kann, ohne wahrnehmbare Änderung der Gitterstruktur. Die Autoren bemerken auch, daß das Salz ein Mol Wasser »zeolitisch« verlieren kann.

Weitere Hydrate sind in der älteren Literatur ebenfalls beschrieben. Verläßlicher scheint aber die Feststellung von THIARD u. Mitarbeiter [12] zu sein, daß nämlich ein 14- und ein 12-Hydrat durch ihre Diffraktogramme charakterisiert werden können; sie sind mit den entsprechenden Hydraten des Chrom(III)sulfats isomorph. THIARD u. Mitarbeiter zeigten, daß keine kristallisierten Hydrate des Aluminiumsulfats mit weniger als 12 Mol Kristallwasser existieren; beim Verlust von mehr Wasser tritt Amorphisierung ein. Über die Zusammensetzung des höchsten Hydrats s.w.u.

Eigene Untersuchungen

Die Bestimmung der genauen Formel des unter gewöhnlichen Umständen stabilen Aluminiumsulfat-Hydrats bereitet Schwierigkeiten, da der Wassergehalt der höheren Hydrate prozentuell wenig verschieden ist, dabei kann das Präparat auch hygroskopisches Wasser enthalten.

Die verläßlichste Methode zur Bestimmung der Zusammensetzung ist die Bestimmung des Volumens der kristallographischen Elementarzelle, zusammen mit der experimentellen Dichte. Zu diesem Zweck sind natürlich gute — wenn auch kleine — Kristalle nötig. Diffraktogramme kann man bei niedriger Symmetrie nicht ohne weiteres indizieren; sie genügen aber zur sicheren Identifizierung und außerdem können die Kanten und Winkel der Elementarzelle mit ihrer Hilfe sehr weitgehend verfeinert werden.

Die Versuche zur Erhaltung von Kristallen aus Aluminiumsulfatlösungen haben wenig Erfolg gebracht. Eine stattliche Zahl von Kristallisationsversuchen — etwa 40 — unter verschiedenen Bedingungen ergaben fast ausnahmslos nur unregelmäßig verwachsene Lamellen. Die Änderung der Löslichkeit mit der Temperatur ist sehr groß und die Zahl der sich bildenden Keime ebenfalls, so daß man Einkristalle kaum herstellen kann. Es ist lediglich gelungen, zwei äußerst dünne, rhomboidförmige Lamellen zu erhalten, die zu Oszillationsaufnahmen geeignet waren; aus diesen konnte die Identitätsperiode in der Richtung der Achse c zu 6,0 Å bestimmt werden. Auch eine Weißenberg-Aufnahme wurde angefertigt, die Bestimmung der übrigen Parameter war aber wegen der Verzwillingung und wegen der Schwäche der Reflexionen nicht genügend sicher.

Die Dichte von kleinen, künstlichen Kristallen wurde mit der Flotationsmethode in Bromoform-Toluol-Gemisch bestimmt und ergab sich zu 1,771 $g \cdot cm^{-3}$ bei 21 °C, in guter Übereinstimmung mit der Angabe von GORDON 1,77 $g \cdot cm^{-3}$.

Nun habe ich natürlichen Alunogen aus verschiedenen Fundorten untersucht, zunächst ein faseriges Mineral aus Böhmen, das ich Herrn Prof. SCHRADER (Freiberg, DDR) verdanken kann. Dies hat ein Faserdiagramm ergeben mit der Faserperiode von $c = 6{,}0$ Å; die sehr zahlreichen Reflexionen an den Schichtlinien konnten in diesem Stadium noch nicht indiziert werden. Herr Dr. Cs. RAVASZ aus dem Ung. Nationalmuseum hat mir freundlicherweise kleine Kristalle von einer Alunogen-Stufe aus Böhmen überlassen, wofür ich ihm auch an dieser Stelle danke. Unter diesen haben wir einen zwar verzwillingten, aber gut brauchbaren Kristall gefunden und davon Weißenberg-Aufnahmen gemacht. Diese konnten vollständig indiziert werden; sie ergaben für die Elementarzelle die folgenden Achsen und Winkel, die durch die Indizierung eines Diffraktogramms (Tabelle I) von einem reinen, künstlichen Aluminiumsulfathydrat-Präparat verfeinert wurden:

$$a = 7{,}420 \pm 0{,}004 \text{ Å} \qquad \alpha = 90{,}00 \pm 0{,}03^\circ$$

$$b = 26{,}900 \pm 0{,}04 \text{ Å} \qquad \beta = 97{,}30 \pm 0{,}13^\circ$$

$$c = 6{,}105 \pm 0{,}004 \text{ Å} \qquad \gamma = 91{,}80 \pm 0{,}07^\circ$$

Volumen der Zelle 1207,98 $Å^3$ Gewicht der Zelle $2139{,}4 \pm 5{,}8 \cdot 10^{-24}$ g

Tabelle I

Diffraktogramm von $Al_2(SO_4)_3 \cdot 17H_2O$

$2\ \vartheta_o^\circ$	$\sin^2 \vartheta_o$	$\sin^2 \vartheta_c$	$\Delta \cdot 10^5$	Int_{Fl}	d Å	hkl
6,58	0,00329	0,00329	0	100	13,426	020
9,88	00741	00740	— 1	2	8,948	030
12,06	01104	01099	— 5	2	7,335	100
12,38	01163	01162	— 1	2	7,145	$\bar{1}10$
12,58	01200	01200	0	1	7,033	110
13,17	01315	01315	0	8	6,718	040
13,50	01382	01389	+ 7	1	6,555	$\bar{1}20$
13,88	01460	01466	+ 6	<1	6,377	120
14,70	01637	01621	−16	<1	6,023	001
14,80	01659	—	—	<1	—	—
19,80	02956	02949	— 7	86	4,482	060
		02959	+ 3			041
20,20	03075	03058	−17	9	4,394	$\bar{1}50$
		03060	−15			101
20,51	03169	03165	— 4	5	4,328	111
		03168	— 1			$\bar{1}\bar{3}1$
20,75	03243	03251	+ 8	4	4,279	150
21,13	03362	03344	−18	1	4,202	121
21,42	03454	03434	−20	1	4,145	$1\bar{2}1$
22,36	03759	03732	−27	4	3,974	$1\bar{3}1$
		03759	0			$14\bar{1}$
22,78	03900	03868	−32	5	3,902	131
		03943	+43			$1\bar{6}0$
24,20	04394	04355	−39	4	3,675	$15\bar{1}$
		04395	+ 1			200
24,52	04509	04515	+ 6	2	3,628	210
		04516	+ 7			$15\bar{1}$
24,72	04582	04562	−20	5	3,599	$0\bar{6}1$
		04601	+19			061
25,25	04777	04801	+24	1	3,525	220
25,76	04969	04992	+23	9	3,457	$1\bar{7}0$
26,49	05250	05229	−21	15	3,363	151
		05244	— 6			$1\bar{6}\bar{1}$
		05251	+ 1			230
		05263	+13			080
		05263	+13			170
28,20	05894	05864	−30	1	3,162	161
		05885	— 9			161
		05885	— 9			240
28,81	06189	06207	+18	5	3,097	$\bar{1}80$
29,00	06269	06257	−12	3	3,077	$\bar{2}50$
		06297	+28			$1\bar{7}\bar{1}$
29,52	06491	06485	— 6	10	3,024	002
		06516	+25			180
		06521	+30			$17\bar{1}$
29,82	06621	06643	+22	2	2,995	250
		06661	+40			090
30,18	06778	06737	−41	2	2,960	$2\bar{1}1$
		06821	+43			211
30,52	06928	06904	−24	2	2,927	$\bar{1}02$
		06932	+ 4			$1\bar{7}\bar{1}$
30,66	06990	06972	−18	1	2,914	$1\bar{1}\bar{2}$
		06998	+ 8			112
31,04	07152	07123	−36	1	2,879	$\bar{2}60$
		07206	+47			$0\bar{3}2$
		07207	+48			$12\bar{2}$

$2\ \vartheta_0^0$	$\sin^2 \vartheta_0$	$\sin^2 \vartheta_c$	$\Delta \cdot 10^5$	Int_{Fl}	d Å	hkl
31,47	07355	07337	−18	2	2,841	081
31,85	07628	07514	−14	1	2,806	$1\bar{8}\bar{1}$
		07563	+35			231
		07568	+40			$25\bar{1}$
32,40	07787	07771	−16	1	2,762	$18\bar{1}$
		07775	−12			$0\bar{4}2$
		07827	+40			042
32,64	07897	07933	+36	1	2,741	190
33,34	08229	08223	− 6	2	2,685	0, 10, 0
		08253	+24			$0\bar{9}1$
		08265	+36			102
		08270	+41			$14\bar{2}$
34,12	08607	08574	−33	2	2,626	052
		08645	+37			122
35,42	09248	—	—	1	2,532	—
35,95	09528	09477	−51	2	2,496	$1\bar{4}2$
		09518	−10			$1\bar{9}1$
		09518	−10			$\bar{2}02$
36,03	09565	09568	+ 3	3	2,493	$2\bar{1}\bar{2}$
		09576	+11			$15\bar{2}$
36,62	09870	09877	+ 7	3	2,452	0, 10, 1
		09909	+37			261
36,80	09963	09950	−13	2	2,441	0, 11, 0
		09925	−37			191
		09940	−23			$16\bar{2}$
		09966	+ 3			280
		09988	+25			300

Die $\sin^2 \vartheta_c$-Werte wurden mit der Gl. $\sin^2 \vartheta_c = 0{,}010987\, h^2 + 0{,}000822\, k^2 + 0{,}016213\, l^2 + 0{,}000193\, hk + 0{,}000033\, kl + 0{,}003400\, hl$ berechnet. Die Intensitäten Int_{Fl} sind mit den Flächen der Reflexionen proportional.

Nehmen wir 2 Formeleinheiten in der Zelle an, so ist das berechnete Gewicht der Zelle im Falle von

16-Hydrat	$2093{,}2 \cdot 10^{-24}$ g
17-Hydrat	2153,0
18-Hydrat	2212,4

Man sieht also, daß wir es mit dem 17-Hydrat zu tun haben; die beiden anderen angeführten Hydrate würden ein um rund 3% kleineres bzw. höheres Gewicht für die Zelle ergeben, was außerhalb der obigen (maximalen) Versuchsfehler liegt. Die für das 17-Hydrat berechnete röntgenographische Dichte ist $d_x = 1{,}782$ g · cm^{-3}, der Unterschied gegen die gemessene Dichte 1,771 g · cm^{-3} ist also gering und liegt in der erwarteten Richtung. Die Zelle enthält 58 [O^{2-}, OH^-, H_2O], es entfällt auf eines ein Volumen von $21{,}31 \cdot 10^{-24}$ cm^3, ein ebenfalls vernünftiger Wert.

Es sei hier erwähnt, daß ein anderer, kleiner Kristall von der erwähnten Alunogen-Stufe eine andere u.zw. monokline Zelle ergab; die Zusammensetzung dieses Kristalls wurde noch nicht sicher bestimmt; es handelt sich aber wahrscheinlich um ein basisches Aluminiumsulfat.

Derivatographische Untersuchung

Die Dehydratation des Aluminiumsulfat-17-Hydrats wurde mit dem Derivatographen von PAULIK, PAULIK und ERDEY [13] verfolgt. Es wurden 500 mg von einem künstlichen, mehrmals umkristallisierten Präparat mit einer Temperaturerhöhung von 12 °C pro Minute erhitzt, ein weiteres Derivatogramm wurde mit 4,5 °C pro Minute aufgenommen.

Die Wasserabgabe beginnt schon unter 40° C und wird mit steigender Temperatur immer schneller. Bei 130 °C finden wir einen Bruch auf den DTG- und DTA-Kurven, danach folgt bei 140 °C bzw. 143 °C ein sehr starkes Minimum auf den zwei Kurven. Der Wassergehalt — ablesbar von der TG-Kurve — entspricht bei 130 °C dem 14-Hydrat und bei 140 °C etwa dem 12-Hydrat. Keines von diesen Hydraten ist aber stabil, da ihr Dampfdruck so hoch ist, daß sie bei den angegebenen Temperaturen ständig Wasser verlieren. Bei 320 °C zeigt sich ein kleineres Minimum auf der DTG-Kurve und bei 330 °C ein ähnliches auf der DTA-Kurve. Die Zusammensetzung bei 320 °C entspricht nach der TG-Kurve dem 3-Hydrat; hier zeigt diese Kurve eine scharfe Inflexion. Danach wird die Wasserabgabe langsamer und es fängt bei 400 °C eine fast waagerechte Stufe an, die bis 700 °C dauert. Die Zusammensetzung ändert sich innerhalb dieses Temperaturbereiches wenig und entspricht bei 600 °C dem wasserfreien $Al_2(SO_4)_3$; die Gewichtsabnahme betrug hier 47,0% gegenüber dem für das 17-Hydrat berechneten Wert 47,25%. — Weitere Erhitzung ruft langsam sich erhöhenden SO_3-Verlust hervor, der bei etwa 800 °C stürmisch wird, bis bei 937 °C an der DTG-Kurve und bei 940 °C an der DTA-Kurve scharfe Minima auftreten. Kurz danach wird das Gewicht der Probe konstant (bis 1200 °C gemessen); der Rückstand ist Al_2O_3 und beträgt 15,6% (berechnet für das 17-Hydrat 15,73%); s. Abb. 1.

Aus der Bestimmung der kristallographischen Elementarzelle und aus der derivatographischen Untersuchung ergibt sich also eindeutig, daß das bei gewöhnlicher Temperatur stabile Hydrat 17 Molekel Kristallwasser enthält. Die weiteren, im Derivatogramm erscheinenden Hydrate sind wenig stabil. WATELLE-MARION und THIARD [12] haben Pulverdiagramme des von ihnen für 16-Hydrat gehaltenen höchsten Hydrats, weiterhin des 14- und des 12-Hydrats mitgeteilt. Leider sind ihre Messungen wenig genau; die Reflexionen werden nur von 6,1 Å Netzebenenabstand angefangen bis 4,0 bzw. 4,4 Å nur auf ein Zehntel Å angegeben, obzwar man mit dem Diffraktometer die Meßgenauigkeit ± 0,002 Å ohne weiteres erreichen kann. Allerdings sieht man aus den Tabellen der letztgenannten Autoren, daß ihre Präparate nicht einheitlich waren. Die stärkeren Linien ihres »16-Hydrats« stimmen ohne Ausnahme mit denen unseres 17-Hydrats überein. Außerdem sind aber noch einige Fremdlinien vorhanden, die zum 14-Hydrat gehören. Das Röntgendiagramm des 12-Hydrats der französischen Autoren zeigt dagegen auch die starken Linien des

14-Hydrats; übrigens ist das 12-Hydrat schon weniger gut kristallisiert, da bei der starken Dehydratisierung auch undefinierte, amorphe Teile auftreten. Unsere Diagramme des 17- und 14-Hydrats sind vollständig indiziert, ersteres mit der aus den Weißenberg-Aufnahmen gefundenen triklinen Zelle, letzteres mit einer rhombischen Zelle (Tabelle II). Das Diffraktogramm des 12-Hydrats s. in Tabelle III.

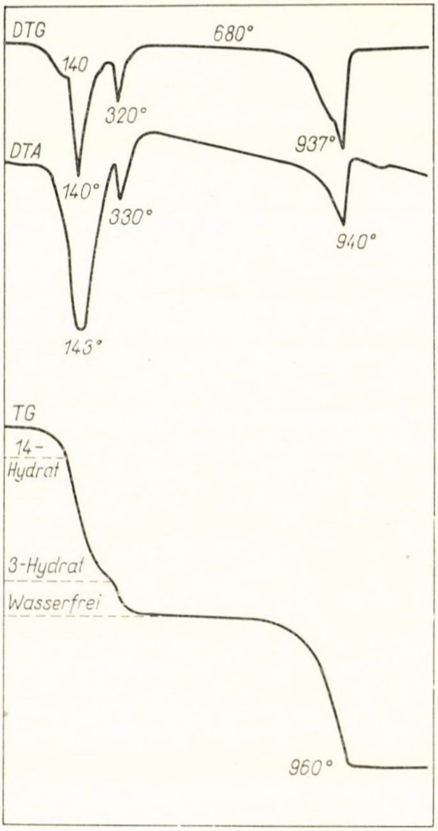

Abb. 1. Derivatogramm des $Al_2(SO_4)_3 \cdot 17\,H_2O$

Durch weitere Erhitzung bei etwa 120 °C haben wir auch ein dem 3-Hydrat entsprechend zusammengesetztes Präparat hergestellt. Das Diffraktogramm zeigt keine Kristallreflexionen, sondern nur verwaschene amorphe Ringe.

Bei über 500 °C dehydratisiertes Aluminiumsulfat, welches schon wasserfrei ist, ist wiederum kristallin; die Reflexionen und Intensitäten sind in Tabelle IV zusammengefaßt.

Man kann also feststellen, daß Aluminiumsulfat nur ein — verhältnismäßig stabiles — Hydrat, u. zw. $Al_2(SO_4)_3 \cdot 17H_2O$, besitzt; weitere, definierte, aber sehr wenig stabile Hydrate sind das 14-Hydrat und das 12-Hydrat. Dann folgt ein amorphes Gebiet und bei Abwesenheit des Wassers eine Umkristallisierung.

Tabelle II

Diffraktogramm von $Al_2(SO_4)_3 \cdot 14H_2O$

$2\,\vartheta_0^0$	$\sin^2 \vartheta_0$	$\sin^2 \vartheta_c$	$\Delta_{c-o}\,10^5$	Int_{Fl}	d Å	hkl
7,24	0,00399	0,00398	− 1	26	12,203	100
12,68	01219	01216	− 3	1	6,977	020
14,48	01588	01592	+ 4	11	6,114	200
15,80	01889	01896	+ 7	1	5,606	210
16,85	02147	02138	− 9	1	5,259	022
19,00	02724	02736	+12	1	4,668	030
20,02	03021	03038	+17	2	4,433	221
21,10	03352	03364	+12	7	4,208	131
21,82	03582	03582	± 0	100	4,071	300
22,27	03730	03730	± 0	5	3,990	222
23,03	03985	03992	+ 7	9	3,860	014
24,19	04291	04390	− 1	2	3,677	114
25,48	04863	04864	+ 1	1	3,494	040
27,37	05594	05584	−10	2	3,257	214
29,16	06337	06368	+31	<1	3,060	400
29,52	06491	06496	+ 5	4	3,024	224
32,10	07644	07658	+14	<1	2,787	215
32,69	08014	07998	−16	<1	2,737	150
33,87	08485	08498	−13	1	2,645	035
		08504	+19			422
35,78	09437	09422	−15	1−2	2,213	522
45,68	15067	15056	−11	1	1,895	018
52,35	19459	19456	− 3	2	1,746	080

Die Indizierung erfolgte mit der Gleichung
$\sin^2 \vartheta_c = 0{,}00398\ h^2 + 0{,}00304\ k^2 + 0{,}002305\ l^2$

Tabelle III

Diffraktogramm von $Al_2(SO_4)_3 \cdot 12H_2O$

$2\,\vartheta_0^0$	$\sin^2\vartheta_0$	Int_{Fl}	d Å
15,23	01756	9	5,799
16,34	02020	26	5,383
18,10	02474	1	4,899
23,01	03978	72	3,853
24,66	04560	100	3,608

GORDON [8] schreibt, daß zerriebenes Alunogen bei gewöhnlicher Temperatur in 2 bis 7 Tagen 6,33% Wasser verloren hat und über konzentriertem H_2SO_4 in 21 Tagen weitere 0,82%. Das entspricht ebenfalls einem Gemisch von 17-Hydrat und 14-Hydrat. Unsere eigenen Versuche zeigten, daß zerriebenes, künstliches 17-Hydrat bei Zimmertemperatur in 7 Tagen 2,34% an Gewicht verloren hat; die Luft war bei uns wahrscheinlich nicht so trocken, wie bei den Versuchen von GORDON.

Tabelle IV

Diffraktogramm von $Al_2(SO_4)_3$ *(wasserfrei)*

$2\vartheta^\circ_0$	$\sin^2 \vartheta_0$	d Å	Int_F
15,23	01756	5,815	40
21,06	03340	4,215	15
25,10	04721	3,545	23
25,50	04871	3,491	100
30,72	07016	2,909	21
33,72	08412	2,656	21
34,32	08705	2,611	16
35,10	09093	2,555	1
38,05	10626	2,364	2
38,66	10957	2,328	4
40,75	12122	2,213	6
44,24	14179	2,046	7
45,43	14910	1,996	3
46,65	15677	1,947	4
47,72	16363	1,905	2
48,50	16869	1,876	2
50,12	17941	1,819	3
51,30	18739	1,780	1
52,15	19320	1,752	7
53,18	20035	1,721	2
55,38	21594	1,658	6
56,28	22244	1,634	5
57,79	23350	1,594	1
58,95	24211	1,565	2
60,38	25396	1,532	5
60,82	25615	1,522	3
61,90	26449	1,498	1
62,35	26797	1,489	2
63,75	27886	1,459	1
65,02	28885	1,434	4
66,08	29728	1,413	3
66,85	30344	1,399	5
68,55	31716	1,368	1
69,30	32327	1,355	1
69,62	32604	1,349	2
70,05	32941	1,342	6

Für die Weißenberg-Aufnahmen danke ich Herrn GY. ARGAY und für die Derivatogramme Frau Dr. P. FEJES.

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ANALYSIS OF MIXTURES OF THE STRUCTURAL ISOMERS OF N-ALLYL-*dl*-CAMPHORAMIC ACID, I

THERMOANALYTICAL METHOD

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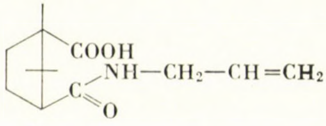
A simple and rapid method has been found for the assay of binary mixtures of the two structural isomers of N-allyl-*dl*-camphoramic acid. The accuracy of the method is ±5%.

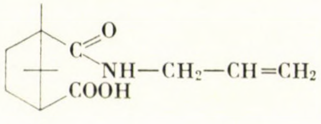
Introduction

N-allyl-*dl*-α-camphoramic acid was first prepared in 1910 [1]. It was shown [2] that the reaction mixture of WOOTON contained the α and β isomers together and the pure α-isomer was obtained only after several recrystallizations.

We searched for a method permitting the quantitative assay of the two structural isomers, *viz.* N-allyl-*dl*-α-camphoramic acid (**I**) and N-allyl-*dl*-β-camphoramic acid (**II**), in the presence of each other.



I



II

No sufficient difference can be noticed between **I** and **II** to permit their assay by the usual analytical procedures. Of the customary physico-chemical methods, the most effective would be the estimation of the acid dissociation constant. In our case the difference between the two pK_a's is too small to allow development of a convenient analytical procedure on this basis. Therefore we tried to solve the problem by the thermoanalytical technique.

Thermal methods have become wide-spread only during the last ten years. Organic compounds have been rarely analyzed by this technique owing to problems which rendered the evaluation of the results difficult [3]. To our knowledge, the thermoanalytical method has been very little used for the quantitative analysis of mixtures of structural isomers.

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* Abstracted from a thesis by R. G. HENEIN (U. A. R.) in fulfilment of the requirements for the degree of Doctor of Philosophy, Institute of Pharmaceutical Technology, Medical University, Budapest.

Experimental

We prepared **I** and **II** according to HENEIN *et al.* [4]. Pure **I** and **II** were mixed in proper amounts to give a series of mixtures increasing by 5% in one of the components. To ensure homogeneity, the mixtures were dissolved in acetone, dried and pulverized in an agate mortar.

The experiments were performed using a GYEM 6016 derivatograph. The sample (300 mg) under examination was placed in a platinum thimble of the special form used for ordinary derivatographic measurements. This also made possible the examination of melts. We used Al_2O_3 ignited over 1200 °C as inert material. The temperature was raised during the period of examination (100 min) at a constant rate of 3 °C/min. As the samples decompose soon after melting, it was not possible to construct a cooling curve, thus only the melting points were considered. Great care was taken to minimize experimental errors which may arise owing to differences in particle size, compactness, or in weighing the samples.

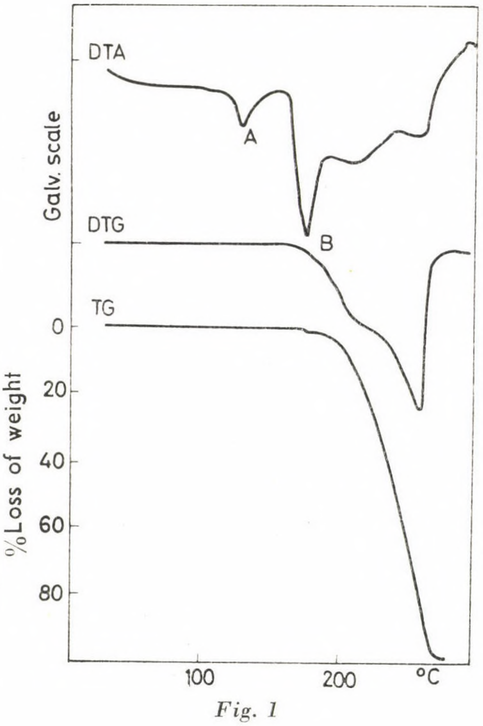

Fig. 1

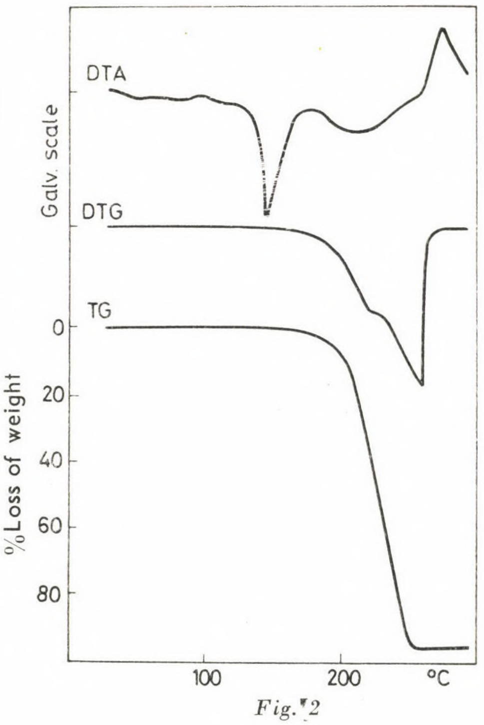

Fig. 2

Results and discussion

The derivatograms of pure **I** and **II** were significantly different (see Figs 1 and 2). In order to observe the enthalpic changes occurring as a result of heating, we followed the heating up processes using a Boeticus block. The endothermic change of **I** occurring at 125 °C (Fig. 1, peak A) indicates a polymorphic transformation, since at this temperature the microcrystals melt, and are immediately replaced by needle crystals which remelt at 176 °C (Fig. 1, peak B). **II** melts at 144 °C without any polymorphic transformation.

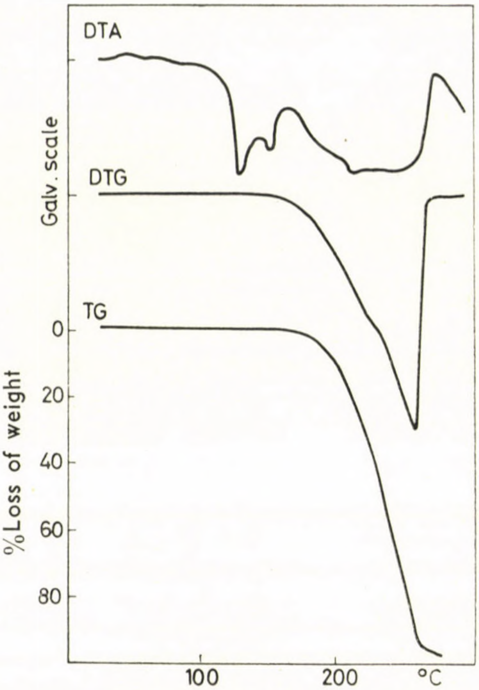

Fig. 3

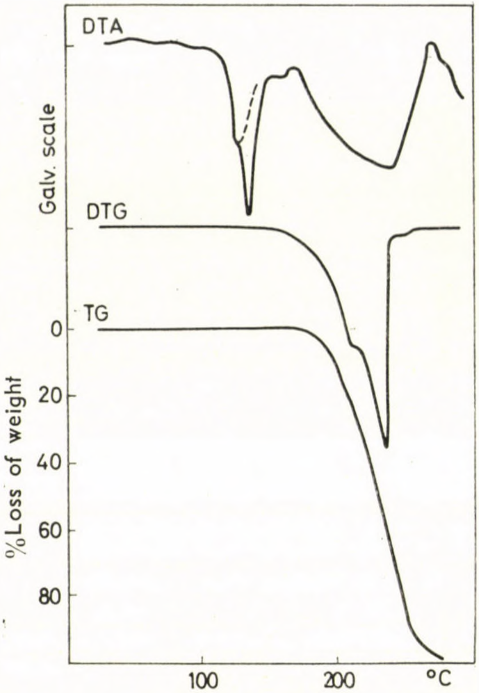

Fig. 4

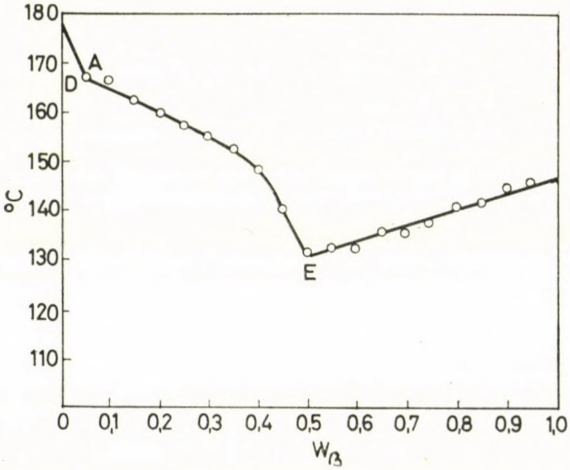

Fig. 5

We examined then the different mixtures of **I** and **II** and noticed the positions of the DTA peaks in relation to the composition, as it can be seen in Figs 3 and 4. The DTA peaks indicate endothermic changes which occur without change in weight, as shown by the TG curve. The curve in Fig. 5

shows the melting temperatures as obtained from the DTA peaks as a function of the composition: thus it is somewhat similar to the melting temperature curve, but it is not exactly the same.

It can be seen that the curve has two critical points, at compositions 50% **I**, and 95% **I**. A discontinuity in the liquidus curve at A (peritectic point) indicates the existence of a compound formed. Melts with compositions between points A and D have three phases, and the system is invariant. Point E is the eutectic point.

The curve can be used to analyze mixtures of unknown composition with an accuracy of ±5%, which is the lower limit of accuracy stated by the manufacturers of the instrument.

*

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THE SORPTION OF METAL IONS FROM SOLVENT MIXTURES ON CELLULOSE ION EXCHANGERS

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The sorption of metal ions (Cu^{2+}, Co^{2+}) on cellulose ion exchangers from different solvents has been investigated. It is concluded that not only water, but also the solvents methanol, ethanol, acetone, or formamide are suitable ion exchange media. In most of the solvents P-, SE-, and C-cellulose were the most advantageous ion exchangers for retaining the metal ions. In some cases, the anion exchanger DE-cellulose could also be used for this purpose. Both the percentage and the rate of sorption are reduced when the dielectric constant of the solvent is decreased, as it has been observed in the case of aliphatic alcohols.

Non-aqueous solvents are recently often used as components of the media for ion exchange processes. Mostly solvent mixtures, one of the components being water, have been suggested. Possibilities for the separation of metal ions in solvent acid mixtures were reported by **Korkisch** *et al.* [1—3]. Separation of metal ions was accomplished by **Muzzarelli** [4] on a cellulose ion exchanger using ether–acid mixtures.

In our previous papers the microanalytical uses of cellulose ion exchangers were considered. The identification and removal of traces of metals from distilled water and organic substances (drugs) had been reported earlier. Our recent investigations have included the use of organic solvents, allowing the detection of metal impurities in water-insoluble organic substances, by means of cellulose ion exchangers [5—7].

The identification and removal of small amounts of heavy metals are of great importance in the telecommunication industry. Comparative tests were carried out to select the most suitable cellulose ion exchanger for the removal of metal ions from a particular solvent, and to find the most convenient solvents best allowing the identification and removal of metal ions from organic substances. Since no data were available concerning the rate of ion exchange on cellulose exchangers in different solvents, the time dependence of the exchange had to be investigated.

Our main purpose was the detection and removal of heavy metals; copper and cobalt were used in the present study. The experiments were performed at low metal ion concentrations, and air-dry ion exchangers were used in the hydrogen form. The water content of the solvents was adjusted to 0.05 mole fraction.

Experimental

Reagents

$CoCl_2 \cdot 6H_2O$, analytical grade
$CuCl_2 \cdot 3H_2O$, analytical grade
C-cellulose (carboxycellulose; 0.23 meq/g) [7]
DE-cellulose Whatman (diethylaminoethylcellulose; 0.70 meq/g)
CM-cellulose Whatman (carboxymethylcellulose; 0.46 meq/g)
P-cellulose Whatman (cellulosephosphate; 0.33 meq/g)
SE-cellulose Nagel (sulphoethylcellulose; 0.14 meq/g)
Rexyn resin (carboxylic resin; R-102 (H); 12.1 meq/g)

All solvents used were of analytical grade; when necessary, they were purified by distillation, or by passing through a cellulose ion exchange column.

Procedure

0.100 g of C-cellulose or another exchanger was added to 20.0 ml of organic solvent containing 100 μg of metal ion.

The mixture was allowed to stand for a certain period without shaking, then the exchanger was separated by filtration, and the metal retained on the exchanger was measured. The metal ion was eluted by dilute mineral acid; both cobalt and copper were determined spectrophotometrically, the former as $Co(DMG)(HDMG)I_2^-$ [8] and the latter as $Cu(DDC)_2$ (DMG = dimethylglyoxime; DDC = diethyldithiocarbamate). In most of the runs the metal content of the filtrate was also determined. In comparing the cellulose cation exchangers 0.046 meq cellulose exchanger was added to 50 ml of a $5 \cdot 10^{-1}$ *N* metal ion solution, the contact time was 24 hours.

Results and discussion

Tables I and II show the percentage absorption of metal ions from different solvents. The results indicate that both the extent of sorption and the period required to attain equilibrium in different solvents depend on the quality of the solvent.

According to IZMAILOV [9], the ion exchange constant is inversely proportional to the dielectric constant of the solvent and to the distance between the counter ions and the functional group. The change in the energy of ion-dipole interaction, when a particular ion becomes attached to an ion exchanger, should also be considered. This effect is negligible when resins of high degree of cross-linking are used. Further the difference in the solvation energies of the exchangeable ions, and the difference in the swelling energies of the exchangers should be taken into account. When H-form exchangers are used, the proton affinity of the solvent is another important factor. Two effects may counteract: the dielectric constant and the chemical properties (basicity, complex forming ability) of the solvent. *E.g.*, cobalt ion is absorbed on C-cellulose from dimethylformamide, but copper is retained in the liquid phase, owing to differences in the complex stabilities.

CHARLOT and TREMILLON [10] divide solvents into three groups according to their effects on the salts dissolved: (1) Solvents causing complete dissociation, $\varepsilon > 40$; (2) partial dissociation. $\varepsilon \sim 15$–40; and (3) practically no

Table I

Absorption of Co^{2+}, %
(100 μg Co^{2+}; 20.00 ml solvent; 0.10 g C-cellulose)

Contact time, min.	Water	Formamide	Dimethylformamide	Methanol	Ethanol	n-Propanol	n-Butanol	Acetone	Dioxan
				Co^{2+} retained %					
1	84.3	61.1	58.1	12.9	6.1	5.3	3.2	28.2	12.8
5	86.4	67.0	73.6	14.9	7.0	5.9	3.3	32.0	15.1
10	84.8	69.4	72.6	18.0	10.6	5.9	4.3	35.5	16.6
30	—	66.5	75.2	29.1	15.0	7.2	4.5	38.1	21.3
60	—	69.5	78.9	33.0	18.0	7.5	5.5	44.5	24.3
120	—	69.1	78.9	34.3	18.6	9.7	6.5	51.6	30.8
180	—	70.2	79.0	38.7	19.9	10.1	6.6	59.6	36.3
240	—	70.5	85.2	39.7	20.2	10.3	6.6	62.6	38.4
300	—	70.8	84.1	40.5	23.7	12.1	7.1	66.5	41.4
360	—	71.0	84.2	41.6	23.3	13.4	8.1	66.3	41.1
960	85.4	72.3	84.2	41.8	38.7	14.9	11.0	68.6	61.7
12 days	86.2	75.1	84.2	42.1	75.3	69.5	38.7	79.3	70.0

dissociation at all, $\varepsilon < 15$. From solvents belonging to Group (1), such as water and formamide, the sorption of metal ions is considerable, the rate of ion exchange is high, the equilibrium is attained within 1 minute. Using the solvents of Group (2) (dimethylformamide, aliphatic alcohols and acetone), the rate of sorption is lower, and the amount of metal ion fixed within 1 day is less than with solvents of Group (1). A regular decrease in the quantity of sorbed metal is to be seen going from methanol to butanol. This is due to

Table II

Absorption of Cu^{2+}, %
(100 μg Cu^{2+}; 20.00 ml solvent; 0.10 g C-cellulose)

Contact time, min.	Water	Methanol	Ethanol	n-Propanol	n-Butanol	Acetone
			Cu^{2+} retained %			
1	93.1	22.0	19.3	10.5	7.0	24.1
5	90.2	22.0	20.8	11.3	7.8	30.5
10	—	32.1	21.5	11.8	8.6	32.8
60	—	42.0	34.6	15.9	11.1	32.8
120	—	44.0	35.8	17.2	13.1	37.7
180	—	48.0	35.5	23.1	13.1	41.4
1440	91.2	73.9	71.5	38.9	30.9	66.7

a decrease in the dielectric constants and solvent basicity, and an increase in viscosity. The partial dissociation of metal salts in these solvents accounts for the slow equilibration. Dioxan and pyridine were chosen as solvents in Group (3). Only a few per cent of copper was sorbed from dioxan and pyridine, however, a considerable amount of cobalt was retained by the exchanger from dioxan.

In organic solvents not only ion exchange but also adsorption phenomena play an important part. At low metal ion concentrations, it is difficult to measure quantitatively the amount of hydrogen ion liberated in the ion exchange process. Approximate figures for the extent of adsorption can be obtained, however, by measuring the amount of metal ion retained on the cellulose powder. The results are given in Table III. The adsorption of $CoCl_2$ and $CuCl_2$ on cellulose is negligible from solvents of high dielectric constant. From acetone and dioxan the adsorption of $CoCl_2$ is significant. In acetone also the retained chloride was determined. The adsorbed $CoCl_2$ could be eluted with acetone.

The behaviour of $CoCl_2$ is peculiar in non-aqueous solvents [10]. In ethanol, acetone and *n*-propanol $CoCl_2$ undergoes dimerization and this leads to the following equilibria:

$$2\,CoCl_2 \rightleftharpoons Co_2Cl_4 \rightleftharpoons CoCl^+ + CoCl_3^-$$

This means that cobalt is retained on anion exchangers also in the above-mentioned solvents. DECl and DEOH were used in these investigations, and the results are given in Table IVa. On DEOH cellulose, cobalt is retained in

Table III

Absorption of Co^{2+} and Cu^{2+} on cellulose powder from various solvents
(Contact time: 16 hours; 100 μg metal ion; 20.0 ml solvent; 0.10 g cellulose powder)

Solvent	ε	Cu^{2+}	Co^{2+}
		retained %	
Water	80.0	17.3	12.7
Methanol	32.6	7.0	8.5
Ethanol	24.3	3.5	12.4
n-Propanol	20.1	2.0	10.9
n-Butanol	17.1	1.9	3.9
Formamide	109.5	0.0	0.0
Dimethylformamide	36.7	0.0	12.6
Acetone	20.7	31.5	79.2
Dioxan	2.2	14.0	72.7

Table IVa

Absorption of Co^{2+} on diethylaminoethylcellulose (DE-cellulose) from different solvents
(Contact time: 24 hours; 100 μg Co^{2+}; 20.0 ml solvent, 0.10 g DE-cellulose)

Solvent	Retained %	
	DE-cellulose (Cl^- form)	DE-cellulose (OH^- form)
Water	0.0	9.5
Methanol	0.0	34.3
Ethanol	42.3	70.3
n-Propanol	14.6	48.7
n-Butanol	13.8	59.3
Formamide	0.0	0.0
Dimethylformamide	5.5	79.7
Acetone	45.9	92.0
Dioxan	63.9	75.3

the form of its chloro complex, on the other hand, it is adsorbed on the exchanger as a slightly soluble hydroxide. Namely, using the anion exchanger in OH form, metal sorption can be observed even from solvents in which the dimerization of $CoCl_2$ does not occur.

For the case of using $Co(NO_3)_2$ instead of $CoCl_2$, the percentage values of sorption are shown in Table IVb. In most ion exchangers (see also Tables III and V) higher values were obtained. The formation of cobalt nitrato complexes can be neglected. Cobalt is not absorbed from ethanol on $DENO_3$ cellulose

Table IVb

Absorption of Co^{2+} from $Co(NO_3)_2$ solutions

(Contact time: 24 hours; 100 μg Co^{2+}; 20.0 ml solvent; 0.10 g ion exchanger)

Solvent	Retained % on			
	Cellulose powder	C-cellulose	DE-cellulose (NO_3^- form)	DE-cellulose (OH^- form)
Methanol	10.6	48.8	0.0	35.8
Ethanol	10.8	39.3	5.0	75.8
n-Propanol	11.4	27.5	6.0	59.3
n-Butanol	4.9	17.6	5.5	53.3
Acetone	60.8	84.6	52.0	79.8
Dioxan	54.0	70.0	66.2	61.7
Water	16.8	85.6	0.0	10.0

when $Co(NO_3)_2$ is applied, but a considerable sorption can be observed on DECl when $CoCl_2$ is used.

Experiments were made to compare the sorption of cobalt ion on Rexyn carboxylic resin and on CM-cellulose from different solvents. The results are given in Table V, where the figures obtained using C-cellulose are also included. The difference in the percentage of sorption does not reflect the great differences in the capacity of exchangers (see Experimental).

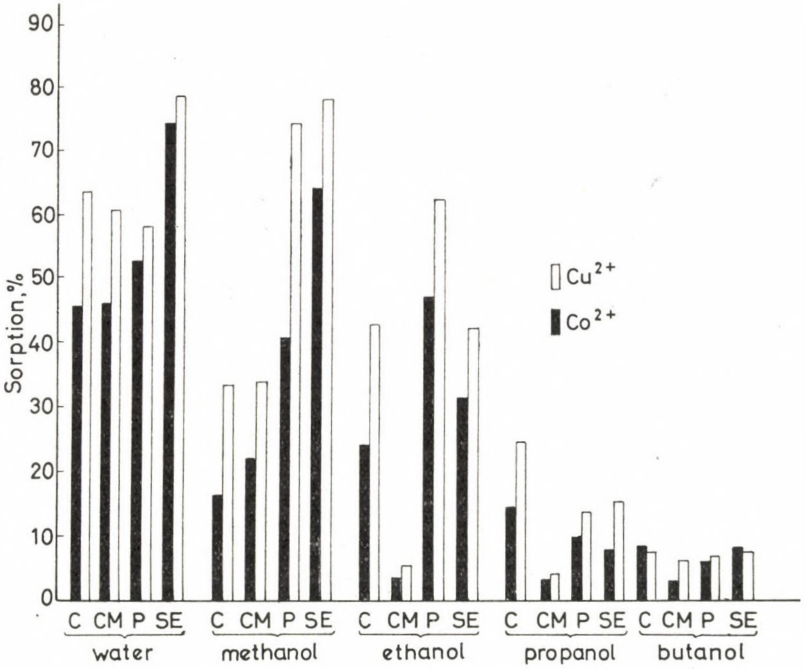

Fig. 1. Sorption of Co^{2+} and Cu^{2+} on different cellulose ion exchangers

Finally, to find the most suitable cellulose cation exchanger for the collection of metal ions from solvents, comparative measurements were made with exchangers containing equivalents of active groups. The results are compiled in Fig. 1. All exchangers were in H-form, and for this reason the acid strength of the active group had a great influence on the sorption. This fact is reflected in the figures obtained for the sorption of cobalt in water. Copper(II) ion is readily bound by carboxyl groups, therefore the adsorption of copper on C-cellulose and CM-cellulose is higher than expected.

Table V

Absorption of Co^{2+} from solvents
(Contact time: 16 hours; 100 μg Co^{2+}; 20.0 ml solvent; 0.10 g ion exchanger)

Solvent	Retained % on		
	Rexyn (COOH-resin)	CM-cellulose	C-cellulose
Water	93.8	96.3	85.4
Methanol	53.5	56.3	41.8
Ethanol	82.4	8.7	38.7
n-Propanol	61.7	6.9	14.9
n-Butanol	22.6	7.9	11.0
Formamide	79.2	60.4	72.3
Dimethylformamide	82.4	49.4	84.2
Acetone	31.1	35.1	68.6
Dioxan	8.9	31.9	61.7

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ANWENDUNG DER OSZILLOMETRISCHEN ENDPUNKTSANZEIGE IN DER ASCORBINOMETRIE, III

BESTIMMUNG VON QUECKSILBER(II)-IONEN

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Der Endpunkt der ascorbinometrischen Bestimmung geringer Mengen von Quecksilber(II)-Ionen wurde oszillometrisch angezeigt. Die Bestimmung kann auf zweierlei Arten durchgeführt werden: es kann mit Ascorbinsäuremaßlösung bis zur Reduktion zu metallischem Quecksilber titriert werden, oder mit chloridhaltiger Ascorbinsäuremaßlösung bis zur Reduktion zu Quecksilber(I)-Ionen. Die Quecksilber(II)-Ionenkonzentration der zu titrierenden Lösungen betrug 10^{-3}—10^{-2} *n*; die Meßgenauigkeit 1—2%.

Über die Bestimmung von Quecksilber(II)-Ionen mit oszillometrischer Endpunktsanzeige liegen verschiedene Arbeiten vor. Japanische Verfasser verwendeten dabei Kaliumchlorid- und Kaliumcyanid-Maßlösungen [1] bzw. Kaliumrhodanid-Maßlösungen [2, 3] in Konzentrationen von 0,01 *n* und 0,1 *n*. Andere japanische Verfasser verwendeten Pikrinsäure- [4] bzw. Äthylentetramin [5] Maßlösung und erhielten Ergebnisse mit einem mittleren Meßfehler von 2%. Blaedel und Malmstadt [6, 7, 8] schlugen ebenfalls Natriumchlorid- und Kaliumrhodanid-Maßlösungen für die Bestimmung von Quecksilber(II)-Ionen vor. Lane [10] titrierte Quecksilber(II)-Ionen in Form von Kupferpropylendiaminjodomerkurat in Eisessig, mit Perchlorsäure-Maßlösung, während Hall und Gibson [11] das Dinatriumsalz der Äthylendiamintetraessigsäure als Maßlösung anwendeten.

In sämtlichen angeführten Arbeiten wurden die Quecksilber(II)-Ionen mit Fällungstitration bzw. komplexometrisch bestimmt. Über reduktometrische Bestimmungen berichten die Verfasser nicht.

Erdey und Buzás [12] fanden die Möglichkeit einer ascorbinometrischen Bestimmung von Quecksilber(II)-Ionen durch die Anwendung von Variaminblau als Redoxindikator, wobei die Endpunktsanzeige dadurch ermöglicht wird, daß sich das Redoxpotential im Endpunkt sprunghaft ändert. Bei der oszillometrischen Endpunktsanzeige ist dagegen die starke Änderung der Leitfähigkeit im Laufe der Titration maßgebend. In der Reaktion

$$Hg^{2+} + C_6H_8O_6 \rightleftarrows Hg + C_6H_6O_6 + 2H^+$$

treten hochbewegliche Wasserstoffionen an die Stelle der weniger beweglichen Quecksilber(II)-Ionen, wodurch die Leitfähigkeit wesentlich gesteigert wird. Nach dem Erreichen des Endpunkts ändert sich die Leitfähigkeit durch die Zugabe weiterer Mengen von Ascorbinsäure nur geringfügig [13], folglich erscheint im Endpunkt ein wohldefinierter Knickpunkt der Titrationskurve.

Die Titration wird in chloridfreier Lösung bis zur Abscheidung von metallischem Quecksilber durchgeführt, da die Ascorbinsäure die Quecksilber(II)-Ionen in Gegenwart von Chloridionen nur zu Quecksilber(I)-Ionen reduziert. Letztere werden in Form von Quecksilber(I)chlorid ausgeschieden; eine weitere Reduktion zu metallischem Quecksilber geht selbst bei hohen Ascorbinsäure-Überschüssen nicht vor sich [12, 14].

Die Redoxpotentiale, Löslichkeiten und Komplexstabilitätsangaben der einzelnen Vorgänge sind die folgenden:

$$\begin{array}{ll}
\mathrm{C_6H_8O_6 \rightleftarrows C_6H_6O_6 + 2H^+ + 2e} & E^\circ = +0{,}19\ \mathrm{V}\ (\mathrm{pH}\ 4) \\
 & \ +0{,}36\ \mathrm{V}\ (\mathrm{pH}\ 0) \\
\mathrm{Hg^{2+} + e \rightarrow 1/2Hg_2^{2+}} & E^\circ = +0{,}92\ \mathrm{V} \\
\mathrm{1/2Hg_2^{2+} + e \rightarrow Hg^\circ} & E^\circ = +0{,}79\ \mathrm{V} \\
\mathrm{2HgCl_2 + 2e \rightarrow Hg_2Cl_2 + 2Cl^-} & E^\circ = +0{,}63\ \mathrm{V} \\
\mathrm{Hg_2Cl_2 + 2e \rightarrow 2Hg^\circ + 2Cl^-} & E^\circ = +0{,}268\mathrm{V} \\
\quad \text{Für } \mathrm{Hg_2Cl_2} : \mathrm{L_{25\,^\circ C}} = 2 \cdot 10^{-18} & \\
\quad \text{Für } \mathrm{HgCl_2}\ : \mathrm{K_{25\,^\circ C}} = 2.6 \cdot 10^{-15} &
\end{array}$$

Die Normalpotentiale lassen erkennen, daß die Ascorbinsäure imstande ist, selbst die Quecksilber(II)chlorid-Komplexe zu reduzieren, wogegen das Quecksilber(I)chlorid mit Ascorbinsäure in schwach saurer Lösung überhaupt nicht zu metallischem Quecksilber reduzierbar ist.

Diese Tatsache bot die Möglichkeit, die Bestimmung der Quecksilber(II)-Ionen mit oszillometrischer Endpunktsanzeige unter Anwendung von Ascorbinsäure als Maßlösung auf zweierlei Arten durchzuführen, und zwar einerseits in chloridfreiem Medium bis zur Abscheidung von metallischem Quecksilber, andererseits mit einer chloridhaltigen Ascorbinsäuremaßlösung bis zur Abscheidung von Quecksilber(I)chlorid.

Lösungen und Meßgeräte

1. Quecksilber(II)nitrat-Stammlösung. Metallisches Quecksilber wurde in Salpetersäure gelöst. Der Wirkungswert der Lösung wurde durch Titrieren mit 0.1 *n* Ascorbinsäuremaßlösung in Gegenwart von Variaminblau als Indikator bestimmt. Die Quecksilber(II)-Ionenkonzentration der Stammlösung betrug 11,21 mg/ml.

2. 0,1 *n* Ascorbinsäuremaßlösung. Der Titer der Lösung wurde auf 0,1 *n* Kaliumjodatlösung eingestellt [13].

3. 0,1 *m* Chlorid enthaltende, 0,1 *n* Ascorbinsäuremaßlösung. Es wurde eine ungefähr 0.5 *n* Ascorbinsäurelösung hergestellt, ihr Wirkungswert mit 0,1 *n* Kaliumjodatlösung bestimmt, die berechnete Menge Natriumchlorid zugefügt und die Lösung auf 0,1 *n* oder 0,05 *n* verdünnt.

Anschließend wurde der Wirkungswert der Lösung von neuem bestimmt. Auch die zeitliche Veränderung der auf die beschriebene Weise hergestellten chloridhaltigen Ascorbinsäurelösung wurde untersucht. Dabei wurde gefunden, daß der Wirkungswert der Lösung im Laufe von zwei Tagen um 0,01 abgenommen hatte, von $f = 1{,}000$ auf den Wert von $f = 0{,}990$.

4. Die oszillometrischen Messungen wurden mit zwei verschiedenen Geräten durchbeführt, und zwar mit dem Gerät nach Tarnay und Juhász [5], dessen Grundfrequenz 5 MHz geträgt und mit dem Oszillotitrator nach Pungor [15] mit der Grundfrequenz von 130 MHz.

5. Die konduktometrischen Messungen wurden mit dem Gerät »Konduktometer« purchgeführt.

6. Bei der potentiometrischen Titration wurde der Potentialunterschied zwischen einer glatten Platinelektrode und einer gesättigten Kalomel-Referenzelektrode mit dem Gerät »Pehavi« gemessen.

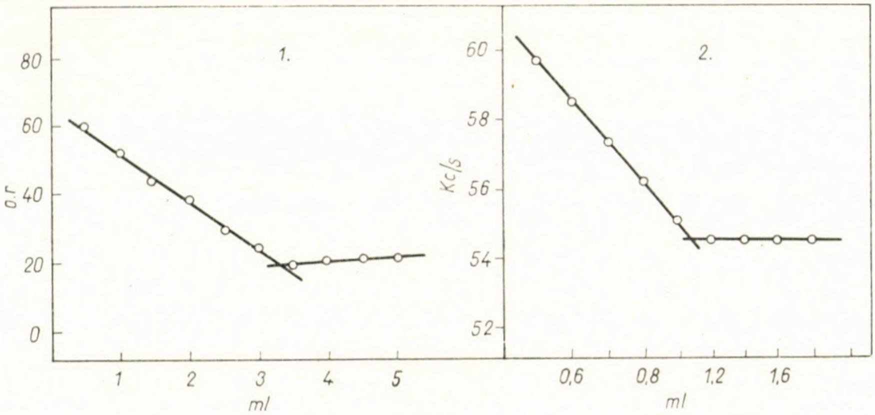

Abb. 1. Titrationskurven von Quecksilber(II)-Ionen mit 0.1 *n* Ascorbinsäuremaßlösung; 1 — im 130 MHz-Gerät, 2 — im 5 MHz-Gerät

Bestimmung der Quecksilber(II)-Ionen in chloridfreiem Medium

Es wurden 2,2–12,45 mg bzw. 11–33 mg Quecksilber(II)-Ionen enthaltende Mengen der Stammlösung in die 20 bzw. 100 ml fassenden Zellen der Geräte eingeführt, mit soviel destilliertem Wasser verdünnt, daß die Oberfläche der Lösung über den Kondensatorringen stand und zwecks Erleichterung der Niederschlagsbildung wurde eine Messerspitze Glaspulver zugefügt. Darauf wurde der Magnetrührer in Gang gesetzt und gewartet, bis sich der Zeiger des Geräts einstellte. Erst dann wurde mit der Titration begonnen, wobei die 0,1 *n* Ascorbinsäuremaßlösung aus einer Mikrobürette in Portionen von 0,1–0,2 ml zugegeben wurde. Die Titrationskurven sind in Abb. 1 gezeigt.

Die Bestimmung wird in schwach saurer, jedoch höchstens 0,02 *n* salpetersaurer Lösung durchgeführt. Die Meßergebnisse enthält Tabelle I.

Um die Meßgenauigkeit zu bestimmen, wurden 12 Parallelmessungen mit 10^{-3} *n* Lösungen durchgeführt. Die Streuung σ ergab sich zu $\pm 7{,}5\%$, die Streuung des Mittelwerts σ_K zu $\pm 2.2\%$ (Tabelle II).

Tabelle I

Bestimmung von Quecksilber(II)-Ionen mit Ascorbinsäuremaßlösung, mit dem 5-MHz-Gerät
Konzentration der Hg^{2+}-Ionen $1 \cdot 10^{-3}$—$5 \cdot 10^{-3}\ n$

Einwaage mg Hg^{2+}	Gefunden mg Hg^{2+}	Abweichung %
2,26	2,25	—0,05
2,26	2,28	+0,1
5,09	5,10	+0,2
5,09	5,16	+1,3
11,32	11,28	—0,3
11,32	11,43	+0,9
12,45	12,53	+0,6
12,45	12,40	—0,4

Bestimmung von Quecksilber(II)-Ionen mit Ascorbinsäuremaßlösung, mit dem 130-MHz-Gerät
Konzentration der Hg^{2+}-Ionen $1 \cdot 10^{-3}$—$5 \cdot 10^{-3}\ n$

Einwaage mg Hg^{2+}	Gefunden mg Hg^{2+}	Abweichung %
11,02	10,99	—0,3
11,02	10,99	—0,3
22,81	22,77	—0,2
22,81	22,87	+0,3
33,06	32,97	—0,3
33,06	33,27	+0,6

Tabelle II

Bestimmung von Quecksilber(II)-Ionen mit Ascorbinsäuremaßlösung, mit dem 130-MHz-Gerät
Hg^{2+}-Konzentration der Lösung $3 \cdot 10^{-3}\ n$

Einwaage mg Hg^{2+}	Gefunden mg Hg^{2+}	Gefunden mg Hg^{2+}
22,81	22,77	22,87
	22,77	22,87
	22,77	22,87
	22,80	22,87
	22,80	22,98
	22,80	22,98

Mittelwert: 22.84 mg Hg^{2+}

$$\sigma = \sqrt{\frac{\Sigma \varepsilon_i^2}{n-1}} = \pm 0{,}075 \quad \sigma\% = \pm 7{,}5\%$$

$$\sigma_K = \frac{\sigma}{\sqrt{n}} = \pm 0{,}022 \quad \sigma_K\% = \pm 2{,}2\%$$

Bestimmung der Quecksilber(II)-Ionen mit chloridhaltiger Ascorbinsäuremaßlösung

Die Quecksilber(II)-Ionen bilden mit Chloridionen stabile Komplexe. Ist die Konzentration der Chloridionen in der zu titrierenden Lösung hoch, so geht die Reduktion mit Ascorbinsäure nur sehr langsam vor sich.

Wird jedoch die Ascorbinsäuremaßlösung mit einem Chloridionengehalt hergestellt, der den reduzierten Quecksilber(II)-Ionen äquivalent ist, d. h. nur zum Abscheiden des Quecksilber(I)chlorid-Niederschlags ausreicht, oder liegen die Chloridionen in der Meßlösung nur in geringem Überschuß vor, so verläuft die Reduktion der Quecksilber(II)-Ionen zu Quecksilber(I)-Ionen schnell. Da das Quecksilber(I)chlorid aus der Lösung abgeschieden wird, kann die Reduktion der Quecksilber(II)-Ionen bei der Stufe der Quecksilber(I)-Ionen gestoppt werden.

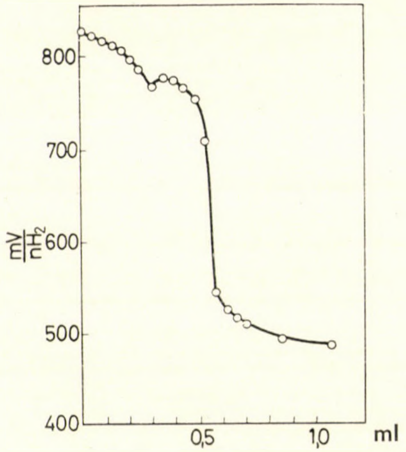

Abb. 2. Potentiometrische Titration von Quecksilber(II)-Ionen mit 0.1 *n* chloridhaltiger Ascorbinsäuremaßlösung

Um zu entscheiden, ob die Reaktion stöchiometrisch verläuft, wurden potentiometrische Titrationen durchgeführt.

Lösungen mit bekanntem Quecksilber(II)nitrat-Gehalt wurden mit der chloridhaltigen 0,1 *n* Ascorbinsäuremaßlösung titriert (Abb. 2). Wie ersichtlich, weisen die Titrationskurven an dem Ort, der dem Übergang $Hg^{++} + Hg^{+}$ entspricht, einen hohen Potentialsprung auf. Durch Steigerung des Chloridionengehalts der Maßlösung wird dieser Potentialsprung nicht verändert, es verschiebt sich nur der erste, niedrigere Knickpunkt der Kurve und das Gleichgewicht stellt sich langsamer ein.

Die Änderung der Leitfähigkeit im Laufe der oszillometrischen Titration ist hauptsächlich durch die leitfähigkeitssteigernde Wirkung der in der Reaktion entstehenden Wasserstoffionen bedingt, jedoch steigt die Leitfähigkeit auch nach dem Endpunkt, infolge des Natrium- und Chloridionengehalts der Maßlösung, wenn auch in geringem Maße. Der Verlauf der konduktometrischen und der mit dem 5-MHz-Gerät erhaltenen Titrationskurve entspricht dieser Erscheinung. Bei den mit dem Oszillotitrator ausgeführten Titrationen können jedoch — infolge der für dieses Gerät charakteristischen glockenförmigen Empfindlichkeitskurven — die Titrationsparameter so eingestellt werden, daß der zweite Abschnitt der Titrationskurven parallel zur Abszisse oder in entgegengesetzter Richtung verläuft, wodurch die Auswertung der Kurven wesentlich erleichtert wird (Abb. 3).

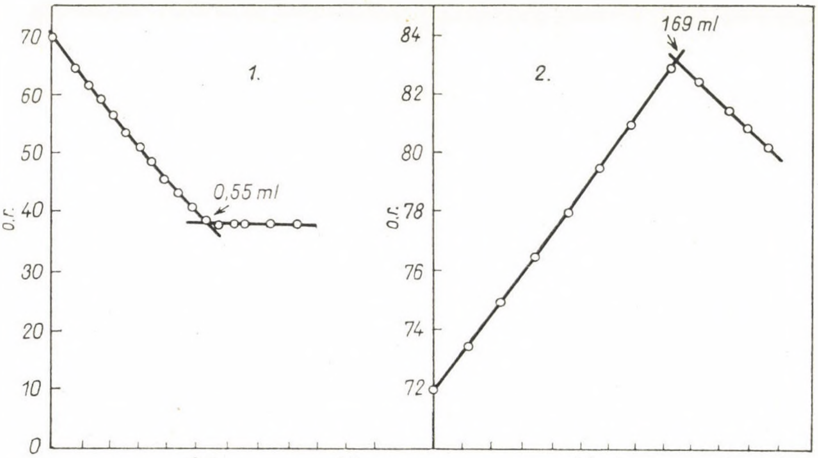

Abb. 3. Titration von Quecksilber(II)-Ionen mit 0.1 *n* chloridhaltiger Ascorbinsäuremaßlösung mit dem 130-MHz-Gerät, in der 20-ml-Meßzelle

Durch Zugabe verschiedener Mengen chloridhaltiger Lösung zu der zu titrierenden Quecksilber(II)-Lösung wurde festgestellt, daß die Bestimmung selbst dann durchführbar ist, wenn 50% der Quecksilber(II)-Ionen in Form des Quecksilber(II)chlorid-Komplexes gebunden sind. Bei der Abnahme des Wirkungswertes der Ascorbinsäure entsteht ein Chloridionenüberschuß, jedoch liegt dieser — bei dem üblichen Verbrauch von 1—2 ml Maßlösung bei der oszillometrischen Bestimmung von geringen Ionenmengen — weit unterhalb der Störgrenze. Die Titrationskurven werden zwar mit zunehmendem Chloridionenüberschuß verzerrt, der Endpunkt aber wird nicht verschoben (Abb. 4).

Die Bestimmung der Quecksilber(II)-Ionen wurde ebenso durchgeführt, wie es für chloridfreie Maßlösungen beschrieben wurde. Die Meßergebnisse sind in Tabelle III angeführt. Um die Genauigkeit der Methode zu bestimmen,

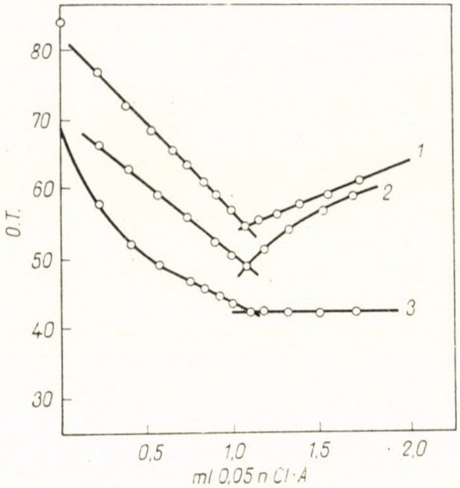

Abb. 4. Titration von Quecksilber(II)-Ionen mit 0.05 *n* chloridhaltiger Ascorbinsäuremaßlösung mit dem 130-MHz-Gerät. Wirkung des Chloridionenüberschusses auf die Titrationskurven — 1 — ohne Überschuß — 2 — 10% der Hg^{2+}-Ionen im Quecksilber(II)chlorid-Komplex gebunden — 3 — 50% der Hg^{2+}-Ionen im Quecksilber(II)chlorid-Komplex gebunden

wurden 12 Parallelmessungen mit 10^{-3} *n* Hg^{2+}-Lösung durchgeführt. Die Streuung σ betrug $\pm 4{,}24\%$, die Streuung des Mittelwerts $\sigma_K \pm 1{,}2\%$ (Tabelle IV).

Tabelle III

Bestimmung von Quecksilber(II)-Ionen mit chloridhaltiger Ascorbinsäuremaßlösung, mit dem 130-MHz-Gerät

Konzentration der Hg^{2+}-Ionen 10^{-2}—$5 \cdot 10^{-3}$ *n*

Einwaage mg Hg^{2+}	Gefunden mg Hg^{2+}	Abweichung %
5,66	5,60	—1,0
5,66	5,69	+0,5
5,66	5,74	+1,2
11,21	11,17	—0,35
11,21	11,27	+0,5
22,42	22,44	+0,1
22,98	22,86	—0,5
33,74	33,90	+0,4
33,74	33,81	+0,2

Tabelle IV

Bestimmung von Quecksilber(II)-Ionen mit chloridhaltiger Ascorbinsäuremaßlösung, mit dem 130-MHz-Gerät
Konzentration der Hg^{2+}-Ionen $5 \cdot 10^{-3}\, n$

Einwaage mg Hg^{2+}	Gefunden mg Hg^{2+}	Gefunden mg Hg^{2+}
11,21	11,15	11,20
	11,17	11,20
	11,17	11,20
	11,17	11,25
	11,17	11,27
	11,20	11,27

Mittelwert: 11,19 mg Hg^{2+}

$$\sigma = \sqrt{\frac{\Sigma \varepsilon_i^2}{n-1}} \pm 0{,}042 \qquad \sigma\% = \pm 4{,}24\%$$

$$\sigma_K = \frac{\sigma}{\sqrt{n}} = \pm 0{,}012 \qquad \sigma_K\% = \pm 1{,}2\%$$

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ELECTRON EXCHANGE REACTION BETWEEN IRON(II) AND IRON(III) IONS IN FORMAMIDE

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The kinetics of the electron exchange reaction between iron(II) and iron(III) ions has been studied in formamide. The reaction is first order in both reactants and depends slightly on acid concentration. The rate of exchange is much lower in formamide than in water. The enthalpy and entropy of activation is 5.2 ± 1.4 kcal/mole and -41 ± 5 e.u., respectively. The results contradict the electrostatic polarization theories of electron transfer reactions which predict higher rate in formamide than in water. The pH dependence can be interpreted by the band model, which gave a reasonable value of 13 Å for the reactant distance in the activated complex.

Introduction

The various theoretical models on the mechanism of electron transfer reactions can be classified into two groups: one of them involves those theories which presume an *indirect transfer*, mediated by a particle unnecessary for the initial and final state of the reaction, while in the other theories a *direct transfer* is assumed. The intermediate particles supposed by the former theories are H-atoms [1—3] or H_3O and OH radicals [4—9] which transport the electron or (in the case of OH) the hole. So the calculation of rate (if possible at all) is essentially based on the properties of these ions and radicals in aqueous solutions. In the theories of direct transfer mainly the Coulombic repulsion between the reactant ions and the polarizability of the medium in the vicinity of the ions are assumed to be the rate-determining factors [10—19].

Thus there is a fundamental difference in the predictions how a change in the solvent would influence the electron exchange process. For indirect transfer, the change in the solvent would result in the change of the intermediate species and the reaction rate could be both higher and lower depending on whether the formation [4—8] or migration [1—3] of the intermediers is easier or not. However, for direct transfer mechanism, the behaviour of the rate would be governed by the dielectric properties of the solvent, namely the rate would decrease when decreasing the dielectric constant.

This gives a possibility to test the applicability of the different theories just by comparing the kinetic parameters of some electron transfer reactions in aqueous solutions and in other solvents. Only a few measurements have been performed so far in non-aqueous or mixed solvents.

Meier and **Kahn** [20] investigated the kinetics of the two-electron exchange reaction between tin(II) and tin(IV) in dehydrated ethanol. Unfortunately, there is no possibility to compare their results with the rate obtained in water, because this reaction has not been studied in aqueous solutions.

The rate law of the uranium(IV)—uranium(VI) exchange has been determined by **Wear** [21] in aqueous ethanol, ethylene glycol and acetone mixed solvents. The reaction is highly accelerated by the addition of the non-aqueous component.

Cohen *et al.* [22] pointed to a discrepancy in the direct transfer theories, in connection with their results on the neptunium(V)—neptunium(VI) system. This reaction takes place with the same rate in different mixed solvents of various macroscopic dielectric constants and becomes lower when the concentration of the organic component reaches the range where the selective solvation of water ceases. The conclusion of the polarization theory that the neighbourhood outside the first coordination sphere of the reactant ions has a marked influence on the rate is in contradiction with these experiments. The assumption that the electron transfer proceeds by the **Grotthus** mechanism [2—4] does not harmonize with these results either, since a relatively long route is thus supposed for the H-atom to be done that would have to be broken by the organic molecules built-in in the chain of water molecules.

Considering the iron(II)—iron(III) exchange, some investigations have been made by **Horne** [23], and **Wada** and **Reynolds** [24]. This reaction is inhibited by adding methanol, ethanol, *n*-propanol or acetone to the aqueous solution [23], but the rate constant does not follow the law $\ln k = a + b/D$ as predicted by the direct transfer theories. Similar contradiction has been shown by discussing the results obtained in dimethyl sulphoxide medium [23], where the energy and entropy of activation has been measured to be 9.6 kcal/mole and —20 e.u., respectively. Comparing these figures with those of 9.9 and —25, respectively, for aqueous solution and considering that the dielectric constant of the dimethyl sulphoxide is about half of the value of water, neither Coulombic repulsion nor polarization phenomena seem to be significant.

Since all the above-mentioned experimental results have been obtained in solvents with lower dielectric constant than that of water, the influence of a solvent with extremely high dielectric constant on the reaction rate seemed to be of particular interest. For this reason formamide was chosen for our experiments being a good solvent for inorganic salts and possessing a dielectric constant of 117 at 25 °C.

Experimental

Materials. Formamide was purified by vacuum distillation. Its water content was less than 0.06 g per 100 ml. All the other reagents were of analytical grade.

The Fe_2O_3 isotope preparation used in some runs contained 10 per cent Fe-59, 88 per cent Fe-55, 1.28 per cent Co-60, and 0.17 per cent Mn-54. After dissolution in hydrochloric acid $FeCl_3$ was extracted from an 8 *M* HCl solution by di-isopropyl ether. After back extracting the iron(III) chloride into water, $Fe(OH)_3$ was precipitated and dissolved in formamide, containing equivalent amount of hydrochloric acid. In other runs carrier-free $^{59}FeCl_3$ was applied to label iron(III).

Stock solutions. Iron(III) chloride stock solution was prepared two days before use. Its concentration was 0.01 *M* for Fe(III), 0.01 *M* or 0.1 *M* for (excess) HCl, and 1 *M* for $NaClO_4$.

1 *M* HCl stock solution was made by introducing dried gaseous hydrogen chloride into formamide, and diluted with formamide to obtain the proper concentration.

Separation. The separation of iron(II) and iron(III) in aqueous solution based on complexing iron(II) with dipyridyl, and either precipitating iron(III) as hydroxide [25] or extracting the iron(III) acetyl-acetone complex with carbon tetrachloride [26], cannot be applied in formamide, because the stability of the iron(III) formamide complex is high enough to hinder the formation of the corresponding species even in dilute aqueous formamide. The *o*-oxyquinoline forms a complex with iron(III) even in formamide, the formation however is completed only in 15 minutes and during this time the oxidation of iron(II) in its dipyridyl complex can be observed. In the presence of Fe^{2+}, however, the reaction of the iron(III) with *o*-oxyquinoline is fast. (Probably the iron(III) formamide complex is substitution inert and Fe^{2+} ions catalyze the ligand exchange by electron exchange.) Thus, the separation technique was as follows: To 2 ml aqueous solution of 5×10^{-2} *M* α,α'-dipyridyl 2.0 ml sample, containing about 10^{-3} *M* iron(II) and -(III) was added. The excess dipyridyl was complexed with 2 ml of a 2×10^{-2} *M* aqueous solution of inactive Fe^{2+} and iron(III) was extracted with 5 ml chloroform containing 5 per cent *o*-oxyquinoline.

After the separation of the two phases, the activity of the phase containing iron(III) was counted. The activity of the stock solutions was adjusted so as to obtain a count-rate of about 4000 cpm with each of the samples.

Runs. Each run was started by mixing 25 ml of iron(III) solution with 25 ml of iron(II) one. The concentrations of iron ions varied from 10^{-3} to 4×10^{-3} *M* and that of hydrochloric acid from 10^{-4} to 2×10^{-3} *M*. In all runs the concentrations of $NaClO_4$ was 0.1 *M*. The two parts of the reaction mixture contained all the components except the iron ions in the same concentrations. The two solutions, containing each component except iron(II), had been deaerated by hydrogen for two hours, then solid iron(II) sulphate was added and after one hour the reaction was started.

The iron(II) concentration of the solution was controlled spectrophotometrically.

Results

The results obtained could be fitted to a rate equation being first order both in iron(II) and iron(III). By replacing $NaClO_4$ with NaCl, no effect of chloride catalysis has been observed which could be interpreted by the great stability of the iron(III) formamide complex (see the separation method).

The second order rate constants, measured at 50, 60, 70 and 80 °C, are given in Table I as the function of acidity. The large experimental errors are probably due to the applied separation method. Thus, the scattering of the measured points of the MacKay equation was unusually large for such a relatively slow reaction. A typical plot is shown in Fig. 1.

In some experiments the influence of water was tested. In 90 and 95 per cent formamide solutions the reaction is acid-catalyzed, but the increase in rate is less than twice.

As it can be concluded from the data in Table 1, there is a slight, though significant dependence of *k* on acidity. Plotting lg *k versus* —lg $[H^+]$ (Fig. 2), one gets about —0.2 for the order of hydrogen ion.

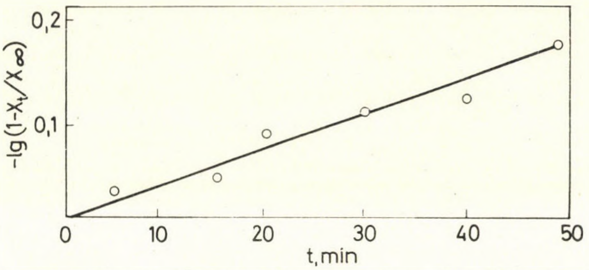

Fig. 1. Typical plot according to the MacKay equation. Iron(II): 7×10^{-4} *M*, iron(III): 1.3×10^{-3} *M*, hydrogen ion: 6×10^{-4} *M*, $NaClO_4$: 0.1 *M*, t = 50 °C

Table I

t, °C	$[H^+] \times 10^4$ *M*	$[Fe^{2+}] \times 10^4$ *M*	$[Fe^{3+}] \times 10^4$ *M*	$k \times 10^2$, lit/mole sec
50	20	9.0	11.0	4.8 ± 0.5
	20	8.2	12.6	5.2 ± 1.8
	10	7.0	14.1	4.3 ± 1.0
	8.0	9.5	10.8	6.1 ± 0.6
	6.0	7.0	13.0	7.1 ± 0.7
	2.0	8.8	12.2	6.5 ± 1.0
	1.0	8.0	12.4	8.5 ± 3.0
	1.0	8.3	11.6	6.7 ± 0.4
	1.0	17.6	12.4	7.1 ± 0.4
	1.0	35.6	23.2	5.4 ± 2.0
60	20	7.0	13.9	6.5 ± 1.9
	10	8.7	11.6	7.2 ± 0.9
	5.0	8.4	12.3	11.7 ± 1.9
	2.0	8.1	11.0	7.2 ± 0.8
	1.0	8.0	12.7	10.0 ± 0.3
70	20	9.1	11.5	9.8 ± 2.0
	10	7.2	12.3	12.3 ± 2.4
	10	8.9	12.3	11.6 ± 2.5
	5.0	7.1	10.4	7.3 ± 1.0
	5.0	6.5	13.5	9.6 ± 0.7
	2.0	8.6	11.4	11.2 ± 2.9
	2.0	8.8	11.9	10.0 ± 1.5
	1.0	7.8	12.8	12.0 ± 2.0
80	20	7.7	12.3	10.3 ± 0.9
	10	7.0	12.9	14.9 ± 1.4
	5.0	9.4	11.1	10.6 ± 2.0
	2.0	6.0	14.6	13.3 ± 1.2
	1.0	7.0	13.0	11.6 ± 2.5

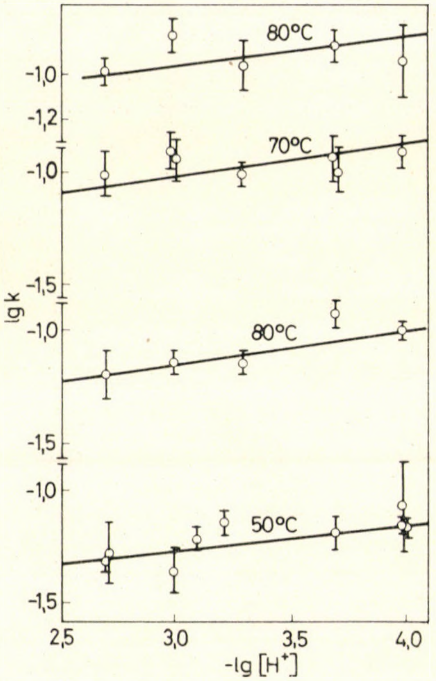

Fig. 2. Acid dependence of the rate constant at different temperatures

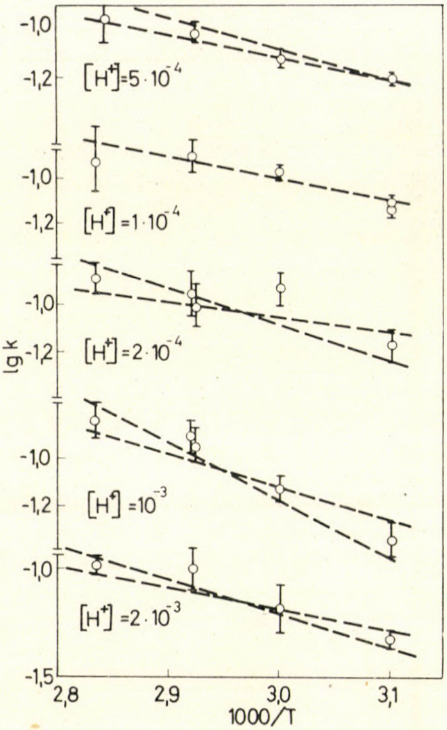

Fig. 3. Arrhenius plots at different acidities

The Arrhenius plot at different acidities shows similar uncertainty, however, the energy of activation, given in Table II, seems to be independent of acid concentration, the weight average value being 5.8 ± 1.4 kcal/mole.

Table II

Hydrogen ion concentration, *M*	E_a, kcal/mole
2×10^{-3}	5.66 ± 1.32
1×10^{-3}	8.05 ± 1.95
5×10^{-4}	5.93 ± 0.91
2×10^{-4}	5.13 ± 2.39
1×10^{-4}	5.36 ± 0.57

Discussion

The main conclusion from the results is that the reaction proceeds *much slower than in water* contrary to the predictions of the theories supposing direct transfer. These are namely the following:

The tunneling theory of EYRING *et al.* [10] results a reactant distance in the activated complex of about 4 Å for formamide medium. Since this is the approximate diameter of one formamide molecule, it suggests an inner sphere mechanism, while the whole theory has been outlined for outer sphere transfer, *i.e.* there is a fundamental contradiction.

According to the MARCUS theory [11—15], the free energy of activation is also predicted to become smaller with increasing dielectric constant. Although the smaller energy of activation is in accordance with such a lowering of the Coulombic repulsion, the large negative value of the entropy of activation, being about —41 e.u. in the case under discussion, while, in water, only —25 e.u., cannot be interpreted. According to MARCUS the entropy would depend on the temperature dependence of the dielectric constant [12]. For the $1/D$ *vs* T function has approximately the same slope for both water and formamide [27], the entropy of activation ought to be around —14 e.u. in both cases. If the difference between the calculated and observed values arises from the effect of the inner coordination sphere — for which calculation cannot be done, because their exact structure is unknown — this portion of the free energy of activation should not stand but for entropy term which is very unlikely. More or less the same discrepancies appear in the other theories of the direct transfer group [16—19] as well.

Considering the "band model", published by one of us (I.R.) [4—8], there are also some difficulties to determine the theoretical values of the enthalpy and entropy of activation, because some necessary data are unknown. This model is based on the assumption that electron transfer proceeds through the intermediate formation of H_3O or OH radical by electron or hole transfer, respectively. In formamide, the analogous species would be

$$(\mathrm{HOCNH_3})^+_{\mathrm{solvated}} + \text{electron or } (\mathrm{HOCNH})^-_{\mathrm{solvated}} + \text{hole}$$

Since the energy of these systems as well as the oxidation-reduction potential of the iron(II)—iron(III) couple are unknown, the height of the potential barrier to be overcome by the electron cannot be given.

There is still an opportunity to test the applicability of this model, since it yields a rule for the pH dependence of the rate [5]. For the top of the barrier is determined by the electronic energy corresponding to the intermediate species mentioned above, and the Fermi level of these is shifted by changing acidity, the tunneling probability and so the entropy of activation is modified at various hydrogen ion concentrations. This can be explicitly given as follows: the total entropy of activation, $\Delta S^{\ddagger}$, consists of three parts [7]:

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

where $\Delta S^{\ddagger}$ corresponds to the collision probability and is given by:

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

In this equation c_* is the so-called normalized concentration for which we have:

$$c_* = (d^3 N_A \cdot 10^{-3})^{-1}, \text{ mole/litre} \tag{3}$$

where d is the distance between the reactant ions in the activated complex and N_A is the Avogadro number. Measuring d in Å, one gets:

$$\Delta S_t^{\ddagger} = 27.32 \lg d - 29.29. \tag{4}$$

$\Delta S_i^{\ddagger}$ in Eq. (1) stands for the change in rotational degrees of freedom when forming the activated complex from the free reactants. If outer sphere transfer is assumed, we have:

$$\Delta S_i^{\ddagger} \simeq 0. \tag{5}$$

$\Delta S_e^{\ddagger}$ is the electronic transfer probability term that could be given by the tunneling formula:

$$\Delta S_e^{\ddagger} = \mathbf{R} \frac{4\pi}{\mathbf{h}} d \sqrt{2\,m\,(U - E_a \pm 2.3\,\mathbf{kT} \cdot \mathrm{pH})} \tag{6}$$

where **h** is the Planck constant, m is the mass of the electron, and E_a is the energy of activation. The barrier height, U is given for electron transfer:

$$U = E_+ - E_{\text{donor},\,e} \tag{7}$$

and for hole transfer:

$$U = E_{\text{donor},h} - E_- \tag{8}$$

where E_+ is the electronic energy due to the lionium radical (in water H_3O) E_- is that of the liate radical (OH) under standard conditions, while $E_{\text{donor},\,e}$ and $E_{\text{donor},\,h}$ are the electronic energies of the electron or hole donor reactants, respectively. The sign before the pH term in Eq. (6) is positive, when the reaction takes place, in fact, by electron transfer and negative, when hole transfer is in operation.

Unless solvolytic reaction occurs pH dependence would appear only in the entropy term of the free energy of activation, according to Eqs (1), (4), and (6). Since the energy of activation of the reaction under discussion exhibits no significant change with pH, it can likely be the case discussed above.

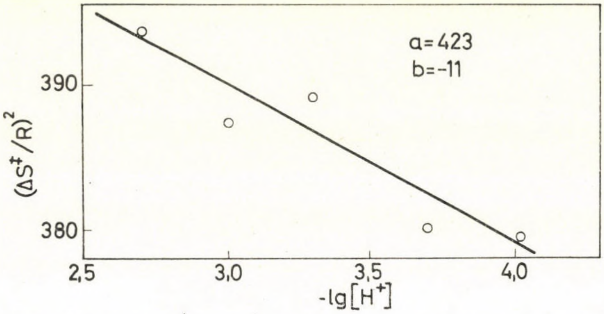

Fig. 4. The dependence of the entropy of activation on pH according to Eq. (11)

Let us introduce *a* and *b* with the following meaning:

$$a = \frac{32\,\pi^2}{\mathbf{h}^2}\, d^2 m\,(U - E_a) \tag{9}$$

and

$$b = 2.3\,\mathbf{kT}\,\frac{32\,\pi^2}{\mathbf{h}^2}\, d^2 m, \tag{10}$$

and let us suppose $\Delta S^{\ddagger}_{t}$ to be zero for the first iteration step, we have:

$$[\Delta S^{\ddagger}/R]^2 = a \pm b \cdot \mathrm{pH}. \tag{11}$$

Plotting the experimental data according to Eq. (11) a straight line is obtained (Fig. 4) the slope of which gives $d = 13.4$ Å and the intercept $U = 2.23$ e.v. Calculating $\Delta S^{\ddagger}_{t}$ from Eq. (4), one gets 1.6 e.u. that is smaller than the errors in determining the entropies, so the iteration need not be continued.

Since $d \cong 13$ Å means the presence of three formamide molecules between two iron ions, this result can be considered as a very reasonable one, because, in this case, the reactants approach each other up to the penetration of the second coordination spheres.

As it is shown in Fig. 4, the sign of *b* is negative which corresponds to the hole transfer path in analogy with the reaction in water [4].

Thus it can be stated that the band model does not contradict the experimental results, moreover the interpretation of the pH dependence yields reasonable data on the reactant distance and barrier height in the activated complex.

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CALCULATION OF THE INFLUENCE OF THE OHMIC RESISTANCE OF THE CELL IN A.C. POLAROGRAPHY IN THE CASE OF REVERSIBLE ELECTRODE REACTION

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The theoretical relationships derived for the first and second harmonic a.c. flowing through a cell under the effect of a small amplitude sinusoidal voltage superimposed on the d.c. polarizing potential in the case of a reversible polarographic reaction were amended by correction terms taking into account the ohmic resistance of the cell. Calculations according to the correction terms show that the decrease of the first and second harmonic a.c. amplitudes under the effect of the ohmic resistance of the cell is greater when the angular frequency of the a.c. voltage and the concentration of the depolarizer are increased and when the number of the electrons involved in the electrode reaction is higher. Further the difference of the d.c. potentials corresponding to the peaks of the second harmonic a.c. amplitudes is increased at increasing cell resistance. The difference is the greater the higher are the angular frequency of the a.c. voltage and the concentration of the depolarizer, further the number of electrons involved in the electrode reaction.

In a previous communication [1] we gave a theoretical treatment of the dependence of the first and second harmonic components of the alternating current flowing through the cell, when a sinusoidal voltage of small amplitude is superimposed onto the polarizing d.c. potential, upon the angular frequency and the amplitude of the a.c. voltage, the overpotential, the transfer coefficient and the exchange current density, in the case of diffusion and charge transfer polarizations. The results were discussed in detail for the case of reversible polarographic reactions. The formulas obtained for the amplitudes of the first and second harmonic a.c. current densities, i_1 and i_2, are in agreement with the data published in the literature:

$$i_1=\eta_{\sim}\left\{\left[\frac{(zF)^2}{\sqrt{2}RT}\sqrt{\omega}\left(C_{10}\sqrt{D_1}+C_{20}\sqrt{D_2}\right)\frac{\sqrt{\frac{D_2}{D_1}}\frac{C_{20}}{C_{10}}e^{\frac{zF}{RT}\eta_{=}}}{\left(1+\sqrt{\frac{D_2}{D_1}}\frac{C_{20}}{C_{10}}e^{\frac{zF}{RT}\eta_{=}}\right)^2}\right]^2+\right.$$

$$\left.+\left[\frac{(zF)^2}{\sqrt{2}RT}\sqrt{\omega}\left(C_{10}\sqrt{D_1}+C_{20}\sqrt{D_2}\right)\frac{\sqrt{\frac{D_2}{D_1}}\frac{C_{20}}{C_{10}}e^{\frac{zF}{RT}\eta_{=}}}{\left(1+\sqrt{\frac{D_2}{D_1}}\frac{C_{20}}{C_{10}}e^{\frac{zF}{RT}\eta_{=}}\right)^2}+\omega C\right]^2\right\}^{1/2} \tag{1}$$

and

$$i_2 = \eta_\sim^2 \frac{(zF)^3}{2\sqrt{2}(RT)^2}\sqrt{\omega}\,(C_{10}\sqrt{D_1} + C_{20}\sqrt{D_2})\,\cdot$$

$$\cdot\,\frac{\sqrt{\dfrac{D_2}{D_1}\dfrac{C_{20}}{C_{10}}}\,e^{\frac{zF}{RT}\eta_=}\cdot\left|1 - \sqrt{\dfrac{D_2}{D_1}\dfrac{C_{20}}{C_{10}}}\,e^{\frac{zF}{RT}\eta_=}\right|}{\left(1 + \sqrt{\dfrac{D_2}{D_1}\dfrac{C_{20}}{C_{10}}}\,e^{\frac{zF}{RT}\eta_=}\right)^3}\,. \qquad (2)$$

where D_1 and D_2 and C_{10} and C_{20} are the diffusion coefficients and the concentrations in the bulk of the solution of the reduced and oxidized forms, respectively, of the component taking part in the electrode reaction, z is the number of electrons involved in the electrode reaction, ω is the angular frequency of the a.c. voltage, $\eta_\sim$ is the amplitude of the a.c. voltage, $\eta_=$ is the time average value of the overpotential, T is the temperature on the Kelvin scale, R is the universal gas constant, F is the Faraday constant and C is the capacity of the double layer.

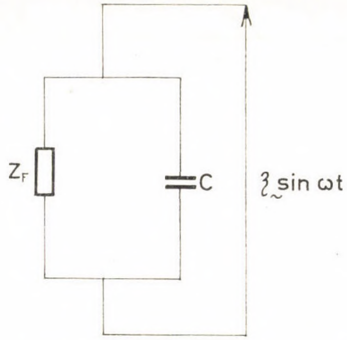

Fig. 1. Equivalent circuit of the electrode, the cell resistance being equal to zero

These equations are valid only when the a.c. voltage, $\eta_\sim$ sin ωt, superimposed on the polarizing potential, appears without any distortion on the electrode impedance composed of the faradaic impedance Z_F and the capacity of the double layer C connected parallelly (Fig. 1). However, the total a.c. voltage η^0 sin ωt imposed on the cell is not applied to the electrode impedance since a considerable ohmic drop arises on the ohmic resistance of the solution and of the electrode as well as on that of the measuring instrument employed for the current measurement. Denoting the sum of these resistances by R_0, the cell can be represented by the equivalent circuit shown in Fig. 2.

The resistance R_0 can be decreased by employing a supporting electrolyte of relatively high conductivity and using a potentiostat for the measurements. The cell composed of three electrodes used in potentiostatic measurements renders possible the compensation for the effect of the external resistances connected to the cell and allows for the regulation of the potential of the working electrode independently from the potential drop caused by the current flowing through the resistance of the solution between the electrode under investigation and the auxiliary electrode. However, the ohmic drop on the solution between the tip of the Luggin capillary connected to the reference electrode and the electrode under investigation cannot be compensated. It is theoretically impossible to attain that R_0 be zero, since by increasing frequency of the a.c. voltage even when R_0 is very small it becomes commensurable to the electrode impedance and thus the ohmic drop is no more negligible. Therefore the experimental data can be compared to theory only if the expressions given by Eqs (1) and (2) are corrected for the ohmic drop appearing on R_0.

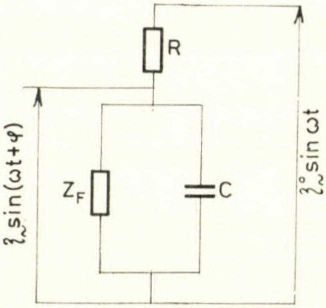

Fig. 2. Equivalent circuit of the electrode in the case of cell resistance *R*

Several authors attempted to correct for the ohmic potential drop on the resistance R_0. Delahay and Adams [2] derived a graphical method to account for this factor. Schmidt and Stackelberg [3] employed a correction term neglecting the faradaic impedance and taking into consideration only the potential drop arising on the resistance of the solution (R_0) and the capacity of the double layer (C). Bauer and Elving [4] apply an approximate correction not accounting for the phase angle difference between the voltages appearing on the resistance R_0 and the electrode impedance.

The correction terms described in the above papers apply only to the first harmonic component (of angular frequency ω) of the a.c. current flowing through the electrode.

In the present paper we derive correction terms for Eqs (1) and (2) relating to the first and second harmonic a.c. current densities taking into account the cell impedance precisely.

The correction term relating to the first harmonic a.c. current density can easily be derived, noting (*cf.* Fig. 2) that the a.c. voltage amplitude $\eta_\sim$ in Eq. (1) appearing on the double layer can be calculated from the a.c. voltage amplitude applied to the cell if the voltage divider formed by R_0, Z_F and C is known.

$$\left|\frac{\eta_{\sim}}{\eta_{\sim}^{0}}\right| = \left|\frac{\dfrac{Z_F\dfrac{1}{j\omega C}}{Z_F+\dfrac{1}{j\omega C}}}{R_0+\dfrac{Z_F\dfrac{1}{j\omega C}}{Z_F+\dfrac{1}{j\omega C}}}\right| = \frac{1}{\left|1+R_0\left(\dfrac{1}{Z_F}+j\omega C\right)\right|}\,, \tag{3}$$

where $j=\sqrt{-1}$ and $\dfrac{1}{Z_F}$ is the faradaic admittance,

$$\frac{1}{Z_F}=\frac{1}{R_P}+j\omega C_P \tag{4}$$

i.e. the resultant of the polarization resistance R_P and the pseudocapacity C_P in parallel connection. The latter terms can be derived from Eq. (1) since the quotient of the amplitudes of the a.c. potential and a.c. current yields the absolute value of the electrode impedance formed by the parallel connection of the faradaic admittance and the double layer capacity. Thus

$$\left|\frac{i_1}{\eta_{\sim}}\right| = \left|\frac{1}{Z_e}\right| = \left|\frac{1}{Z_F}+j\omega C\right| = \sqrt{\left(\frac{1}{R_P}\right)^2+(\omega C_P+\omega C)^2}\,. \tag{5}$$

Whence comparing Eqs (1) and (5)

$$\frac{1}{R_p}=\omega C_p=\frac{(zF)^2}{\sqrt{2}RT}\sqrt{\omega}(C_{10}\sqrt{D_1}+C_{20}\sqrt{D_2})\,\frac{\sqrt{\dfrac{D_2}{D_1}\dfrac{C_{20}}{C_{10}}e^{\frac{zF}{RT}\eta_{=}}}}{\left(1+\sqrt{\dfrac{D_2}{D_1}\dfrac{C_{20}}{C_{10}}e^{\frac{zF}{RT}\eta_{=}}}\right)^2}\,. \tag{6}$$

Now Eqs (4) and (6) are introduced into Eq. (3):

$$\eta_{\sim}=\frac{\eta_{\sim}^{0}}{\left|\left(1+\dfrac{R_0}{R_P}\right)+j\left(\dfrac{R_0}{R_P}+\omega R_0 C\right)\right|}=\frac{\eta_{\sim}^{0}}{\sqrt{\left(1+\dfrac{R_0}{R_P}\right)^2+\left(\dfrac{R_0}{R_P}+\omega R_0 C\right)^2}}\,. \tag{3a}$$

Thus Eq. (1) relating to the first harmonic component of the a.c. current density takes the following form:

$$i_1 = \eta^0_\sim \frac{\sqrt{\left(\frac{1}{R_P}\right)^2 + \left(\frac{1}{R_P} + \omega C\right)^2}}{\sqrt{\left(1 + \frac{R_0}{R_P}\right)^2 + \left(\frac{R_0}{R_P} + \omega R_0 C\right)^2}} \,. \tag{1a}$$

Two effects are to be taken into account in order to obtain the correction term relating to the second harmonic component of the a.c. current density:

a) first, the decrease of the a.c. voltage amplitude according to Eq. (3) is to be considered. Thus introducing Eq. (3a) into Eq. (2) we obtain the corrected term i_2^*

$$i_2^* = \frac{(zF)^3}{2\sqrt{2}\,(RT)^2} \sqrt{\omega}\,(C_{10}\sqrt{D_1} + C_{20}\sqrt{D_2}) \frac{\sqrt{\frac{D_2}{D_1}\frac{C_{20}}{C_{10}}}\, e^{\frac{zF}{RT}\eta_=} \cdot \left|1 - \sqrt{\frac{D_2}{D_1}\frac{C_{20}}{C_{10}}}\, e^{\frac{zF}{RT}\eta_=}\right|}{\left(1 + \sqrt{\frac{D_2}{D_1}\frac{C_{20}}{C_{10}}}\, e^{\frac{zF}{RT}\eta_=}\right)^3} \cdot \tag{2a}$$

$$\cdot \frac{\eta^{0^2}_\sim}{\left(1 + \frac{R_0}{R_P}\right)^2 + \left(\frac{R_0}{R_P} + \omega R_0 C\right)^2} ;$$

b) moreover, i_2^* is further decreased under the shunting effect of the resistance R_0. In order to account for this effect the equivalent circuit of the cell has to be transformed in view of the second harmonic component (Fig. 3).

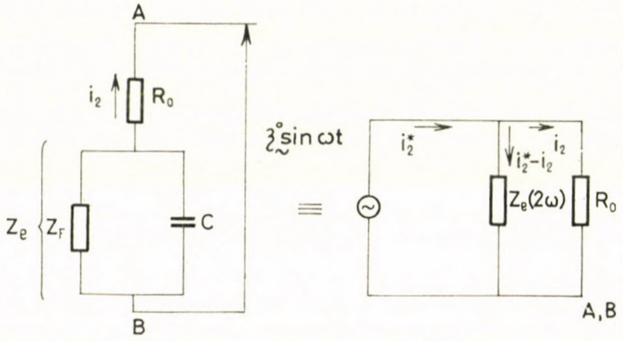

Fig. 3. Equivalent circuit of the electrode relating to the second harmonic component of the a.c. current

A sine-wave voltage of angular frequency ω that does not contain higher harmonic components is imposed onto the points *A* and *B* of the cell *i.e.* onto the resultant of R_0 and Z_e connected in series. Thus *A* and *B* are at equal potentials as far as the second harmonic a.c. component is concerned and they can be considered as short circuited in the equivalent circuit. Accordingly, in this case the resistance R_0 and the electrode impedance Z_e (2ω) can be represented in parallel connection. The electrode impedance $Z_e\ (2\omega)$ is given by the following formula

$$\frac{1}{Z_e(2\omega)} = \frac{1}{Z_p(2\omega)} + j2\omega C, \tag{7}$$

i.e. it is defined as in Eq. (5) but at the angular frequency 2ω of the second harmonic. The appearance of the second harmonic component in the a.c. current flowing through the cell is a consequence of the non-linearity of the electrode impedance, thus the latter can be represented as a current generator producing a current i_2^* and having an internal resistance equal to $Z_e\ (2\omega)$. According to the equivalent circuit of Fig. 3, taking into consideration Kirchoff's law, we have

$$i_2 R_0 = (i_2^* - i_2) Z_e(2\omega),$$

where i_2 is the second harmonic current flowing through the electrode. Hence

$$i_2 = \frac{|\,i_2^*\,|}{1 + \dfrac{R_0}{Z_e(2\omega)}} = \frac{i_2^*}{1 + \dfrac{R_0}{R_P(2\omega)} + j\left(\dfrac{R_0}{R_p} + 2\omega R_0 C\right)},$$

and thus the absolute value of the second harmonic current density is

$$|\,i_2\,| = \frac{|\,i_2^*\,|}{\sqrt{\left(1 + \dfrac{R_0}{R_p(2\omega)}\right)^2 + \left(\dfrac{R_0}{R_p(2\omega)} + 2\omega R_0 C\right)^2}}. \tag{8}$$

Finally uniting the correction terms derived in paragraphs *a)* and *b)* we obtain

$$|i_2| = \frac{(zF)^3}{2\sqrt{2}(RT)^2}\sqrt{\omega}(C_{10}\sqrt{D_1} + C_{20}\sqrt{D_2}) \frac{\sqrt{\dfrac{D_2}{D_1}\dfrac{C_{20}}{C_{10}}\,e^{\frac{zF}{RT}\eta_=}} \cdot \left|1 - \sqrt{\dfrac{D_2}{D_1}\dfrac{C_{20}}{C_{10}}\,e^{\frac{zF}{RT}\eta_=}}\right|}{\left(1 + \sqrt{\dfrac{D_2}{D_1}\dfrac{C_{20}}{C_{10}}\,e^{\frac{zF}{RT}\eta_=}}\right)^3} \cdot \tag{2b}$$

$$\cdot \frac{\eta_\sim^{0^2}}{\left[\left(1 + \dfrac{R_0}{R_p(\omega)}\right)^2 + \left(\dfrac{R_0}{R_p(\omega)} + \omega R_0 C\right)^2\right]\sqrt{\left(1 + \dfrac{R_0}{R_p(2\omega)}\right)^2 + \left(\dfrac{R_0}{R_p(2\omega)} + 2\omega R_0 C\right)^2}} \cdot$$

Formulas (1a) and (2b) represent the amplitude of the first and second harmonic a.c. current densities resp. flowing through the cell under the effect of a sine wave a.c. voltage of amplitude $\eta_\sim^0$, superimposed on the direct potential $\eta_=$ as a function of z, C_{10}, C_{20}, $\sqrt{\omega}$, $\eta_=$, $\eta_\sim^0$ and R_0.

It is convenient to rewrite Eqs (1a) and (2b) by introducing the variable $\Delta\eta = \eta_= - \eta_{1/2}$ instead of the overpotential $\eta_=$ where $\eta_{1/2}$ is the polarographic half-wave potential defined by (*cf.* DELAHAY [5]):

$$\eta_{1/2} = \frac{RT}{zF}\ln\frac{C_{10}}{C_{20}} + \frac{RT}{zF}\ln\sqrt{\frac{D_1}{D_2}}\,.$$

Thus Eqs (6) and (2b) take the following form

$$\frac{1}{R_p} = \omega C_p = \frac{(zF)^2}{\sqrt{2RT}}\sqrt{\omega}\left(C_{10}\sqrt{D_1} + C_{20}\sqrt{D_2}\right)\frac{e^{\frac{zF}{RT}(\eta_{=}-\eta_{1/2})}}{\left(1 + e^{\frac{zF}{RT}(\eta_{=}-\eta_{1/2})}\right)^2}\,; \tag{6a}$$

$$|i_2| = \frac{(zF)^3}{2\sqrt{2}(RT)^2}\sqrt{\omega}\left(C_{10}\sqrt{D_1} + C_{20}\sqrt{D_2}\right)\frac{e^{\frac{zF}{RT}(\eta_{=}-\eta_{1/2})}\cdot\left|1 - e^{\frac{zF}{RT}(\eta_{=}-\eta_{1/2})}\right|}{\left(1 + e^{\frac{zF}{RT}(\eta_{=}-\eta_{1/2})}\right)^3}\,. \tag{2c}$$

$$\cdot\frac{\eta_{\sim}^{0^2}}{\left[\left(1+\frac{R_0}{R_p(\omega)}\right)^2 + \left(\frac{R_0}{R_p(\omega)} + \omega R_0 C\right)^2\right]\cdot\sqrt{\left(1+\frac{R_0}{R_p(2\omega)}\right)^2 + \left(\frac{R_0}{R_p(2\omega)} + 2\omega R_0 C\right)^2}}\,.$$

Calculations were made in order to evaluate Eqs (1a) and (2c) since the formulas containing many variables are rather complicated. The results of these calculations are represented in Figs 4 to 13 plotted as a function of each variable. (For sake of convenience the values $D = 1\cdot10^{-5}$ cm^2 sec^{-1} and $\eta_{\sim}^{0} = 1\cdot10^{-2}$ V were assumed.)

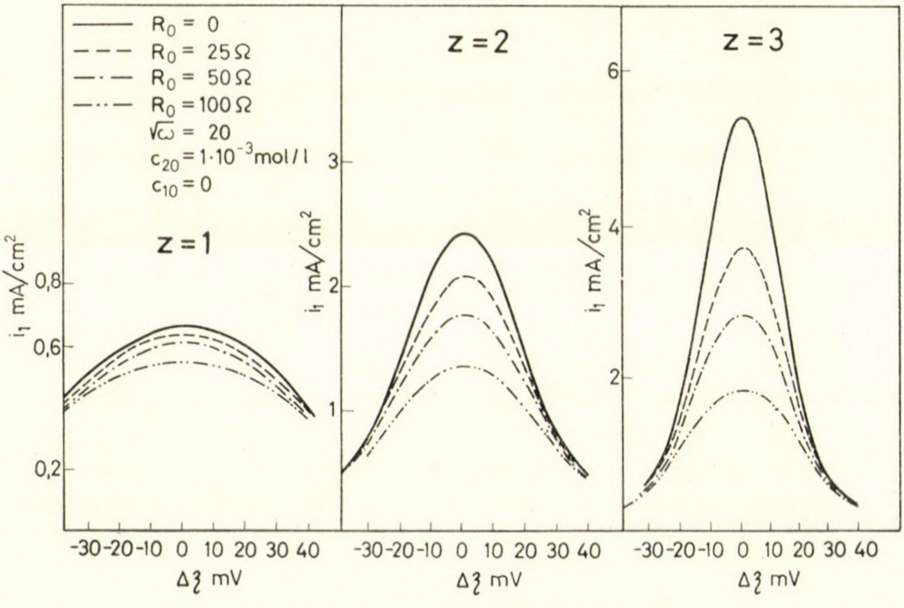

Fig. 4. The current density of the first harmonic a.c. component (i_1) plotted *vs.* the d.c. potential for $R_0 = 0$,25, 50 and 100 Ohm resp. ($C_{10}=0$, $C_{20} = 1\cdot10^{-3}$ mole/l and $\sqrt{\omega} = 20$.) a) $z = 1$; b) $z = 2$; c) $z = 3$

Fig. 4 shows the amplitude of the first harmonic a.c. component as a function of $\Delta\eta_{=}$ in case of $z = 1, 2$ and 3 resp. for $R_0 = 0, 25, 50$ and $100\ \Omega$ resp. while $C_{10} = 0$, $C_{20} = 1 \cdot 10^{-3}$ mole/1, $\sqrt{\omega} = 20$. It is apparent from Fig. 4 that the amplitude of the first harmonic a.c. current density decreases by increasing R_0 and z. This result is easily understood on the basis of Eqs (3a) and (6a) since the voltage amplitude appearing on the double layer is decreasing when z and R_0 are increased.

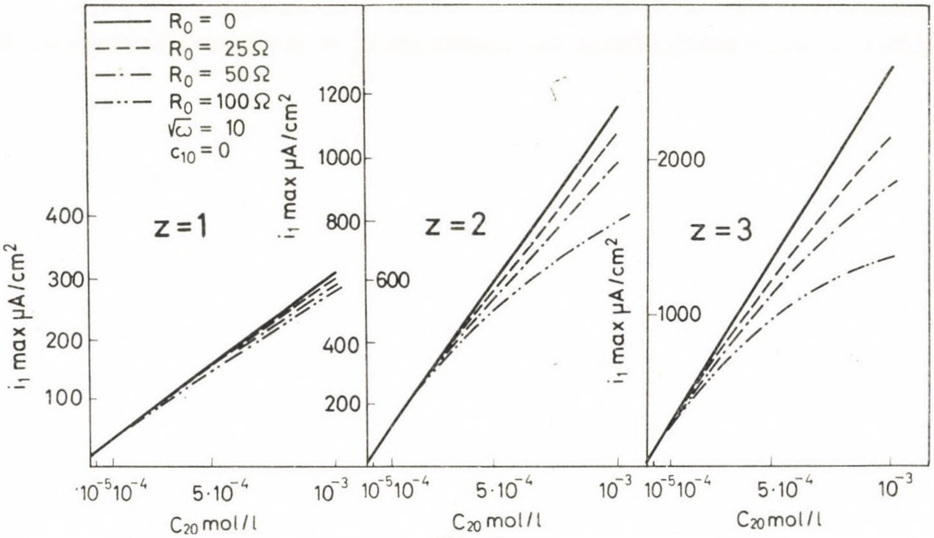

Fig. 5a

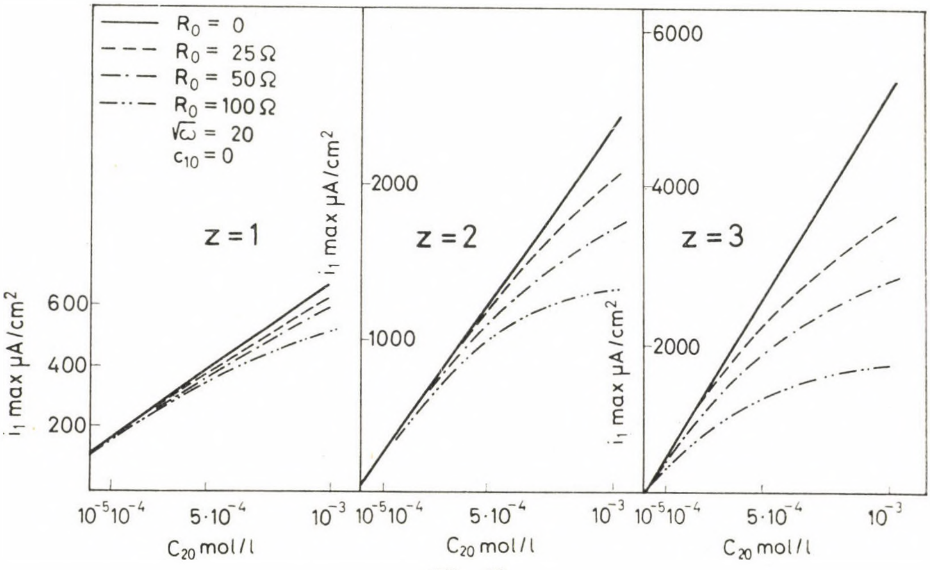

Fig. 5b

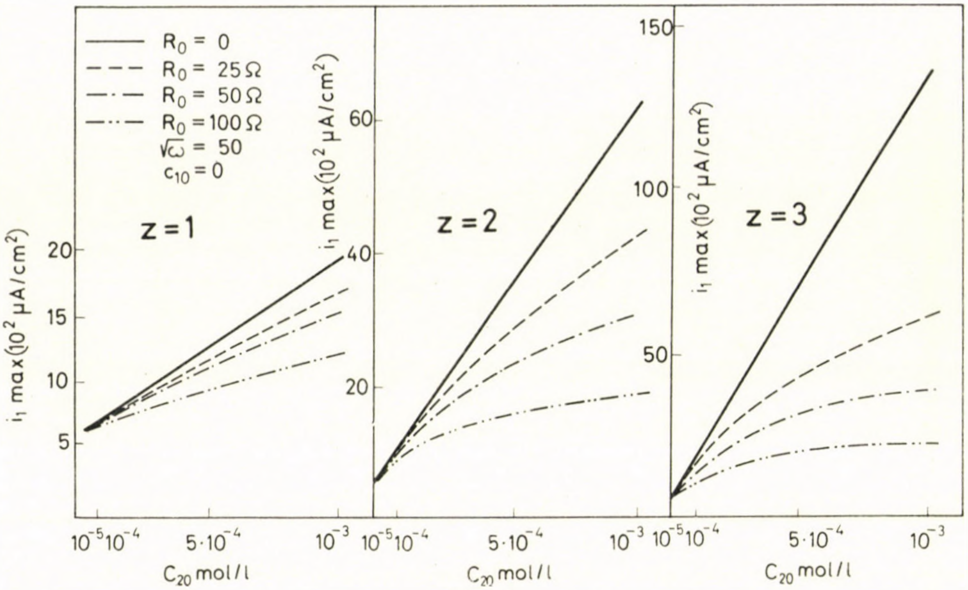

Fig. 5c

Fig. 5. The maximum of the current density of the first harmonic a.c. component ($i_1^{\max}$) plotted *vs.* the concentration C_{20} ($C_{10} = 0$) for $R_0 = 0$, 25, 50 and 100 Ohm resp. a) $\sqrt{\omega} = 10$ and $z = 1$, 2, and 3, resp. b) $\sqrt{\omega} = 20$ and $z = 1$, 2, and 3, resp. c) $\sqrt{\omega} = 50$ and $z = 1$, 2, and 3, resp.

Figs 5 and 6 represent the maximum values of the first harmonic a.c. component $i_1^{\max}$ as a function of the concentration C_{20} and the square root of the angular frequency $\sqrt{\omega}$, respectively, for different values of R_0. It is apparent that at low concentrations and low frequencies the deviation from the curve pertaining to $R_0 = 0$ is small, however, by increasing the frequency and the concentration the deviation from the theoretical values will be the greater the higher R_0 is. It is noteworthy that $i_1^{\max}$ tends to a limiting value by increasing frequency since, considering Eq. (1a)

$$\lim_{\omega\to\infty} i_1 = \lim_{\omega\to\infty} \eta^0_\sim \frac{\sqrt{\left(\frac{1}{R_p}\right)^2+\left(\frac{1}{R_p}+\omega C\right)^2}}{\sqrt{\left(1+\frac{R_0}{R_p}\right)^2+\left(\frac{R_0}{R_p}+\omega R_0 C\right)^2}} = \frac{\eta^0_\sim}{R_0},$$

i.e. at sufficiently high frequencies the electrode impedance is practically short-circuited by the impedance $\frac{1}{\omega C}$ of the double layer capacity C and thus the current is only determined by the resistance R_0.

The lower frequencies are needed for this effect the higher are the concentration of the solution as well as the number of electrons involved in the cell reaction.

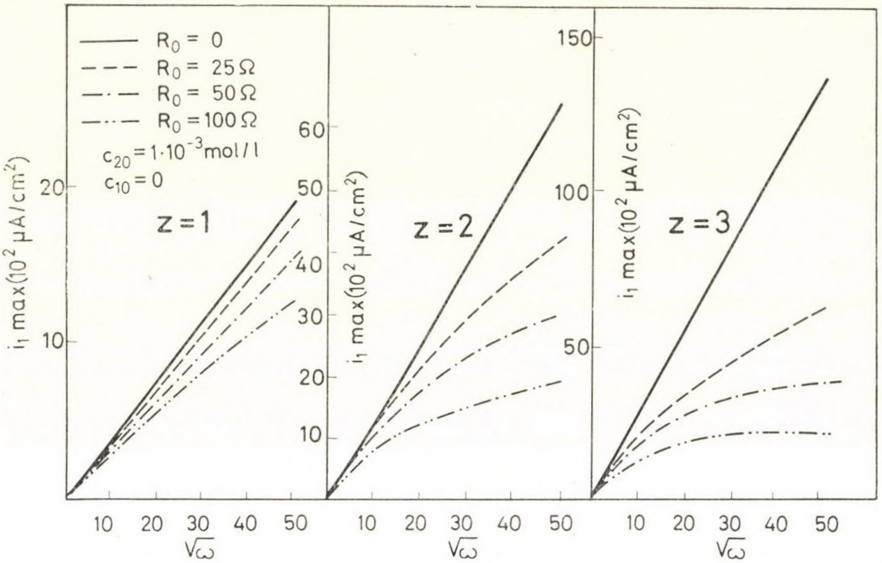

Fig. 6a

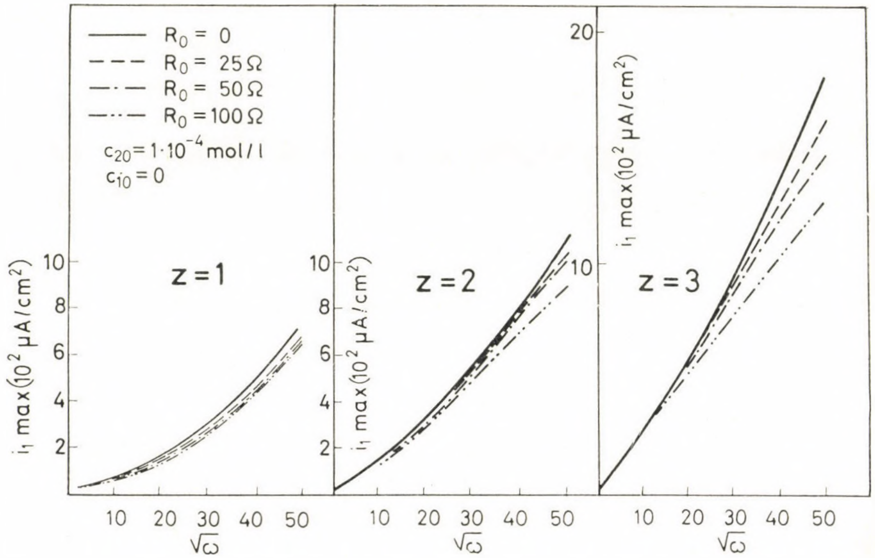

Fig. 6b

Fig. 6. The maximum of the current density of the first harmonic a.c. component ($i_1^{\max}$) plotted *vs.* the square root of the angular frequency of the a.c. voltage for $R_0 = 0$, 25, 50 and100 Ohm resp. a) $C_{20} = 1 \cdot 10^{-3}$ mole/l ($C_{10} = 0$) and $z = 1$, 2, and 3, resp. b) $C_{20} = 1 \cdot 10^{-4}$ mole/l ($C_{10} = 0$) and $z = 1$, 2, and 3, resp.

It is noteworthy that at low concentrations $i_1^{\max}$ is proportional to the angular frequency instead of the square root of the latter even at low frequencies. This phenomenon can be explained if we consider that in the present case the faradaic current is negligible as compared to the current flowing through the double layer capacity the latter being proportional to the angular frequency.

In Fig. 7 the amplitude of the second harmonic component of the a.c. current density i_2 is plotted as a function of the d.c. potential for the theoretical case when $R_0 = 0$ at a given concentration and frequency.

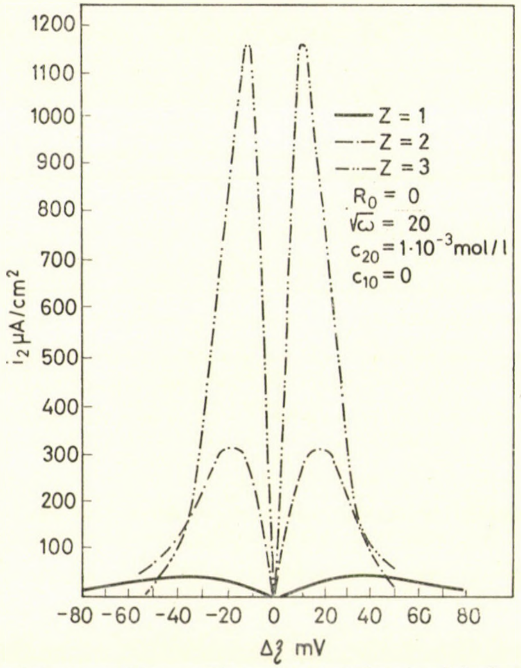

Fig. 7. The amplitude of the second harmonic a.c. current density (i_2) plotted *vs.* the d.c. potential for $z = 1$, 2 and 3 resp. in the case of $C_{10} = 0$, $C_{20} = 1 \cdot 10^{-3}$ mole/l, $\sqrt{\omega} = 10$ and $R_0 = 0$

Fig. 8 shows the deformation of the curves in Fig. 7 under the influence of R_0 in the case of $\sqrt{\omega} = 20$. It is apparent that at low concentrations the effect is hardly noticeable, however, i_2 is decreasing and the difference in the potentials corresponding to the maximum amplitudes and the half-wave potential is increasing at higher concentrations. The phenomenon becomes more pronounced at higher values of z.

Fig. 9 represents the same effect at higher and lower frequencies ($\sqrt{\omega} = 10$ and $\sqrt{\omega} = 50$), respectively. It is apparent that the decrease in i_2 as well as the increase in the difference of the peak potential, and the half-wave potential at higher frequencies are the greater the larger are the values of R_0 and z.

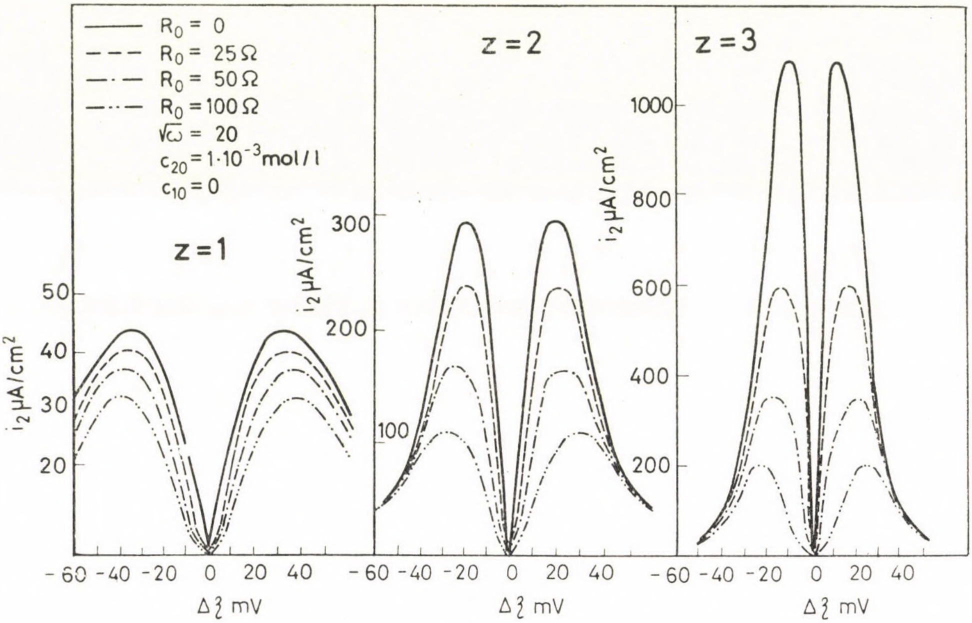

Fig. 8a

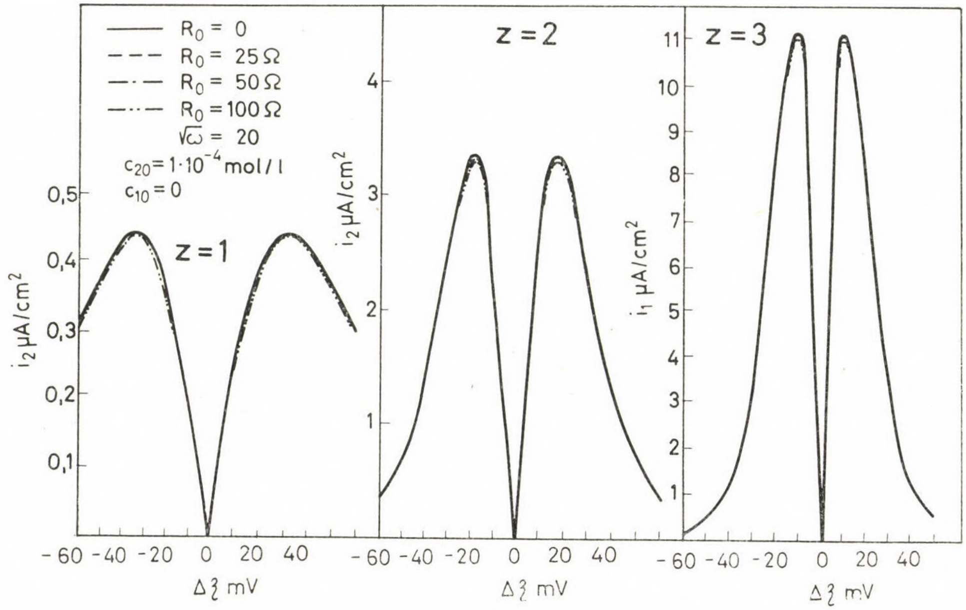

Fig. 8b

Fig. 8. The amplitude of the second harmonic a.c. current density (i_2) plotted *vs.* the d.c. potential in the case of $\sqrt{\omega} = 20$, for $R_0 = 0$, 25, 50 and 100 Ohm, resp. a) $C_{20} = 1 \cdot 10^{-3}$ mole/l, ($C_{10} = 0$) and $z = 1$, 2 and 3, resp. b) $C_{20} = 1 \cdot 10^{-4}$ mole/l, ($C_{10} = 0$) and $z = 1$, 2 and 3, resp.

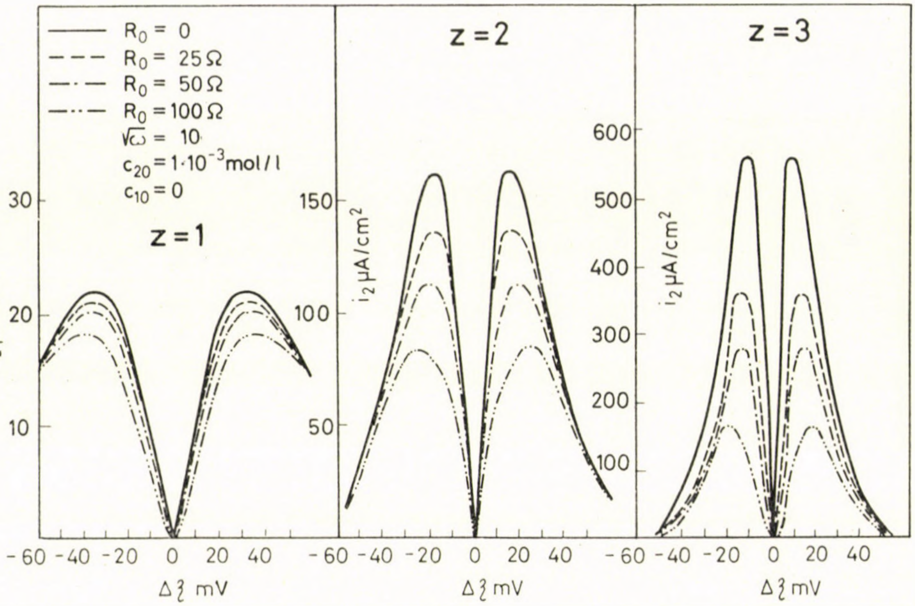

Fig. 9a

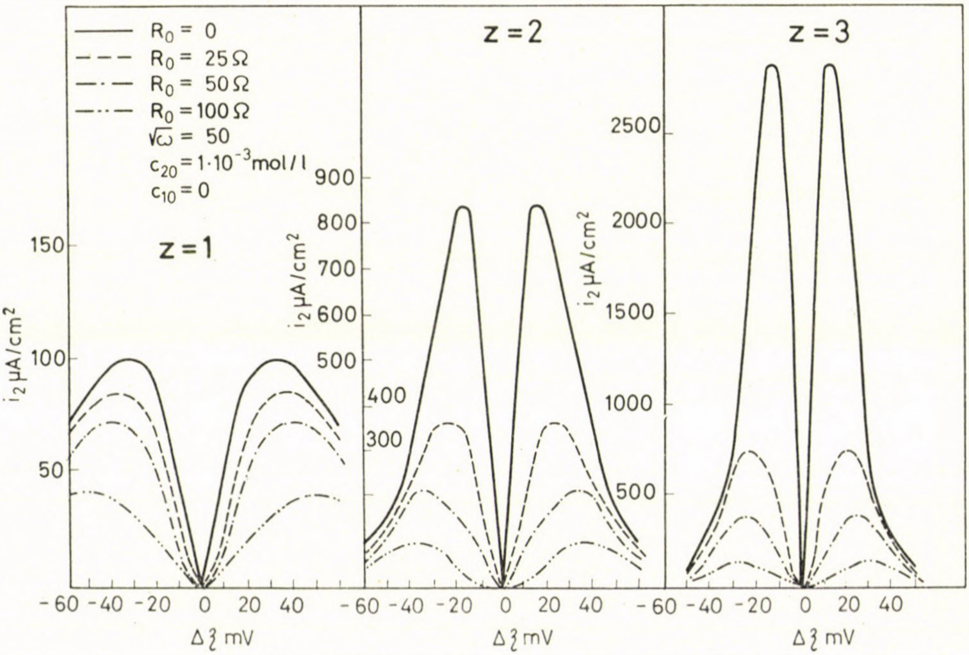

Fig. 9b

Fig. 9. **The amplitude of the second harmonic a.c. current density (i_2) plotted *vs.* the d.c. potential for $R_0 = 0$, 25, 50 and 100 Ohm resp. a) $\sqrt{\omega} = 10$ and $z = 1$, 2 and 3, resp. b) $\sqrt{\omega} = 50$ and $z = 1$, 2 and 3, resp.**

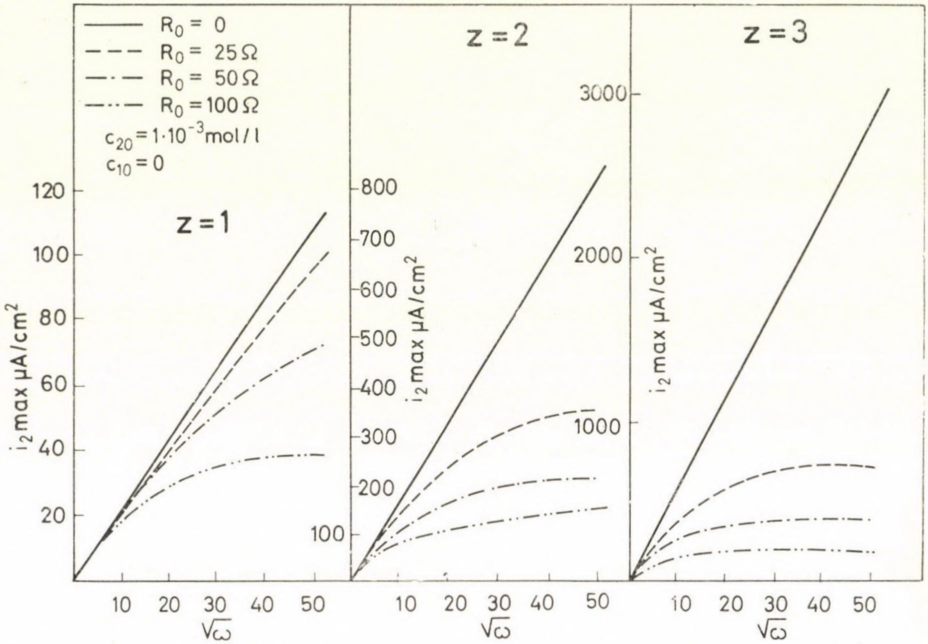

Fig. 10. The maximum amplitude of the second harmonic a.c. current density (i_2^{max}) plotte *vs.* the square root of the angular frequency for $R_0 = 0$, 25, 50 and 100 Ohm, resp. ($C_{10} = 0$ $C_{20} = 1 \cdot 10^{-3}$ mole/l) a) $z = 1$; b) $z = 2$; c) $z = 3$

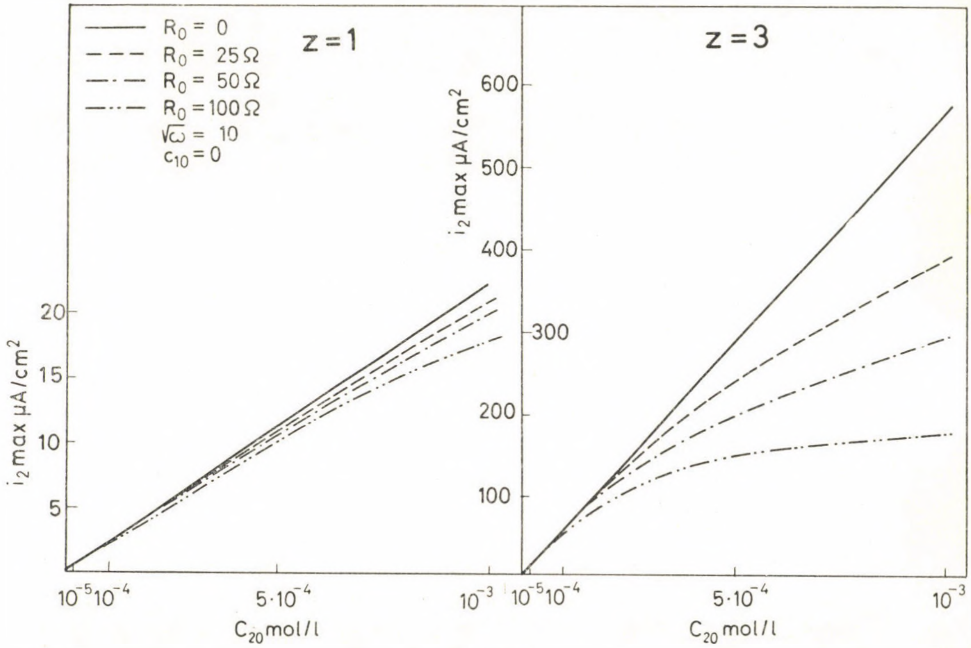

Fig. 11a

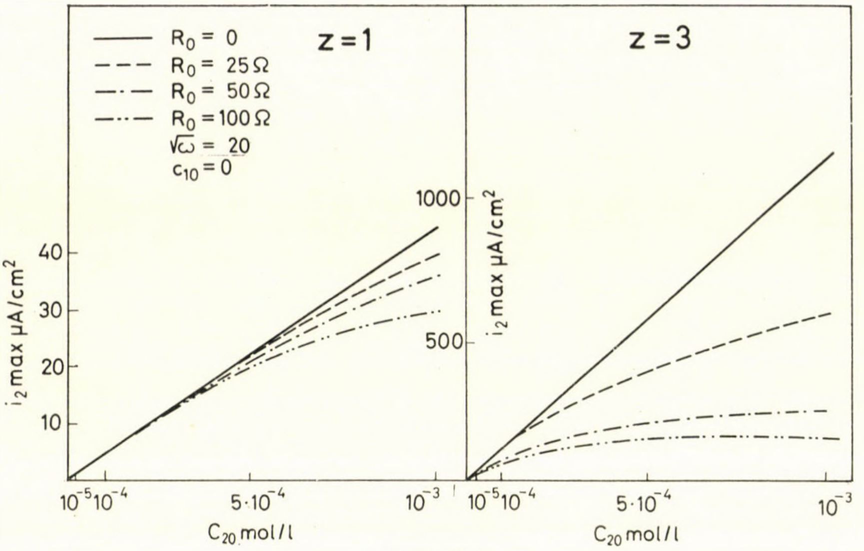

Fig. 11b

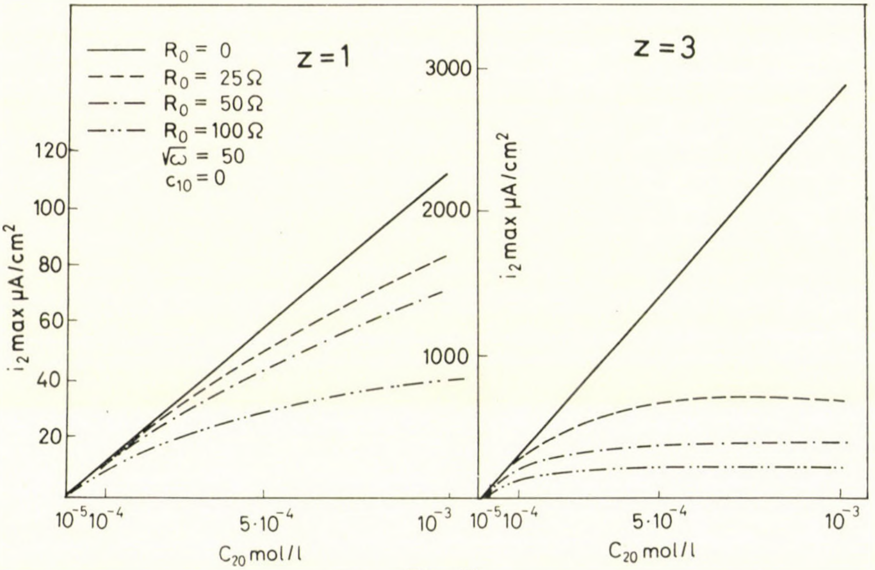

Fig. 11c

Fig. 11. The maximum amplitude of the second harmonic a.c. current density $(i_2^{\max})$ plotted *vs.* the concentration C_{20} $(C_{10} = 0)$ for $R_0 = 0$, 25, 50 and 100 Ohm, resp. a) $\sqrt{\omega} = 10$ and $z = 1$ and 3; b) $\sqrt{\omega} = 20$ and $z = 1$ and 3; c) $\sqrt{\omega} = 50$ and $z = 1$ and 3

Figs 10 and 11 represent the maximum amplitudes $(i_2^{\max})$ of the second harmonic a.c. component plotted as a function of the frequency and of the concentration, respectively. The deviation from the theoretical values (*i.e.* when $R_0 = 0$) is increasing by increasing values of R_0, z and $\sqrt{\omega}$.

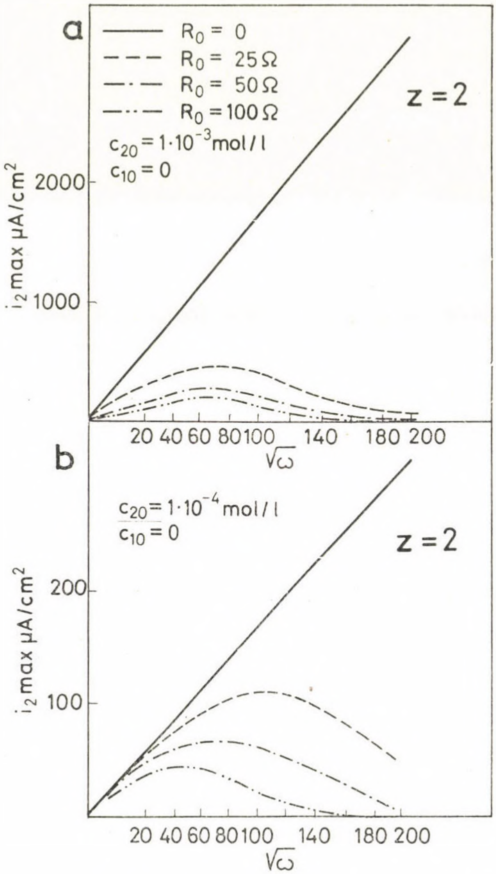

Fig. 12. The maximum amplitude of the second harmonic a.c. current density ($i_2^{\max}$) plotted *vs.* the square root of the angular frequency of a.c. voltage in case of $z = 2$ and for $R_0 = 0$, 25, 50 and 100 Ohm, resp. a) $C_{20} = 1 \cdot 10^{-3}$ mole/l, $C_{10} = 0$; b) $C_{20} = 1 \cdot 10^{-4}$ mole/l, $C_{10} = 0$

It is noteworthy that the ohmic correction becomes very significant at high frequencies ($\sqrt{\omega} = 100$, $\sqrt{\omega} = 200$), since the faradaic impedance is short-circuited by the impedance of the double layer capacity and thus the second harmonic component of the a.c. current flowing through the electrode tends to zero. Hence maximum values of the amplitudes of the current density ($\dot{i}_2^{\max}$) plotted as a function of the square root of the angular frequency exhibit a maximum in the case of $R_0 \neq 0$. Fig. 12 represents the values of $\dot{i}_2^{\max}$ plotted as a function of $\sqrt{\omega}$ at various values of R_0 when $z = 2$ and $C_{20} = 1 \cdot 10^{-3}$ mole/l and $1 \cdot 10^{-4}$ mole/l resp.

In Figs 13 and 14 the difference of the potentials corresponding to the maximum of the amplitudes of the second harmonic a.c. current density and the halfwave potential is plotted as a function of the concentration and of the frequency, respectively. No deviation is found from the theoretical value

$0.034/z$ V [1] at low concentrations even at $\sqrt{\omega} = 50$ and $R_0 = 100$; the deviation from this value, however, is increasing at higher concentrations when R_0, z and $\sqrt{\omega}$ are increased. These data support the results of Brown *et al.* [9] while according to Bauer and Foo [6] the value of $0.034/z$ is independent from the conductivity of the supporting electrolyte and the capacity of the double layer. This statement is valid at sufficiently low frequencies and concentrations only.

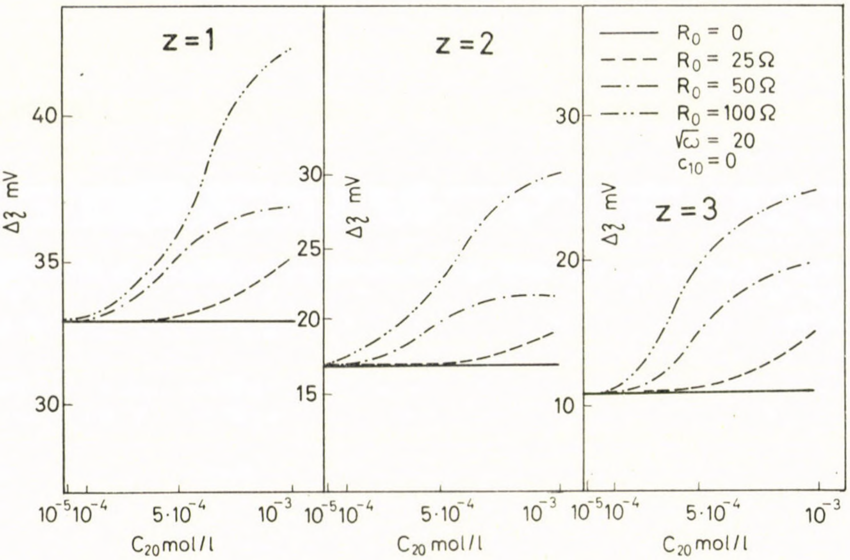

Fig. 13a

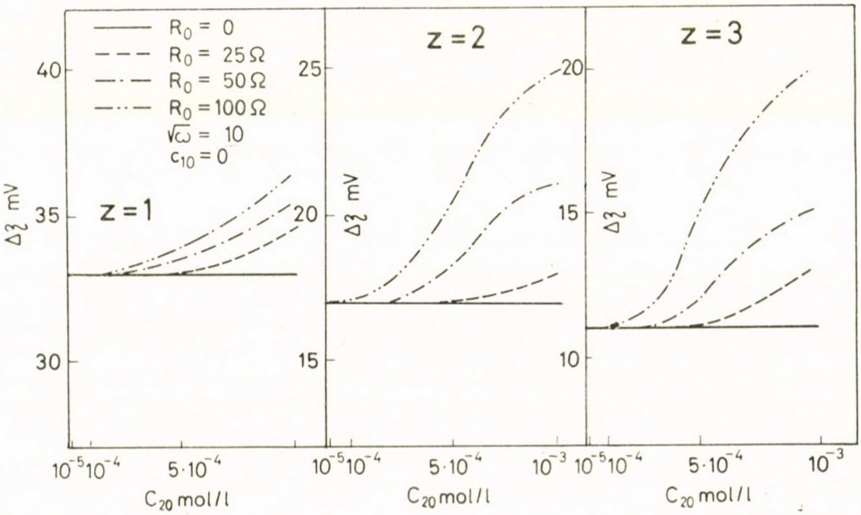

Fig. 13b

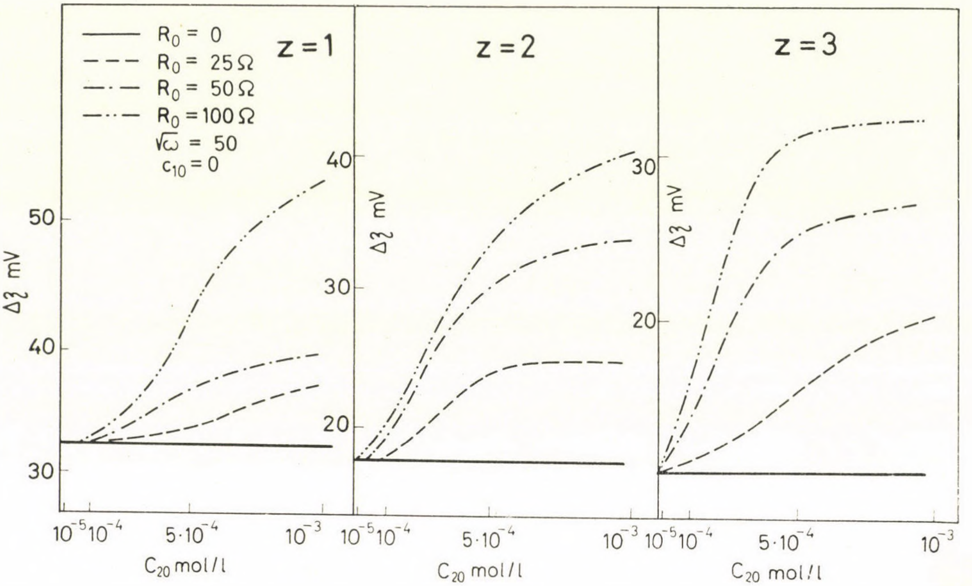

Fig. 13c

Fig. 13. Deviation of the potential corresponding to the maximum amplitude of the second harmonic a.c. current density from the theoretical value, 0.034/z, plotted as a function of the concentration C_{20} ($C_{10} = 0$), for $R_0 = 0$, 25, 50 and 100 Ohm, resp. a) $\sqrt{\omega} = 10$ and $z = 1$, 2 and 3, resp. b) $\sqrt{\omega} = 20$ and $z = 1$, 2 and 3, resp. c) $\sqrt{\omega} = 50$ and $z = 1$, 2 and 3, resp.

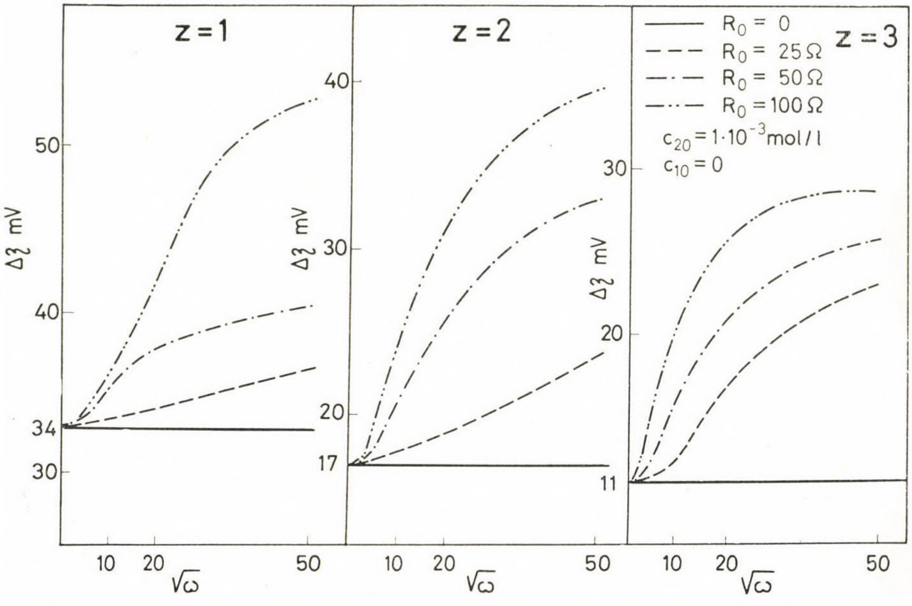

Fig. 14. Deviation of the potential corresponding to the maximum amplitude of the second harmonic a.c. current density from the theoretical value, 0.034/z plotted as a function of the square root of the angular frequency of a.c. voltage, for $R_0 = 0$, 25, 50 and 100 Ohm, resp. ($C_{10} = 0$, $C_{20} = 1 \cdot 10^{-3}$ mole/l.) a) $z = 1$; b) $z = 2$; c) $z = 3$

Our calculations led to the conclusion that the ohmic drop appearing on the resistance R_0 is considerably altering the theoretical relationships represented by Eqs (1) and (2). These deviations are negligible at low frequencies and low concentrations only, provided that R_0 is sufficiently low.

Hence, it is advisable to employ a low-resistance cell in a.c. polarography in order to obtain a linear relationship between the concentration of the depolarizer and the harmonic components of the a.c. current as suggested by BREYER and BAUER [7] as well as by other workers [2, 3, 8, 9]. To this end it is preferable to select a supporting electrolyte having high conductivity and to employ a dropping mercury electrode of low resistance [8]. Further the a.c. voltage superimposed on the d.c. polarizing potential is to be applied by means of a potentiostat (*i.e.* the potential appearing between the reference and the measuring electrode should always be the sum of the d.c. potential and the sine-wave a.c. voltage) since in this case the resistance R_0 is practically composed of the resistance of the solution between the tip of the reference electrode and the measuring electrode, further of the resistance of the dropping mercury electrode.

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KINETISCHE ANALYSE EINIGER FOLGEREAKTIONEN, IV

DIE KONKURRENTEN FOLGEREAKTIONSSYSTEME $A \rightarrow C$, $A + C \rightarrow E$ UND $A + B \rightarrow C$, $A + C \rightarrow E$

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Die konkurrenten Folgereaktionssysteme $A \rightarrow C$, $A + C \rightarrow E$ bzw. $A + B \rightarrow C$, $A + C \rightarrow E$ wurden kinetisch untersucht und es wurde festgestellt, daß die exakte Lösung der bezüglichen Differentialgleichungssysteme im Falle des $A \rightarrow C$, $A + C \rightarrow E$ Systems mit Hilfe der unvollständigen *Gamma*-Funktion, im Falle des $A + B \rightarrow C$, $A + C \rightarrow E$ Systems mit Hilfe der unvollständigen *Beta*-Funktion anzugeben ist.

Im dritten Teil unserer Mitteilung [1] haben wir die kinetische Analyse des konkurrenten Folgereaktionssystems

$$A + A \rightarrow C \qquad\qquad A + C \rightarrow E \tag{1}$$

eingehend behandelt: wir gaben die Aufstellung des Differentialgleichungssystems und dessen exakte Lösung an und analysierten ausführlich die Abhängigkeit der Konzentrationen der in den Reaktionen teilnehmenden Substanzen voneinander und von der Zeit.

In dieser Arbeit befassen wir uns nun mit der kinetischen Analyse von zwei weiteren konkurrenten Folgereaktionssystemen; wir behandeln die Aufstellung und exakte Lösung des bezüglichen Differentialgleichungssystems; wegen der chemischen Analogie, die mit dem in der vorangegangen Mitteilung behandelten Fall besteht, befassen wir uns hier jedoch nicht mit der eingehenden Analyse der Ergebnisse.

1. Das System A → C, A + C → E

Es seien die geschwindigkeitsbestimmenden konsekutiven Schritte der vollständigen chemischen Reaktion

$$A \rightarrow C \tag{2}$$

$$A + C \rightarrow E \tag{3}$$

Vorgänge erster und zweiter Ordnung. Die zur Entstehung von je einem Mol des Zwischenproduktes C verbrauchte Menge der Substanz A sei a_1 Mol, die zum Verbrauch des Zwischenproduktes C benötigte Menge der Substanz A sei a_2 Mol, ferner sei mit e Mol die Menge der Substanz E bezeichnet, die dabei entstanden ist; die jeweiligen molaren Konzentrationen der verschiedenen Substanzen seien mit den entsprechenden großen Buchstaben (A, C, E), ihre Anfangskonzentrationen hingegen mit dem Index o (A_0, C_0, E_0) bezeichnet; so können die Änderungsgeschwindigkeiten der in den Reaktionen (2) und (3) teilnehmenden Substanzen folgendermaßen aufgeschrieben werden:

$$-\frac{dA}{dt} = a_1 k_1 A + a_2 k_2 A C \tag{4}$$

$$\frac{dC}{dt} = k_1 A - k_2 A C \tag{5}$$

$$\frac{dE}{dt} = e k_2 A C\,. \tag{6}$$

Zwischen diesen Geschwindigkeiten ist folgender Zusammenhang festzustellen:

$$-\frac{dA}{dt} = a_1 \frac{dC}{dt} + \frac{a_1 + a_2}{e} \frac{dE}{dt} E \tag{7}$$

woraus durch Integration, weiters durch Berücksichtigung der Anfangsbedingungen (am Anfang der Reaktion $C_0 = E_0 = 0$) folgende stöchiometrische Relation zwischen den Konzentrationen zu gewinnen ist:

$$A_0 - A = a_1 C + \frac{a_1 + a_2}{e} E\,. \tag{8}$$

Zwecks Lösung des Differentialgleichungssystems seien die Gleichungen (4) und (5) vereinigt:

$$-\frac{dC}{dA} = \frac{k_1 A - k_2 A C}{a_1 k_1 A + a_2 k_2 A C}\,. \tag{9}$$

Falls wir die Bezeichnung

$$\varkappa = \frac{k_2}{k_1} \tag{10}$$

einführen, kann (9) nach Vereinfachung mit $k_1 A$ in folgender Form aufgeschrieben werden:

$$-\frac{dC}{dA} = \frac{1 - \varkappa C}{a_1 + a_2 \varkappa C}\,. \tag{11}$$

Dies wird nach Trennung der Veränderlichen integriert und auf diese Weise folgender $A = A(C)$ Zusammenhang gewonnen:

$$A = A_0 + a_2 C + \frac{a_1 + a_2}{\varkappa} \ln |1 - \varkappa C| . \tag{12}$$

Hiervon ist mit Hilfe der stöchiometrischen Relation (8) folgender $E = E(C)$ Zusammenhang zu gewinnen:

$$E = -e \left(C + \frac{1}{\varkappa} \ln |1 - \varkappa C| \right) . \tag{13}$$

Zwecks Feststellung der Zeitabhängigkeit der Konzentrationen sei unser Ergebnis laut (12) in die Differentialgleichung (5) substituiert:

$$\frac{dC}{dt} = k_1 (1 - \varkappa C) \left(A_0 + a_2 C + \frac{a_1 + a_2}{\varkappa} \ln |1 - \varkappa C| \right) \tag{14}$$

und die neue Veränderliche

$$\Omega = \frac{\beta_2 + \ln |1 - \varkappa C|}{\beta_1} \tag{15}$$

eingeführt, wo

$$\beta_1 = \frac{a_2}{a_1 + a_2} \tag{16}$$

und

$$\beta_2 = \frac{a_2 + \varkappa A_0}{a_1 + a_2} \tag{17}$$

ist. Mit der laut (15) definierten neuen Veränderlichen kann C folgendermaßen ausgedrückt werden:

$$C = \frac{1}{\varkappa} (1 - \varepsilon_\Omega^+) \tag{18}$$

wo ε_Ω^+ (bzw. ε_Ω^-) folgenden exponentiellen Ausdruck bedeutet:

$$\varepsilon_\Omega^\pm = \exp \left[\pm (\beta_1 \Omega - \beta_2) \right] . \tag{19}$$

Mit Hilfe dieser Ausdrücke kann die Differentialgleichung (14) auf eine einfachere Form gebracht werden:

$$\frac{d\Omega}{dt} = k_1 \frac{a_2}{\beta_1} \varepsilon_\Omega^+ (1 - \Omega \varepsilon_\Omega^-) . \tag{20}$$

Nach Trennung der Veränderlichen gewinnen wir aus (20) das Integral

$$I(\Omega) = \frac{\beta_1}{a_2} \int \frac{\varepsilon_\Omega^-}{1 - \Omega \varepsilon_\Omega^-} \, d\Omega = \Theta + I(\Omega_0) . \tag{21}$$

Die Bedeutung des in diesem Zusammenhang vorkommenden Θ ist folgende:

$$\Theta = k_1 t. \tag{22}$$

Es kann gezeigt werden, daß das Integral $I(\Omega)$ auch in folgender Form aufgeschrieben werden kann:

$$I(\Omega) = \frac{\beta_1}{a_2} \sum_{n=0}^{\infty} \exp\,[\beta_2(n+1)] \int \Omega^n \exp\,[-\beta_1(n+1)\Omega]\,d\Omega\,. \tag{23}$$

Der Wert des hier bezeichneten Integrals kann mit Hilfe der sog. unvollständigen Gamma-Funktion [2] angegeben werden, in allgemeiner Form ($\nu > 0$):

$$\int_0^x z^{\nu-1} \exp\,(-\mu z)\,dz = \mu^{-\nu}\gamma(\nu, \mu x)\,. \tag{24}$$

Da in unserem Fall die Veränderliche x der unvollständigen Gamma-Funktion Ω ist, ihre Parameter hingegen

$$\nu = n + 1 \tag{25}$$

$$\mu = \beta_1(n+1) \tag{26}$$

sind, kann das Integral (23) mit Hilfe der unvollständigen Gamma-Funktion folgendermaßen aufgeschrieben werden:

$$I(\Omega) = \frac{\beta_1}{a_2} \sum_{n=0}^{\infty} \exp\,[\beta_2\,(n+1)]\,\frac{1}{\beta_1^{n+1}(n+1)^{\,n+1}}\,\gamma[n+1, \beta_1\,(n+1)\,\Omega]. \tag{27}$$

Die in (27) vorkommende unvollständige Gamma-Funktion — wegen des Spezialwertes von ν laut (25) — kann mit Hilfe folgender Formel berechnet werden:

$$\gamma[n+1, \beta_1(n+1)\Omega] = n!\left\{1 - \exp\,[-\beta_1(n+1)\,\Omega] \sum_{m=0}^{n} \frac{\beta_1^m\,(n+1)^m}{m!}\,\Omega^m\right\}. \tag{28}$$

Es sei bemerkt, daß die Werte der unvollständigen Gamma-Funktion für die verschiedenen Werte der Veränderlichen und der Parameter in Tabellen aufzufinden sind (z. B. [3] und [4]).

Mit Hilfe des in (27) aufgeschriebenen Integrals kann der die Zeitabhängigkeit enthaltende Zusammenhang (21) in folgender Form aufgeschrieben werden:

$$\Theta = I(\Omega) - I(\Omega_0)\,. \tag{29}$$

Hier bedeutet $I(\Omega_0)$ den Wert des Ausdruckes (27) beim Anfangswert ($t = 0$) der Veränderlichen; dieser Wert is laut (15):

$$\Omega_0 = \frac{\beta_2}{\beta_1}\,, \tag{30}$$

da am Anfang der Reaktion ($t = 0$) $C_0 = 0$ und so $\ln|1 - \varkappa C_0| = 0$ ist.

Die Konzentrationen der in der Reaktion teilnehmenden Substanzen können mit Hilfe der in (15) definierten Veränderlichen Ω wie folgt angegeben werden [die Funktion $C = C(\Omega)$ ist in (18) enthalten]:

$$A = \frac{a_2}{\varkappa}(\Omega - \varepsilon_\Omega^+) \tag{31}$$

bzw.

$$E = \frac{e}{\varkappa}[(\beta_2 - \beta_1\Omega) - (1 - \varepsilon_\Omega^+)]. \tag{32}$$

(18), (31) und (32) geben also die Abhängigkeit der Konzentrationen der in der Reaktion teilnehmenden Substanzen von der Veränderlichen Ω. (29) hingegen gibt die Zeitabhängigkeit der Ω an; auf diese Weise kann die Zeitabhängigkeit aller in der Reaktion teilnehmenden Substanzen berechnet werden.

Wie dies aus der Differentialgleichung (5) feststellbar ist, ergibt sich der Wert des Maximums der Zwischenprodukt-Konzentration als

$$C_m = \frac{1}{\varkappa}. \tag{33}$$

Die Untersuchung der Zusammenhänge $A = A(C)$ laut (12) bzw. $E = E(C)$ laut (13) zeigt hingegen, daß C diesen Maximalwert bei keinerlei $\varkappa$ erreicht. Aus diesen Zusammenhängen kann gleichzeitig festgestellt werden, daß die Zwischenprodukt-Konzentration am Ende der Reaktion jeweils einen begrenzten Wert annimmt und bei keinerlei $\varkappa$ gleich Null wird. Der Zusammenhang $C_\infty = f(\varkappa)$ kann, wegen des transzendenten Charakters der Lösungsfunktionen in expliziter Form nicht angegeben werden.

2. Das System A + B → C, A + C → E

Es seien die geschwindigkeitsbestimmenden konsekutiven Schritte der vollständigen chemischen Reaktion

$$A + B \rightarrow C \tag{34}$$

$$A + C \rightarrow E \tag{35}$$

Prozesse zweiter Ordnung; ferner sei die zur Entstehung von je einem Mol des Zwischenproduktes C verbrauchte Menge der Substanz B (ihre jeweilige Konzentration ist B, die Anfangskonzentration B_0) b Mol (die sonstigen Bezeichnungen stimmen mit dem in Punkt 1 angegebenen überein), somit können die Änderungsgeschwindigkeiten der in den Reaktionen (34) und (35) teilnehmenden Substanzen folgendermaßen aufgeschrieben werden:

$$-\frac{dA}{dt} = a_1k_1AB + a_2k_2AC \tag{36}$$

$$-\frac{dB}{dt} = bk_1AB \tag{37}$$

$$\frac{dC}{dt} = k_1AB - k_2AC \tag{38}$$

$$\frac{dE}{dt} = ek_2AC. \tag{39}$$

Zwischen diesen Geschwindigkeiten können folgende Zusammenhänge festgestellt werden:

$$\frac{dA}{dt} = \frac{a_1 + a_2}{b}\frac{dB}{dt} + a_2\frac{dC}{dt} \tag{40}$$

$$-\frac{dA}{dt} = -\frac{a_1}{b}\frac{dB}{dt} + \frac{a_2}{e}\frac{dE}{dt} \tag{41}$$

$$-\frac{dA}{dt} = a_1\frac{dC}{dt} + \frac{a_1 + a_2}{e}\frac{dE}{dt} \tag{42}$$

woraus durch Integration, weiters durch Berücksichtigung der Anfangsbedingungen (am Anfang der Reaktion ist $C_0 = E_0 = 0$) die folgenden stöchiometrischen Zusammenhänge zwischen den Konzentrationen gewonnen werden können:

$$A - A_0 = \frac{a_1 + a_2}{b}(B - B_0) + a_2C \tag{43}$$

$$A_0 - A = \frac{a_1}{b}(B_0 - B) + \frac{a_2}{e}E \tag{44}$$

$$A_0 - A = a_1C + \frac{a_1 + a_2}{e}E. \tag{45}$$

Es seien die Gleichungen (37) und (38) zwecks Lösung des Differentialgleichungssystems vereinigt:

$$-\frac{dC}{dB} = \frac{k_1AB - k_2AC}{bk_1AB}. \tag{46}$$

Falls wir die neue Veränderliche

$$\psi = \frac{C}{B} \tag{47}$$

einführen und ferner berücksichtigen, daß auf Grund von (47) (da $C = B\psi$)

$$\frac{dC}{dB} = \psi + B\frac{d\psi}{dB} \tag{48}$$

ist, so kann unsere Gleichung (46) in folgender Form geschrieben werden:

$$-\psi - B\frac{d\psi}{dB} = \frac{1 - \varkappa\psi}{b}\,. \tag{49}$$

Nach Ordnung und nach Trennung der Veränderlichen gelangen wir aus (49) zu folgender Relation:

$$-\frac{dB}{B} = -\frac{b d\psi}{1 + (b - \varkappa)\psi}\,. \tag{50}$$

Nach Integration von (50) gewinnen wir den $B = B(\psi)$ Zusammenhang:

$$B = B_0[1 - (\varkappa - b)\psi]^{\frac{b}{\varkappa - b}}. \tag{51}$$

Falls wir für die relative Konzentration der Substanz B die Bezeichnung

$$B_r = \frac{B}{B_0} \tag{52}$$

einführen, gewinnen wir auf Grund von (51) und (47) die $\psi = \psi(B_r)$ und $C = C(B_r)$ Relationen:

$$\psi = \frac{1}{\varkappa - b}\left(1 - B_r^{\frac{\varkappa - b}{b}}\right) \tag{53}$$

und

$$C = \frac{B_0}{\varkappa - b} B_r \left(1 - B_r^{\frac{\varkappa - b}{b}}\right). \tag{54}$$

Es seien zwecks Feststellung der Relation $A = A(B_r)$ die Gleichungen (36) und (37) vereinigt:

$$\frac{dA}{dB} = \frac{a_1 k_1 AB + a_2 k_2 AC}{b k_1 AB}\,. \tag{55}$$

Dies kann auf Grund von (52) und (53) — nach Vereinfachung mit $k_1 AB$ — folgendermaßen aufgeschrieben werden:

$$\frac{1}{B_0}\frac{dA}{dB_r} = \frac{a_1}{b} + \frac{a_2}{b}\frac{\varkappa}{\varkappa - b}\left(1 - B_r^{\frac{\varkappa - b}{b}}\right). \tag{56}$$

Nach Integration gewinnen wir hieraus folgenden $A = A(B_r)$ Zusammenhang:

$$A = A_0 - B_0\left[\frac{(a_1 + a_2)\varkappa - a_1 b}{b(\varkappa - b)}(1 - B_r) - \frac{a_2}{\varkappa - b}\left(1 - B_r^{\frac{\varkappa}{b}}\right)\right]. \tag{57}$$

Durch Einführung der Bezeichnungen

$$\alpha_1 = \frac{A_0}{B_0} + \alpha_2 + \alpha_3 \tag{58}$$

$$-\alpha_2 = \frac{(a_1 + a_2)\varkappa - a_1 b}{b(\varkappa - b)} \tag{59}$$

$$\alpha_3 = \frac{a_2}{\varkappa - b} \tag{60}$$

kann unser Ergebnis (57) folgendermaßen aufgeschrieben werden:

$$A = B_0\left(\alpha_1 - \alpha_2 B_r - \alpha_3 B_r^{\frac{\varkappa}{b}}\right). \tag{61}$$

Das Ergebnis (61) sei, zwecks Feststellung der Konzentrationen, in die Differentialgleichung (37) substituiert:

$$-\frac{dB_r}{dt} = bk_1 B_0 \left(\alpha_1 - \alpha_2 B_r - \alpha_3 B_r^{\frac{\varkappa}{b}}\right) B_r . \tag{62}$$

Es sei ferner die neue Veränderliche

$$\zeta = 1 - \frac{\alpha_3}{\alpha_1} B_r^{\frac{\varkappa}{b}} \tag{63}$$

eingeführt. Somit wird

$$B_r = \left(\frac{\alpha_1}{\alpha_3}\right)^{\frac{b}{\varkappa}} (1 - \zeta)^{\frac{b}{\varkappa}} \tag{64}$$

und

$$\frac{dB_r}{dt} = -\frac{b}{\varkappa}\left(\frac{\alpha_1}{\alpha_3}\right)^{\frac{b}{\varkappa}} (1 - \zeta)^{\frac{b - \varkappa}{\varkappa}} \frac{d\zeta}{dt}, \tag{65}$$

mit deren Hilfe die Differentialgleichung (62) folgendermaßen umgestaltet werden kann:

$$-\frac{d\zeta}{dt} = k_1 \varkappa \alpha_2 B_0 \left(\frac{\alpha_1}{\alpha_3}\right)^{\frac{b}{\varkappa}} (1 - \zeta)^{1 + \frac{b}{\varkappa}} \left[1 - \frac{\alpha_1}{\alpha_2}\left(\frac{\alpha_1}{\alpha_3}\right)^{-\frac{b}{\varkappa}} \zeta (1 - \zeta)^{-\frac{b}{\varkappa}}\right]. \tag{66}$$

Nach Trennung der Veränderlichen und durch Bezeichnung bzw. Durchführung der Integrale gewinnen wir folgendes Ergebnis:

$$\Theta = \frac{1}{\varkappa \alpha_2 B_0} \left(\frac{\alpha_1}{\alpha_3}\right)^{-\frac{b}{\varkappa}} [J(\zeta_0) - J(\zeta)], \tag{67}$$

wo die Bedeutung von Θ wie in (22) ist und der Anfangswert ($t = 0$) der Veränderlichen ζ laut (63)

$$\zeta_0 = 1 - \frac{\alpha_3}{\alpha_1} \tag{68}$$

bedeutet, ferner $J(\zeta)$ das folgende Integral bezeichnet:

$$J(\zeta) = \int \frac{(1-\zeta)^{-\left(\frac{b}{\varkappa}+1\right)}}{1 - \alpha_4 \zeta (1-\zeta)^{-\frac{b}{\varkappa}}} \, d\zeta \tag{69}$$

wo die Bedeutung von α_4 die folgende ist:

$$\alpha_4 = \frac{\alpha_1}{\alpha_2} \left(\frac{\alpha_1}{\alpha_3}\right)^{-\frac{b}{\varkappa}} . \tag{70}$$

Es kann gezeigt werden, daß das Integral $J(\zeta)$ in folgender Form aufgeschrieben werden kann:

$$J(\zeta) = \sum_{n=0}^{\infty} \alpha_4^n \int \zeta^n (1-\zeta)^{-\left[\frac{b}{\varkappa}(n+1)+1\right]} d\zeta \, . \tag{71}$$

Der Wert des obigen Integrals kann mit Hilfe der sog. unvollständigen Beta-Funktion [5, 6] angegeben werden, in allgemeiner Form:

$$\int_0^x z^{p-1} (1-z)^{q-1} dz = B_x(p, q) . \tag{72}$$

Da in unserem Fall die Veränderliche x der unvollständigen Beta-Funktion ζ ist, ihre Parameter hingegen

$$p = n + 1 \tag{73}$$

$$q = -\frac{b}{\varkappa}(n+1) , \tag{74}$$

kann das Integral (71) mit Hilfe der unvollständigen Beta-Funktion folgendermaßen aufgeschrieben werden:

$$J(\zeta) = \sum_{n=0}^{\infty} \alpha_4^n B_{\varrho}\left[n+1, -\frac{b}{\varkappa}(n+1)\right] . \tag{75}$$

Es sei hier bemerkt, daß die Werte der unvollständigen Beta-Funktion bezüglich der verschiedenen Werte der Veränderlichen und der Parameter in Tabellen aufzufinden sind (z. B. [7]).

Die Konzentrationen der in den Reaktionen teilnehmenden Substanzen können mit Hilfe der in (63) definierten Veränderlichen ζ wie folgt angegeben werden:

$$A = B_0 \left[\alpha_1 \zeta - \alpha_2 \left(\frac{\alpha_1}{\alpha_3}\right)^{\frac{b}{\varkappa}} (1-\zeta)^{\frac{b}{\varkappa}}\right] \tag{76}$$

$$B = B_0 \left(\frac{\alpha_1}{\alpha_3}\right)^{\frac{b}{\varkappa}} (1 - \zeta)^{\frac{b}{\varkappa}} \tag{77}$$

$$C = \frac{B_0}{b - \varkappa} \left(\frac{\alpha_1}{\alpha_3}\right)(1 - \zeta)\left[1 - \left(\frac{\alpha_1}{\alpha_3}\right)^{\frac{b}{\varkappa} - 1} (1 - \zeta)^{\frac{b}{\varkappa} - 1}\right] \tag{78}$$

$$E = \frac{e}{a_2}\left[\left(A_0 - \frac{a_1}{b} B_0\right) - \alpha_1 B_0 \zeta + \left(\frac{\alpha_1}{\alpha_3}\right)^{\frac{b}{\varkappa}} \left(\alpha_2 + \frac{a_1}{b}\right) B_0 (1 - \zeta)^{\frac{b}{\varkappa}}\right]. \tag{79}$$

Die Relationen (76)—(79) geben also die Abhängigkeit der Konzentrationen der in der Reaktion teilnehmenden Substanzen von der Veränderlichen ζ an: die Relation (67) hingegen zeigt die Zeitabhängigkeit der Veränderlichen ζ. Auf diese Weise kann die Zeitabhängigkeit der Konzentration aller, in der Reaktion teilnehmenden Substanzen berechnet werden.

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ON THE PARAMETER FORM OF FORCE CONSTANTS MATRIX, IX

THE CONNECTION BETWEEN NORMAL AND SYMMETRY COORDINATES

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An investigation of the connection between the symmetry and normal coordinates has led to the conclusion that the force constant sets belonging to a given assignment can be restricted to narrower limits. Since the signs of the columns of the transs formation matrix between symmetry and normal coordinates are not fixed it follows that all the possible force constants can be formed by parameters having their valuee between the limits $-\pi/2$ and $+\pi/2$. Methods are given for the calculation of th. parameters characterizing the connection between symmetry and normal coordinates -

Normal coordinates give complete information about the vibrational motion of a molecule. The normal coordinates can only be determined in the knowledge of both the force field and molecular geometry [1]. However, to construct the symmetry coordinates, it is only the molecular geometry that is needed. Accordingly, the connection between symmetry and normal coordinates depends on the force constants, and this fact underlines the importance of its investigation.

In order to investigate the connection between symmetry and normal coordinates, let us denote the column matrix of symmetry coordinates and that of normal coordinates by S and Q, respectively. As it is known, the transformation between the two column matrices is given by

$$Q = L S,$$

where L is an n-dimensional matrix, which can be obtained by solving the secular problem

$$G F L = L \Lambda. \qquad (1)$$

G can be constructed in the knowledge of the molecular geometry and the masses of the atoms: the elements of matrix F are the force constants; Λ is a diagonal matrix whose elements can readily be obtained from the normal frequencies, and the columns of matrix L are the eigenvectors of matrix GF [1]. The order of the symmetry coordinates is determined by the sequence of the rows (or columns) of matrix G, and that of the normal coordinates by the elements of matrix Λ.

In our previous paper [2] it has been pointed out that matrix L can be written as

$$L = g U, \qquad (2)$$

where $g = G^{1/2}$, and U is an orthogonal matrix satisfying the equation

$$gFgU = U\Lambda ,$$

From this relation we get all the matrices F reproducing the measured normal frequencies:

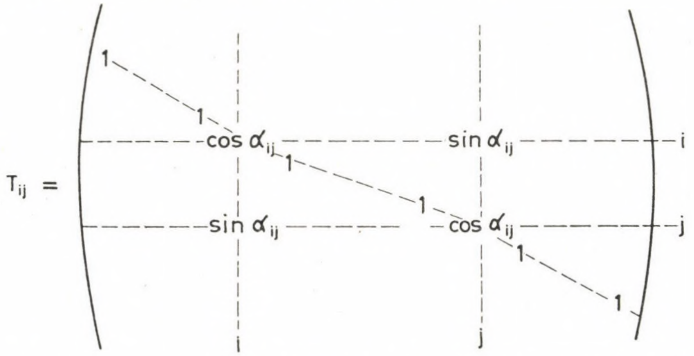
$$F = g^{-1}\,U\Lambda U^{T}g^{-1} \tag{3}$$

where U is an arbitrary proper orthogonal matrix (*i.e.* one with the determinant equal to $+1$), and U^T means the transpose of U.

The following two parameter representations of matrices U are known [3]:

(a) Angle parameters

Let us define the T_{ij} elementary rotation matrix as follows:



where α_{ij} is the ij-th parameter. All the possible n-dimensional matrices U can be given as a product of (n) elementary rotational matrices:

$$U = T_{12}T_{13}\ \ldots\ T_{1n}T_{23}\ \ldots\ T_{2n}\ \ldots\ T_{n-1,\ n}. \tag{4}$$

(b) Antisymmetric parameters

The matrices U can also be formed by antisymmetric matrices, K:

$$U = (E - K)\,(E + K)^{-1} = 2(E + K)^{-1} - E$$

where the elements of K are the n parameters having any arbitrary real values:

$$K = \begin{pmatrix} 0 & t_{12} & \ldots & t_{1n} \\ -t_{12} & 0 & \ldots & t_{2n} \\ \ldots & \ldots & \ldots & \ldots \\ -t_{1n} & -t_{2n} & \ldots & 0 \end{pmatrix}$$

It follows from the foregoing that Eq. (2) gives all the possible matrices L as function of the proper orthogonal matrices U. As it was expounded in our previous papers [2, 4, 6], the assignment between the symmetry coordinates belonging to the rows of matrices G and F and the normal coordinates belonging to the normal frequencies in matrix Λ, is the closest, if $U = E$, where E denotes the unit matrix. In this case $L = g$, which means that the starting position is fixed by matrix G. The exact matrix L of the molecule is determined by the difference between the exact force constants and the elements of matrix

$$F_0 = g^{-1} \Lambda g^{-1},$$

which can be obtained from Eq. (3) by substituting $U = E$. This difference is measured by matrix U, therefore, with a given matrix G, it is matrix U that must be examined in order to obtain information about matrix L.

It is known that a proper orthogonal matrix defines a rigid rotation of an orthogonal coordinate system about its origin [3]. An arbitrary U_{ki} element of matrix U is equal to the cosinus of the angle between the k-th axis of the reference coordinate system and the i-th axis of the rotated one. In the case of an n-dimensional problem, matrix U defines the rotation of an orthogonal coordinate system in the n-dimensional space. Let the starting reference system be fixed by $U = E$. It follows from the foregoing and from our previous papers [5, 6] that this $U = E$ position corresponds to the assignment centre with the closest connection between the k-th symmetry coordinate and k-th normal one ($k = 1, 2, \ldots, n$). If the rotation of the coordinate system from this position is small, the projection of every rotated axis is the greatest to the reference axis from which it has been rotated out. It is also possible that after rotation the k-th rotated axis coincides with the reference axis i_k ($k=1, 2, \ldots, n$), where $i_1, i_2, \ldots, i_n$ denote an arbitrary permutation of numbers 1, 2, ..., n. In this case U belongs to the centre of the assignment, ordering the k-th symmetry coordinate to the i_k-th normal one ($k = 1, 2, \ldots, n$).

On the basis of these considerations, we can say that the k-th normal coordinate has the closest connection with i-th symmetry coordinate, if the k-th column of matrix U has its element of greatest absolute value in the i-th row.

When the assignment is uncertain, several columns may have elements of maximum value in the same row, but it does not occur in the case of a definite assignment. In the latter case, it is advisable to rearrange the order of the columns of matrix U in such a way that the diagonal elements in each column should have the greatest absolute values. In this way, of course, the sequence of the elements in matrix Λ will be changed, thus the k-th symmetry coordinate and the k-th normal one ($k = 1, 2, \ldots, n$) will have again the closest connections. As matrix U never means reflection but only rotation, it can always be achieved that all the diagonal elements have positive signs after the aforesaid rearrangement.

According to our previous paper [5], all the matrices U generating matrices F belonging to a given assignment can be formed by the parameters taken from the $\pi/4$ region of the zero point, *i.e.* by

$$-\pi/4 < \alpha_{ij} < \pi/4 \quad i < j,\ j = 2, 3, \ldots, n. \tag{5}$$

This suggestion was made on the basis of an arrangement of the centre points in the space of parameters. It should be noted that near the borders of the various regions, there are cases when the projections of the rotated axes are no longer the greatest to the original ones. Considering this fact, the narrowing of the region given by Eq. (5) is possible. As either the projections to all the axes are equal to $1/\sqrt{n}$, or at least there is one axis to which the projection is greater than $1/\sqrt{n}$, in forming matrices F belonging to a given assignment, it is reasonable to restrict ourselves to the matrices U whose diagonal elements are greater than $1/\sqrt{n}$.

To illustrate the above ideas, let us consider the matrix U formed by the angle parameters $\alpha_{12} = \alpha_{13} = \alpha_{23} = 40°$. The corresponding antisymmetric parameters are: $t_{12} = -0.4828$, $t_{13} = -0.2799$, $t_{23} = 0.7689$.

$$U = \begin{pmatrix} 0.58676 & -0.80889 & 0.03602 \\ 0.49238 & 0.32116 & -0.80889 \\ 0.64280 & 0.49238 & 0.58676 \end{pmatrix}$$

It appears that one of the diagonal elements is smaller than $1/\sqrt{3} = 0.5773$, and the matrix U corresponds to an assignment ordering the 1st, 2nd and the 3rd normal coordinates to the 3rd, 1st and 2nd symmetry ones, respectively. After rearranging the columns in this sense, we get

$$U = \begin{pmatrix} 0.80889 & -0.03602 & 0.58676 \\ -0.32116 & 0.80889 & 0.49238 \\ -0.49238 & -0.58676 & 0.64280 \end{pmatrix}.$$

This matrix can be formed with the angle parameters

$$\alpha_{12} = -29°\,25', \quad \alpha_{13} = -21°\,40', \quad \alpha_{23} = -42°\,25',$$

and with the antisymmetric parameters $t_{12} = -0.1094$, $t_{13} = -0.4141$, $t_{23} = -0.4141$. In the rearranged form, the sum of the absolute values of the parameters is smaller than in the original case, indicating that when starting from the second centre, the rotation required is smaller.

As it can be observed from the foregoing, a given matrix F can be formed by several matrices U differing in the sequence of their columns. As the multiplication of the eigenvectors by a constant is allowed, the same matrix F will be formed by matrices U which only differ in the signs of all elements in some of the columns. In the case of angle parameters it can be proved that, if the absolute values of one or several parameters exceed $\pi/2$, another set of parameters can always be found, all the members of which are from the $\pi/2$ region of the zero point, *i.e.*:

$$-\pi/2 < \alpha_{ij} < \pi/2 \qquad i < j, \qquad j = 2, 3, \ldots, n$$

and the matrix U formed by them differs from the original one only in the signs of all elements in the even numbers of columns. An important consequence of this fact is that all matrices F can be formed by parameters taken from the $\pi/2$ region of the zero point. It can also be shown that, on the other hand, it is not possible to find even two sets of parameters in the $\pi/2$ region which give the same matrix F (naturally Λ remaining unchanged).

Let us suppose that all the parameters forming a given matrix U are from the $\pi/2$ region, with the exception of α_{ij}. Instead of α_{ij} let us take the parameter $\alpha_{ij}+\pi$ which is in the $\pi/2$ region. At the same time, let us change the signs of the parameters α_{ps} with the indices $p = i, j$ and $s = n, n-1, \ldots, j+1$, furthermore those with $s = j$ and $p = j-1, j-2, \ldots \ldots, i+1$. In this case all the new parameters are from the $\pi/2$ region, and they generate a matrix U differing from the original one only in the signs of the i-th and k-th columns. For example, if among the parameters generating a 5-dimensional matrix U, it is only α_{12} for which $|\alpha_{12}| > \pi/2$, let us choose $\alpha_{12}+\pi$ and reverse the signs of parameters $\alpha_{13}, \alpha_{14}, \alpha_{15}, \alpha_{23}, \alpha_{24}, \alpha_{25}$. The new parameters will give a matrix U differing from the previous one only in the signs of the 1st and 2nd columns.

In this way the significant role of matrix U in the connection between symmetry and normal coordinates has been demonstrated. For characterizing a matrix U, its parameters are very convenient. Taking into consideration that all the quantities depending on the force constants can be expressed as function of parameters, it is necessary to calculate the parameters belonging to a solved eigenvalue problem characterized by matrix L. We mention that the parameters belonging to matrix F, obtained at the end of an iteration process, are not at our disposal even in the knowledge of the individual steps [4]. In the following two methods will be given for determining the parameters of matrix $U = g^{-1}L$, which can be calculated from L without difficulty.

(a) The parameters of the skew symmetric matrix K can be formed by simple matrix manipulations:

$$K = (E - U)(E + U)^{-1} = 2(E + U)^{-1} - E.$$

If the problem is of higher dimension, computer calculations are needed. In the case of a three-dimensional problem, the parameters can readily be calculated from the elements of matrix U:

$$t_{12} = \frac{U_{21} - U_{12}}{D}, \qquad t_{13} = \frac{U_{31} - U_{13}}{D}, \qquad t_{23} = \frac{U_{32} - U_{23}}{D},$$

$$\text{where} \quad D = 1 + U_{11} + U_{22} + U_{33}.$$

(b) The calculation of the angle parameters is somewhat more difficult. In carrying out such calculations, we make use of the fact that the parameters $\alpha_{12}, \alpha_{13}, \ldots, \alpha_{1n}$ can be obtained from the first column. Namely, the elements of the first column are the following:

$$\begin{array}{l}
\cos \alpha_{1,n} \cos \alpha_{1,n-1} \ \ldots \ \cos \alpha_{12} \\
\cos \alpha_{1,n} \cos \alpha_{1,n-1} \ \ldots \ \cos \alpha_{13} \sin \alpha_{12} \\
\cos \alpha_{1,n} \cos \alpha_{1,n-1} \ \ldots \ \cos \alpha_{14} \sin \alpha_{13} \\
\cdots\cdots\cdots\cdots\cdots\cdots\cdots \\
\cos \alpha_{1,n} \sin \alpha_{1,n-1} \\
\sin \alpha_{1,n}
\end{array}$$

Let us apply the notation $U = U_1 U_2$, where $U_1 = T_{12} T_{13} \ldots T_{1,n}$. Having obtained the parameters $\alpha_{12}, \alpha_{13}, \ldots, \alpha_{1,n}$ from the first column of matrix U, matrix U_1 can be formed and U_2 can also be determined by

$$U_2 = U_1^T U.$$

As it can be seen, U_2 has tfollowing partitioned construction:

$$U_2 = \left(\begin{array}{c:c} 1 & 0 \\ \hdashline 0 & U_3 \end{array}\right)$$

where matrix U_3 has the same construction as U, therefore, from the first column of U_3 the parameters $\alpha_{23}, \alpha_{24}, \ldots, \alpha_{2,n}$ can be determined. In this way, the n-dimensional problem has been reduced to an $(n-1)$-dimensional one. These steps must be repeated in order to obtain all parameters. Notably, this method can only be applied if all the parameters are from the $\pi/2$ region of the zero point.

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ГИДРОДИНАМИКА ТОНКИХ ПЛЕНОК ЖИДКОСТИ, ТЕКУЩЕЙ ПО ВЕРТИКАЛЬНОЙ ПОВЕРХНОСТИ

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Статья занимается проблемой жидкостной пленки, стекающей по вертикальной поверхности. Сравниваются теории, описывающие исследоваемое явление с собственными и литературными данными. Для средней толщины жидкостной пленки вводится линеаризированное уравнение типа

$$\eta = A \cdot Re^k,$$

характеризующее диапазон течения в области $0 < Re < 80\,000$, где A и k константы.

На основании литературных уравнений и собственных измерений высчитываются значения A и k для 3-х режимов течения. Измерения средней толщины жидкостной пленки как при волновом, так и при безволновом течении показывают, что теория Нуссельта в пределах точности опыта, в режиме, где $Re < 1000$, хорошо описывает течение жидкостной пленки.

Наблюдение и измерение волнового течения на поверхности пленки показало, что характер волн, за исключением места их образования отличается от предсказанного теорией. На основании измерений, проведенных при специальных условиях опыта дается выражение, выражающее зависимость дли ныволны и скорости волнового движения от скорости подачи жидкости, выраженной числом Re.

Вопросы гидродинамики тонких пленок («falling film») за последние несколько лет вызвали к себе повышенный интерес исследователей и с теоретической и с экспериментальной точки зрения. Этот интерес вызывается в первую очередь тем фактом, что скорости тепло- и массопередачи в жидкостной пленке тесно связаны с ее гидродинамикой. Несмотря на большое количество опубликованных теоретических и экспериментальных работ, целый ряд вопросов гидродинамики тонких пленок жидкостей до сих пор удовлетворительно не решен.

Данная статья занимается вопросом средней толшины жидкостной пленки, стекающей по вертикальной поверхности, и волновым движением на поверхности пленки.

I. Средняя толщина жидкостной пленки

1. Обзор литературы

Одним из параметров жидкостной пленки, характеризующих ее гидродинамику является средняя толщина пленки.

На основании теоретических работ Нуссельта [1] возможно вывести уравнение для предсказания средней толщины пленки. Предполагая, что движение жидкости в пленке стационарно, что жидкость в прилегающем к твердой поверхности слое неподвижна и, что на границе жидкость-газ значительных касательных напряжений не имеется, распределение скоростей жидкости в пленке в направлении, перпендикулярном к движению жидкости, выражается следующим уравнением:

$$U = \frac{g}{2\nu}(2my - y^2). \tag{1}$$

На основании уравнения (1) с максимальной скоростью U_M жидкость течет на поверхности жидкость-газ. Отношение между U_M и средней по всей толщине пленки скоростью U_{cp} будет

$$\frac{U_M}{U_{cp}} = \frac{3}{2}, \tag{2}$$

где U_{cp} можно выразить как

$$U_{cp} = \frac{Q}{m}. \tag{3}$$

Средняя толщина жидкостной пленки, текущей по вертикальной поверхности выражается следующим уравнением:

$$m = \left(\frac{3Q\nu}{g}\right)^{1/3}. \tag{4}$$

В случае невертикальной поверхности в знаменатель правой части уравнения (4) входит значение $\sin \alpha$, где α — угол наклона поверхности к горизонту.

Результаты некоторых работ, опубликованных за последнее время [2], [3] указывают на то, в экстремальном случае, когда $\alpha \rightarrow 0$ уравнение (4) не соответствует экспериментальным данным.

Во многих случаях для характеристики течения удобно пользоваться зависимостью коэффициента трения на границе жидкость-стена f от значения числа Re.

Если число Re для жидкостной пленки выражается как

$$Re = \frac{4Q}{\nu}, \tag{5}$$

то в интервале течения, характеризуемым теорией Нуссельта

$$f = \frac{96}{Re}. \tag{6}$$

Теория Нуссельта предполагает, что течение жидкости в пленке ламинарно. В то же время на поверхности жидкостной пленки, начиная с числа $Re =$

$= 20—30$ замечается волновое движение. Это явление привело многих исследователей к предположению, что при появлении волн течение пленки не описывается моделью Нуссельта.

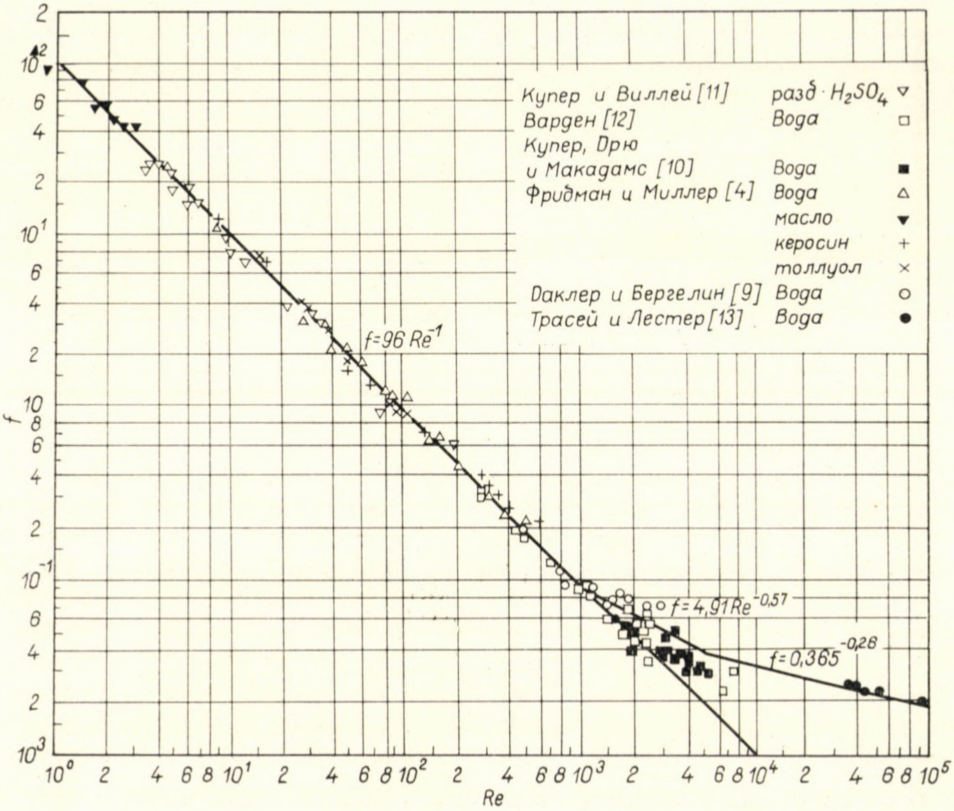

Рис. 1. Зависимость коэффициента трения f от числа Re по данным различных авторов

Проведенное рядом исследователей [4], [5], [6], [7] с целью проверки уравнения (2) измерение скорости жидкости на поверхности пленки привело к противоречивым результатам. Так измерение скорости движения краски [4] и пластмассовых палочек [5], нанесенных на поверхность стекающей пленки жидкости, показало, что до наступления волнового движения уравнение (2) верно, а затем отношение между поверхностной и средней скоростью пленки становится больше 2-х. С другой стороны измерения Портальского [6], недавно подтвержденные результатами Веста и Кола [7], указывают на то, что отношение U_M/U_{cp} как при наличии, так и при отсутствии волн приблизительно равняется значению 1,5.

По поводу методики измерений поверхностной скорости путем нанесения краски или палочек на поверхность пленки можно заметить следующее.

По теории волнового движения скорость волнового фронта превышает скорость поверхности пленки. Таким образом волны, толкая перед собой нанесенные на поверхность пленки капли краски или палочки, увеличивают их скорость. Это подтверждается наблюдением Брауэра [5], что палочки, нанесенные на поверхность пленки, по мере своего движения группируются по фронту волн.

Проведенные различными авторами измерения средней толщины пленки также привели к противоречивым выводам.

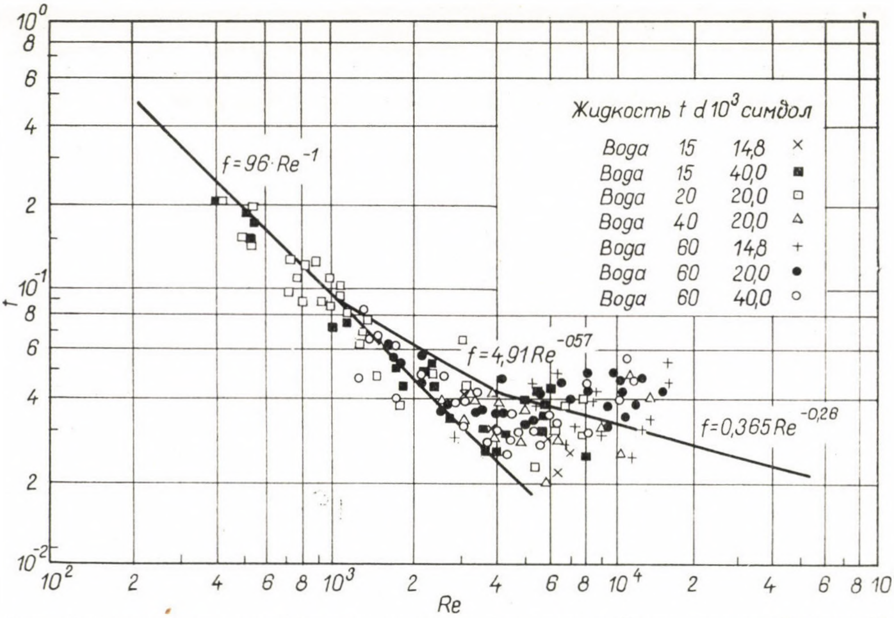

Рис. 2. Зависимость коэффициента трения f от числа Re по данным Брётца [14]

В качестве примера на рис. 1 и 2 изображены пересчитанные результаты различных авторов [4], [9—14]. Как видно из рисунка 1, результаты измерений средней толщины пленки до некоторого определенного числа Re хорошо выражаются уравнением (6). Сходную закономерность показывают и результаты, приведенные на рис. 2, хотя в последнем случае разброс точек значителен.

С другой стороны, результаты ряда работ [5], [15—17], проведенных в том же интервале чисел Re, противоречат теории Нуссельта. Так приведенные на рис. 3 результаты измерений Портальского в интервале $10 < Re < 400$ выражаются лучше теорией Капицы [8], чем теорией Нуссельта. По теории Капицы, характеризующей течение пленки при волновом движении средняя толщина пленки

$$m = \left(\frac{2{,}4\ Q\nu}{g} \right)^{1/3} \tag{7}$$

Для характеристики пленочного течения взамен теории Нуссельта рядом авторов [9], [15], [16] было предложено применение теории универсального профиля скоростей Кармана [18]. Даклер и Бергелин [9], предположив, что пленка жидкости при всех режимах содержит ламинарный, переходный и турбулентный подслой, вывели следующее уравнение:

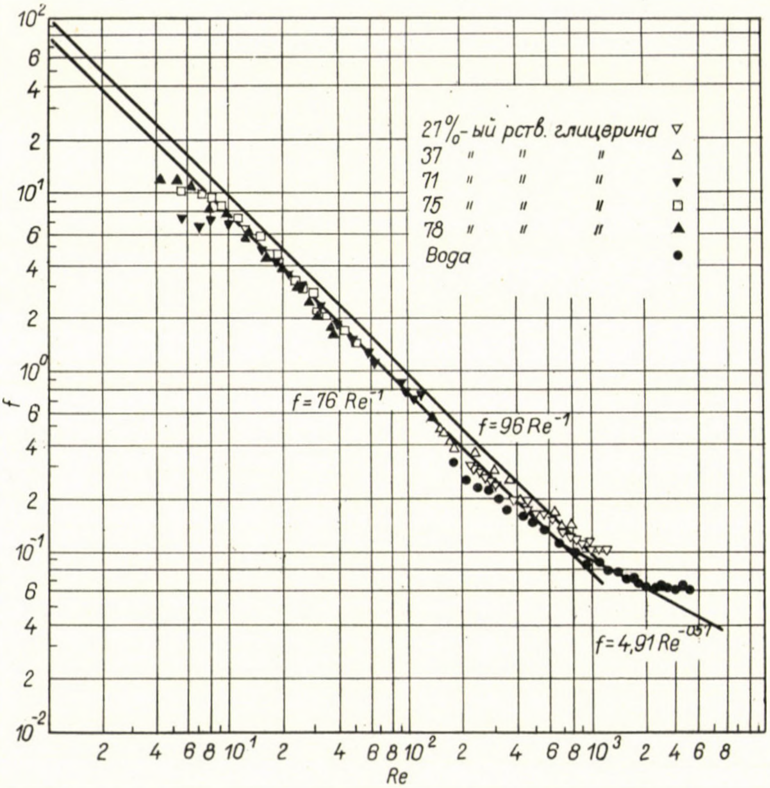

Рис. 3. Зависимость коэффициента трения f от числа Re по данным Портальского [15]

$$Re = 12\eta + 10\eta \ln \eta - 256, \tag{8}$$

где между параметром η и средней толщиной пленки можно вывести зависимость:

$$m = \left(\frac{\eta^2 \nu^2}{g}\right)^{1/3}. \tag{9}$$

На рис. 4 в двойных логарифмических координатах изображено (сплошная линия) уравнение (8). Из графика видно, что с уменьшением числа Re кривая становится почти параллельной оси Re, что на основании уравнения (9) означает следующее: значительное изменение в этой области числа Re приведет к весьма небольшому изменению средней толщины пленки.

Этот вывод противоречит опытным результатам. Так, например, результаты измерений, приведенные на рис. 1, показывают, что в области малых чисел ***Re*** уравнение (8) не применимо.

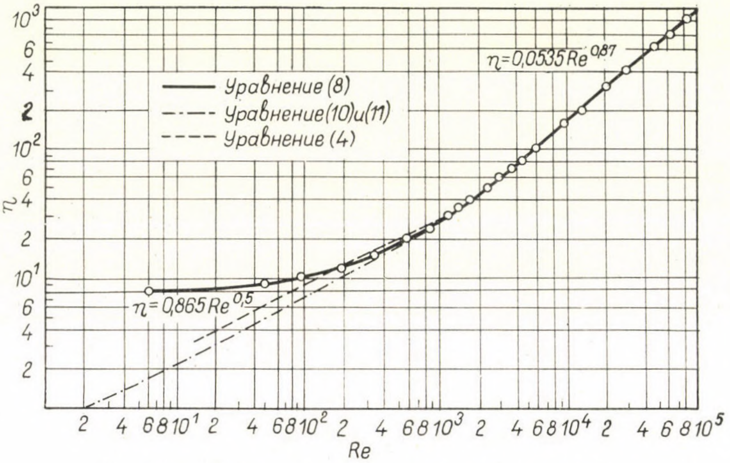

Рис. 4. Зависимость параметра η от числа ***Re***

Портальский [15] преобразовал уравнение (8) Даклера и Бергелина [9]. В результате преобразования для ламинарного режима в области, где $0 < \eta \leq 5$ было получено:

$$Re = 2\eta^2 \tag{10}$$

и для переходного режима, где $5 \leq \eta \leq 30$. (11)

Для турбулентного режима, где $\eta \geq 30$, уравнение (8) осталось действительным. Уравнения (10)—(11) сравниваются с уравнением (8) на рис. 4 (пунктирная линия).

Нетрудно доказать, что уравнение (10) может быть выражено в форме уравнения (4); т. е. в виде

$$m = \left(\frac{2Qv}{g}\right)^{1/3}. \tag{12}$$

Преимущество теории универсального профиля скоростей перед теорией Нуссельта заключается в том, что она действительна не только для ламинарной, но и для переходной и турбулентной области. Величины числа ***Re***, при котором течение перестает быть ламинарным (Re_{kp}), определенные различными авторами отличаются друг от друга (таблица 1).

Результаты измерений, проведенных рядом исследователей [9], [14], [15] в турбулентном режиме при $Re > 2000$, показали повышенную среднюю толщину пленки по сравнению с высчитанной из уравнения (8) толщиной. Например, результаты Брётца (рис. 2) группируются вокруг линии, параллельной оси ***Re***. На основании своих измерений Брётц для режима

Таблица 1

Автор	Re_{kp}
Портальски[15]	1 160
Брауэр[5]	1 600
Живайкин[19]	1 800
Уарден[12]	2 000
Брётц[14]	2 360
Джексон[20]	5 000

$Re > 2360$ предложил эмпирическую формулу

$$m = 0{,}172 \left(\frac{Q^2}{g}\right)^{1/3} . \tag{13}$$

В формуле (13) в числе независимых параметров отсутствует вязкость, т. е. в этой области коэффициент трения не зависит от числа Re и по Брётцу является постоянной величиной, равной 0,048. Сходные результаты получил и Портальски [15] (рис. 3) с той разницей, что у него $f \approx 0{,}06$.

В противоречии с этими выводами результаты измерений, приведенные на рис. 1, показывают, что зависимость коэффициента трения f от числа Re не прекращается и при режиме, где $Re > 2000$.

2. *Введение линеаризированного общего уравнения средней толщины пленки*

Из литературного обзора видно, что ни теория Нуссельта, ни теория универсального профиля скоростей Даклера и Бергелина не в состоянии характеризовать среднюю толщину жидкостной пленки во всем встречающемся в практике диапазоне скоростей. Наряду с этим из уравнений (8)—(11), выведенных из теории универсальной профиля скоростей, функциональная зависимость между средней толщиной пленки и определяющими ее параметрами не может быть выражена в эксплицитной форме. Так как при расчете скоростей тепло- и массообмена в жидкостной пленке как раз эта зависимость имеет важную роль, мы ее выразили линеаризированным приближением уравнения (8). В нашей работе мы попытались ввести общее уравнение, которое применимо для всех областей течения.

Введение общего уравнения средней толщины пленки исходит из следующих предположений:

1. Значением средней толщины пленки можно пренебречь в сравнении с двойным радиусом поверхности, по которой течет пленка. На поверхности жидкость-газ значительных касательных напряжений нет.
2. В ламинарной области течения пленки применима теория Нуссельта.

3. В турбулентном режиме течения жидкостной пленки в области $1000 < Re < 80\,000$ функция $\log \eta$ от $\log Re$ может быть выражена минимальным числом прямых.

На основании вышесказанного зависимость η от Re может быть выражена как

$$\eta = ARe^k. \tag{14}$$

Подставляя уравнение (14) в уравнение (9), получаем:

$$m = \left(\frac{A^2 Re^{2k} \nu^2}{g}\right)^{1/3}. \tag{15}$$

Аналогичным путем выводится уравнение для коэффициента трения:

$$f = 128\, A^2 Re^{2k-2}. \tag{16}$$

Совместным решением уравнений (4) и (15) или уравнений (5) и (16) для ламинарного режима ($Re < 1000$) получается $A = 0{,}865$ и $k = 0{,}5$.

В области больших чисел Re ($10^4 < Re < 10^5$) кривая, изображенная на рис. 4, была замещена прямой. Методом регрессии для этой области мы получили:

$$\eta = 0{,}0535\, Re^{0,87}. \tag{17}$$

Подставляя значения A и k в уравнения (15) и (16) получаем:

$$m = \left(\frac{2{,}85 \cdot 10^{-3}\, Re^{1,74}\, \nu^2}{g}\right)^{1/3}, \tag{18}$$

$$f = 0{,}365\, Re^{-0,26}. \tag{19}$$

В целях проверки полученных уравнений, уравнение (19) сравнивалось с эмпирическими уравнениями, известными из литературы.

Течение жидкостей в трубах при турбулентном режиме характеризуется известным уравнением Блазиуса:

$$f = 0{,}316\, Re^{-0,25}. \tag{20}$$

Живайкин [19] на основании собственных и литературных данных выразил коэффициент трения в турбулентном течении жидкостной пленки следующим эмпирическим уравнением:

$$f = 0{,}360\, Re^{-0,25}. \tag{21}$$

На основании своих измерений Брауэр [5] нашел, что в турбулентном режиме коэффициент трения зависит от числа Re в степени 0,266.

Вышеприведенные примеры показывают, что приближенные уравнения (18) и (19) хорошо совпадают с литературными данными.

Попытка вывести уравнение для жидкостной пленки в интервале $1000 < Re < 10\,000$ на основании приближения кривой на рис. 4 не привела к удовлетворительным результатам. Этот режим течения был нами характеризован на основе экспериментальных результатов.

3. Экспериментальная часть

Экспериментальные методы определения средней толщины жидкостной пленки хорошо описаны в статье Портальского [15].

В наших измерениях мы пользовались методом отсечки питания («hold up»). Схема установки изображена на рис. 5. Жидкостная пленка стекала по внешней поверхности трубки, диаметр которой изменялся между 18,5 и 20,2 мм, а длина между 448 и 694 мм.

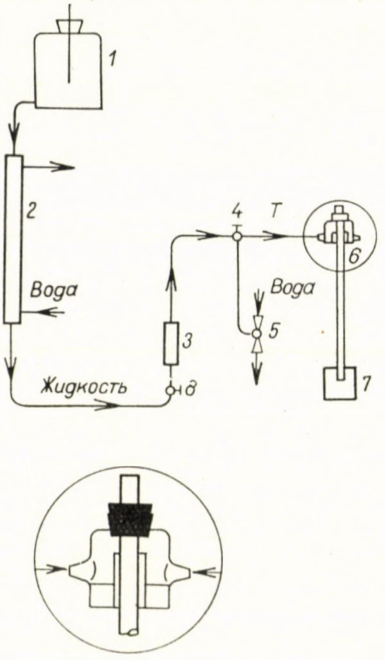

Рис. 5 Схема установки

В измерениях применялись стеклянные и медные трубки. Для распределения жидкости по периметру трубки служила распределительная головка (на рис. 5 изображена отдельно).

Рабочей жидкостью служила вода из водопровода при 10°C и 15°C. Для измерения средней толщины пленки в безволновом режиме к воде добавлялось поверхностно-активное вещество (п. а. в.) марки Никепон.

Измерение проводилось следующим образом: Напорный бак 1 (см. рис. 4) заполнялся жидкостью и открытием клапана *8* жидкость подавалась в колонну *6*. После установления смачивания трубки пленкой по всей её длине, скорость подачи и температуры устанавливались на заранее определенное значение. Поворотом трехходового крана *4* подача жидкости прекращалась (жидкость из распределительной головки отсасывалась эжектором *5*). Одновременно с отсечкой питания начиналось сбирание жидкости, задержавшейся на поверхности трубки, в предварительно взвешенный сборник. Жидкость собиралась в течение 2 минут, затем остаток на поверхности трубки собирался предварительно взвешенной фильтровальной бумагой, затем бумага вновь взвешивалась и количество жидкости добавлялось к задержавшейся жидкости. По меньшей мере 3 измерения проводились при одинаковых условиях и затем брался средний результат.

Среднюю толщину пленки получали делением объема собранной жидкости на рабочую поверхность трубки.

4. Обсуждение результатов измерений

Средняя толщина пленки измерялась в интервале от $Re = 67$ до $Re = 5830$. Результаты измерений в виде значения средней толщины пленки как функции числа Re изображены на рис. 6 в двойных логарифмических координатах. Прямые линии на рисунке отвечают изображению уравнения (4) при 10°C и 15°C. Из рис. 6 видно, что при $Re < 1000$ результаты измерений согласуются с теорией Нуссельта. Переход от ламинарного режима, выражаемый характерным отклонением результатов от прямой, не однозначен. Так результаты измерений, проведенных с металлической трубкой, показывают, что ламинарный режим кончается около $Re \approx 1000$, в то же время значение перехода для результатов, полученных со стеклянной трубкой, лежит около $Re \approx 2000$.

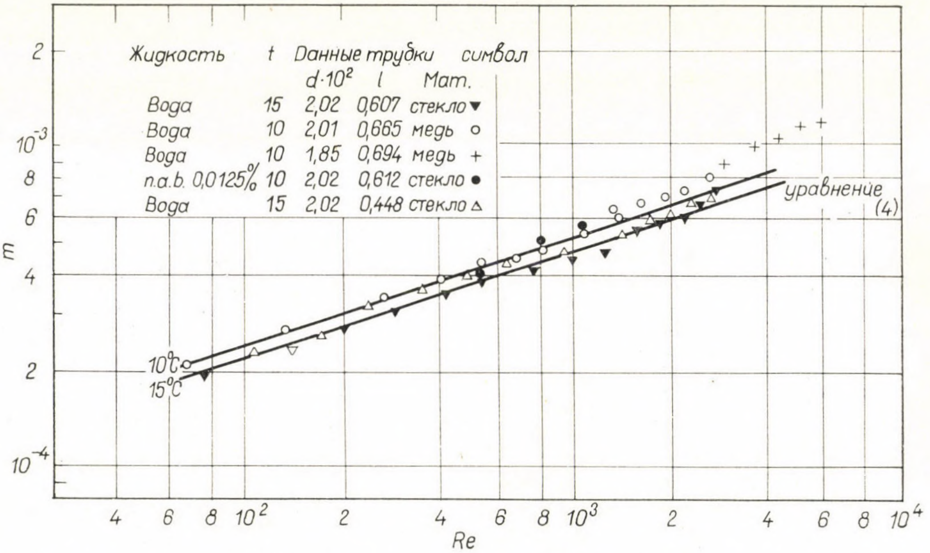

Рис. 6. Зависимость средней толщины пленки от числа Re при двух различных температурах жидкости

Приведенные в таблице 1 данные показывают разнообразие точек перехода, полученных различными авторами. Можно предположить, что это разнообразие вызывается не только разницей в экспериментальной методике (в случае наших измерений методика не менялась), а что на значение критического числа Re влияют и такие факторы как шероховатость поверхности, по которой течет жидкостная пленка. Это предположение поддерживается и результатами Брауэра [5].

Одной из целей измерений было изучение теоретически трудно определяемого переходного режима, расположенного между ламинарным и турбулентным течением в области $1000 < Re < 10\,000$. По техническим причинам измерения были проведены до $Re = 5830$.

На рис. 7 в двойных логарифмических координатах приведены результаты измерений в виде функции η от числа Re. В области $Re = 1076$ — 5830 получилось 26 точек измерения; они приближаются уравнением, полученным с помощью метода наименьших квадратов:

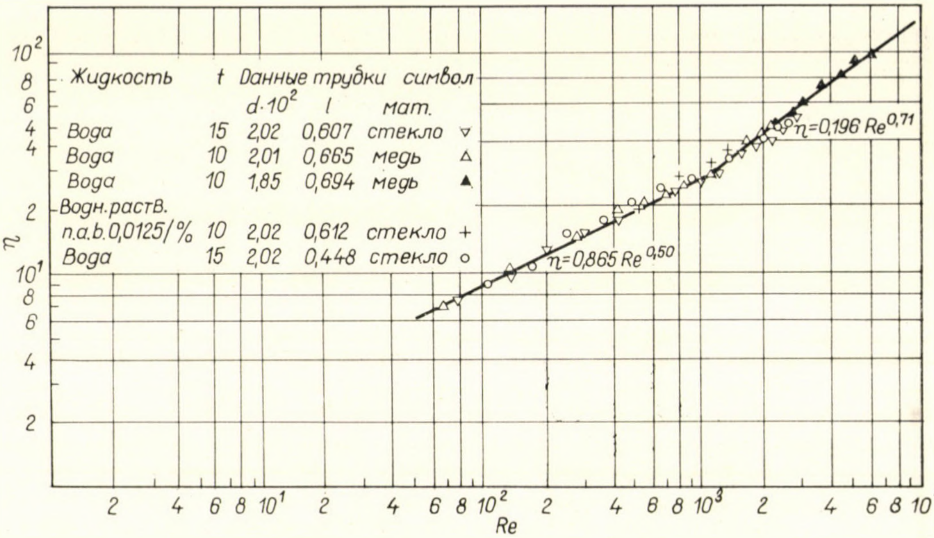

Рис. 7. Зависимость параметра η от числа Re

$$\eta = 0{,}196\, Re^{0{,}71}\,. \tag{22}$$

Подставляя рассчитанные таким путем значения A и k в уравнение (16) получаем:

$$f = 4{,}91\, Re^{-0{,}57}\,. \tag{23}$$

Уравнения, полученные для трех режимов течения, приведены в таблице 2.

Таблица 2

Режим	f	m
Ламинарный $Re < 10^3$	$96\, Re^{-1}$	$\left(\dfrac{0{,}75\, Re\nu^2}{g}\right)^{1/3}$
Переходный $10^3 < Re < 10^4$	$4{,}91\, Re^{-0{,}57}$	$\left(\dfrac{3{,}84 \cdot 10^{-2}\, Re^{1{,}43}\nu^2}{g}\right)^{1/3}$
Турбулентный $10^4 < Re < 10^5$	$0{,}365\, Re^{-0{,}26}$	$\left(\dfrac{2{,}85 \cdot 10^{-3}\, Re^{1{,}74}\nu^2}{g}\right)^{1/3}$

В целях сравнения полученных уравнений с результатами измерений уравнения для f из таблицы 2 нанесены на рис. 1, 2 и 3.

II. Волновое движение на поверхности жидкостной пленки

В предыдущей главе мы упомянули, что на поверхности жидкостной пленки, начиная с определенного числа Re (20—30) появляется волновое движение. Волны заметны на поверхности пленки только на некотором расстоянии от места образования пленки.

Многочисленные измерения показали, что с появлением волн на поверхности пленки скорость тепло- и массопередачи в пленке заметно повышается. Это явление вызывает значительный интерес к волновому движению на поверхности пленки.

1. Обзор литературы

Хотя волновое движение описывается несколькими отличающимися друг от друга теориями [8], [21], [22], в настоящей работе мы остановимся только на выводах из теории Капицы [8], так как эта теория наиболее широко описывает изучаемое явление.

По модели Капицы волновое движение на поверхности пленки является установившимся движением с волнами синусоидального характера. Скорость движения волн постоянна по времени и в 2,4 раза больше средней по всей толщине пленки скорости U_{cp}.

Длина волн по теории равняется:

$$\lambda = 7{,}5 \left(\frac{\nu\delta}{Qg}\right)^{1/2}, \tag{24}$$

а средняя толщина пленки выражается уравнением (7). По теории Капицы волнообразование на поверхности пленки возникает при определенном числе Re и это значение для каждого специального случая может быть высчитано. Так, например, для случая воды при 20°C это значение равно $Re = 23$. Это значение более или менее подтверждается рядом опытных наблюдений [4], [15], [21], [23], [24]. С другой стороны, по мнению Брука [21], волнообразование не ограничено нижней границей — при достаточно большой длине поверхности волны будут образовываться при любом малом значении числа Re. Кроме этого, по его выводам в области $Re < 16{,}5$ для воды амплитуда волн настолько мала, что волны невооруженным глазом не замечаются.

Другой возможностью проверки теории Капицы является измерение средней толщины волнистой пленки. Затруднение заключается лишь в том, что предполагаемые значения из теории Капицы (уравнение (7)) и из теории

Нуссельта (уравнение (4)) отличаются друг от друга лишь на 7%, что меньше погрешности большинства измерений средней толщины пленки. Результаты некоторых измерений, однако, по их авторам [15], [17], [25] лучше характеризуются теорией Капицы, чем теорией Нуссельта.

По теории Капицы волновое движение является периодическим — синусоидальным. По наблюдениям [5], [26], [27], [28] волны такого рода замечаются только в месте их возникновения и на коротком от этого места расстоянии. По мере дальнейшего движения волновое движение теряет свою регулярность.

Измерения длин волн на месте их возникновения показали [26], [29], что в противоречии с уравнением (24) длина волн с изменением объемной скорости не уменьшается, а является приблизительно постоянной величиной.

2. Экспериментальное исследование волнового движения

2.1 Визуальные наблюдения. Волновое движение на поверхности пленки жидкости изучалось на установке, изображенной на рис. 5. Одновременно с образованием жидкостной пленки на ее поверхности и невооруженным глазом наблюдались волны, движущиеся по направлению к движению жидкости. Для улучшения видимости внутренняя часть стеклянной трубки заполнялась матовой белой жидкостью, а пленка окрашивалась перманганатом. Образование волн было заметно на расстоянии нескольких сантиметров от места образования пленки. В зависимости от скорости подачи жидкости это расстояние изменялось.

При малых скоростях подачи жидкости ($Re = 30-40$) волны стекали в форме правильных колец. С увеличением подачи скорость движения волн увеличивалась, нарушалась их правильная кольцеобразная форма. С дальнейшим увеличением подачи жидкости скорость волн настолько увеличивалась, что их наблюдение невооруженным глазом становилось невозможным.

Наименьшим числом Re, при котором еще наблюдалось волновое движение было $Re = 28$. Это значение немного выше значения, предсказанного теорией Капицы, но при меньших подачах пленка разрывалась. Волны при $Re = 28$ были видны не по всему периметру трубки, а только на одной ее части. Сходное неравномерное распределение волн было обнаружено и другими авторами [29], [30]. При этой скорости длина волн по всей трубке была постоянной и приблизительно равнялась величине 10 мм, предсказанной Стэинторпом и Алленом [26]. При повышении подачи жидкости волновое движение восстанавливалось по всему периметру трубки.

Для более подробного изучения волнового движения снимались кино- и фотосъемки с них. На приведенных фотоснимках 1—3 видно место образования волн. Волны имеют периодический характер, длина волн примерно 10 мм. После нескольких сантиметров течения волны теряют свою правильную форму, расстояние между ними увеличивается (фото 4—7). При больших подачах жидкости профиль волн размывается. Визуальные наблюдения позволяют сделать вывод, что за исключением малых чисел ***Re*** и места образования, волновое движение носит неровный характер.

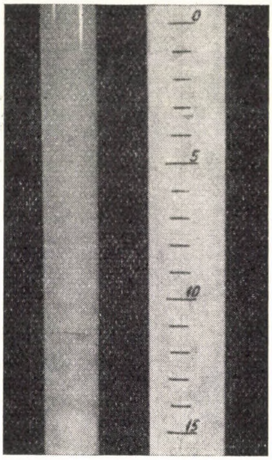

Фото 1

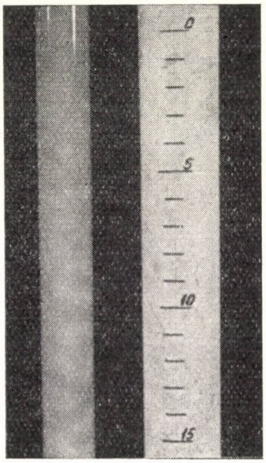

Фото 2

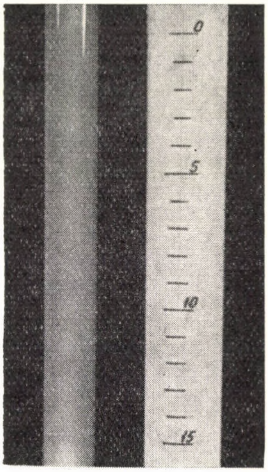

Фото 3

2.2 Измерение волнового движения на поверхности пленки. По теории Капицы, при постоянной подаче жидкости волны на поверхности пленки движутся с постоянной скоростью, которая в 2,4 раза больше средней скорости пленки. На основании визуальных наблюдений можно сделать вывод, что хотя профиль волн особенно при больших числах ***Re*** не показывает правильную форму, волны с примерно одинаковой скоростью следуют друг за другом.

Измерение скорости волн производилось их киносъемкой, где фиксировался пройденный путь волны за определенное время (количество кадров). Съемка производилась при скорости 24 и 48 кадров в секунду. Уже на основании фотоснимков можно было предположить, что волны не движутся с постоянной скоростью по всей длине трубки. Из снимков видно, что при образовании расстояние между волнами (длина волны) примерно постоянно, затем это расстояние увеличивается. Можно сделать вывод о том, что после образования волны проходят промежуток пути с ускорением, а затем их скорость опять становится постоянной.

По наблюдениям Стэинторпа и Аллена [26] волны сначала ускоряются, а затем замедляются. При замедлении волны должны бы накопляться, а этого ни на фото-, ни на киносъемках не замечается. Измерение скорости волн проводилось с окрашенной перманганатом водопроводной водой с тем-

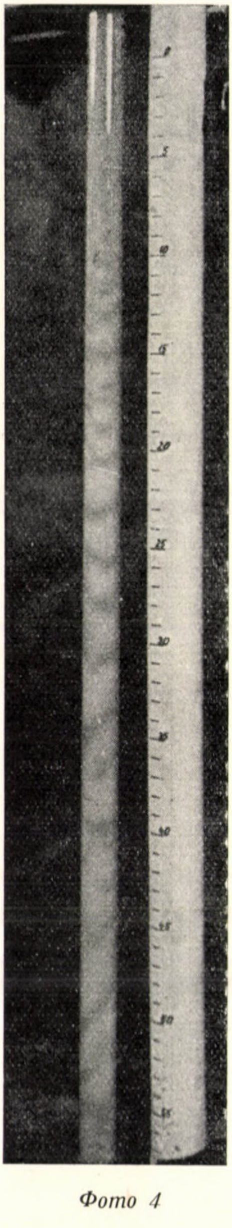
Фото 4

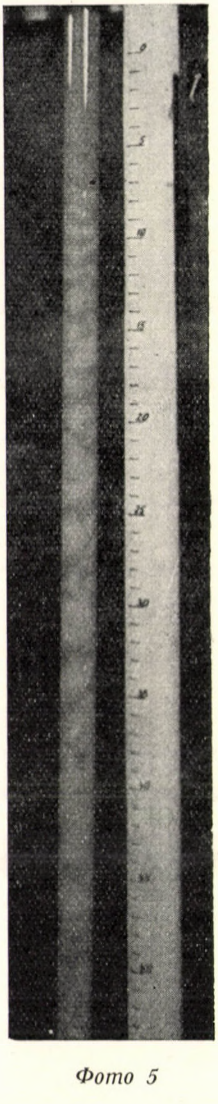
Фото 5

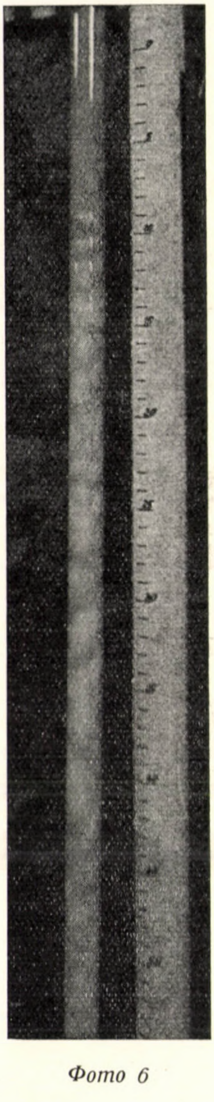
Фото 6

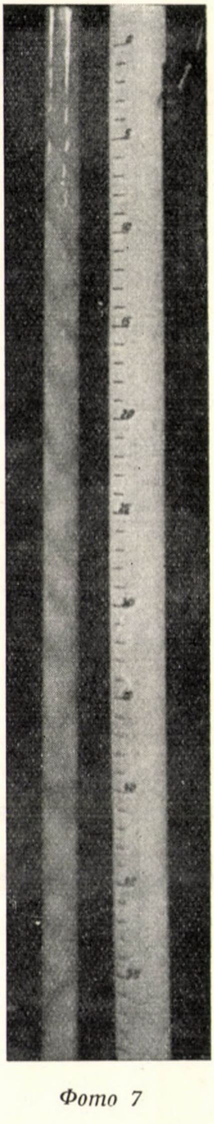
Фото 7

пературой 16°C, текущей по поверхности трубки с внешним диаметром 20,2 мм, длиной 630 мм.

На рис. 8 приведены средние скорости волн, измеренные на отрезках трубки, расположенных на различных расстояниях от места образования пленки. Измерения подтверждают предположение об ускорении волн.

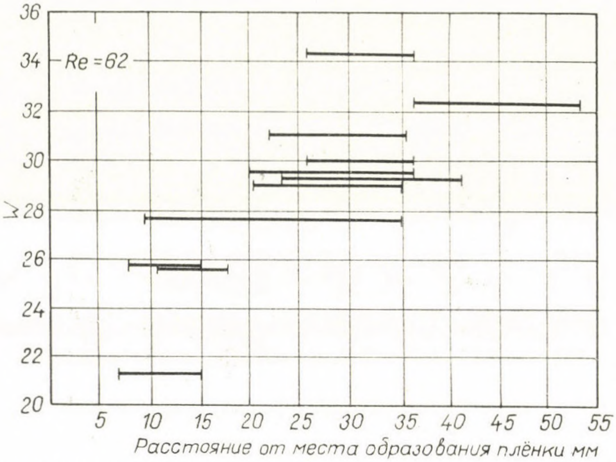

Рис. 8. Скорость движения волн на отрезках поверхности, расположенных на различных расстояниях от места образования пленки

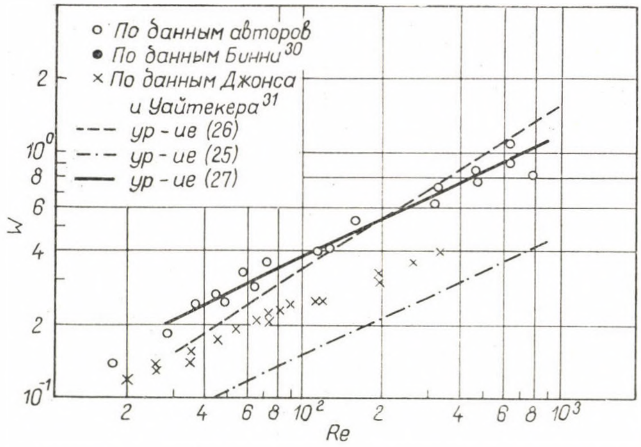

Рис. 9. Зависимость скорости волнового движения от числа **Re**

Результаты измерений скорости волн в зависимости от числа *Re* стекающей пленки приведены на рис. 9.

Уже упомянутые Стэинторп и Аллен [26], на основании своих измерений скорости волн в месте их образования получили эмпирическую формулу:

$$W = 1{,}48 \cdot 10^{-2}\, Re^{0{,}5}. \tag{25}$$

На основании теории Капицы скорость волн:

$$W = 0{,}71\, (\nu g)^{1/3}\, Re^{2/3}. \tag{26}$$

Уравнения (25) и (26) вместе с результатами некоторых авторов [30], [31] приведены на рис. 9. Измеренные нами скорости волн, хотя их зависимость от числа *Re* находится в том же порядке, значительно больше результатов, полученных упомянутыми авторами [26], [31]. Это объясняется тем, что их измерения проводились в области образования волн, а мы измеряли скорость волн в области их стационарных скоростей.

На основании наших измерений, для скорости волн в зависимости от числа Re жидкостной пленки мы получили эмпирическое уравнение:

$$W = BRe^{0,5}, \tag{27}$$

где при условиях нашего опыта $B = 3{,}82 \cdot 10^{-2}$.

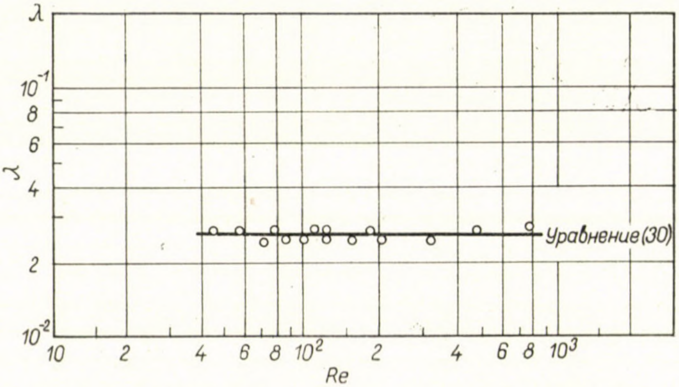

Рис. 10. Зависимость длины волн от числа Re

На основании уравнения для скорости движения волн, возможно получить изменение длины волны в зависимости от числа Re. Для этого мы воспользовались литературным [26] эмпирическим уравнением, характеризующим волновой поток (под волновым потоком подразумевается число волн, проходящее мимо внешнего наблюдателя, за единицу времени):

Волновой поток равен:

$$b = 1{,}3\, Re^{0,5}. \tag{28}$$

Делением уравнения (27) на уравнение (28) получаем выражение для длины волны:

$$\lambda = 2{,}94 \cdot 10^{-2}. \tag{29}$$

По уравнению (29) длина волны не зависит от числа Re жидкостной пленки. В целях проверки этого вывода мы попытались определить среднюю длину волн в области установившегося течения. Для этого на фото- и киносъемках подсчитывалось количество волн на определенном отрезке трубки и затем рассчитывалась средняя длина волны.

Результаты, приведенные на рис. 10, подтверждают независимость длины волны от числа Re. В данном случае для средней длины волны в области $Re = 44-785$ мы получили значение

$$\lambda = 2{,}61 \cdot 10^{-2}. \tag{30}$$

Так как при измерениях волнового движения изменялась только скорость подачи жидкости, то полученные результаты нельзя считать окончательными. Необходимы дальнейшие теоретические и экспериментальные изыскания для выяснения механизма волнового течения жидкостной пленки на поверхности.

SUMMARY

Experimental data taken from the literature and the authors' own results are used to compare different theories of the flow of faning films on vertical surfaces The following equation is proposed to characterize the average thickness of the faning film in the range $0 < \mathrm{Re} < 80{,}000$:

$$\eta = A\mathrm{Re}^k$$

where A and k are constants. The values of A and k are calculated for three flow ranges, using known equations and original data. Measurements of the average thickness of the faning film indicate that the Nusselt theory adequately characterizes the observed phenomena in the range where $\mathrm{Re} < 1000$. The observation of, and the measurements carried out on, the waves formed on the surface of the faning film show that the theory only predicts correctly the location of wave-formation, other characteristics being at variance with the theory. On the basis of the present measurements, the speed and length of the waves are described as functions of the input of liquid.

Обозначения

A	— Константа в уравнении (14)	—
B	— Размерный коэффициент в уравнении (27)	м/сек
Q	— Удельная скорость подачи	м^2/сек
Re	— Число Рейнольдса	—
b	— Волновой поток	1/сек
f	— Коэффициент трения	—
g	— Ускорение силы тяжести	м/сек^2
k	— Константа в уравнении (14)	—
m	— Средняя толщина пленки	м
U	— Линейная скорость течения	м/сек
U_{cp}	— Средняя по толщине пленки линейная скорость течения	м/сек
U_{μ}	— Максимальная скорость течения	м/сек
y	— Расстояние от стенки	м
W	— Скорость волнового движения	м/сек
η	— Значение безразмерного расстояния от стенки на поверхности пленки	—
λ	— Длина волны	м
ν	— Кинематическая вязкость	м^2/сек
δ	— Динамическое поверхностное натяжение	м^3/сек^2

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EINE NÄHERUNGSMETHODE ZUR KINETISCHEN ANALYSE VON FOLGEREAKTIONEN

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Es wurde eine handlichere Näherungsmethode zur kinetischen Analyse von aus zwei uni- und/oder bimolekularen konsekutiven Prozessen bestehenden Folgereaktionen ausgearbeitet. Die Methode wurde an dem Beispiel des auch exakt behandelten Folgereaktionssystems $A + B \rightarrow C$, $C + D \rightarrow E$ dargelegt und auch ihre Fehlergrenze wurde geschätzt.

Die exakte kinetische Behandlung der Folgereaktionen ist, wie in unseren früheren Mitteilungen [1—4] gezeigt wurde, im Falle von Systemen, die aus zwei uni- und/oder bimolekularen konsekutiven Reaktionen bestehen, immer durchführbar. Die exakte Lösung führt aber manchmal zu weniger bekannten höheren Funktionen, deren praktische Anwendung (besonders für einen Chemiker) gewisse rechnungstechnische Schwierigkeiten verursacht. Obwohl diese Schwierigkeiten überwindbar sind, hielten wir es für zweckmäßig, eine Näherungsmethode auszuarbeiten, die bei mehreren Systemen leicht anzuwenden ist.

Diese Näherungsmethode, grundsätzlich eine Polygon-Approximation, soll in der vorliegenden Arbeit beschrieben werden und zwar im Interesse der besseren Verständlichkeit für den Fall des auch exakt behandelten [1] Systems

$$A + B \rightarrow C \tag{1}$$

$$C + D \rightarrow E \tag{2}$$

1. Das Differentialgleichungssystem und die exakte Lösung

Die zur Entstehung von je einem Mol des im Zuge des Gesamtprozesses entstehenden Zwischenproduktes C verbrauchte Menge der Substanz A sei a Mol, die der Substanz B sei b Mol, ferner sei mit d die Menge der Substanz D bezeichnet, die zum Verbrauch von je 1 Mol des Zwischenproduktes benötigt wurde und mit e die Menge der entstandenen Substanz E; die jeweilige molare Konzentration der verschiedenen Substanzen sei mit den entsprechenden großen Buchstaben (A, B, C, D, E) und die Anfangskonzentration mit dem Index o (A_o, B_o, $C_o = 0$, D_o, $E_o = 0$) bezeichnet: zur Bezeichnung der molaren Quantität der bis zum Zeitpunkt t laut (1) entstandenen Substanz C diene die Funktion $x = x(t)$ und zur Bezeichnung der laut (2) bis zum Zeitpunkt t verbrauchten molaren Quantität von C die Funktion $y = y(t)$, d. h. definitionsgemäß sei

$$C = x - y \tag{3}$$

ferner seien die folgenden Bezeichnungen eingeführt:

$$\frac{A_o}{a} = a_o \tag{4}$$

$$\frac{B_o}{b} = b_o \tag{5}$$

$$\frac{D_o}{d} = d_o \tag{6}$$

$$abk_1 = \varkappa_1 \tag{7}$$

$$dk_2 = \varkappa_2 \tag{8}$$

dann kann das Differentialgleichungssystem für die Reaktionen (1) und (2) wie folgt aufgeschrieben werden:

$$\frac{dx}{dt} = \varkappa_1 (a_o - x)(b_o - x) \tag{9}$$

$$\frac{dy}{dt} = \varkappa_2 (x - y)(d_o - y). \tag{10}$$

Die Lösung der Differentialgleichung (9) lautet [bei $t = 0$ ist $x(o) = 0$]:

$$x(t) = a_o b_o \frac{1 - \varepsilon_1(t)}{b_o - a_o \varepsilon_1(t)} \tag{11}$$

bzw. damit

$$A = A_o \frac{(aB_o - bA_o)\,\varepsilon_1(t)}{aB_o - bA_o \varepsilon_1(t)} \tag{12}$$

$$B = B_o \frac{aB_o - bA_o}{aB_o - bA_o \varepsilon_1(t)} \tag{13}$$

wobei $\varepsilon_1(t)$ für folgenden Ausdruck steht:

$$\varepsilon_1(t) = \exp[-\varkappa_1 (b_o - a_o)\,t]. \tag{14}$$

Für die Konzentration des Zwischenproduktes C ist, nach Einführung der neuen Veränderlichen,

$$z = \frac{x - a_o}{b_o - a_o} \tag{15}$$

bzw. der Funktion

$$C(t) = W(z) \tag{16}$$

die folgende Lösung zu gewinnen:

$$C = W(z) = \frac{a_o - b_o}{\beta} z(z-1) \frac{\dfrac{df_1(z)}{dz} + K \dfrac{df_2(z)}{dz}}{f_1(z) + Kf_2(z)} \tag{17}$$

wo die Funktion $f_1(z)$ für alle Werte von z

$$f_1(z) = z^{1-\gamma}(1-z)^{\gamma-\beta-1} \tag{18}$$

bedeutet, die Funktion $f_2(z)$ ist aber für beliebige Werte von z folgend definiert:

im Falle von $|z| < 1$:

$$f_2(z) = {}_2F_1(1, \beta; \gamma; z) \tag{19}$$

im Falle von $z < -1$:

$$f_2(z) = -\frac{1}{z}\, {}_2F_1\left(1, 2-\gamma; 2-\beta; \frac{1}{z}\right) \tag{20}$$

im Falle von $z > +1$:

$$f_2(z) = \frac{1}{z}\, {}_2F_1\left(1, 2-\gamma; 2+\beta-\gamma; 1-\frac{1}{z}\right). \tag{21}$$

Die Deutung der Konstanten in den Ausdrücken (17)—(21) ist, wie folgt:

$$\beta = -\frac{\varkappa_2}{\varkappa_1} \tag{22}$$

$$\gamma = 1 - \frac{\varkappa_2}{\varkappa_1} \frac{d_o - a_o}{b_o - a_o}. \tag{23}$$

Die Funktion ${}_2F_1\,(a, b; c; \zeta)$ in den Gleichungen (19)—(21) ist die sog. hypergeometrische Funktion, die durch die folgende Potenzreihe definiert ist ($c \neq 0, -1, -2, \ldots$):

$$ {}_2F_1(a,b;c;\zeta) = 1 + \frac{ab}{c}\,\frac{\zeta}{1!} + \frac{a(a+1)\,b(b+1)}{c(c+1)}\,\frac{\zeta^2}{2!} + \ldots \tag{24} $$

Der Wert der Konstanten K in (17) wurde aus den Anfangsbedingungen gewonnen:

$$ K = -\frac{\dfrac{df_1(z_o)}{dz}}{\dfrac{df_2(z_o)}{dz}} \tag{25} $$

wobei z_o den Anfangswert von z bedeutet:

$$ z_o = \frac{a_o}{a_o - b_o}\,. \tag{26} $$

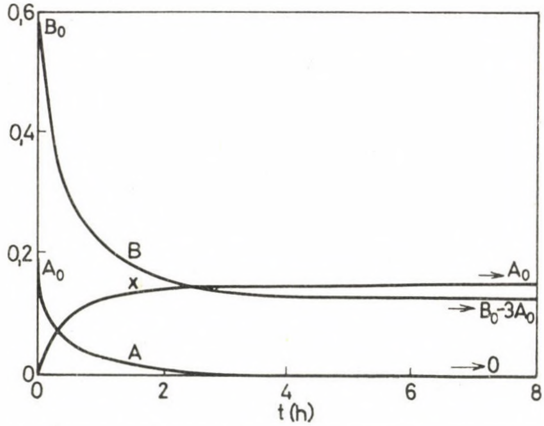

Abb. 1. Beispiel für die zeitliche Änderung von A, B und x

Aus der Lösungsfunktion (17) für C erhält man mit Hilfe der Zusammenhänge (3) und (11) die Funktion $y(t)$:

$$ y(t) = x(t) - C \tag{27} $$

und damit auch die Konzentrationen der Substanzen D und E:

$$ D = D_0 - dy(t) \tag{28} $$

$$ E = ey(t)\,. \tag{29} $$

Die Zeitabhängigkeit der Konzentrationen A, B, C, D und E bzw. der Funktionen x und y ist auf Grund der exakten Lösungen [der Reihe nach: (12), (13), (17), (28) und (29) bzw. (11) und (27)] in den Abbildungen 1 und 2 dargestellt. [Im dargestellten Beispiel einer anorganischen Reaktion [5] betrugen: $A_o = a_o = 0{,}1505$ $(a = 1)$, $B_o = 3\,b_0 = 0{,}5783$ $(b = 3)$, $D_o = 3\,d_o = 0{,}2877$ $(d = 3)$, $E = y$ $(e = 1)$, $k_1 = 5{,}16$, $k_2 = 0{,}28$.]

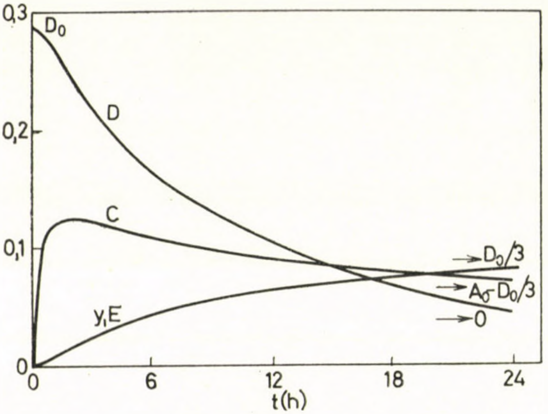

Abb. 2. Beispiel für die zeitliche Änderung von C, D und y

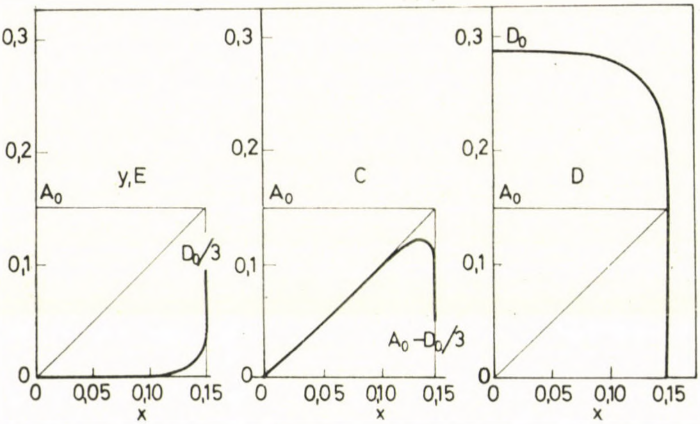

Abb. 3. Beispiel für die Abhängigkeit der Größen C, D, E und y von x

In Abb. 3 werden dieselben Werte des angewandten Beispiels als Funktion der Veränderlichen x dargestellt. Aus dieser Abbildung ist ersichtlich, daß die Lösung laut (17) gut zu behandeln ist, solange der Wert der Veränderlichen x sich dem Grenzwert nicht allzusehr nähert. Es ergeben sich jedoch gewisse rechnerische Schwierigkeiten (die aber nicht unüberwindlich sind), wenn man die exakte Lösung nach (17) bei den dem Grenzwert naheliegenden x-Werten anwendet. Im angeführten Beispiel ändert sich der x-Wert nach

5 Stunden Reaktionszeit praktisch nicht mehr (s. Abb. 1: die Änderung beträgt weniger als 10^{-3} % und wird ständig kleiner), obzwar die Reaktion (2) noch viele Stunden hindurch die Menge des Zwischenproduktes vermindert (Abb. 2).

2. Die annähernde Lösung des Differentialgleichungssystems

Im Zusammenhang mit Abb. 3 wurde schon darauf hingewiesen, daß bei langen Reaktionszeiten die Anwendung der exakten Lösung laut (17) gewisse rechnungstechnische Schwierigkeiten verursacht. Weitere Schwierigkeiten entstehen beim Rechnen mit hypergeometrischen Reihen, wenn die Bestimmung der Reaktionskonstanten auf Grund von experimentellen Daten benötigt wird. Daher wird im folgenden eine handlichere Annäherungsmethode beschrieben. Unseres Erachtens ist diese Methode bei sinngemäßer Anwendung auch dazu geeignet, bei kinetischen Problemen benützt zu werden, die zu exakt nicht lösbaren Differentialgleichungen führen.

2.1 *Die Näherungsfunktion* $\tilde{y} = \tilde{y}(t)$

Die Differentialgleichung (10) wäre, wie aus dem Vergleich mit (9) zu sehen ist, in geschlossener analytischer Form integrierbar, falls

$$x = \text{konstant} \tag{30}$$

sein sollte. Theoretisch wird diese Bedingung nie, praktisch aber dann erfüllt, wenn x seinem Grenzwert schon ziemlich nahegekommen ist (z. B. in dem in Abb. 1 bis 3 vorgeführten Beispiel bei $t > 5$ Stunden Reaktionsdauer). Für ein ganz kleines Zeitintervall wird aber kein großer Fehler begangen, wenn in diesem der x-Wert als konstant betrachtet und die Differentialgleichung, analog zu (9), für das erwähnte Zeitintervall integriert wird, und sodann mit dem erhaltenen Resultat für das nächste — ebenfalls sehr kleine — Zeitintervall neue Anfangsbedingungen bestimmt werden.

Die Grundlage der jetzt beschriebenen Polygon-Approximation bilden die folgenden Relationen:

Die Anfangsbedingungen des n-ten Intervalles

$$\Delta t_n = t_n - t_{n-1}, \tag{31}$$

d. h. die Werte von C und $\frac{1}{d} D$ am Anfang dieses Intervalles seien c_{n-1} bzw. d_{n-1}. Diese können folgenderweise errechnet werden:

$$c_{n-1} = \tilde{x}_{n-1} - \tilde{y}_{n-1} \tag{32}$$

bzw.

$$d_{n-1} = d_\sigma - \tilde{y}_{n-1} \tag{33}$$

wobei

$$\tilde{x}_{n-1} = \frac{x_{n-1} + x_n}{2} \tag{34}$$

bzw.

$$\tilde{y}_{n-1} = \sum_{i=1}^{n-1} \Delta\tilde{y}i \tag{35}$$

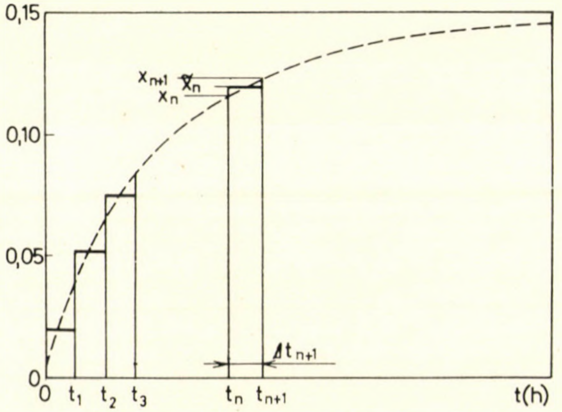

Abb. 4. Beispiel für die Konstruktion der Treppenfunktion $\tilde{x}(t)$

bedeuten. In (34) geben x_{n-1} und x_n die Werte der $x(t)$-Funktion für den Anfang bzw. das Ende des n-ten Intervalles an, daher ist x_{n-1} das arithmetische Mittel der beiden. Im wesentlichen erfolgt hiermit der Übergang von der Funktion $x(t)$ zur Treppenfunktion $\tilde{x}(t)$ (Abb. 4). Hiermit wurde einerseits erreicht, daß unser Verfahren auch für das erste Zeitintervall anwendbar wurde $[x_o = 0$, wogegen $\tilde{x}_o = (x_o + x_1)/2 = x_1/2 \neq 0]$, anderseits aber, da die Ungleichheit

$$\tilde{x}_{n-1} \geqq x_{n-1} \tag{36}$$

besteht, wird bis zu einem gewissen Grade auch berücksichtigt, daß die Bedingung (30) nicht erfüllt ist und daher der Wert von x im fraglichen Intervall tatsächlich anwächst, obzwar wir diesen als eine Konstante in Rechnung ziehen.

$\Delta\tilde{y}_i$ in der Summierung (35) bezeichnet den Zuwachs der Näherungsfunktion $\tilde{y}(t)$ für das i-te Zeitintervall. Mit Hilfe der Anfangsbedingungen (32) und (33) kann nämlich die Differentialgleichung (10) folgenderweise aufgeschrieben werden:

$$\frac{d\tilde{y}}{dt} = \varkappa_2 (c_{n-1} - \tilde{y})\ (d_{n-1} - \tilde{y}) \tag{37}$$

und nach Integrierung für das n-te Zeitintervall ergibt sich

$$\Delta \widetilde{y}_n = c_{n-1} d_{n-1} \frac{1 - \varepsilon_2 (\Delta t_n)}{d_{n-1} - c_{n-1} \varepsilon_2 (\Delta t_n)} \tag{38}$$

wobei

$$\varepsilon_2 (\Delta t_n) = \exp \left[- \varkappa_2 (d_{n-1} - c_{n-1}) \Delta t_n \right] \tag{39}$$

bedeutet. Dieses Verfahren kann bis zu einem Zeitpunkt t_k fortgesetzt werden, in dem die Funktion $x(t)$ praktisch den Grenzwert erreicht, d. h. laut (34)

$$\widetilde{x}_k = \frac{x_k + x_{k+1}}{2} \approx \frac{2x_k}{2} = x_k \approx \lim_{t \to \infty} x(t) \tag{40}$$

ist, wodurch die Funktion $x(t)$ mit der Treppenfunktion $\widetilde{x}(t)$ praktisch zusammenfällt. Die mit den hiernach berechenbaren Anfangsbedingungen

$$c_k = x_k - \widetilde{y}_k \tag{41}$$

$$d_k = d_o - \widetilde{y}_k \tag{42}$$

aufgestellte Differentialgleichung

$$\frac{d\widetilde{y}}{dt} = \varkappa_2 (c_k - \widetilde{y}) \ (d_k - \widetilde{y}) \tag{43}$$

kann für die Zeitwerte $t > t_k$ schon unbestimmt integriert werden, womit die für die Zeitwerte

$$\tau = t - t_k \tag{44}$$

anwendbare Lösung

$$\widetilde{y}(\tau) = c_k d_k \frac{1 - \varepsilon_2 (\tau)}{d_k - c_k \varepsilon_2 (\tau)} \tag{45}$$

gegeben ist, in welcher

$$\varepsilon_2 (\tau) = \exp \left[- \varkappa_2 (d_k - c_k) \tau \right] \tag{46}$$

bedeutet. Im Zuge des durch die Schritte (31) bis (46) charakterisierten Näherungsverfahrens erhielten wir die annähernde Lösungsfunktion $\tilde{y} = \tilde{y}(t)$, welche laut (35) ($\tau \geqq 0$) in der Form

$$\widetilde{y}(t) = \sum_{i=1}^{k} \Delta \widetilde{y}_i + \widetilde{y}(\tau) \tag{47}$$

geschrieben werden kann; unter Zuhilfenahme dieser Gleichung können auch die Näherungswerte der Funktionen C, D und E errechnet werden, indem wir uns der Zusammenhänge (3), (28) und (29) bedienen:

$$\widetilde{C} = x(t) - \widetilde{y}(t) \tag{48}$$

$$\widetilde{D} = D_o - d\widetilde{y}(t) \tag{49}$$

$$\widetilde{E} = e\widetilde{y}(t) \tag{50}$$

2.2 *Fehlerabschätzung der Näherungslösung*

Zur übersichtlichen Durchführung der Fehlerabschätzung bedienen wir uns für die Bezeichnung der Differentialgleichung (10) der Funktion $g(x, y)$:

$$g(x, y) = \frac{dy}{dt} = \varkappa_2 (x - y)\ (d_o - y)\,. \tag{51}$$

Sinngemäß lautet die mit den Näherungsgleichungen $\tilde{x} = \tilde{x}(t)$ und $\tilde{y} = \tilde{y}(t)$ aufgeschriebene Differentialgleichung

$$g(\widetilde{x}, \widetilde{y}) = \frac{d\widetilde{y}}{dt} = \varkappa_2 (\widetilde{x} - \widetilde{y})\,(d_o - \widetilde{y})\,. \tag{52}$$

Wir suchen die maximale Abweichung dieser zwei Funktionen; da die Beziehung $|\alpha + \beta| \leq |\alpha| + |\beta|$ besteht, ist

$$|g(\widetilde{x}, \widetilde{y}) - g(x, y)| \leq |g(x, \widetilde{y}) - g(x, y)| + |g(\widetilde{x}, \widetilde{y}) - g(x, \widetilde{y})|\,. \tag{53}$$

Betrachten wir die erste Differenz der rechten Seite der Ungleichheit (53):

$$|g(x, \widetilde{y}) - g(x, y)| = \varkappa_2\, |(x - \widetilde{y}) + (d_o - y)| \cdot |\widetilde{y} - y|\,. \tag{54}$$

Da der maximale Wert des Unterschiedes des $x - \tilde{y} = \widetilde{C}$ den Wert von $\widetilde{C}_{\max}$ hat (d. h. die Maximalkonzentration des Zwischenproduktes, berechnet nach der Näherungsmethode), und der Höchstwert der $d_o - y$ Differenz d_o beträgt (sowohl $\widetilde{C}_{\max}$ als auch d_o positiv), daher ist

$$|g(x, \widetilde{y}) - g(x, y)| \leq \varkappa_2 (\widetilde{C}_{\max} + d_o) \cdot |\widetilde{y} - y|\,. \tag{55}$$

Der zweite Ausdruck auf der rechten Seite der Ungleichheit (53) kann folgenderweise umgewandelt werden:

$$|g(\widetilde{x}, \widetilde{y}) - g(x, \widetilde{y})| = \varkappa_2 |d_o - \widetilde{y}| \cdot |\widetilde{x} - x|\,. \tag{56}$$

Der maximale Wert dieses Ausdrucks, da $d_o > \tilde{y}$ ist, beträgt:

$$|g(\widetilde{x}, \widetilde{y}) - g(x, \widetilde{y})| \leq \varkappa_2 d_o |\widetilde{x} - x|\,. \tag{57}$$

Die hier vorkommende Differenz $|\tilde{x} - x|$ soll nun untersucht werden. Aus der Definition (34) der Treppenfunktion folgt:

$$|\tilde{x} - x| \leqq \left| \frac{x(t + \Delta t) + x(t)}{2} - x(t) \right| \approx \frac{\Delta t}{2} \frac{dx}{dt} \tag{58}$$

wo Δt das größte Zeitintervall unserer Approximation bezeichnet. Werden in der Gleichung (53) die Ausdrücke (55), (57) und (58) eingesetzt, so ergibt sich als Resultat:

$$|g(\tilde{x},\tilde{y}) - g(x, y)| \leqq \varkappa_2 (\tilde{C}_{\max} + d_o) \cdot |\tilde{y} - y| + \varkappa_2 d_o \frac{\Delta t}{2} \frac{dx}{dt} . \tag{59}$$

Die linke Seite der Ungleichheit (59) ist laut (51) und (52) nichts anderes als

$$|g(\tilde{x},\tilde{y}) - g(x, y)| = \left| \frac{d\tilde{y}}{dt} - \frac{dy}{dt} \right| . \tag{60}$$

Da die Relation $|\alpha| - |\beta| \leqq |\alpha - \beta|$ besteht, kann

$$\left| \frac{d\tilde{y}}{dt} - \frac{dy}{dt} \right| = \left| \frac{d}{dt} (\tilde{y} - y) \right| \geqq \frac{d}{dt} |\tilde{y} - y| \tag{61}$$

geschrieben werden. Wenn zur Bezeichnung der absoluten Differenz zwischen den exakten und den nähernden Lösungen die zeitabhängige Funktion $\Delta_{\text{abs}}(t)$ eingeführt wird, ist

$$|\tilde{y} - y| = \Delta_{\text{abs}}(t) \tag{62}$$

womit auf Grund von (61) die Ungleichung (59) in folgender Form geschrieben werden kann:

$$\frac{d}{dt} \Delta_{\text{abs}}(t) \leqq \varkappa_2 (\tilde{C}_{\max} + d_o)\, \Delta_{\text{abs}}(t) + \varkappa_2 d_o \frac{\Delta t}{2} \frac{dx}{dt} . \tag{63}$$

Es ist beweisbar, daß sich für diese die Lösung

$$\Delta_{\text{abs}}(t) \leqq \varepsilon_3(t) \left[\delta + \varkappa_2 d_o \frac{\Delta t}{2} \int\limits_o^t \frac{dx}{dt'} \frac{1}{\varepsilon_3(t')} dt' \right] \tag{64}$$

ergibt, wo $\varepsilon_3(t)$ folgende Bedeutung hat:

$$\varepsilon_3(t) = \exp [\varkappa_2 (\tilde{C}_{\max} + d_o)\, t] \tag{65}$$

und δ eine Integrationskonstante ist. Da einerseits die Relation $\varkappa_2(\tilde{C}_{\max} + d_o) > 0$ besteht, ist offenbar

$$\int_o^t \frac{dx}{dt'} \frac{1}{\varepsilon_3(t')} dt' \leq \int_o^t \frac{dx}{dt'} dt' = x(t) \tag{66}$$

und da andererseits im Zeitpunkt $t = 0$ sinngemäß $\Delta_{\text{abs}}(t) = 0$ ist, ist der Wert der Integrationskonstante

$$\delta = 0, \tag{67}$$

und deswegen kann die Lösung (64) in folgender Form geschrieben werden:

$$\Delta_{\text{abs}}(t) \leq \frac{1}{2} \varkappa_2 d_o \Delta t \, x(t) \, \varepsilon_3(t) \,. \tag{68}$$

Aus der hiermit für die höchste Fehlergrenze abgeleiteten Schätzung (68) kann einerseits festgestellt werden, daß das ausgearbeitete Näherungsverfahren konvergent ist:

$$\lim_{\Delta t \to o} \Delta_{\text{abs}}(t) = 0 \tag{69}$$

was soviel bedeutet, daß durch Verminderung der Größe der Zeitintervalle die Näherungsmethode Resultate liefert, welche sich dem exakten Resultat nähern, anderseits wird aber durch (68) auch die Abhängigkeit der Güte der Näherung von den Reaktionsparametern angezeigt. Die relative Abweichung (%) der mit der Näherungsmethode erhaltenen $\tilde{C}$ Zwischenprodukt-Konzentrationen $[\Delta_{\text{abs}}(t)]$ wurde gemäß (68) berechnet:

$$\Delta_{\tilde{C},\,\text{rel}}(t) = \frac{\Delta_{\text{abs}}(t)}{\tilde{C}} 100 \tag{70}$$

— im Falle des in den Abb. 1 bis 4 angeführten Beispiels und bei einer Approximation, wobei identisch 0,25stündige Intervalle ($\Delta t = 0{,}25$) benützt wurden — übersteigt nicht 4%, auch bei einer Reaktionsdauer von 5 Stunden [da laut Abb. 1 die Funktion $x(t)$ bei 5 Stunden praktisch den Grenzwert erreicht, mußte die Näherungsmethode nur für 5 Stunden Reaktionsdauer angewandt werden; für die 5 Stunden übersteigende Reaktionsperiode konnte schon die Relation (45) benützt werden]. Tatsächlich übersteigt die Differenz zwischen der mit der Näherungs- und mit der exakten Methode (17) errechneten Werte bei dem in den Abbildungen vorgeführten Beispiel in keinem Falle 1%, was darauf hinweist, daß der sich tatsächlich ergebende Fehler durch die Formel (68) stark überschätzt wird.

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X-RAY CRYSTALLOGRAPHIC COMPUTING PROGRAMS ON THE COMPUTER URAL-2, II

DETERMINATION OF A "BEST FITTED" PLANE TO A SET OF ATOMS BY THE SCHOMAKER ITERATIVE METHOD

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A program was elaborated for the computer URAL-2 that fits a plane to a given set of atoms. The iteration method of SCHOMAKER was used for the computations. The program is written in machine code, and computations of crystals having a monoclinic and higher symmetry can be performed with it. Maximal number of atoms of the set determining the plane is ten, while the distance of ten other atoms from the plane can be computed, too.

The molecule of an organic compound or one part of it is often plane, especially if the molecule contains aromatic rings. In the case of X-ray structure investigations it is necessary to find the plane that fits best to the positions of a set of atoms. The distances of the atoms from this plane give significant informations about the structure and the accuracy of the structure determination.

The problem can be solved most correctly by the method of least squares: The sum of squares of the distances of the chosen atoms to the plane shall be a minimum. SCHOMAKER *et al.* [1] give an iterative solution that makes the convergence very rapid. A program has been elaborated to perform the computations on the computer URAL-2.

The essential mathematical outlines of the iterative procedure is the following.

The position of one atom is given by the coordinates x_k, y_k, z_k, resp., by the vector r_k. The distance of this atom from the plane to be determined is D_k. This plane is defined by its unit normal vector, m and by its perpendicular distance from the origine, d. The atom-to-plane distance is then

$$D = m \cdot r_k - d$$

Such values of m and d are to be found which minimize the function

$$S = \sum_k D_k^2 = \sum_k (m \cdot r_k - d)^2$$

The sum is taken over the chosen atoms of the molecule. The condition that m is a unit vector

$$m \cdot m = 1$$

is taken into account using the method of the LAGRANGE multiplier. By means of the known procedure we get for d the following expression

$$d = m_1\bar{x} + m_2\bar{y} + m_3\bar{z}$$

m_1, m_2, m_3 are the components of the vector m, and $\bar{x}, \bar{y}, \bar{z}$ are the coordinates of the centroid of the set of atoms. For m and for the LAGRANGE multiplier λ we obtain a system of homogeneous linear equations that can be written in matrix notations:

$$(\mathbf{A} - \lambda\mathbf{g})\, m = 0 \tag{1}$$

To obtain the matrix **A** new coordinates of the atoms are introduced related o the centroid of the set of atoms

$$X_k = x_k - \bar{x}, \qquad Y_k = y_k - \bar{y}, \qquad Z_k = z_k - \bar{z}.$$

Denoting the matrix of the coordinates X_k, Y_k, Z_k by **X**

$$\mathbf{A} = \mathbf{X} \cdot \mathbf{X}^*$$

$\mathbf{X}^*$ is the transposed matrix of **X**. (So is $A_{11} = \sum_k X_k^2$, $A_{12} = A_{21} = \sum_k X_k Y_k$, etc.)

The matrix **g** contains the products of the reciprocal lattice vectors a^*, b^*, c^*, that is $g_{11} = a^{*2}$, $g_{12} = g_{21} = a^*b^*$, etc.

If the system of the homogeneous equations has a non-trivial solution, its determinant shall vanish: $|\mathbf{A} - \lambda\,\mathbf{g}| = 0$.

This is a cubic equation for λ and gives three roots $\lambda^{(1)}$, $\lambda^{(2)}$, $\lambda^{(3)}$ and so we obtain three vectors $m^{(1)}$, $m^{(2)}$, $m^{(3)}$. Since the identity $S \equiv \lambda$ can easily be proved, the "best plane" is represented by the smallest λ value, say $\lambda^{(1)}$.

This procedure is tedious (solution of cubic equation, in addition to a set of linear equations). By virtue of the smallness of the $\lambda^{(1)}$ value comparatively to the two others, SCHOMAKER *et al.* suggest the following iteration procedure:

We introduce a new matrix **B** by the identity $\mathbf{B} = \mathbf{A}^{-1}\,\mathbf{g}$; $\mathbf{A}^{-1}$ is the inverse of **A**. (The original publication uses the adjoint matrix being more convenient for hand computation. The inverse matrix is easier calculated in computer programs.) By multiplying (1) from the left with $\mathbf{A}^{-1}$ and using the properties $\mathbf{A} \cdot \mathbf{A}^{-1} = \mathbf{I}$ and $\mathbf{I} \cdot m = m$ (**I** is the unit matrix), after rearranging the equation obtained, we have

$$\mathbf{B} \cdot m \equiv \mathbf{A}^{-1} \cdot \mathbf{g} \cdot m = (1/\lambda) \cdot m \tag{2}$$

As a zero approximation we can choose any vector $m_{(o)}$ that is not perpendicular to $m^{(1)}$. (The approximate orientation of the molecule is known in this stage of the investigations.) $m_{(o)}$ can be written in the form

$$m_{(o)} = c_1 \cdot m^{(1)} + c_2 \cdot m^{(2)} + c_3 m^{(3)}. \tag{3}$$

We repeatedly multiply (3) with $\mathbf{B}$, making use of the property (2). So we obtain the first, second etc. approximations:

$$m_{(1)} \equiv \mathbf{B} \cdot m_{(o)} = (c_1/\lambda^{(1)}) \cdot m^{(1)} + (c_2/\lambda^{(2)}) \cdot m^{(2)} + (c_3/\lambda^{(3)}) \cdot m^{(3)},$$

$$m_{(2)} \equiv \mathbf{B} \cdot m_{(1)} = c_1(1/\lambda^{(1)})^2 \cdot m^{(1)} + c_2(1/\lambda^{(2)})^2 \cdot m^{(2)} + c_3(1/\lambda^{(3)})^2 \cdot m^{(3)},$$

etc.

If the set of atoms is really coplanar, $\lambda^{(1)}/\lambda^{(2)}$ is of the order of 10^{-4}, so for the n^{th} approximation the following expression is valid with high precision:

$$m_{(n)} = c_1 \cdot (1/\lambda^{(1)})^n \cdot m^{(1)}$$

We are going to see that one step is enough to evaluate $m^{(1)}$. The second step gives the value of $\lambda^{(1)}$.

The computer program

We have defined the fundamental vectors of the crystal as unit vectors: $|a| = |b| = |c| = 1$.

The reciprocal lattice fundamental vectors are given by the conditions $a \cdot a^* = b \cdot b^* = c \cdot c^* = 1$.

x_k, y_k, z_k shall be given in Ångstrom unit. The program is made for monoclinic crystals and it is good also for crystals having a monoclinic or higher symmetry.

In the monoclinic case

$$m \cdot m = (1/\sin^2 \beta^*) \cdot (m_1^2 + m_3^2 \; 2 m_1 m_3 \cos \beta^*) + m_2^2,$$

taken $m^{(1)} = m_1 a^* + m_2 b^* + m_3 c^*$.

$$\mathbf{g} = \begin{vmatrix} 1/\sin^2\beta^* & 0 & \cos\beta^*/\sin^2\beta^* \\ 0 & 1 & 0 \\ \cos\beta^*/\sin^2\beta^* & 0 & 1/\sin^2\beta^* \end{vmatrix}$$

β^* is the angle between a^* and c^*.

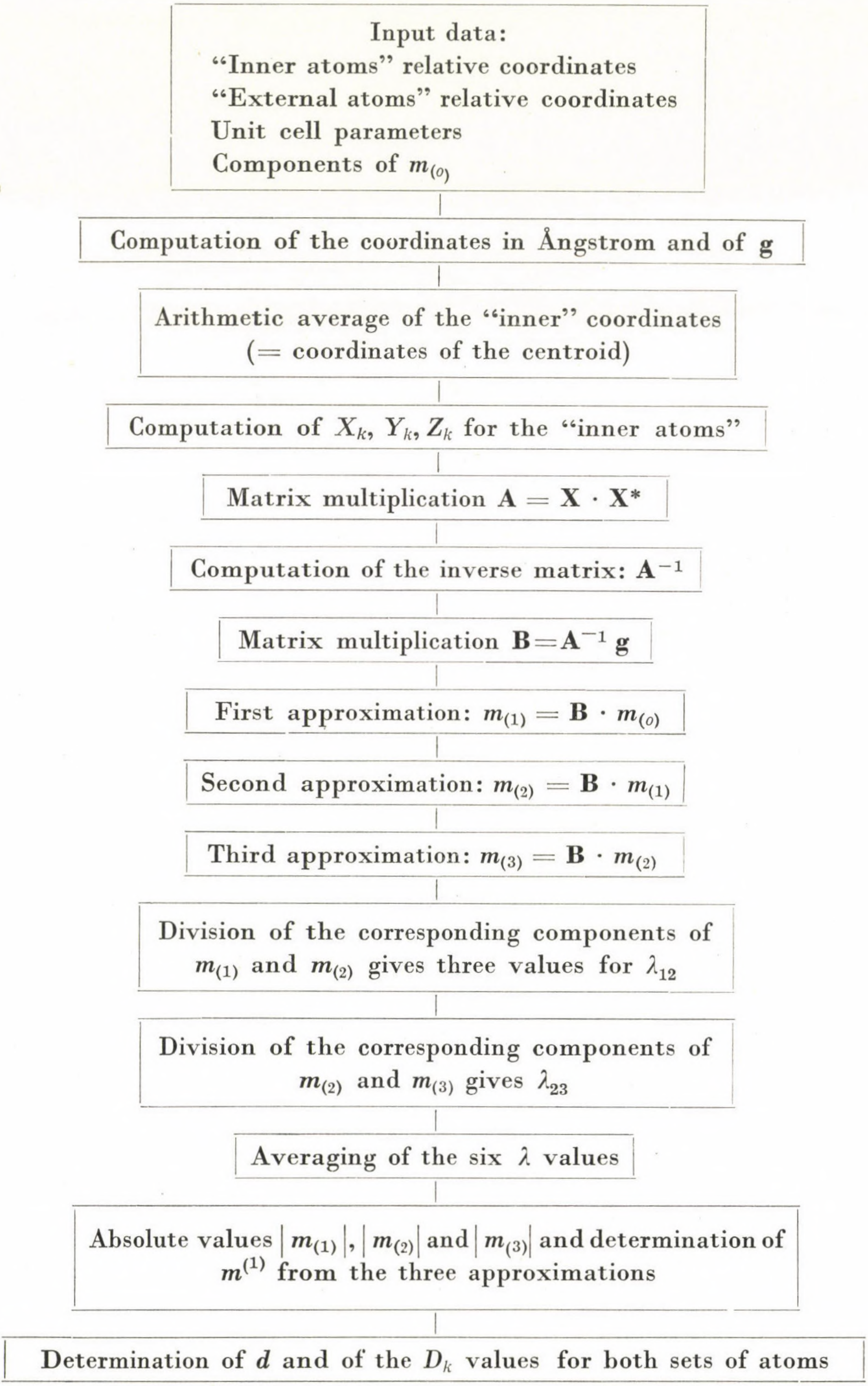
Coordinates of two sets of atoms are given as input data:

a) The set of atoms to which the plane shall be fitted, called further as "inner atoms".

b) The set of the "external atoms" that does not determine the plane but whose distances from the plane are computed, too.

The following block diagram presents the general outlines of the program:

The operations matrix-matrix multiplication and matrix-vector multiplication figure as subroutines. The calculation of the third approximation serves to check the speed of convergence. 10 "inner atoms" and 10 "external" ones can be drawn into the computations.



Input data:
"Inner atoms" relative coordinates
"External atoms" relative coordinates
Unit cell parameters
Components of $m_{(o)}$

Computation of the coordinates in Ångstrom and of $\mathbf{g}$

Arithmetic average of the "inner" coordinates (= coordinates of the centroid)

Computation of X_k, Y_k, Z_k for the "inner atoms"

Matrix multiplication $\mathbf{A} = \mathbf{X} \cdot \mathbf{X}^*$

Computation of the inverse matrix: $\mathbf{A}^{-1}$

Matrix multiplication $\mathbf{B} = \mathbf{A}^{-1}\, \mathbf{g}$

First approximation: $m_{(1)} = \mathbf{B} \cdot m_{(o)}$

Second approximation: $m_{(2)} = \mathbf{B} \cdot m_{(1)}$

Third approximation: $m_{(3)} = \mathbf{B} \cdot m_{(2)}$

Division of the corresponding components of $m_{(1)}$ and $m_{(2)}$ gives three values for λ_{12}

Division of the corresponding components of $m_{(2)}$ and $m_{(3)}$ gives λ_{23}

Averaging of the six λ values

Absolute values $|m_{(1)}|$, $|m_{(2)}|$ and $|m_{(3)}|$ and determination of $m^{(1)}$ from the three approximations

Determination of d and of the D_k values for both sets of atoms

The program has been used for the crystal of the 3-nitro-phenylhydrazon-acetone. The carbon atoms belonging to the benzene rings were taken as "inner atoms", all the others (excluding hydrogens) were the "external" ones. The $\left(\begin{smallmatrix}0\\1\\0\end{smallmatrix}\right)$ direction was chosen for $m_{(0)}$. The results are given in Table I.

Table I

$10^3 \cdot \lambda_{12}$	$10^3 \lambda_{23}$	components of $m^{(1)}$		
		from $m_{(1)}$	from $m_{(2)}$	from $m_{(3)}$
2.0822	2.0834	0.0078	0.0078	0.0078
2.0836	2.0834	0.8920	0.8920	0.8920
2.0827	2.0834	−0.4462	−0.4464	−0.4464

d from $m_{(1)}$ —2.513 Å, from $m_{(2)}$ —2.514 Å, from $m_{(3)}$ —2.514 Å

The data in Table I verify that the first approximation gives $m^{(1)}$ with a precision corresponding to the accuracy of the lattice parameter measurements and the second one gives a good $\lambda^{(1)}$ value.

*

The program is written in the machine code of the computer. The program is available at the Department for Experimental Physics, L. Eötvös University (Budapest VIII., Múzeum krt. 6—8). We are indebted to the coworkers of the University Computing Center for their kind help at the computations.

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HYDANTOINS, THIOHYDANTOINS AND GLYCOCYAMIDINES, XXVII+

REDUCTIVE REARRANGEMENTS OF THE RETROBENZILIC ACID TYPE INDUCED BY LEWIS ACIDS, IV++

SCOPE OF THE ALUMINIUM CHLORIDE INDUCED REACTIONS OF DITHIOHYDANTOINS WITH ARENES

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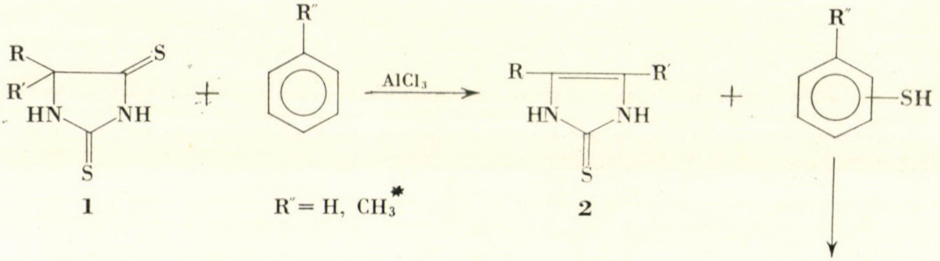
5,5-Diaryldithiohydantoins (where aryl = phenyl and *p*-chlorophenyl), when refluxed with benzene in the presence of aluminium chloride, are desulfurized and rearranged to yield the corresponding 4,5-diaryl-4-imidazoline-2-thiones. 5,5-Dimethyl- and 5,5-dibenzyldithiohydantoin do not yield analogous rearrangement products, whereas 5-aryl-5-methyl-dithiohydantoins (where aryl = phenyl, *p*-tolyl and *p*-chlorophenyl) are desulfurized under migration of the aryl group.

In previous parts of the present series the reductive desulfuration under rearrangement, brought about by treatment of 5,5-diphenyl-4-thiohydantoin or 5,5-diphenyldithiohydantoin (**1a**) [1, 2] or of their *N*- and/or *S*-alkyl derivatives [1—3] in benzene or toluene with aluminium chloride and yielding 4,5-diphenyl-4-imidazolin-2-ones and -2-thiones, respectively (or their *N*- and/or *S*-alkyl derivatives), has been described. In the case of **1a**, the reaction could be formulated as shown in Scheme 1.



1

R″ = H, CH_3*

2

a: R = R′ = C_6H_5
b: R = R′ = p-ClC_6H_4
c: R = R′ = p-$CH_3OC_6H_4$
d: R = C_6H_5; R′ = p-ClC_6H_4
e: R = R′ = CH_3
f: R = R′ = $C_6H_5CH_2$
g: R = CH_3; R′ = C_6H_5
h: R = CH_3; R′ = p-$CH_3C_6H_4$
i: R = CH_3; R′ = p-ClC_6H_4

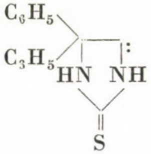
a: R = R′ = C_6H_5
b: R = R′ = p-ClC_6H_4
d: R = C_6H_5; R′ = p-ClC_6H_4
g: R = CH_3; R′ = C_6H_5
h: R = CH_3; R′ = p-$CH_3C_6H_4$
i: R = CH_3; R′ = p-ClC_6H_4

Scheme 1

* With solvent chlorobenzene (R″ = Cl) no reaction occurred under reaction conditions successfully applied for the rearrangement in arenes.

+ For Part XXVI, see [3].
++ Considered as Parts I—III are the papers [1—3].

Since the sulfur eliminated from position 4 of **1a** has been found to sulfurate the solvent arene, it was postulated that this atom became detached from the heterocycle in sextet state. Unfortunately, from this assumption, even if it means the transient formation of an intermediate of type **3** (complexed, of course, in some way to aluminium chloride), the actual state of the phenyl group during migration (with or without the electron pair by which it has been attached to C-5) cannot be deduced. The active site of **3** would be a carbenoid centre which may exhibit either nucleophilic or electrophilic activity [4], therefore, the phenyl group might, in principle, migrate both as an electrophil or as a nucleophil,* the latter, of course, being more probable.



3

In order to gain deeper insight into the mechanism of the reaction, we decided to study the behaviour of derivatives of **1a** carrying different *para* substituents in the phenyl rings.

5,5-Diaryldithiohydantoins are best prepared from the corresponding hydantoins or 2-thiohydantoins by treatment with phosphorus pentasulfide in tetralin [6, 7], the starting compounds themselves being prepared by the Biltz synthesis, *i.e.* by the base-catalyzed condensation of the appropriate benzil with urea and thiourea, respectively [8]. Unfortunately, the introduction of substituents other than alkyl groups into the benzene rings of benzil strongly interferes with the Biltz condensation (*cf.* [9]), or the sulfuration step, or both, therefore, only three such derivatives of **1a**, *viz.* the *p,p'*-dichloro (**1b**), *p,p'*-dimethoxy (**1c**) and *p*-chloro (**1d**) derivatives could be prepared.

5,5-Di(*p*-chlorophenyl)-dithiohydantoin (**1b**), when refluxed with benzene in the presence of aluminium chloride, rearranged normally under desulfuration to **2b**. The monochloro compound **1d** was found to behave analogously. Significant rate enhancement or rate decrease has not been found in either case compared with the reaction of **1a**, at least in the preparative work. The di(*p*-anisyl) derivative **1c**, on the other hand, did not yield the expected **2c** on treatment with aluminium chloride and only untractable tars were formed. In this connection it is important to note that **2c**, prepared independently, is decomposed by treatment with aluminium chloride in hot benzene. Accord-

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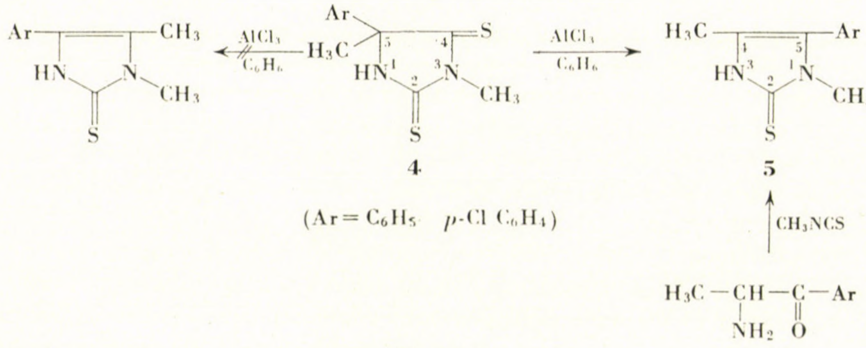
* The situation is somewhat analogous to the so-called electrophilic rearrangements *e.g.* the STEVENS and WITTIG rearrangements. For a critical review, see [5].

ing to the IR spectra of the crude products, the reagent had caused at least partial *O*-demethylation.

Next the behaviour of 5,5-dimethyl- (**1e**) and 5,5-dibenzyldithiohydantoin (**1f**) was investigated but, under the conditions successfully applied for the transformations of **1a**, **1b** and **1d**, neither was found to rearrange into the expected **2e** and **2f**, respectively.

On the other hand, the "mixed" 5-methyl-5-aryl derivatives (**1g**—**1i**) could easily be rearranged under desulfuration into the corresponding 4-imidazoline-2-thiones (**2g**—**2i**).

From our experience that the 5,5-diaryl derivatives (**1a, 1b** and **1d**) are unstable towards aluminium chloride, whereas the dimethyl derivative (**1e**) is stable towards the same reagent, it seemed practically certain that, in the case of **1g**—**1i**, it is always the aryl group which migrates. Treatment of the 3-methyl derivatives **4**, instead of compounds **1g**—**1i**, with aluminium chloride and an independent synthesis of the products **5** afforded a rigorous proof for the selective migration of the aryl groups (Scheme 2).



Scheme 2

Experimental*

Preparation of hydantoins and 2-thiohydantoins**

5,5-Di(p-chlorophenyl)-2-thiohydantoin

To a suspension of 4,4′-dichlorobenzil [10] (27.9 g; 0.1 mole) (prepared by selenium dioxide oxidation of the corresponding desoxybenzoin in dioxane solution) and thiourea (20.0 g; 0.26 mole) in methanol (400 ml) there was added an aqueous solution (50 ml) of potassium hydroxide (20.0 g; 0.36 mole), and the mixture was refluxed for 2 hrs. The hot solution was decolorized with Norite, diluted with water (2 l) and the pH adjusted to 4 by the addition of acetic acid, to obtain a colourless precipitate (32.5 g; 96.5%), m.p. 304—305°C (from aqueous methanol).

$C_{15}H_{10}Cl_2N_2OS$ (337.20). Calcd. Cl 21.25; N 8.31; S 9.51. Found Cl 21.01; N 8.55; S 9.65%.

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* All m.p.'s are uncorrected.

** Only the preparation of hydantoins and 2-thiohydantoins thus far unknown and the compounds prepared by new procedures are described.

S-*Methyl derivative*

The above product (2.6 g; 7.8 mmoles) and sodium hydroxide (0.31 g; 7.8 mmoles) were dissolved in a mixture of methanol (30 ml) and water (1 ml), and treated with methyl iodide (0.53 ml; 8.5 mmoles). After standing overnight, the mixture was diluted with water (100 ml) and the oily precipitate allowed to solidify in a refrigerator, to yield 2.6 g (95%) of a product which could be conveniently purified by sublimation at 4 Torr and 165°; m.p. 85—86 °C.

$C_{16}H_{12}Cl_2N_2OS$ (351.3). Calcd. N 7.98; S 9.13. Found N 7.76; S 9.13%.

Hydrolysis

The *S*-methyl derivative (1.50 g; 4.3 mmoles) was refluxed in a mixture of conc. HCl (4.5 ml) and ethanol (7.5 ml) for 5 hrs., during which period the evolution of methanethiol gradually ceased. After cooling, the mixture was diluted with water (10 ml) to yield 1.33 g (97%) of *5,5-di(p-chlorophenyl)-hydantoin*, m.p. 320 °C (from butanol), lit. m.p. [11]: 322°.

$C_{15}H_{10}Cl_2N_2O_2$ (321.2). Calcd. Cl 22.08; N 8.72. Found Cl 22.10; N 8.44%.

5,5-Dibenzyl- and 5-aryl-5-methylhydantoins were prepared according to Method *A* described by GOODSON *et al.* [12], see Table I.

5-Aryl-3,5-dimethylhydantoins were prepared by dissolving the corresponding 5-aryl-5-methylhydantoin in an equivalent amount of 10% aqueous NaOH, followed by the addition of 1 mole of methyl iodide, and allowing the mixture to stand, with occasional shaking, for about 15 hrs.; the product crystallized gradually from the solution (see Table I).

Preparation of dithiohydantoins

5,5-Dimethyl- (**1e**) and 5-methyl-5-phenyldithiohydantoin (**1g**) are known substances; the former has been prepared by the procedure described in the literature [17].

The other dithiohydantoins were prepared by sulfuration of the corresponding hydantoins or 2-thiohydantoins by phosphorus pentasulfide in tetralin. The detailed description of the preparation of 5,5-di(*p*-chlorophenyl)-dithiohydantoin serves as an example; for the preparation of the other dithiohydantoins, see Table II.

5,5-Di(p-chlorophenyl)-dithiohydantoin (**1b**)

A mixture of 5,5-di(*p*-chlorophenyl)-2-thiohydantoin (13.5 g; 40 mmoles), phosphorus pentasulfide (10.7 g; 48 mmoles) and dry tetralin (100 ml) was stirred for 2 hrs. at 195—200°. After cooling, the yellow homogeneous mixture was diluted with petroleum ether (50 ml) to yield a crystalline product (12.7 g) which was purified by dissolving it in 5% aqueous NaOH (200 ml), treating the solution with Norite, and adjusting the pH of the filtrate by the addition of acetic acid to 4. Yield: 12.3 g (80%) of **1b**, m.p. 282 °C (from benzene).

$C_{15}H_{10}Cl_2N_2S_2$ (353.30). Calcd. Cl 20.07; N 7.93; S 18.15. Found Cl 20.36; N 7.83; S 17.93%.

Rearrangements of the dithiohydantoins (cf. [2])

Mixtures prepared from the appropriate dithiohydantoin, dry toluene (20—30 ml for 1 g of the dithiohydantoin) and freshly sublimed aluminium chloride (2.2—2.5 mmoles for 1 mmole of the dithiohydantoin) were refluxed for 1.5—2 hrs. and, after cooling, poured into diluted (3 : 1) aqueous HCl (150 ml for 1 g of the starting dithiohydantoin). After stirring for 15 min., the colourless crystalline precipitates were sucked off, washed with water and, after recrystallization, identified by m.p. and mixed m.p. and/or by comparing their IR spectra with those of the appropriate authentic 4-imidazoline-2-thiones, prepared as described below. For details, see Table III.

When the above procedure was applied to 5,5-dibenzyldithiohydantoin (**1f**), a crystalline substance was obtained which proved to be different from the expected rearrangement product (**2f**). The structure elucidation of this product is in progress.

Table I

Preparation of some hydantoins

Substituent	Method[a)]	Yield	M. p.	Recryst. solvent	Lit. m. p.	Formula (Mol. wt.)	Calcd./Found C	H	N	References
5,5-Dibenzyl	*A*	89%	316 °C	ethanol	208—209 °C					13
5-Methyl-5-phenyl	*A*	53%	196 °C	ethanol	187 °C					14
5-Methyl-5-(*p*-tolyl)	*A*	70%	205 °C	ethanol	203—204 °C	$C_{11}H_{12}N_2O_2$ (204.23)	64.68 64.79	5.92 5.88	13.72 13.43	15
5-(*p*-Chlorophenyl)-5-methyl	*A*	86%	272 °C	ethanol	260—261 °C	$C_{11}H_9ClN_2O_2$ (224.65)	53.46 53.95	4.03 4.32	b)	15
3,5-Dimethyl-5-phenyl	*B*	86%	184 °C	50% methanol	188 °C	$C_{11}H_{12}N_2O_2$ (204.23)	64.68 64.27	5.92 5.93	13.72 13.42	16
3,5-Dimethyl-5-(*p*-chlorophenyl)	*B*	70%	187 °C	ethanol	—	$C_{11}H_{11}ClN_2O_2$ (238.67)		c)	11.74 11.35	—

a) Method *A* is identical with the Method *A*, described by GOODSON *et al.* [12]; Method *B*: *N*-methylation by methyl iodide in 15% aqueous sodium hydroxide solution.

b) Cl, Calcd. 15.78. Found 15.55%.

c) Cl, Calcd. 14.87. Found 14.98%.

Table II

Preparation of dithiohydantoins by sulfuration

Substituent	Starting compound	Temperature	Work up of the reaction mixture a)	Yield	M. p.	Recryst. solvent	Formula (Mol. wt.)	Calcd./Found			
								C	H	N	S
5,5-Di(*p*-anisyl) (**1c**)	2-Thiohydantoin [18]	165—170 °C b)	*A* c)	75%	192 °C	benzene	$C_{17}H_{16}N_2O_2S_2$ (344.45)	59.27 59.27	4.68 4.69	8.13 7.85	18.63 18.43
5-(*p*-Chlorophenyl)-5-phenyl (**1d**)	2-Thiohydantoin [19]	195—200 °C	*A*	64%	252 °C	aqueous methanol	$C_{15}H_{11}ClN_2S_2$ (318.85)	56.50 56.25	3.48 3.76		20.11 20.28
5,5-Dibenzyl (**1f**)	Hydantoin [13]	180—190 °C	*B*	96%	198—201 °C	aqueous methanol	$C_{17}H_{16}N_2S_2$ (312.45)	65.34 65.84	5.16 5.07	8.97 8.80	20.52 20.38
5-Methyl-5-phenyl (**1g**) [17]	Hydantoin [14]	190 °C	*B*	78%	173—174 °C d)	aqueous methanol					
5-Methyl-5-(*p*-tolyl) (**1h**)	Hydantoin [15]	190 °C	*B*	70%	198—199 °C	aqueous methanol	$C_{11}H_{12}N_2S_2$ (236.36)	55.89 55.63	5.12 4.89	11.85 11.80	27.13 27.14
5-(*p*-Chlorophenyl)-5-methyl (**1i**)	Hydantoin [15]	190 °C	*B*	83%	218 °C	ethanol	$C_{10}H_9ClN_2S_2$ (256.78)	46,77 47.09	3.53 3.59	e)	24.93 24.97
3,5-Dimethyl-5-phenyl (**4**; Ar = C_6H_5)	Hydantoin [16]	190 °C	*B*	70%	129 °C	aqueous methanol	$C_{11}H_{12}N_2S_2$ (236.36)	55.89 56.03	5.12 5.31	11.85 11.69	27.13 27.06
5-(*p*-Chlorophenyl)-3,5-dimethyl (**4**; Ar=*p*-ClC_6H_4)	Hydantoin	190 °C	*A*	70%	136 °C	methanol	$C_{11}H_{11}ClN_2S_2$ (270.80)		f)	10.35 10.03	23.68 24.04

a) Method *A*: The clear solution obtained at the end of the reaction was allowed to cool and then diluted with petroleum ether, whereupon the crystallization of the crude product began. It was purified by reprecipitating it from its solution in 5% aqueous NaOH by acetic acid. Method *B*: The clear supernatant of the hot reaction mixture was decanted and allowed to stand. On cooling, the product directly crystallized; dilution with petroleum ether was unnecessary.

b) At higher temperatures extensive charring occurred.

c) According to TLC, the material of m. p. 184—186 °C, obtained on recrystallization from benzene, still contained approximately 2% of the starting material as an impurity, but it could easily be purified by chromatographing its chloroform solution through a column of aluminium oxide (Brockmann II grade) and eluting with chloroform, the individual fractions being examined by TLC. Recovery: 80%.

d) Lit. m. p. 173—174 °C [17] e) Cl, Calcd. 13.80, Found 13.44%. f) Cl, Calcd. 13.09. Found 12.24%.

Table III

Rearrangement of the dithiohydantoins

Starting compound	mmoles	Product	Yield	M. p.	Recryst. solvent	Formula	Mol. wt.	Calcd./Found				
								C	H	N	S	Cl
1b	4	**2b**	90%[a)]	324 °C	acetic acid	$C_{15}H_{10}Cl_2N_2S$	321.3				9.98 10.18	22.07 22.16
1d	1	**2d**	91%	306—307 °C	ethanol	$C_{15}H_{11}ClN_2S$	286.76			9.77 9.67	11.18 11.26	12.36 12.13
1g	10	**2g**	87%	293 °C[b)]	aqueous methanol	$C_{10}H_{10}N_2S$	190.26	63.12 63.54	5.29 5.50	14.72 14.50	16.85 16.60	
1h	4	**2h**	95%	314 °C	aqueous ethanol	$C_{11}H_{12}N_2S$	204.30	64.66 64.60	5.92 5.60	13.71 13.02	15.69 15.88	
1i	4.7	**2i**	86%	308 °C	95% ethanol	$C_{10}H_9ClN_2S$	224.72					15.77 15.74
4 (Ar = C_6H_5)	10	**5** (Ar = C_6H_5)	100%[c)]	228 °C	aqueous methanol	$C_{11}H_{12}N_2S$	204.30	64.66 64.58	5.92 5.93	13.71 13.81	15.69 15.58	
4 (Ar = *p*-ClC_6H_4)	1	**5** (Ar = *p*-ClC_6H_4)	79%	292 °C	95% ethanol	$C_{11}H_{11}ClN_2S$	238.74	55.33 55.09	4.64 4.76	11.73 11.16	13.43 13.38	

a) On evaporation of the toluene phase of the filtrate of the crude product, 7% of the starting substance could be recovered.

b) Lit. m. p. [23]: 290—295 °C.

c) Part of the product crystallized directly when the reaction mixture was poured into dilute HCl; the rest was obtained by evaporating the toluene phase of the filtrate of the first crop and recrystallizing the residue.

When 5,5-dimethyldithiohydantoin was treated with aluminium chloride and the mixture poured into aqueous HCl, no crystalline precipitate was obtained. The toluene phase was therefore separated, washed until neutral and, after drying over $MgSO_4$, evaporated. The oily residue could be sublimed in vacuum and its m.p. proved it to be identical with the starting substance. The aqueous phase, after separation from the toluene phase, was extracted thoroughly with ether and the ethereal solution worked up as usual, to yield a crystalline residue which, again, proved to be identical with the starting substance, the total recovery of the latter being almost 100%. The same result was obtained in an attempt to perform the reaction in boiling xylene.

Synthesis of authentic 4-imidazoline-2-thiones

The 4,5-diaryl derivatives **2b—d** were prepared by condensing the appropriate benzoin with thiourea. The preparation of 4,5-di(*p*-chlorophenyl)-4-imidazoline-2-thione (**2b**), described in detail below, serves as an example. The 4-aryl-5-methyl derivatives **2g—i** were prepared, starting with the appropriate propiophenone, by isonitrosation and subsequent reduction according to the method of HOUSE and BERKOWITZ [20] and, finally, by reacting the α-ammonio-propiophenone chlorides (**6** · HCl) thus obtained with potassium thiocyanate.

The 5-aryl-1,4-dimethyl derivatives **5** were prepared starting with the same compounds, **6** · HCl, and reacting them with methyl isothiocyanate.

Of the α-isonitrosopropiophenone intermediates, the following were already known: α-isonitrosopropiophenone [21] and α-isonitroso-*p*-chloropropiophenone [22]; of the α-ammoniopropiophenone chloride intermediates, only the compound unsubstituted in the benzene ring has been described previously [23].

Among the 4-aryl-5-methyl derivatives again the compound unsubstituted in the benzene ring (**2g**) [23] has been known.

α-Isonitroso-p-methylpropiophenone, m.p. 118 °C (from chloroform; $C_{10}H_{11}N_2O$ (177.20). Calcd. C 67.77; H 6.25; N 7.90. Found C 67.83; H 6.25; N 7.90%.

α-Ammonio-p-methylpropiophenone chloride (**6** · HCl; Ar = p-CH_3-C_6H_4), m.p. 217 °C (by precipitation from an ethanolic solution with ether). $C_{10}H_{14}ClNO$ (199.67). Calcd. Cl 17.75; N 7.01. Found Cl 18.04; N 7.06%.

α-Ammonio-p-chloropropiophenone chloride (**6** · HCl; Ar = p-ClC_6H_4), m.p. 208 °C (purified as above). $C_9H_{11}Cl_2NO$ (220.10). Calcd. Cl 32.31; N 6.36. Found Cl 32.45; N 6.18%. Lit. m.p.: 245 °C [22].

4,5-Di(p-chlorophenyl)-4-imidazoline-2-thione (**2b**)

4,4′-Dichlorobenzoin [10]* (1.0 g; 3.7 mmoles) and thiourea (0.42 g; 5.5 mmoles) were thoroughly mixed and the mixture melted in an oil bath. At 195—200 °C a vigorous evolution of steam started. Another portion of finely pulverized thiourea was added, and the temperature raised to 210 °C. Accomplishment of the reaction was indicated by gradual solidification of the melt. After cooling, the solid was pulverized, treated with methanol (10 ml) and filtered off. The product could be purified by reprecipitation from its alkaline solution by acid to yield 0.60 g (51%) of **2b**, m.p. 324 °C (from ethanol).

$C_{15}H_{10}Cl_2N_2S$ (321.3). Calcd. Cl 22.07; S 9.98. Found Cl 22.44; S 9.72%.

4,5-Di(p-anisyl)-4-imidazoline-2-thione (**2c**) was prepared in essentially the same way, starting with anisoin, in 50% yield, m.p. 266—7 °C (from methanol), lit. m.p. [26]: above 280 °C.

$C_{17}H_{16}N_2O_2S$ (312.4). Calcd. N 8.97; S 10.26. Found N 8.65; S 10.25%.

4-(p-Chlorophenyl)-5-phenyl-4-imidazoline-2-thione (**2d**) was prepared similarly to the 4,5-di(*p*-chlorophenyl) analogue, **2b**, starting with 4-chlorobenzoin [25], in 35% yield. M.p. 306—307 °C (from ethanol).

$C_{15}H_{11}ClN_2S$ (286.76). Calcd. Cl 12.36; N 9.77; S 11.18. Found Cl 12.13; N 9.67; S 11.26%.

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* 4,4′-Dichlorobenzoin was prepared from 4,4′-dichlorodesoxybenzoin [24] by bromination with *N*-bromosuccinimide and benzoyl peroxide in carbon tetrachloride to obtain α-bromo-*p,p*′-dichlorodesoxybenzoin (yield: 87%, m.p. 84° [from ligroin]. $C_{14}H_9BrCl_2O$ [344.0]. Calcd. C 48.81; H 2.63; halogen as Cl 30.88. Found C 48.65; H 2.86; halogen as Cl 31.04). This compound was then converted into the required dichlorobenzoin in 82% yield according to the general method described by JENKINS [25].

4-Methyl-5-(p-tolyl)-4-imidazoline-2-thione (**2h**)

A mixture of **6** · HCl (Ar = p-$CH_3C_6H_4$) (0.45 g; 2.2 mmoles), potassium thiocyanate (0.22 g; 2.3 mmoles), water (10 ml) and ethanol (5 ml) was refluxed 1 hr. and subsequently evaporated to dryness. The residue was recrystallized from aqueous ethanol to yield 0.10 g (23%) of **2h**, m.p. 314 °C. For the analysis results, see Table III.

4-(p-Chlorophenyl)-5-methyl-4-imidazoline-2-thione (**2i**) was prepared similarly in 50% yield, m.p. 306 °C (from 95% ethanol).

1,4-Dimethyl-5-phenyl-4-imidazoline-2-thione (**5**; Ar = C_6H_5)

A mixture of α-ammoniopropiophenone hydrochloride (**6** · HCl; Ar = C_6H_5) [23] (0.31 g) 1.8 mmoles), methyl isothiocyanate (0.14 g; 1.9 mmoles), triethylamine (0.2 g; 2 mmoles) and methanol (10 ml) was refluxed for 1 hr. When a part of the solvent was evaporated, the product crystallized on cooling to yield 0.19 g (50%), of **5** (Ar = C_6H_5), m.p. 227 °C (from aqueous methanol).

5-(p-Chlorophenyl)-1,4-dimethyl-4-imidazoline-2-thione (**5**; Ar = p-ClC_6H_4) was prepared similarly in 23% yield, m.p. 286 °C (from ethanol).

*

The microanalyses were performed by Miss K. ÓFALVI, Mrs. S. VISZT-SIMON and Mrs. I. ZAUER-CSÜLLÖG, and the IR spectra were taken by Mrs. M. SZIRÁNYI-KISS. The authors wish to express their thanks for the valuable assistance of the persons named, as well as to Mrs. MEGYES-PAPP and Miss Zs. SZALAY for their technical assistance in the experiments.

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HETEROCYCLIC SPIRO COMPOUNDS, VI*

α- AND β-SPIROXAZONE

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In principle, six tautomeric forms (two spirane and four open-chain forms) can participate in the tautomerism of spiroxazone. Two of the tautomers are stable; when isolated, these (α-spiroxazone with spirane structure, **Ia**, and β-spiroxazone of an open structure, containing an endocyclic C=N bond, **Ic**) retain their structures at room temperature.

In the case of the open structure of spiroxazone, the stability of the two desmotropic forms is due to a relatively high potential barrier hindering the rearrangement of the C=N bonds, and in the case of the cyclic hydrazide group, to the greater stability of the semi-iminohydrine tautomer as well as to the difference in proneness to addition of the C=N double bond depending on its exo or endo position. The position of the C=N bond has been elucidated by NMR spectra and by investigating the alcohol addition reaction.

Spiro-(1,2,3,4-tetrahydrophthalazine-1,2'-oxazolidine)-4-one, or spiroxazone (**I**), whose structure has been verified by preparative methods and IR spectroscopy, is converted in basic medium into a compound that is identical with spiroxazone if the melting point, other physical properties and chemical characteristics are considered, yet it has an IR spectrum (Fig. 1) very similar to but not quite identical with that of spiroxazone (Fig. 2).

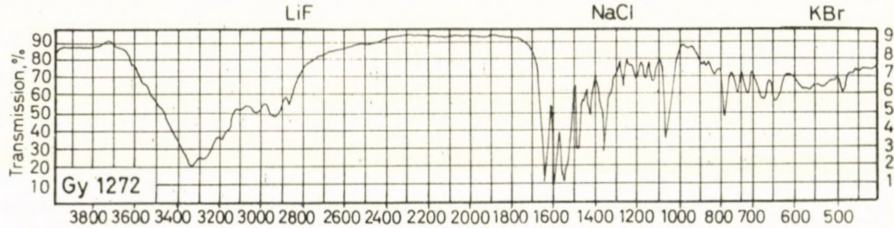

Fig. 1. IR spectrum of β-spiroxazone

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* Part I Acta Chim. Acad. Sci. Hung. **39,** 93—108 (1963).
Part II Acta Chim. Acad. Sci. Hung. **39,** 109—128 (1963).
Part III Acta Chim. Acad. Sci. Hung. **39,** 453—464 (1963).
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The elemental analyses and the UV (Fig. 3) and IR spectra of the derivatives, *e.g.* of the monoacetates [1], are the same for both compounds. This suggests that this is a case of tautomerism. In order to distinguish one compound from the other, the parent substance will be designated as α-spiroxazone, and the name β-spiroxazone is proposed to denote the new compound produced in basic media.

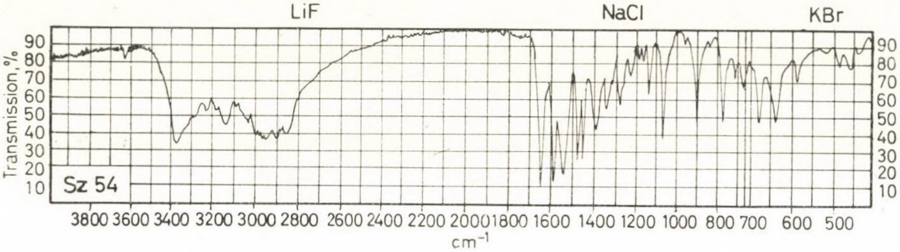


Fig. 2. IR spectrum of α-spiroxazone

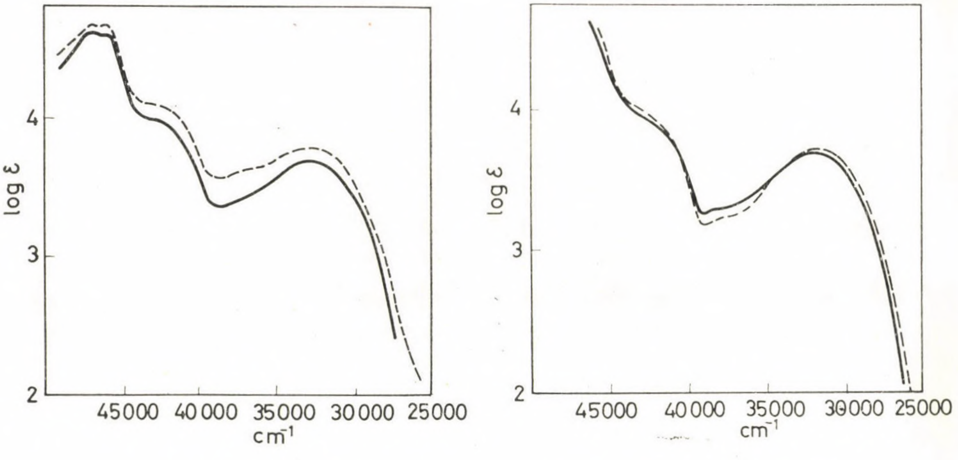
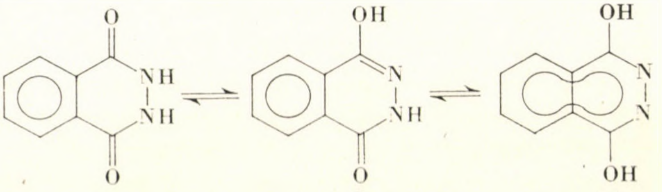
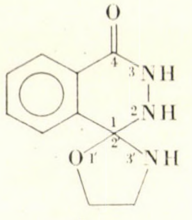


Fig. 3. UV spectra of α- (———) and β-spiroxazone (— — —)
a: in 0.1 *N* HCl
b: in 0.1 *N* NaOH

Spiroxazone (**I**) is a combination of two structural elements (**IIa** and **IIIa**) that show a tendency to tautomerize. One of these is a cyclic hydrazide. Such compounds, *e.g.* maleic hydrazide or phthalic hydrazide [2], form a possible tautomeric system of three components. According to the literature [3, 4, 5] the three tautomers differ in stability and their equilibrium is a function of the solvent. The NMR spectrum of phthalic hydrazide recorded in dimethyl sulphoxide suggests a di-oxo structure (**IIa**), whereas in ethanol or in propylene

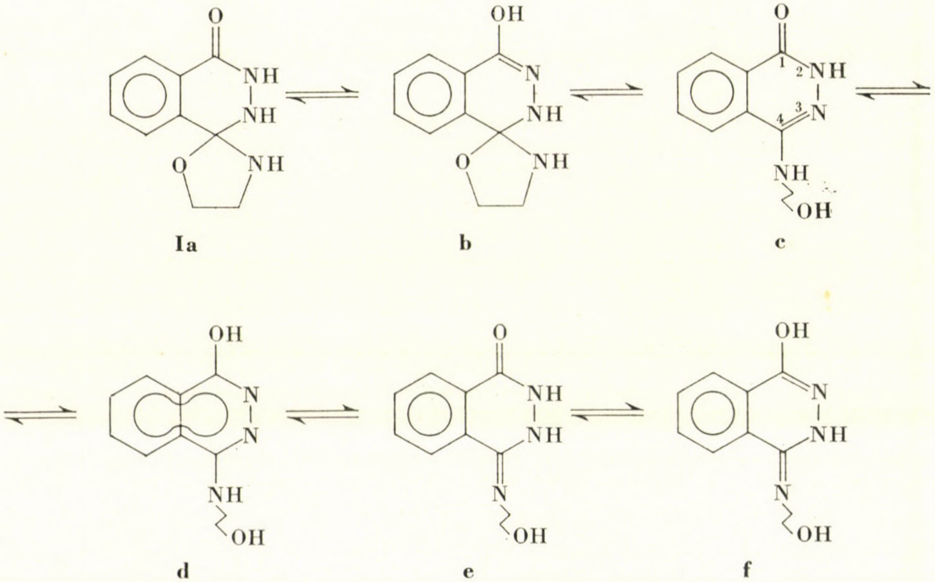


IIa **b** **c**



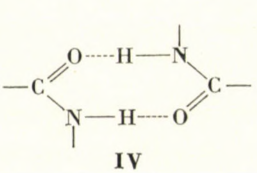
I

IIIa **b**

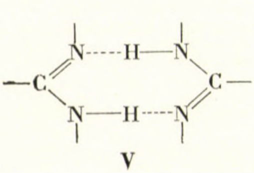


Ia **b** **c**

d **e** **f**



IV



V

carbonate, the semi-enolized form (**IId**) predominates, as it was also found by ELVIDGE [4]. ELVIDGE expresses some doubt in connexion with ROWE's statement [5] that in a neutral or acid medium phthalic hydrazide should be present in the 1,4-dihydroxy form (**IIc**). This tautomer has only been definitely identified in the form of its derivatives.

On the basis of consistent experimental results, of the three possible tautomers the half-enolized form, **IIb**, might be regarded as the most stable. Thus, generally, in the case of cyclic hydrazides mostly the tautomer analogous to **IIb** will be formed. This so-called "*semi-iminohydrine rule*" plays a decisive part in the chemical behaviour of cyclic hydrazides.

The other structural element of spiroxazone is the oxazolidine ring. A tautomeric change (**IIIa** $\rightleftharpoons$ **IIIb**) in this structure has been reported by BERGMANN [6].

A combination of the possible tautomeric changes of the two structural elements would theoretically suggest for spiroxazone the formation of a complex equilibrium system comprising six tautomers. Two of these would be spirane (**Ia** and **Ib**), and the remaining four semi-cyclic amidrazon tautomers (**Ic**—**If**).

In order to decide which of the six tautomers represent the structure of α- and β-spiroxazone, synthetic and spectroscopic studies have been undertaken.

Since α-spiroxazone is converted by bases into the β-compound, it seemed reasonable to suppose that β-spiroxazone corresponds to one of the iminohydrine tautomers (**Ib**, **Id** and **If**), and that the two modifications are members of one of the amide-iminohydrine tautomeric pairs (**Ia** and **Ib**; **Ic** and **Id**; **Ie** and **If**).

However, the conversion proved to be irreversible: β-spiroxazone could not be re-converted by acid into α-spiroxazone. This and other findings, together with the IR spectra, contradicted our first supposition.

The IR spectra do not allow unequivocal distinction between the tautomeric structures discussed, because the stretching vibration bands which are most characteristic of the OH and NH groups, the amide-I band of the amide group and the stretching vibration band of the straight-chain tautomers, further that of the C=N bond in the enol forms, appear nearly at the same frequency values and with equal intensities.

In the NMR spectra of α- and β-spiroxazone samples dissolved in dimethyl sulphoxide (Figs 4 and 5), not counting the absorption of the solvent itself, five maxima or groups of maxima are discernible. Among these the proton of the amide group (*i.e.* that of the NH at position 3) absorbs at lowest field: the signal appears at $\delta = 11.6$ ppm in both spectra, at the same place where it appears in the case of phthalic hydrazide used as a model, and generally in the case of amides of a similar structure [7]. (It might be noted that the coincident signals of the two NH protons in phthalic hydrazide, and the symmetric structure of the signals of the aromatic protons prove, in accordance with data of the literature [3], that the solution in dimethyl sulphoxide contains the diamide tautomer, and the semi-iminohydrine tautomer does not occur in verifiable quantities.) The fact that at 11.6 ppm there is a signal in the spectra of the α- as well as in those of the β-compound, seems to exclude the possibility of the occurrence of tautomers **Ib, Id** and **If** in α- and β-spiroxazone.

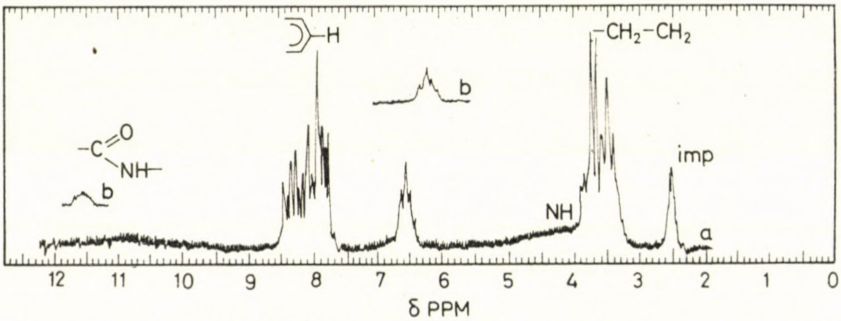


Fig. 4. NMR spectrum of α-spiroxazone
a: in DMSO-d_6 at 100 °C
b: in DMSO at 25 °C

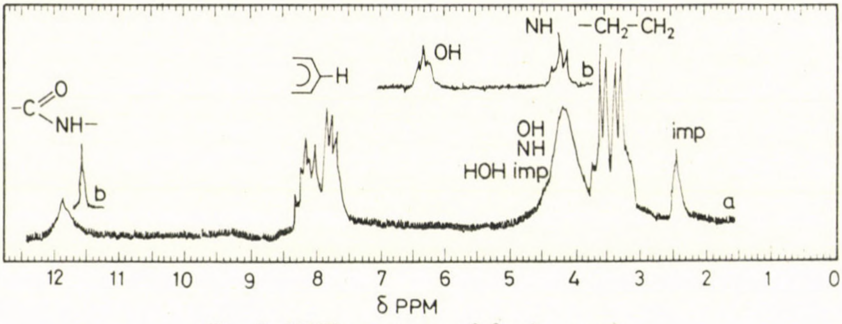


Fig. 5. NMR spectrum of β-spiroxazone
a: in DMSO-d_6 at 25 °C
b: in DMSO at 25 °C

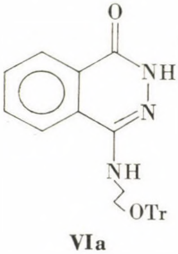
The multiplet signal system of the aromatic protons appears between 450 and 510 cps with the same band structure in the two spectra. However, the spectra are different in other regions, and this supports the conclusion made on the basis of the IR spectra, *i.e.* that α- and β-spiroxazone have different structures.

The spectrum of the β-compound (in anhydrous $(CH_3)_2SO$) has two triplets at about 6.5 and 4.7 ppm; these may be assigned on the basis of spin-spin splitting (J = 6 cps), to NH or OH protons adjacent to two methylene groups. These signals disappear on the addition of D_2O. This is an unequivocal indication that the structure of β-spiroxazone must be **Ic** (the two signals are attributed to the protons —CH_2—OH, and —CH_2—NH, respectively), since only one triplet can be expected for **Ia** and **Ie**.

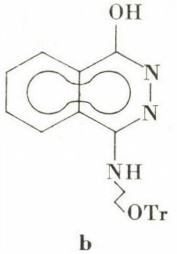
The triplet at about 6.5 ppm in the spectrum of α-spiroxazone (in anhydrous $(CH_3)_2SO$*) is the same as that shown by the β-compound. Instead of the signal group at 4.7 ppm in the β-spectrum (whose pattern is similar to that of the 6.5 ppm group), the α-spectrum has a diffuse, though well discernible, maximum between 210 and 330 cps, its high-field side being merged into the coalescent absorption of the methylene groups and solvent, and of the water present as a contaminant of the solvent.

The appearance of the triplet at about 6.5 ppm can be interpreted with either structure **Ia** (—CH_2NH) or **Ie** (—CH_2—OH). Therefore, in the case of α-spiroxazone the NMR spectra do not allow decision between these two alternatives.

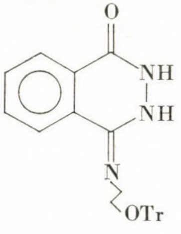
It is important to note that the foregoing statements only apply to solutions in dimethyl sulphoxide, and there is no proof that these spiroxazones exist in the same tautomeric forms in the solid phase. Nevertheless, it is highly probable that α- and β-spiroxazone in the solid phase cannot exist, at least not in any significant proportion, in the iminohydrine tautomeric forms **Ib**, **Id** and **If**. This is indicated by the appearance of a diffuse NH stretching vibration band with secondary maxima at low wave numbers in their IR spectra, characteristic of an amide group in the 3,4-position. This band is characteristic of cyclic dimeric associations (**IV**) of lactams [7—8] that can only be formed in the case of **Ia**, **Ic** and **Ie** [8—15]. Though an analogous association structure (**V**) with a similar NH stretching vibration band is also possible with amidines and amidrazons (*i.e.* with **Id** and **If**) [10], such association structures are highly improbable in the present case, since intermolec-



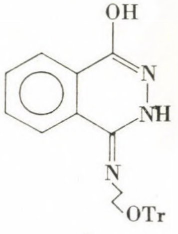
VIa



b



c



d

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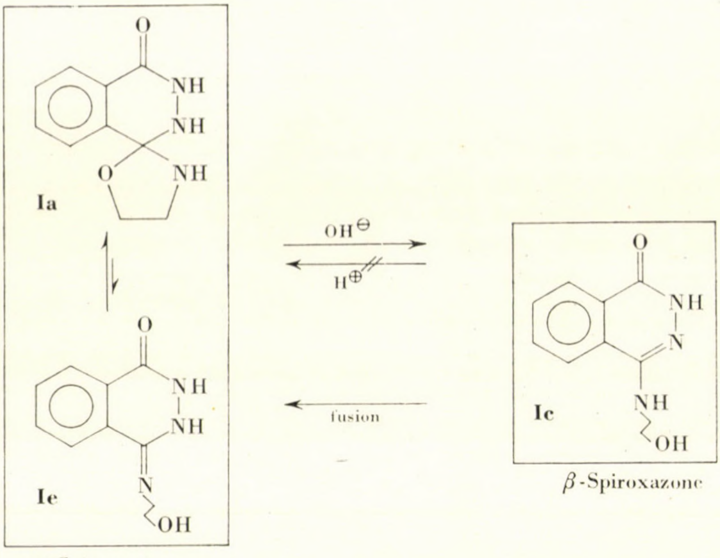
* The triplet structure can be more clearly recognized in the spectrum obtained in $(CD_3)_2SO$; this is probably the consequence of the higher purity (less water content) of this solvent.



α-Spiroxazone

β-Spiroxazone

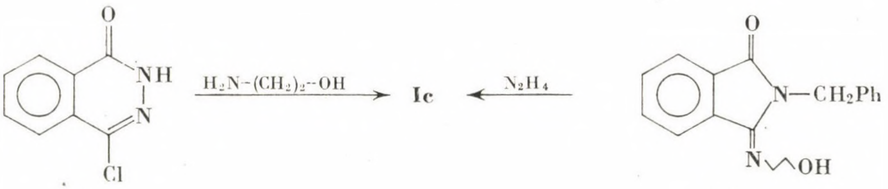
ular association by the C-4 hydroxyl groups gives rise to stronger and more stable hydrogen bonds. Structure **Ic** is not likely either, as the presence of the endocyclic C=N bond does not favour the formation of association structure **IV**.

A certain amount of information concerning these structures is furnished by the intense band between 1100 and 1000 cm^{-1} in the IR spectra of α- and β-spiroxazone. In the α-spiroxazone spectrum this band presents very sharp outlines at 1070 cm^{-1}, while in that of β-spiroxazone it is slightly more diffuse at 1065 cm^{-1}. This absorption can equally be ascribed to the $\nu C-O(H)$ vibration of the OH of a primary alcohol, or to the $\nu_{as}C-O-C$ vibration maximum of the ether bond in the spiro ring. This alternative possibility of assignment prevents again decision between the open-chain and cyclic tautomer. However, the pattern and frequency of the two bands in the two spectra are not the same, thus it is highly probable that they have different origin in the two compounds, *i.e.* in one case this band is assignable to a $\nu C-O(H)$, and in the other to a $\nu_{as}C-O-C$ vibration. The presence of two inserted methylene groups in structures **Ic**–**If** seems sufficient to justify the view that the $\nu C-O(H)$ band should remain unchanged, especially since there is no significant change in the association conditions either. Similarly, in the spectra corresponding to structures **Ia** and **Ib**, no change of the $\nu_{as}C-O-C$ band can be expected. If we also take into account that the IR spectrum of α-spiroxazone has a very intense band also at 910 cm^{-1}, which is most probably due to $\nu_{s}C-O-C$ vibration, being absent in the IR spectrum of the β-compound, then it seems obvious that the tautomeric structure **Ia** is the correct choice for α-spiroxazone.

The formation of tautomer **Id** containing a heteroaromatic ring is also improbable for chemical reasons, as it has been shown [3] by NMR spectra of maleic hydrazide that the semi-iminohydrine and the diamide tautomers are the stable structures, since mesomerism of the amide group allows more favourable energy states than given by delocalization of the π-electrons in the hetero ring [16].

Summing up, the NMR spectra recorded on samples dissolved in dimethyl sulphoxide, and the IR spectra recorded on solid samples in KBr pellets, show that most probably a high proportion of β-spiroxazone molecules have the open **Ic** structure, while α-spiroxazone is the **Ia** spirane compound or, less likely according to the IR spectra, the **Ie** exocyclic amidrazon tautomer, or a mixture of these two.

According to data in the literature [17] and earlier results [18], the extent of the addition of nucleophilic reagents, *e.g.* of alcohols, to a C=N group depends on the exocyclic or endocyclic position of this double bond. Since addition to an exocyclic C=N double bond occurs more readily, the structural position of the C=N group can be concluded from the degree of alcohol addition.



VII VIII

The same O-trityl derivative (**VI**) is produced in pyridine medium from both α-spiroxazone and β-spiroxazone. For tritylated spiroxazone the equilibrium of four tautomers (**VIa**–**VId**) must be considered. Since, on recrystallization from alcohol the trityl derivative retains one mole of alcohol and this is fixed *by addition* and not as alcohol of crystallization, the exocyclic tautomers **VIc** and **VId** seem to represent the true structures best.

Thus the exocyclic position of the C=N bond is considered the cause of quantitative alcohol addition. This is also supported by the fact that the trityl compound, before alcohol addition, can be hydrolyzed with hydrochloric acid to α-spiroxazone. According to our spectroscopic studies, α-spiroxazone may have a spirane (**Ia**) or an open exocyclic amidrazon (**Ie**) structure. Since α-spiroxazone does not add any alcohol, the open structure **Ie** can be excluded. Owing to the strong tendency of its exocyclic C=N bond for additions, structure **Ie** is not stable and it is immediately converted by ring closure into the spirane **Ia**. The cleavage of the spirane ring and ring closure of the straight-chain tautomer are both reversible processes, therefore α-spiroxazone can be considered to be an equilibrium system consisting of tautomers **Ia** and **Ie**, with the spirane form predominating.

On the basis of spectroscopic studies, we have assigned the open **Ic** structure, containing an endocyclic C=N bond, to β-spiroxazone. In accordance with this, when this compound is boiled in alcohol, it takes up 6.6% of alcohol by addition. The low yield of this addition reaction is explained by the low reactivity of the endocyclic C=N double bond.

Obviously, the exo-endo tautomerism of the C=N bond in spiroxazone is much more hindered than in amidines, hydrazidines, and amidrazons. Otherwise, it would not be possible to prepare α- and β-spiroxazone separately, since they would be interconvertible.

The possibility of interconversion is given. The conversion (β → α) opposite to ring cleavage (α → β) occurring in basic medium, can be effected by chemical reactions, *e.g.*, by the hydrolysis of the trityl derivative of spiroxazone, or by the fusion of β-spiroxazone.

Our synthetic work included the preparation of β-spiroxazone in order to prove its structure. This synthesis has been achieved from 4-chloro-1(2H)-phthalazinone (**VII**) as the starting compound [19].

The product thus prepared had the same IR spectrum as β-spiroxazone.

The reaction of 2-benzyl-3-(β-hydroxyethyl)-phthalamidine (**VIII**) with hydrazine [21], formerly studied by us on the basis of a publication by FLITSCH [20], can also be regarded as a synthesis proving the structure, since the formation of β-spiroxazone has been observed in the course of this reaction.

Experimental*

α-Spiroxazone [Spiro-(1,2,3,4-tetrahydrophthalazine-1,2′-oxazolidine)-4-one; **Ia**]

(*a*) Freshly prepared 2-*o*-carboxyphenyl-Δ^2-oxazoline (19.1 g; 0.1 mole) was suspended in ethanol (90 ml), and a solution of 100% hydrazine hydrate (4.14 g; 0.09 moles) in ethanol (15 ml) was added under vigorous stirring during 5 min. A yellow solution was obtained which soon gave a deposit of α-spiroxazone (15.8 g; 85.4%). Recrystallization from water yielded colourless needles, m.p. 254—256 °C.

$C_{10}H_{11}N_3O_2$ (205.2). Calcd. C 58.5; H 5.4; N 20.5. Found 58.6; H 5.5; N 20.3%.

(*b*) β-Spiroxazone (1.00 g) was fused at 260 °C in a Wood's alloy bath and kept at this temperature for 15 min. The solidified melt was twice recrystallized from water using decolourizing carbon, to obtain colourless needles, m.p. 254—256 °C (0.82 g; 82%).

(*c*) The trityl derivative of spiroxazone (448 mg; 1 mmole), recrystallized from a mixture of chloroform and ether, was refluxed in a mixture of cc. HCl (5 ml) and water (1 ml). During boiling, the mixture turned yellow, but this colour slowly faded and an oily phase separated. After 3 hrs of boiling, the mixture was cooled and the precipitated triphenylcarbinol filtered off on a glass filter. The crystals were extracted with abs. ethanol. The undis-

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* All m.p.'s were determined on a Boëtius apparatus.

solved spiroxazonium chloride was added to the filtered HCl solution, which was then several times evaporated in vacuum, with the addition of water, to dryness. The residue was recrystallized from water to obtain colourless needles, m.p. 254—256 °C (0.16 g; 78%).

Beilstein's halogen test was negative. (A positive result indicates that recrystallization from water must be repeated.)

The substances prepared according to these three methods have the same IR spectra. When crystallized from alcohol, no alcohol is retained by the crystals.

β-Spiroxazone. [4-(2-hydroxyethylamino)-1(2H)-phthalazinone; **Ic**]

(*a*) This compound was formed in the reaction of 2-*o*-carboxyphenyl-Δ^2-oxazoline (191 g; 1 mole) with an excess of hydrazine (1.1 mole) in alcohol (1 l) [22].

(*b*) From a solution in dry pyridine (dried over KOH), α-spiroxazone crystallized as spectroscopically homogeneous β-spiroxazone.

(*c*) A mixture of β-spiroxazone (100 mg) and cc. HCl (2 ml) was boiled for 30 min. The solution was evaporated to dryness under reduced pressure several times, water being added after each evaporation but the last. The residue contained no halogen, and was obtained as colourless crystals from water (85 mg; 85%), m.p. 254—256 °C. According to the IR spectrum, this product was pure β-spiroxazone.

Mixture of α- and β-spiroxazone

(*a*) As shown by the IR spectrum, the product (100 mg) obtained from the hydrolysis with HCl of the alcohol adduct of the trityl derivative (500 mg) of spiroxazone (*cf.* hydrolysis of tritylated spiroxazone) consisted mainly of α-spiroxazone, but it was contaminated with a considerable quantity of β-spiroxazone.

(*b*) A hot solution of β-spiroxazone (2.05 g) and KOH (1.68 g) in water (50 ml) was quickly mixed with cc. HCl (30 ml). The excess of HCl was removed by repeated distillation under reduced pressure. The dry residue was recrystallized from hot water (150 ml) to obtain 1.70 g (83%) of the product, m.p. 254—256 °C. According to the IR spectrum it consisted of -spiroxazone containing some α-spiroxazone as an impurity.

Trityl derivative of spiroxazone (VI)

α-Spiroxazone or β-spiroxazone (2.05 g; 10 mmoles) was dissolved in abs. pyridine (50 ml), and trityl chloride (5.58 g; 20 mmoles) was added. Next day the product was precipitated by the addition of water, dried, and recrystallized from a mixture of chloroform and ether to obtain 3.50 g (78.2%) of colourless plates, m.p. 213 °C.

$C_{29}H_{25}N_3O_2$ (447.5). Calcd. C 77.8; H 5.6; N 9.4. Found C 77.6; H 5.6; N 9.5%.

Boiling in HCl, rapidly hydrolyzed the product to α-spiroxazone and tritanol. Recrystallization from alcohol gave colourless needles containing one molecule of alcohol. The ethoxyl content of the alcohol adduct remained unchanged when the product was kept at 65 °C over phosphorus pentoxide in vacuum for 5 hrs, or when it was three times recrystallized from a mixture of abs. chloroform and ether, or chloroform and petroleum ether. The alcohol content could be removed by drying over phosphorus pentoxide in vacuum at 100 °C for 10 hrs.

$C_{29}H_{25}N_3O_2 \cdot C_2H_5OH$ (493.6). Calcd. EtO 9.1. Found EtO 9.0%.

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N-GLYCOSIDE, XIV

UNTERSUCHUNGEN AN β-D-GLUCOPYRANOSYLMORPHOLIN

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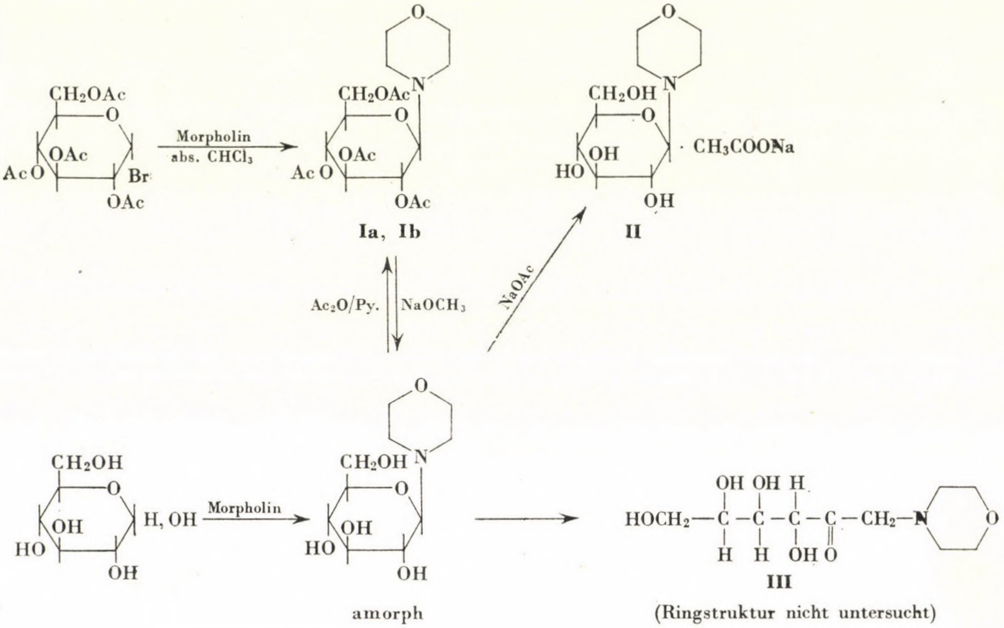
Darstellung und Eigenschaften des 2,3,4,6-Tetra-O-acetyl-β-D-glucosylmorpholins (**I**) und des β-D-Glucopyranosylmorpholins werden beschrieben. Letzteres liefert ein kristallines, stöchiometrisch zusammengesetztes Natriumacetat-Additionsprodukt (**II**). **I** tritt in zwei verschiedenen Modifikationen auf. **I** läßt sich nach Entacetylieren in die bereits bekannte 1-Desoxy-1-morpholino-D-fructose (**III**) umlagern.

Hodge und Rist berichten über die Darstellung von Glucosiden verschiedener sekundärer Amine und ihrer Amadori-Umlagerungsprodukte [1, 2]. Vom Morpholin und Glucose bzw. Mannose ausgehend stellten sie jedoch nur das Amadori-Umlagerungsprodukt, die 1-Desoxy-1-morpholino-D-fructose dar. Staněk und Černý haben später [3] 2,3,4,6-Tetra-O-acetyl-β-D-glucopyranosylmorpholin (**Ia**) durch die Umsetzung von 2,3,4,6-Tetra-O-acetyl-α-D-glucopyranosylbromid mit 2 Mol Morpholin in Ätherlösung synthetisiert. Andere Angaben über Glucoside des Morpholins sind in der Literatur nicht beschrieben. Daher hatten wir uns das Studium der Umsetzungen und Derivate des D-Glucopyranosylmorpholins zum Ziel gesetzt.

Die Herstellung von kristallinem D-Glucopyranosylmorpholin bzw. seines Tetraacetats haben wir nach verschiedenen bekannten Verfahren versucht. Die Methoden, die von freien Zuckern bzw. von Zuckeracetaten vom verschiedenen Typ ausgehen [4, 5, 6, 7, 8], führten zu keinem Ergebnis.

Die Synthese von **Ia** gelang in 50% Ausbeute durch Umsetzung von 2,3,4,6-Tetra-O-acetyl-α-D-glucopyranosylbromid mit überschüssigem Morpholin (4 Mol) in $CHCl_3$-Lösung, analog der Darstellung des Hepta-O-acetylcellobiosylpiperidins [9]. Bei der Methode nach Koenigs und Knorr [10] bzw. nach deren Varianten (mit KOH oder Ag_2O bzw. Ag_2CO_3) lagen die Ausbeuten bedeutend niedriger (0—15%). Ähnliche Kupplungsversuche mit 2,3,4,6-Tetra-O-acetyl-β-D-glucopyranosylchlorid [11, 12, 13] verliefen erfolglos. Direkte Kupplung von wasserfreier D-Glucose mit Morpholin und Acetylieren des amorphen Reaktionsproduktes führte aber zum Ziel und **Ia** wurde in 60% Ausbeute dargestellt.

2,3,4,6-Tetra-O-acetyl-β-D-glucopyranosylmorpholin wurde in zwei Modifikationen (**Ia** und **Ib**) beobachtet, die in beiden Richtungen ineinander überführbar sind. Modifikation **Ia** schmilzt bei 121—122,5 °C; bei Temperatur-



erhöhung wandelt sie sich in **Ib** um: die klare Schmelze verfestigt sich und schmilzt bei 134—135 °C. Beide Formen sind kristallsolvensfrei. Die IR-Spektren beider Modifikationen (in KBr) sind völlig identisch und zeigen für die N-substituierten Morpholinderivate charakteristischen Banden bei 2850, 1117, 1080 und 867 cm^{-1} [14]. Auf Grund der Analogie zu Glucosiden anderer sekundärer Amine kann das Vorliegen einer β-Glucopyranosid-Struktur als sicher angenommen werden.

Desacetylierung von **I** mit Natriummethylat in abs. Methanol lieferte auch bei Aufarbeitung unter sorgfältigem Ausschluß der Luftfeuchtigkeit nur ein amorphes und äußerst hygroskopisches acetylfreies Produkt.

Die direkte Reaktion von Morpholin mit Glucose lieferte das gleiche Produkt. Beim Acetylieren dieser Substanz in Pyridin-Acetanhydrid erhielten wir ein Tetra-O-acetat das sich mit dem oben dargestellten **I** als identisch erwies.

Eine stabile, kristalline Form des β-D-Glucopyranosylmorpholins konnte in Form seiner Natriumacetat-Additionsverbindung (**II**) durch Desacetylieren von **I** und anschließender Zugabe von molarer Menge Natriumacetat isoliert werden. Nach der Analyse besitzt **II** die Zusammensetzung $C_{10}H_{19}O_6N \cdot \cdot CH_3COONa$. Die Substanz ist bedeutend weniger hygroskopisch und ohne Veränderung der Zusammensetzung umkristallisierbar. Ihre Lösung in abs. Methanol ist stabil, auch in Wasser tritt nur eine sehr langsame Veränderung der spezifischen Drehung auf; jedoch steigt der pH schnell an. Somit dürften neben Hydrolyse gleichzeitig andere Umlagerungen stattfinden.

Nach Desacetylieren von **I** mit Natriummethylat kann das sirupöse Entacetylierungsprodukt — nach HODGE und RIST [2] in Alkohol und Diäthylmalonat erhitzt — durch AMADORI-Umlagerung in mäßiger Ausbeute in 1-Desoxy-1-morpholino-D-fructose (**III**) überführt werden.

Beschreibung der Versuche

2,3,4,6-Tetra-O-acetyl-β-D-glucopyranosylmorpholin (Ia)

A) Zur Lösung von 10 g (0,02 Mol) 2,3,4,6-Tetra-O-acetyl-α-D-glucopyranosylbromid in 50 ml abs. Chloroform gibt man in einem Guß 7 ml (0.08 Mol) Morpholin und läßt 30 Std. bei 20 °C stehen. Allmählich scheidet sich Morpholin HBr aus. Von diesem wird abfiltriert, die Chloroformlösung einige Male mit Wasser gewaschen, mit $CaCl_2$ getrocknet und im Vak. bis zum sirupösen Rückstand eingeengt, der bald erstarrt. Nach zweimaligem Umkristallisieren aus je 10 ml abs. Alkohol erhält man farblose Kristalle.

Ausbeute 5.1 g (50% d. Th.). Die Substanz schmilzt bei 121—122,5 °C; meist erstarrt die Masse von einem kleinen verbliebenen Kristallisationszentrum aus sofort wieder, um bei 135—136 °C von neuem zu schmelzen. $[\alpha]_D = -3{,}8$ °C ($c = 9$, $CHCl_3$). Lit. [3] Schmp. 120 °C; $[\alpha]_D = -21{,}3$ °C ($CHCl_3$).

($C_{18}H_{27}O_{10}N$, 417.4):
Ber. C 51,79% H 6,52% N 3,35% CH_3CO 41,2%,
Gef. C 52,01% H 6,54% N 3,22% CH_3CO 41,0%.

B) 2,34 g 2,3,4,6-Tetra-O-acetyl-α-D-glucopyranosylbromid werden in 7 ml Aceton gelöst, mit 0,5 ml Morpholin und dann unter Eiskühlung tropfenweise mit 2,4 ml 2,5 *n* Kalilauge versetzt. Nach 48stündigem Schütteln dampft man die neutral reagierende Lösung im Vak. bis zum Verschwinden des Acetongeruches ein, löst den Rückstand in Chloroform und schüttelt schnell mit 1%iger KOH-Lösung und dann mehrmals mit Wasser aus. Aufarbeitung der Chloroformlösung wie oben.

Ausbeute 0,35 g (15% d. Th.), $[\alpha]_D = -3{,}3$°C ($c = 4{,}6$, $CHCl_3$); Schmp. 121—122 °C bzw. 134—135° C. Bei Mischschmelzpunktsbestimmung keine Depression.

C) 2,0 g fein gepulverte wasserfreie D-Glucose werden mit 2 ml Morpholin verrieben, bis leichte Erwärmung auftritt. Nun erhitzt man unter Feuchtigkeitsausschluß auf dem Wasserbad in Intervallen so, daß die Temperatur der Mischung 12 Min. lang zwischen 70 und 80 °C liegt. Es entsteht ein klarer fast farbloser Sirup, den man nach dem Erkalten mit einer gekühlten Mischung von 7 ml Acetanhydrid und 14 ml abs. Pyridin übergießt. Man schüttelt bis zur Lösung und kühlt dabei anfänglich so, daß die Temperatur nur allmählich auf etwa 25 °C sinkt. Ist alles gelöst, stellt man 16 Std. in den Kühlschrank und läßt dann noch 8 Std. bei 20 °C stehen. Nun wird bei 50 °C Badetemperatur im Vak. eingedampft, der sirupöse Rückstand in 20 ml Chloroform gelöst, dieses mit Wasser, Bicarbonatlösung und wieder mit Wasser ausgeschüttelt, mit $CaCl_2$ getrocknet und mit Kohle geklärt. Im Vak. destilliert man das Chloroform ab und kristallisiert den bald erstarrenden Rückstand zweimal aus je 5 ml abs. Alkohol um.

Ausbeute 2,8 g (60% d. Th.), Schmp. 121—122 °C bzw. 135—136 °C; $[\alpha]_D = -3{,}7$° ($c = 4$, $CHCl_3$). Bei Mischschmelzpunktsbestimmung keine Depression.

Darstellung von Modifikation Ib

Eine gewogene Menge (etwa 100 mg) von 2,3,4,6-Tetra-O-acetyl-β-D-glucopyranosylmorpholin (Modifikation **Ia**) wird in einem engen, oben offenen Glasrohr in ein Paraffinbad von 100 °C gebracht und dieses innerhalb von 30 Minuten auf 140 °C erhitzt. Ist die Masse vollständig geschmolzen, läßt man das Röhrchen im Exsikkator erkalten. Es tritt kein wägbarer Gewichtsverlust auf. Schmp. 135—136 °C; $[\alpha]_D = -3{,}9$° ($c = 1{,}5$, $CHCl_3$).
Ber. C 51,79% H 6,52% N 3,35%,
Gef. C 51,90% H 6,54% N 3,29%.

Umwandlung von Modifikation Ib in Ia

80 mg **Ib** werden in einigen Tropfen heißem Alkohol gelöst. Beim Erkalten scheidet sich Modifikation **Ia** aus.

Ausbeute 73 mg (91% d. Th.), Schmp. 121—122 °C bzw. 136 °C; $[\alpha]_D = -4{,}1°$ ($c = 2{,}4$, $CHCl_3$). Die Substanz gibt keine Schmelzpunktdepression mit dem auf anderem Wege hergestellten **Ia**.

β-D-Glucopyranosylmorpholin-Natriumacetat Additionsprodukt (II)

1,1 g **Ia** werden in 25 ml abs. Methanol mit 0,3 ml 3,5 *n* abs. methanolischer Natriummethylat-Lösung bis zur Auflösung geschüttelt und 1 Std. bei 20 °C stehen gelassen. Nach Neutralisieren mit einer Mischung von Eisessig und abs. Methanol gegen Phenolphthalein wird die Lösung im Vak. eingedampft. Die zurückbleibende flockige Masse löst man in 50 ml abs. (über wasserfreiem K_2CO_3 getrocknetem) *n*-Butanol, erwärmt auf 60 °C und versetzt mit 1.5 ml einer 1 *n* Lösung von wasserfreiem Natriumacetat in abs. Methanol. Die Menge des bei der Neutralisation des Natriummethylats entstehenden und des zugesetzten Natriumacetats ist so berechnet, daß das Glucosid in 5%igem Überschuß vorhanden ist. Beim Erkalten scheidet sich das Präparat in schönen tafelförmigen Kristallen aus, die man am nächsten Tag absaugt.

Ausbeute 0,787 g (95% d. Th.). Die Substanz schmilzt bei 158—159 °C unter Zersetzung. $[\alpha]_D = -3{,}5°$ ($c = 0{,}5$, abs. Methanol 5 Min. → 48 Std.) bzw. $-3°$ ($c = 0{,}2$. Wasser; 5 Min.) → 0° (24 Std.).

($C_{10}H_{19}O_6N \cdot CH_3COONa$ 331.3):
Ber. C 43,50% H 6,69% N 4,23% CH_3CO 13,0% Sulfat-Asche 21,74%,
Gef. C 42,92% H 6,63% N 4,25% CH_3CO 13,1% Sulfat-Asche 22,22%.

1-Desoxy-1-morpholino-D-fructose (III)

2 g **Ia** werden in 50 ml abs. Methanol mit 0,15 ml einer 3,5 *n* Lösung von Natriummethylat in abs. Methanol wie oben verseift. Nun dampft man die Lösung im Vak. zum Sirup ein, löst diesen in einer Mischung von 4,5 ml abs. Alkohol und 4,5 ml abs. Diäthylmalonat und hält 2 Std. auf dem Wasserbad bei leichtem Rückfluß. Die braungelbe Lösung versetzt man nach dem Erkalten mit 20 ml abs. Äther und läßt zwei Tage im Kühlschrank stehen. Die Kristalle werden abgesaugt und zweimal aus abs. Methanol umkristallisiert.

Ausbeute 0.407 g (34% d. Th.), Schmp. 145—146 °C (unter Zersetzung), $[\alpha]_D = -115°$ ($c = 0{,}5$, abs. Pyridin 5 Min.) → $-51°$ (48 Std.). Die Daten der Substanz zeigen gute Übereinstimmung mit der von HODGE und RIST [2] dargestellten 1-Desoxy-1-morpholino-D-fructose (Schmp. 145—146 °C, $[\alpha]_D = -117°$ ($c = 2{,}0$, abs. Pyridin, 12 Min.) → $-50{,}8°$ (48 Std.)). Mischschmelzpunktsdepression tritt nicht auf.

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HERSTELLUNG UND REAKTIONEN VON LITHIUMSALZEN AROMATISCHER SULFENSÄUREN

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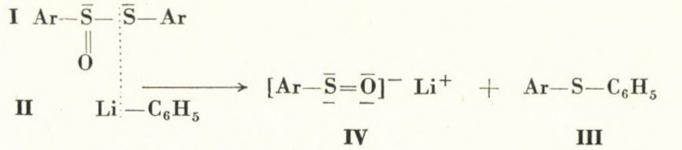
Bei der Reaktion von Thiolsulfinsäureestern mit Lithiumphenyl konnten bisher wenig bekannte Lithiumsalze von einfach gebauten Sulfensäuren isoliert werden. Es wurde festgestellt, daß diese Verbindungen nur in der Abwesenheit von Luft entstehen bzw. aufbewahrt werden können. Es wurden verschiedene Reaktionen der Lithiumsulfenate, namentlich ihre Hydrolyse, Autoxydation, Disproportionierung und Reaktion mit verschiedenen Halogeniden untersucht. Auf Wirkung von Wasser entstehen Thiolsulfinate, auf Wirkung von Luft Lithiumsulfinate, beim Erhitzen Sulfinsäure und Disulfid. Mit organischen Verbindungen, die bewegliche Halogenatome enthalten, entstehen im Stickstoffstrom Sulfoxyde, in Gegenwart von Luft Sulfone. Bei der Reaktion mit schwefelhaltigen Säurehalogeniden entsteht mit Sulfinsäurechlorid Thiolsulfonat, mit Sulfonsäurechlorid »Disulfid-Trioxyd«.

Theoretischer Teil

Die chemischen Eigenschaften der Thiolsulfinsäureester (Thiosulfinate) wurden erst im letzten Jahrzehnt eingehender untersucht [1, 2, 3]. In unserem Institut befassen wir uns seit Jahren mit diesen Verbindungen [4, 5]. Unter anderem schien es interessant, zu entscheiden, in welcher Richtung das Elektronenpaar der Schwefel-Schwefel-Bindung induktiv polarisiert ist. Auch interessierte uns die Frage, ob das Sulfenyl-Schwefelatom oder das Sulfinyl-Schwefelatom das nukleophile Zentrum des Moleküls ist. Um sie zu entscheiden, wurde die Spaltung der Schwefel-Schwefel-Bindung mit verschiedenen Reagenzien untersucht. Die Versuchsergebnisse zeigten, daß der nukleophile Charakter des Thiolsulfinat-Moleküls nicht ausschließlich dem Sulfenyl- bzw. Sulfinyl-Schwefelatom zugeordnet ist [6].

Um das Problem eingehender zu prüfen, wurde versucht, die Thiolsulfinate mit Phenyllithium zu spalten. Es wurde z. B. die Lösung von *p*-Toluylthiolsulfinsäure-*p*-toluylester (**Ia**) in absolutem Benzol mit der berechneten Menge Lithiumphenyl (**II**) unter trockenem Stickstoff in Reaktion gebracht. Als Produkt der lebhaften Reaktion konnte neben *p*-Toluylphenylsulfid (**III**) das Lithiumsalz der *p*-Toluylsulfensäure (**IVa**) isoliert werden [7, 8]. Bei der Reaktion von Phenylthiolsulfinsäurephenylester mit Lithiumphenyl spielt sich ein analoger Vorgang ab. Das Lithiumsalz wird in Form eines leichten weißen Pulvers abgeschieden, und kann von Sulfid leicht getrennt werden [Gl. (1)].



$$\underset{\mathrm{I}}{Ar-\underset{\underset{O}{\|}}{\bar{S}}-\bar{S}-Ar} + \underset{\mathrm{II}}{Li-C_6H_5} \longrightarrow \underset{\mathrm{IV}}{[Ar-\bar{S}=\bar{O}]^- Li^+} + \underset{\mathrm{III}}{Ar-S-C_6H_5} \tag{1}$$

a) Ar = *p*-Toluyl
b) Ar = Phenyl

Das Arylsulfinyllithium (**IV**) ist eine äußerst hygroskopische feste Substanz. Sie kann aus dem Reaktionsgemisch in ziemlich reiner Form isoliert werden. Der Lithiumgehalt des Rohproduktes zeigt gute Übereinstimmung mit dem berechneten Wert.

Literaturangaben [9, 10, 11] weisen darauf hin, daß nur einige Sulfensäuren bzw. sulfensaure Salze isoliert werden können, die durch die Gegenwart von bestimmten funktionellen Gruppen (z. B. Chinon) stabilisiert werden. Sehr wahrscheinlich sind die Sulfensäuren, die keine derartige »stabilisierende« Gruppe enthalten, wegen ihrer starken Neigung zur Disproportionierung gar nicht existenzfähig. Die im Laufe unserer Untersuchungen isolierten, einfach gebauten Sulfensäuren ermöglichen eine eingehendere Untersuchung dieser Verbindungen.

Um die Eigenschaften der Lithiumsalze der Sulfensäuren zu untersuchen, wurden folgende Reaktionen durchgeführt.

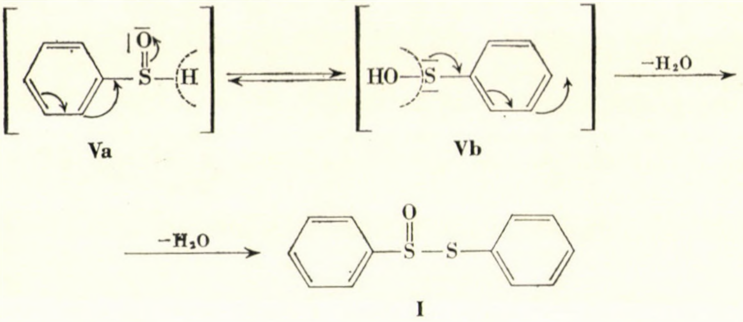
Hydrolyse

Auf Einwirkung von Wasser hydrolysieren die Sulfensäuresalze unter Bildung des Thiolsulfinsäureesters (**I**) schnell. Die Reaktion geht schon auf Einwirkung von feuchter Luft vor sich. Die Hydrolyse wird vermutlich durch die Bildung von Sulfensäure (**V**) gemäß Gl. (2) eingeleitet, wonach die beiden tautomeren Formen der Sulfensäure (**Va** und **Vb**) gemäß Gl. (3) unter Wasserabgabe in Thiolsulfinat (**I**) überführt werden. Das tautomere Gleichgewicht kommt wahrscheinlich dadurch zustande, daß das Sulfenatanion an beiden Punkten protoniert wird, in höherem Maße, jedoch am basischen Zentrum, d. h. am Sauerstoff. Im Gleichgewicht dominiert deshalb vermutlich die tautomere Form **Vb**.

Es konnte experimentell bewiesen werden [12], daß das tautomere **Vb** mit Protonen oder elektrophilen Reaktionspartnern unter Abspaltung von Hydroxylionen reagiert. So ergibt z. B. die Reaktion mit dem Proton der Sulfinsäure Thiolsulfonat ($Ar-SO_2-S-Ar$). Ist ein solcher Partner nicht zugegen, so reagieren die beiden tautomeren Formen der »in-situ«-Sulfensäure [5] miteinander und es entsteht Thiolsulfinat (siehe [2] Band 2, S. 371).

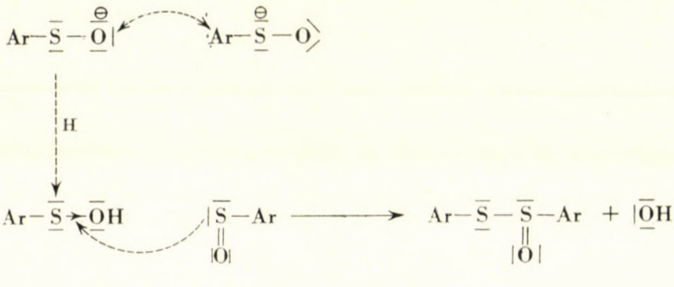
Unsere Untersuchungen können mit der Arbeit von Shelton und Davies [11] in Zusammenhang gebracht werden. Diese amerikanischen Forscher bestätigten auf Grund von IR-Spektren die gleichzeitige Gegenwart beider tautomeren Formen der tert. Butylsulfensäure.

$$\underset{\mathbf{IV}}{\left[\mathrm{Ar}-\overline{\underline{\mathrm{S}}}=\overline{\underline{\mathrm{O}}}\right]^{\ominus}}\mathrm{Li}^{\oplus} \xrightarrow{H_2O} \underset{\mathbf{V}}{\left[\mathrm{Ar}-\overline{\underline{\mathrm{S}}}=\overline{\underline{\mathrm{O}}}\right]^{\ominus}}\mathrm{H}^{\oplus} + \mathrm{LiOH} \qquad (2)$$



(3)

Es kann auch ein anderer Ablauf der Entstehung des Thiolsulfinats angenommen werden. So kann z. B. das Sulfenation mit nukleophilem Charakter durch die Wirkung von Wasser am stärker elektronaffinen Sauerstoffatom protoniert werden, und die so gebildete Sulfensäure kann mit dem Sulfenatanion eines anderen Moleküls in Wechselwirkung treten. Im letzteren ist das Schwefelatom das nukleophile Zentrum, folglich kann in der Reaktion — unter Abspaltung eines Hydroxylanions — eine Schwefel-Schwefel-Bindung zustande kommen [Gl. (4)].



(4)

Autoxydation

Beim Stehen an der Luft, in Abwesenheit von Feuchtigkeit, autoxydieren die Salze der Sulfensäure im Laufe von einigen Stunden vollständig zum Lithiumsalz der Sulfinsäure [(**VI**) Gl. (5)].

$$\underset{\mathbf{IV}}{[\mathrm{Ar}-\mathrm{S}=\mathrm{O}]^{-}\ \mathrm{Li}^{+}} \xrightarrow{\text{Stehen an der Luft}} \underset{\mathbf{VI}}{[\mathrm{Ar}-\mathrm{SO}_2]^{-}\ \mathrm{Li}^{+}} \qquad (5)$$

Die Bildung der Sulfinsäure wurde auf zwei verschiedenen Wegen bestätigt. Ein Teil des nach dem Stehen an der Luft erhaltenen Produktes wurde in Gegenwart von wenig Salzsäure in Wasser gelöst und anschließend wurde Eisen(III)chlorid-Lösung zugefügt. Dabei wird das Eisen(III)sulfinat in Form eines orangeroten Niederschlags fast quantitativ abgeschieden [13]. Ein anderer Teil des Produkts wurde in der Hitze mit verschiedenen Alkyl- und Arylhaloiden versetzt, wobei das entsprechende Sulfon und nicht Sulfoxyd entstand [siehe Gl. (4)].

Disproportionierung

Die Salze der Sulfensäure wurden ohne Lösungsmittel im Stickstoffstrom am Wasserbad erhitzt. Unter diesen Umständen tritt Disproportionierung der Verbindung ein. Aus dem Reaktionsgemisch konnte — nach Zugabe von wenig Salzsäure und Eisen(III)chlorid enthaltendem Wasser — Eisen(III)-sulfinat (**VII**) und Disulfid (**VIII**) isoliert werden [Gl. (6)].

$$
\begin{gathered}
2[\mathrm{Ar{-}S{=}O}]^- \, \mathrm{Li}^+ \xrightarrow[100^\circ]{N_2} [\mathrm{Ar{-}SO_2}]^- \, \mathrm{Li}^+ + [\mathrm{Ar{-}S}]^- \, \mathrm{Li}^+ \longrightarrow \\
\xrightarrow{H_2O} \mathrm{Ar{-}SO_2H} + \mathrm{ArSH} \xrightarrow{FeCl_3} \underset{\textbf{VII}}{[\mathrm{ArSO_2}]_3\mathrm{Fe}} + \underset{\textbf{VIII}}{(\mathrm{ArS})_2}
\end{gathered}
\tag{6}
$$

Das Disulfid entsteht aus dem primär entstandenen Thiophenol durch die oxydative Wirkung des zum Abscheiden der Sulfinsäure im Überschuß angewendeten Eisen(III)chlorids.

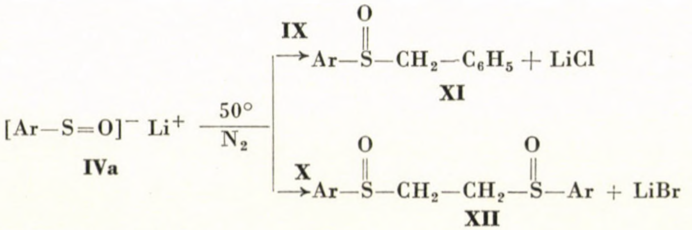
Reaktion mit Alkylhaloiden*

Es wurde bereits erwähnt, daß bei der Reaktion des autoxydierten sulfensauren Salzes mit Verbindungen, welche bewegliche Halogenatome enthalten, anstelle von Sulfoxyd, Sulfon entsteht. Dieses Produkt ist offensichtlich das Ergebnis der Autoxydation des Sulfenatsalzes zum Sulfinatsalz.

Daher wurde, abweichend vom obigen Prozeß, während der ganzen Reaktionszeit bei 50 °C unter Stickstoff gearbeitet. Unter diesen Umständen erfolgt keine Autoxydation, und es entsteht — gemäß Gl. (7) — Sulfoxyd (**XI** und **XII**). (Außer dem Sulfoxyd erscheinen im Reaktionsgemisch auch Produkte der Disproportionierung — Disulfid, Sulfinsäure, Sulfon — in wechselnden Mengen.)

---

* Zu den weiteren Versuchen wurde das Lithiumsalz der *p*-Toluylsulfensäure (**IVa**) gewählt, da das entsprechende Thiolsulfinat (**Ia**) stabil ist und — im Gegensatz zur Verbindung **Ib** — wenig zur Disproportionierung neigt.



$$[\mathrm{Ar{-}S{=}O}]^-\,\mathrm{Li}^+\ (\mathbf{IVa})\ \xrightarrow[\mathrm{N_2}]{50^\circ}\ \begin{cases}\xrightarrow{\mathbf{IX}}\ \mathrm{Ar{-}\overset{\overset{O}{\|}}{S}{-}CH_2{-}C_6H_5 + LiCl}\ (\mathbf{XI})\\ \xrightarrow{\mathbf{X}}\ \mathrm{Ar{-}\overset{\overset{O}{\|}}{S}{-}CH_2{-}CH_2{-}\overset{\overset{O}{\|}}{S}{-}Ar + LiBr}\ (\mathbf{XII})\end{cases} \qquad (7)$$

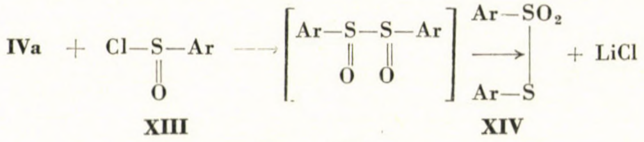
IX = Benzylchlorid
X = Äthylenbromid

Durch die in den vorangehenden Abschnitten behandelten Reaktionen konnte die Struktur der hergestellten Salze der Sulfensäuren zufriedenstellend geklärt werden.

Reaktion mit Arylsulfinyl- und -sulfonylhalogeniden

Das Salz der Sulfensäure wurde bei Zimmertemperatur, unter Stickstoff, mit verschiedenartigen schwefelhaltigen Säurehaloiden in Reaktion gebracht.

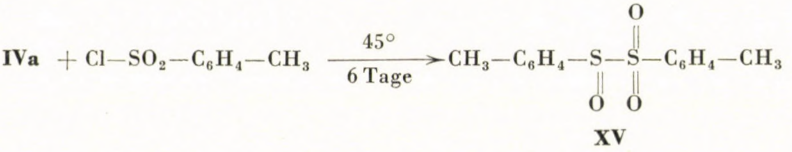
a) Bei der Reaktion von Lithiumsulfenat und Arylsulfinylchlorid (**XIII**) enstand das entsprechende Thiolsulfonat (**XIV**). Vermutlich lagert sich das primär entstehende »Disulfoxyd« zum stabilen Thiolsulfonat [Gl.(8)] [14, 15].



$$\mathbf{IVa} + \underset{\mathbf{XIII}}{\mathrm{Cl{-}\underset{\underset{O}{\|}}{S}{-}Ar}} \longrightarrow \left[\mathrm{Ar{-}\underset{\underset{O}{\|}}{S}{-}\underset{\underset{O}{\|}}{S}{-}Ar}\right] \longrightarrow \underset{\mathbf{XIV}}{\begin{array}{l}\mathrm{Ar{-}SO_2}\\ \quad\ |\\ \mathrm{Ar{-}S}\end{array}} + \mathrm{LiCl} \qquad (8)$$

Ar = *p*-Toluyl—

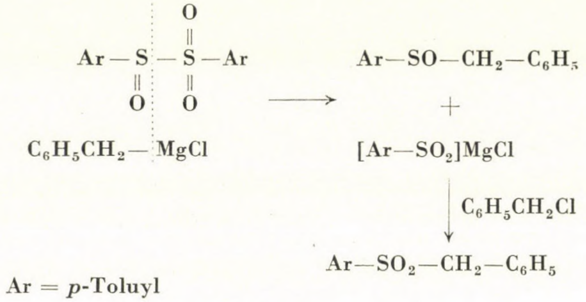
b) Verbindung **IVa** und *p*-Toluolsulfochlorid wurden — im geschlossenen Rohr, in Äther suspendiert — unter milden Bedingungen in Reaktion gebracht. Aus dem Reaktionsgemisch wurde — gemäß Gl. (9) — *p*-Toluylsulfinyl-*p*-toluylsulfon (**XV**) isoliert.



$$\mathbf{IVa} + \mathrm{Cl{-}SO_2{-}C_6H_4{-}CH_3} \xrightarrow[6\,\mathrm{Tage}]{45^\circ} \underset{\mathbf{XV}}{\mathrm{CH_3{-}C_6H_4{-}\underset{\underset{O}{\|}}{S}{-}\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}{-}C_6H_4{-}CH_3}} \qquad (9)$$

Die Verbindung **XV** erwies sich als identisch mit der zuerst durch KNOEVENAGEL und POLLACK [16] hergestellten Verbindung, deren richtige Struktur durch BREDERECK und Mitarbeiter [17] auf Grund ihres IR-Spektrums geklärt und als »Disulfid-trioxyd« genannt wurde.

Bei der Untersuchung der Eigenschaften der Verbindung **XV** wurde festgestellt, daß sie bei der Reaktion mit Benzylmagnesiumchlorid auf charakteristische Art zum Salz der Sulfinsäure und zu *p*-Toluylbenzylsulfoxyd umgesetzt wurde. Um das Sulfinat zu charakterisieren, wurde es durch weitere Reaktion mit Benzylchlorid zu *p*-Toluylbenzylsulfon umgesetzt (Gl. (10)).



(10)

Experimenteller Teil

(Schmelzpunkte unkorrigiert)

1. Reaktion von p-Toluylthiolsulfinsäure-p'-toluylester (Ia) mit Lithiumphenyl

Zur Lösung von 2,62 g (0,01 *M*) Thiolsulfinat in 50 ml absolutem Äther wurden unter Rühren und in trockener Stickstoffatmosphäre 0,84 g (0,01 *M*) Lithiumphenyl, in absolutem Äther gelöst, tropfenweise zugegeben. (Die ätherische Lösung des Lithiumphenyls ist fast bromidfrei; ihre Konzentration wurde nach Versetzen mit Wasser alkalimetrisch bestimmt.) In der lebhaften Reaktion entstand ein heller pulverartiger Niederschlag. Nach kurzem Stehen wurde der Äther dekantiert und das feste Produkt mit absolutem Äther noch zweimal schnell gewaschen. Ausbeute 0,65 g (44,5%) fast weißes Pulver. Der Lithiumgehalt wurde nach dem Veraschen in Form von Sulfatasche bestimmt.

p-Toluylsulfensaures Lithium (**IVa**). Analyse: C_7H_7SOLi (145,05). Berechnet Li 4,75, gefunden Li 5,16.

Die Hauptmenge des nach dem Eindampfen der ätherischen Waschflüssigkeit zurückbleibenden Rohproduktes besteht aus *p*-Toluylphenylsulfid (1,2 g 60%). Die Verbindung wurde durch Vakuumdestillation gereinigt. Ihr Siedepunkt ist mit dem Literaturwert [18] identisch. Analyse: $C_{13}H_{12}S$ (200,15). Berechnet S 16,03, gefunden S 15,65.

2. Reaktion von Phenylthiolsulfinsäurephenylester (Ib) mit Lithiumphenyl

2,3 g (0,01 *M*) der Verbindung **Ib** wurden mit 0,83 g (0,01 *M*) Lithiumphenyl auf die in 1) beschriebene Weise in Reaktion gebracht und weiterverarbeitet. Ausbeute: 0,35 g (28%) phenylsulfensaures Lithium. Analyse: C_6H_5SOLi (132,11). Berechnet Li 5,25 gefunden Li 5,10. Diphenylsulfid (**IIIb**) 1,3 (69,8%). Siedepunkt identisch mit dem Literaturwert [18]. Analyse: $C_{12}H_{10}S$ (186,27). Berechnet S 17,2, gefunden S 16,9.

3. Hydrolyse des Lithiumsalzes der Sulfensäure

Je 0,32 g der Verbindungen **IVa** und **IVb** wurden mit Gemischen von 50 ml Wasser und 5 ml verdünnter Essigsäure 10 Minuten lang geschüttelt. Die unlöslichen Produkte wurden mit Äther extrahiert. Der lösungsmittelfreie Rückstand besteht aus 0,20 g **Ia** bzw. 0,21 g **Ib** (Ausbeute nahezu quantitativ). Gemische mit authentischen Präparaten zeigten keine Schmelzpunktdepression [5].

4. Autoxydation des Lithiumsalzes der Sulfensäure

1,4 g (0,01 *M*) der Verbindung **IVa** bzw. 1,3 g (0.01 *M*) der Verbindung **IVb** wurden unter Ausschluß der Feuchtigkeit an der Luft stehen gelassen. Nach einigen Stunden wurden die Verbindungen in je 100 ml Wasser, welches mit 2 ml verdünnter Salzsäure angesäuert war, suspendiert, einige Minuten lang geschüttelt und mit je 5 g kristallinem Eisen(III)-chlorid versetzt. Der entstehende orangerote Niederschlag wurde abfiltriert. Ausbeuten: 1,4 g bzw. 1,2 g Eisen(III)sulfinat (theoretische Menge 1,7 bzw. 1,6 g). Zur wäßrigen Suspension des Niederschlages wurde Ammoniaklösung zugefügt. Aus der vom ausgeschiedenen Eisen(III)-hydroxyd abfiltrierten Lösung kristallisierten die Sulfinsäuren nach dem Ansäuern mit Salzsäure aus. Mischungen mit authentischen Präparaten zeigten keine Schmelzpunktdepression [19].

5. Disproportionierung des Lithiumsalzes der Sulfensäure

1,4 g (0,01 *M*) der Verbindung **IVa** bzw. 1,3 g (0,01 *M*) der Verbindung **IVb** wurden ohne Lösungsmittel, im trockenen Stickstoffstrom zwei Stunden lang auf dem Wasserbad erhitzt. Nach dem Abkühlen wurde das Produkt mit einer Lösung von 5 g kristallinem Eisen-(III)chlorid in Wasser zersetzt, das mit Salzsäure angesäuert war. Das abfiltrierte Eisen(III)-sulfinat wurde mit Äther gewaschen und das Filtrat mit Äther extrahiert. Isolierte Produkte: 0,9 g (100%) bzw. 0,75 g (95%) Eisen(III)sulfinat und 0,3 g (50%) *p,p*'-Ditoluyldisulfid (Schmelzpunkt 44—45 °C) bzw. 0,4 g (74%) Diphenyldisulfid (Schmelzpunkt 60—61 °C). Die Sulfinsäuren und Disulfide waren mit authentischen Produkten identisch [19, 20, 21].

6. Reaktion des Lithiumsalzes der Sulfensäure mit Alkylhalogeniden

Die in der nachstehenden Tabelle angegebenen Mengen der sulfensäuren Salze wurden in absolutem Benzol gelöst und mit der nötigen Menge des entsprechenden Halogenids versetzt. Das Reaktionsgemisch wurde 48 Stunden lang im trockenen Stickstoffstrom bei Temperaturen von 50—80 °C gehalten. Das ausgeschiedene Salz wurde abfiltriert und der Rückstand nach dem Abdestillieren des Lösungsmittels mit Petroläther versetzt, wobei das Sulfoxyd in kristalliner Form abgeschieden wurde.*

In einigen Versuchen wurde das Halogenid im Überschuß angewandt und zusammen mit dem Lösungsmittel durch Wasserdampfdestillation entfernt.

Bei Anwendung von Produkten, die durch Stehen an der Luft autoxydiert waren, konnten folgende drei Sulfone isoliert werden:

a) **p-Toluylbenzylsulfon.** Schmelzpunkt 142—143 °C, identisch mit dem Literaturwert [22]. Ausbeute: 52% $C_{14}H_{14}O_2S$ (246,31). Berechnet S 13,0, gefunden S 13,6.

Tabelle I

Sulfensaures Salz, g (*M*)	Halogenid g (*M*)	Isoliertes Produkt, g (%)	Schmelzpunkt, Lösungsmittel	Charakterisierung
IVa 1,4 (0,01)	**IX** 1,6 (0,01)	**XI** 1,5 (65,2)	136—137 °C Äther mit wenig Methanol	Identisch mit authentischem *p*-Toluylbenzylsulfoxyd [18]
IVa 2,8 (0,02)	**X** 1,9 (0,01)	**XII** 0,5 (16,3)	150—151 °C Methanol	$C_{16}H_{16}O_2S$ (306,44) Ber. C 62,6 Gef. C 62,5 Ber. H 5,9 Gef. H 5,8 α,β-bis(*p*-Toluylsulfinyl)-äthan [26]

Die prozentuellen Ausbeuteangaben wurden auf das Salz der Sulfensäure bezogen.

---

* Ein Teil der durch Disproportionierung entstandenen Nebenprodukte blieb im Petroläther gelöst bzw. konnte durch Waschen mit Wasser entfernt werden. Das Sulfon wurde vom Sulfoxyd durch empirische Chromatographie auf Silikagel mit einem Gemisch aus Benzol und Petroläther getrennt.

b) **α,β-bis-(p-Toluylsulfonyl)äthan.** Schmelzpunkt 194—195 °C, identisch mit dem Literaturwert [23]. Ausbeute: 20% $C_{16}H_{18}O_4S_2$ (338,44). Berechnet S 18,9, gefunden S 19,3.

c) **2,4-Dinitrophenyl-4'-toluylsulfon.** Schmelzpunkt 179—180 °C. Ausbeute: 45% $C_{13}H_{10}O_6N_2S$ (322.15). Berechnet S 9,9, gefunden S 9,8.

7. Reaktion des Lithiumsalzes der Sulfensäure mit Arylsulfinylchlorid

13,1 g (0,05 *M*) des Thiolsulfinats **Ia** wurden in 50 ml absolutem Benzol gelöst und in trockener Stickstoffatmosphäre tropfenweise mit der Lösung von 4,1 g (0,05 *M*) Lithiumphenyl in absolutem Äther versetzt. Ohne Isolierung des Lithiumsalzes wurden 8,7 g (0,05 *M*) *p*-Toluylsulfinsäurechlorid (**XIII**), in 40 ml absolutem Benzol gelöst, tropfenweise zugegeben. Unter dauerndem Rühren wurde das Reaktionsgemisch 24 Stunden lang bei 50 °C gehalten. Das ausgeschiedene Lithiumchlorid wurde abfiltriert. Der lösungsmittelfreie Rückstand kristallisierte nach Zugabe von Petroläther aus. Ausbeute 5,1 g (36,7%). Schmelzpunkt (aus Methanol umkristallisiert) 75—76 °C, identisch mit authentischem *p*-Toluylthiolsulfonsäure-*p*-toluylester [24].

8. Reaktion des Lithiumsalzes der Sulfensäure mit p-Toluolsulfochlorid

1,4 g (0,01 *M*) Lithiumsulfenat (**IVa**) und 1,9 g (0,01 *M*) Tosylchlorid wurden in absolutem Äther suspendiert und im geschlossenen Rohr 6 Tage lang bei 50 °C gehalten. Danach wurde das Lösungsmittel bei Zimmertemperatur, unter Ausschluß der Feuchtigkeit abdestilliert. Der Rückstand erstarrte beim Abkühlen. Er wurde mehrmals mit eiskaltem Äther gewaschen. Schmelzpunkt nach dem Umkristallisieren aus einem Gemisch von Benzol und Petroläther (1 : 4) 77—78 °C. Ein Gemisch mit *p*-Toluylsulfinyl-*p*-toluylsulfon, welches nach dem Verfahren von KNOEVENAGEL [16] bzw. BREDERECK [17] hergestellt wurde, zeigte keine Schmelzpunktdepression.

9. Reaktion der Verbindung XV mit Benzylmagnesiumchlorid

2,9 g (0,01 *M*) der nach KNOEVENAGEL [16] hergestellten Verbindung wurden in absolutem Äther gelöst, bei Zimmertemperatur tropfenweise mit der Lösung von 1,5 g (0,01 *M*) Benzylmagnesiumchlorid versetzt und eine Stunde lang in mäßigem Sieden gehalten. Das Reaktionsgemisch wurde filtriert, wobei 2,1 g (100%) Magnesiumchlorid-*p*-toluylsulfinat in Form eines farblosen Pulvers erhalten wurde. Diese Verbindung geht beim Erwärmen mit salzsäurehaltigem Wasser schnell in Lösung. Mit festem Eisen(III)chlorid kann das Eisensalz der Sulfinsäure abgeschieden und das Magnesium aus dem Filtrat quantitativ zurückgewonnen werden. Durch Kochen mit überschüssigem Benzylchlorid unter Rückfluß setzt sich die Verbindung zu *p*-Toluylbenzylsulfon um. Schmelzpunkt 142—143 °C, identisch mit dem unter 6a) erhaltenen Sulfon.

Der Abdampfrückstand des ätherischen Filtrats betrug 2,0 g (87%). Aus Äther mit wenig Methanol umkristallisiert, betrug der Schmelzpunkt 136—137 °C. Die Verbindung war mit dem unter Punkt 6 erhaltenen *p*-Toluylbenzylsulfoxyd identisch.

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REACTIONS CATALYZED BY STRONG ACIDS, IN NONAQUEOUS MEDIA, III*

SYNTHESIS OF 1,4-DIHYDRO-1-PHENYL-3(2*H*)-ISOQUINOLINONE AND ITS DERIVATIVES FROM AROMATIC ALDEHYDES AND ARYL ACETONITRILES IN THE PRESENCE OF POLYPHOSPHORIC ACID CATALYST

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A procedure has been elaborated for the synthesis of 1,4-dihydro-1-phenyl-3(2*H*)-isoquinolinone and its substituted derivatives from aromatic aldehydes and arylacetonitriles in polyphosphoric acid. Fourteen new derivatives of the parent compound have been synthesized by the procedure. The structures of the products obtained from *m*-methylbenzyl cyanide and homoveratronitrile (3,4-dimethoxybenzyl cyanide) have been elucidated on the basis of the infrared spectra. It has been proved that the reaction proceeds through the intermediary product benzylidene-bis-phenylacetamide, which can also be prepared in other ways. In polyphosphoric acid, this compound readily undergoes ring closure to 1,4-dihydro-1-phenyl-3(2*H*)-isoquinolinone, and phenylacetamide is split off simultaneously.

In a preceding communication [1] of this series it was reported that the reaction of benzaldehyde and benzyl cyanide in abs. acetic acid and in the presence of boron fluoride or sulphuric acid gave benzylidene-bis-phenylacetamide. When the above aldehyde and nitrile were allowed to react in polyphosphoric acid (PPA) of high acidity, an exothermic reaction occurred and a yellow product was obtained which melted at 165 °C. The product was identical neither with α-phenylcinnamonitrile obtainable in basic medium, nor with benzylidene-bis-phenylacetamide accessible in acetic acid solution in the presence of BF_3 or H_2SO_4 catalyst. According to the infrared spectrum (Fig. 1), the compound contains no nitrile group. The characteristic bands in the infared spectrum at 3050 cm^{-1}, 3180 and 1665 cm^{-1} indicated the presence of a carboxamide group. A further characteristic feature of the spectrum was the band system in the region between 800 and 700 cm^{-1}, arising from the out-of-plane deformational vibrations of the hydrogen atoms attached to the aromatic ring. Of these, the bands at 750 and 700 cm^{-1} might presumably be assigned to a monosubstituted, and the band at 740 cm^{-1} to a 1,2-disubstituted aromatic ring.

As the infrared spectrum indicated the presence of a carboxamide group, it was assumed that condensation had been accompanied by hydratation of

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the nitrile group. In first approximation this assumption was supported by the identical melting point of the product with that of α-phenylcinnamamide and furthermore that it could be produced by the reaction of phenylacetamide and benzaldehyde, as well. The only contradiction to the supposed structure was the observation that, in disagreement with literary data, it could not be converted into the corresponding nitrile by heating with phosphorus pentoxide in toluene. Further doubts arose concerning the structure of the compound when the melting point of the product obtained with *p*-nitrobenzaldehyde differed from that of α-phenyl-*p*-nitrocinnamamide reported in the literature.

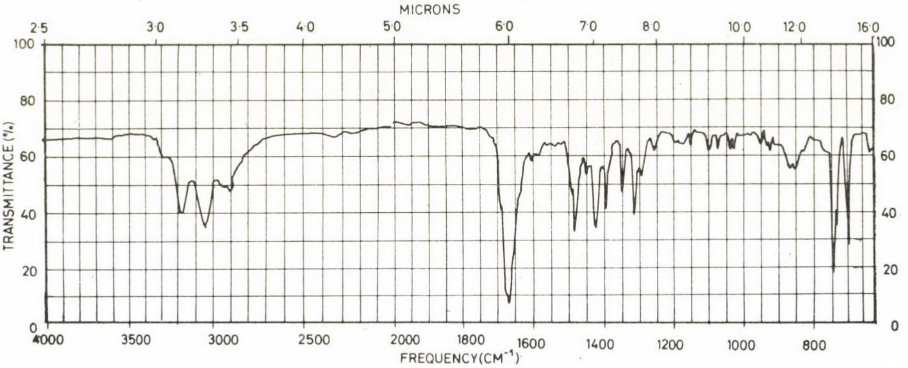


Fig. 1. IR spectrum of 1,4-dihydro-1-phenyl-3(2*H*)-isoquinolinone in KBr

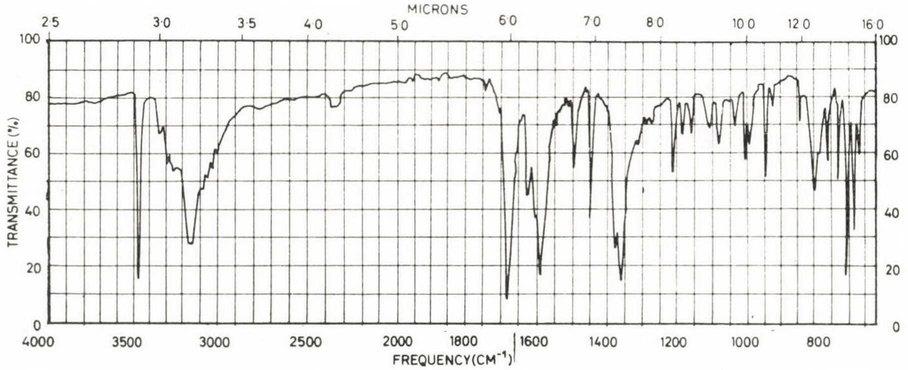


Fig. 2. IR spectrum of *cis*-α-phenylcinnamamide in KBr

Therefore, *trans*-α-phenylcinnamic acid was partially isomerized to the *cis* derivative by heating [2], the isolated and purified *cis* isomer was transformed to the acid chloride with phosphorus pentachloride, and the latter converted to *cis*-α-phenylcinnamamide with ammonia. This compound showed considerable melting point depression with our product, and the infrared spectra to be entirely different (Figs 1 and 2).

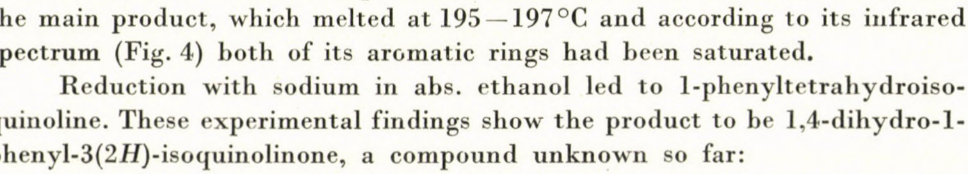
The next step in the elucidation of the structure of the product was the determination of the molecular weight. After the failure of the application of several methods (Rast, boiling point elevation), mass spectroscopic determination showed the molecular weight to be 223, corresponding to the empirical formula $C_{15}H_{13}NO$. The results of elemental analysis were consistent with the above empirical formula. In order to check the role of the active methylene group, the reaction was also carried out with phenylisobutyronitrile, which has no active methylene group; the product thus obtained was identical in character with the parent compound both according to analysis and infrared spectroscopy.

It was also found that the compound was slightly basic; on treatment with dry hydrogen chloride in abs. benzene, the colourless hydrochloride was obtained. This salt proved rather unstable: on exposure to air it gradually decomposed to the parent compound, with the simultaneous re-appearance of the yellow colour. The compound was resistant to acids and bases, it could be recovered unchanged after refluxing with dilute or concentrated acids for longer periods, or after heating in a sealed ampoule at 125 °C for 8 hours. Treatment with lithium aluminium hydride in tetrahydrofuran or heating with palladium on charcoal in decaline left the compound unchanged.

Hydrogenation with Raney nickel at 125 °C and 100 atm. for 8 hours afforded a new product melting at 137—139 °C. The most characteristic changes in the infrared spectrum of the hydrogenated substance (Fig. 3), as compared with that of the parent compound, were the following: the band at 2940 cm^{-1} indicating the presence of the methylene group was considerably strengthened, and only a single, strong band at 740 cm^{-1} remained in the region between 800 and 700 cm^{-1}.

These changes indicated the saturation of the monosubstituted aromatic ring. When the hydrogenation was effected at 140—150 °C and 120 atm., in addition to the above compound, a further new derivative was formed as the main product, which melted at 195—197 °C and according to its infrared spectrum (Fig. 4) both of its aromatic rings had been saturated.

Reduction with sodium in abs. ethanol led to 1-phenyltetrahydroisoquinoline. These experimental findings show the product to be 1,4-dihydro-1-phenyl-3(2*H*)-isoquinolinone, a compound unknown so far:



Unlike the case of 3,4-dihydro-1(2*H*)-isoquinolinones (isocarbostyrils), there are only a few data in the literature concerning the preparation of 1,4-dihydro-3(2*H*)-isoquinolinones. The parent compound was first synthesized by VON BRAUN and REICH [3] by thermal cyclization of *o*-aminomethylphenylacetic acid, or by the alkaline hydrolysis of its ester hydrochloride in alcohol solution. In addition, among the derivatives containing no substituent on the nitrogen atom, 4,4-diphenyl-1-methyl- and 1,4-dihydro-4-phenyl-3(2*H*)-isoquinolinones are known. The former was synthesized by PETYUNIN *et al.* [4] by the ring closure of benzylic acid γ-phenylethylamide with sulphuric acid, while the 4-phenyl derivative by GARDENT and HAMON [5] by the cyclization of mandelic acid benzylamide by means of phosphoric acid.

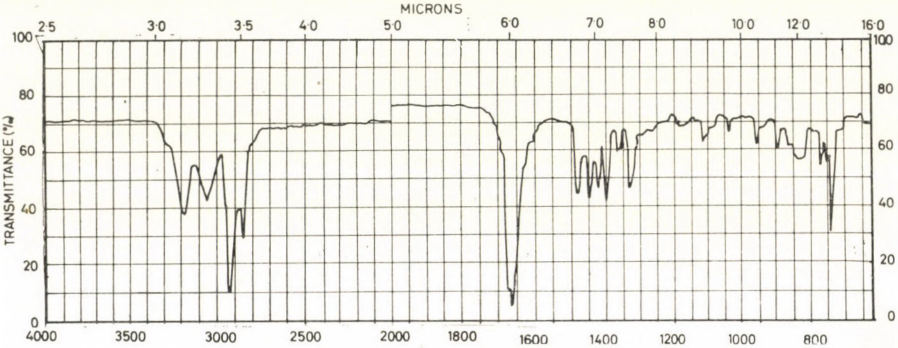


Fig. 3. IR spectrum of 1-cyclohexyl-1,4-dihydro-3(2*H*)-isoquinolinone in KBr

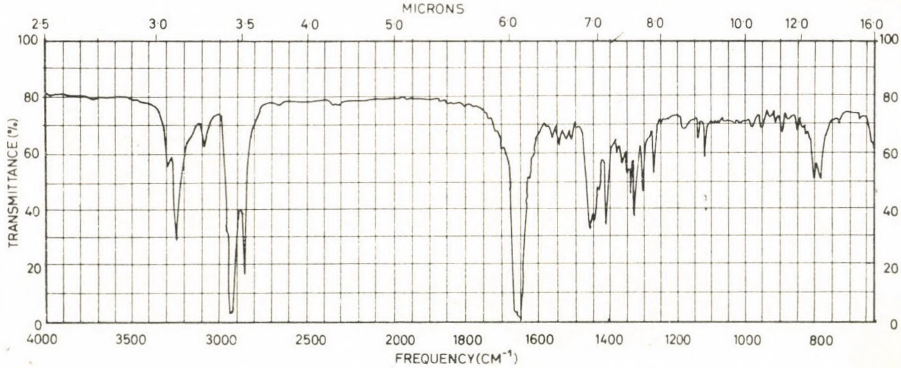
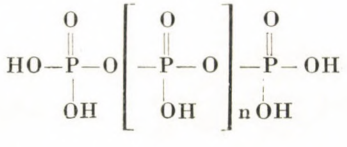


Fig. 4. IR spectrum of 1-cyclohexyl-1,4,5,6,7,8-hexahydro-3(2*H*)-isoquinolinone in KBr

After having elucidated the structure of the product, the optimum conditions of the reaction were investigated. First of all, the effect of the varied composition of the polyphosphoric acid catalyst was examined.

As it is known [6], the composition of polyphosphoric acid depends on the ratio of the starting materials, *i.e.* phosphoric acid and phosphorus pentoxide. The composition is usually characterized by the per cent ratio of phosphorus pentoxide. Mixtures with less than 85% P_2O_5 contain only linear polyphosphoric acids besides ortho- and pyrophosphoric acids. In the case of higher anhydride contents, the mixture also contains cyclic and cross-linked polymers. According to HUHTI and GARTAGANIS [7], the linear polymers are characterized by the following general formula:



$$HO-\underset{OH}{\overset{O}{\overset{\|}{P}}}-O\left[-\underset{OH}{\overset{O}{\overset{\|}{P}}}-O\right]_n-\underset{OH}{\overset{O}{\overset{\|}{P}}}-OH$$

A polyphosphoric acid with 82% P_2O_5 content consists, in about 64%, of 3- to 10-membered polymers ($n = 1-7$). In the case of 84% P_2O_5 content, the ratio of polymers with $n = 7$ or higher amounts to about 20%.

In the following, the various polyphosphoric acids will be characterized by the ratio of 85% phosphoric acid (ml) and phosphorus pentoxide (g) used in their preparation. The P_2O_5 contents of these polyphosphoric acids are shown in Table I.

Table I

Percentage P_2O_5 contents of polyphosphoric acids

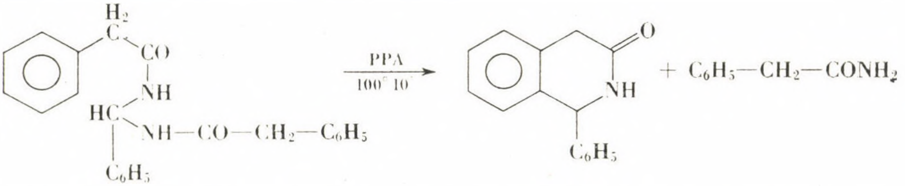
	Polyphosphoric acid			100% orthophosphoric acid	85% phosphoric acid
	1 : 2	1 : 1.5	1 : 1		
P_2O_5%	82.8	80.0	76.0	72.5	61.6

On attempting to carry out ring closure with the catalysts listed in Table I, it was found that cyclization did not occur with 85% phosphoric acid, but it proceeded with 100% acid (orthophosphoric acid). Almost the same results were obtained with this latter and various polyphosphoric acids, the only difference being that when the highly viscous 1 : 2 and 1 : 1.5 polyphosphoric acids were used the mixtures became even thicker during the reaction causing difficulties in handling. This effect was not observed with 1 : 1 polyphosphoric acid. As the reaction is exothermic and thus thorough stirring is required, 1 : 1 polyphosphoric acid was used in our further experiments.

Next the question was studied, whether the reaction could be accomplished with substituted derivatives of benzaldehyde and benzyl cyanide. It was found that nitro, halogen and alkyl substituents in the aldehyde component did not affect the reaction, while anisaldehyde, *o*-methoxybenzaldehyde and phenylacetaldehyde failed to give the corresponding derivatives. With substituted benzyl cyanide derivatives it was found that methoxy, nitro and chlorine substituents in *p*-position prevented the reaction or other products were obtained, while methyl and 3,4-dimethoxybenzyl cyanide afforded the expected products. The latter was also accessible from pyridine carboxaldehyde. Data of the parent compound and its derivatives are summarized in Table II.

In the infrared spectrum of 1-phenyl-1,4-dihydro-3(2*H*)-isoquinolinone derivatives substituted in the nucleus, the νNH stretching vibration bands appear at 3200—3190 and 3080—3060 cm^{-1}, and the amide-I band at 1680—1650 cm^{-1}. (The infrared spectra were taken in KBr pellets with a Perkin-Elmer 237 instrument.) The band at 1430 cm^{-1} appearing in the spectrum of the parent compound is absent in the spectrum of the 1-phenyl-1,4-dihydro-4,4-dimethyl-3(2*H*) derivative, therefore it presumably originates from the $\beta_s CH_2$ deformation vibration of the methylene group between the $>C=O$ group and the aromatic ring. This band appears in the spectrum of various derivatives in the region between 1430 and 1410 cm^{-1}. The $\gamma(=CH)$ deformation vibration bands depending on, and characteristic of, the pattern of substitution also appear between 880 and 700 cm^{-1}. In the spectrum of the nitro derivatives the ν_s and ν_{as} stretching vibration bands appear at 1510 and 1350 cm^{-1} in the case of the compound obtained from *p*-nitrobenzaldehyde and at 1540 and 1360 cm^{-1} in that from the *m*-isomer. The spectrum of the fluorine derivative has the νC—F stretching vibration bands at 1220 and 1160 cm^{-1}.

Examination of the reaction conditions showed that phenylacetamide could be isolated as a by-product of the reaction catalyzed by polyphosphoric acid. It was assumed that this compound had been formed from the excess benzyl cyanide under the effect of the polyphosphoric acid. When, however, the ratio of benzyl cyanide was lowered, the yield of isoquinolinone also decreased, and the maximum yield of the latter was obtained when the molar ratio of benzaldehyde and benzyl cyanide was 1 : 2. This indicates the formation of some intermediary product under the reaction conditions applied, from 1 mole aldehyde and 2 moles of the nitrile, which then transforms to the end-product with the elimination of phenylacetamide. The correctness of this assumption was supported by the fact that at lower temperatures benzylidene-bis-phenylacetamide could be isolated from the crude product. On the basis of our experiments we assumed that this compound is formed first in polyphosphoric acid, too, but under the cyclizing effect of polyphosphoric acid it is converted into the isoquinolinone derivative, while a phenylacetamide molecule is split off. Indeed, when benzylidene-bis-phenylacetamide was heated at 100 °C in polyphosphoric acid, it was converted into 1-phenyltetrahydroisoquinolinone within 10 minutes.



As it has been mentioned *p*-chlorobenzyl cyanide failed to yield the corresponding isoquinolinone derivative. Therefore, benzylidene-bis-(*p*-chlorophenyl)-acetamide was synthesized indirectly [1] and then heated in polyphosphoric acid. Comparison of the infrared spectrum of the bis-amide (Fig. 5) with that of the product obtained on working up the polyphosphoric acid melt (Fig. 6) showed that the conversion of the bis-amide was again very fast, occurring within 10 minutes. The most characteristic changes in the spectrum were the appearance of the double carbonyl band of identical intensity at 1660 and 1655 cm^{-1}, the disappearance of the band at 1555 cm^{-1} (presumably assignable to the secondary amide group, an amide-II band) and the simultaneous appearance of the amide-II band at 1630 cm^{-1}, characteristic of primary amides.

These changes are also reflected in the region between 3500 and 3000 cm^{-1} which is characteristic of the N—H stretching vibrations: instead of the bands

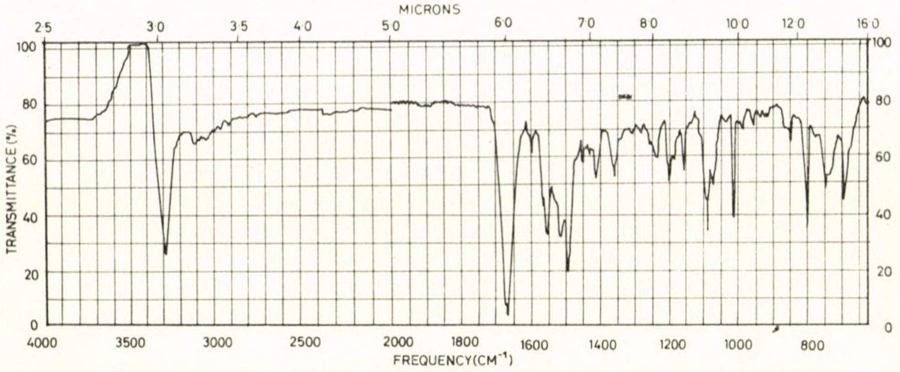


Fig. 5. IR spectrum of benzylidene-bis(*p*-chlorophenyl)-acetamide in KBr

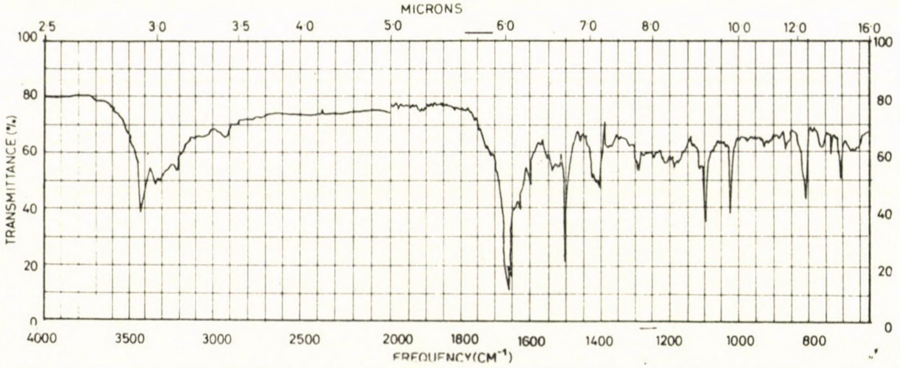


Fig. 6. IR spectrum in KBr of the product obtained in the reaction of benzylidene-bis-(*p*-chlorophenyl)-acetamide in polyphosphoric acid

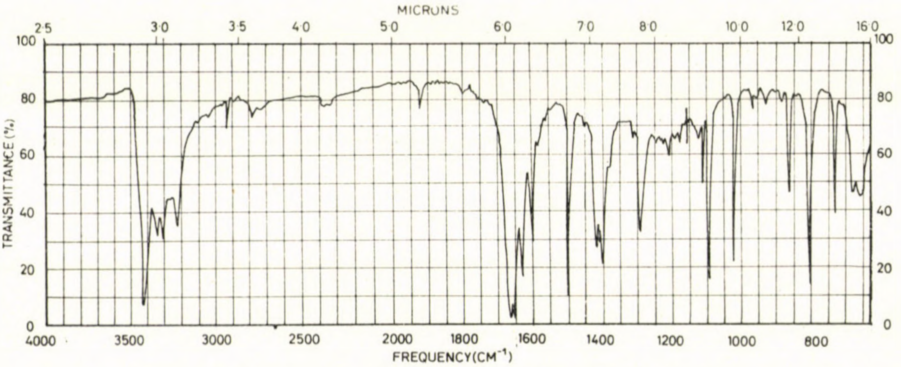
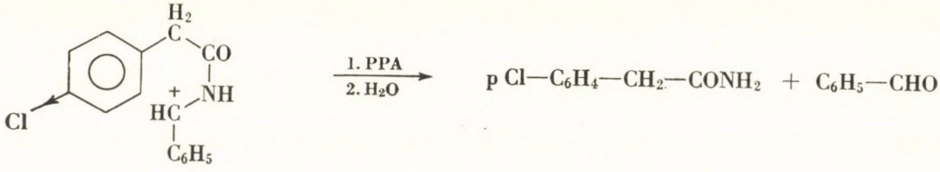
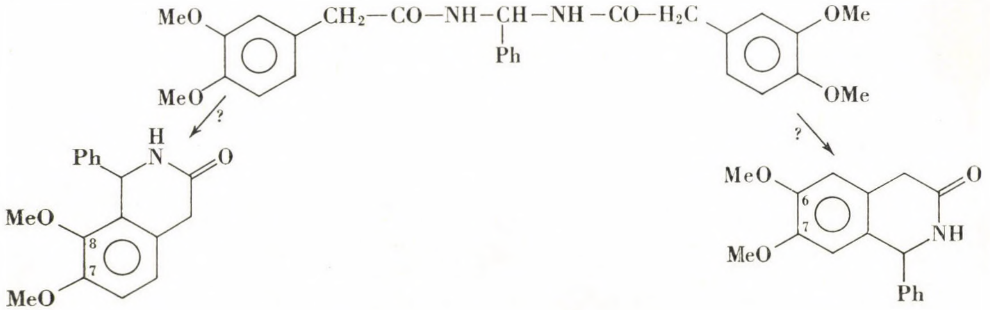
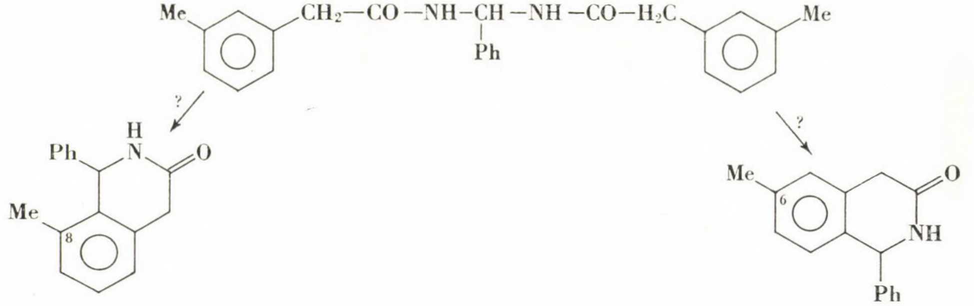


Fig. 7. IR spectrum of *p*-chlorophenylacetamide in KBr

at 3285 and 3100 cm^{-1}, ascribed to secondary amides, a strong band appeared at 3410 cm^{-1} and three bands of medium intensity at 3320, 3300 and 3210 cm^{-1}, respectively. According to the spectral data, the bis-amide transformed to a primary amide in polyphosphoric acid. On comparing the spectrum of the product (Fig. 6) with that of *p*-chlorophenylacetamide (Fig. 7), the conclusion may be drawn that the reaction of benzylidene-bis-(*p*-chlorophenyl)acetamide in polyphosphoric acid resulted, instead of ring closure, in a conversion to *p*-chlorophenylacetamide. This reaction path is presumably due to the deactivating influence of the chlorine atom on the carbonium ion which is produced from the bis-amide under the effect of polyphosphoric acid; this affects most just the carbon atom which participates in the cyclization reaction. Thus splitting to *p*-chlorophenylacetamide and benzaldehyde proceeds faster than ring closure to the corresponding isoquinolinone derivative.







Of the compounds listed in Table II, elucidation of the structures of the isoquinolinones obtained from 3,4-dimethoxybenzyl cyanide and *m*-methylbenzyl cyanide required further investigations. Namely, depending on the site of ring closure, dimethoxybenzyl cyanide may afford either the 6,7-

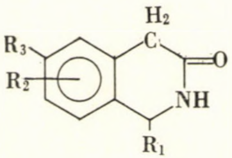


Table II

R_1	R_2	R_3	Yield, %	M.p.,* °C	Colour	Formula	Calcd./Found C%	Calcd./Found H%	Calcd./Found N%	Hal%
C_6H_5	H	H	52	164	yellow	$C_{15}H_{13}NO$	80.71 80.70	5.83 5.98	6.27 6.16	
m-$O_2NC_6H_4$	H	H	63	184	white	$C_{15}H_{12}N_2O_3$	67.70 67.82	4.48 4.53	10.45 10.20	
p-$O_2NC_6H_4$	H	H	66	180	orange	$C_{15}H_{12}N_2O_3$	67.70 68.05	4.48 4.62	10.45 10.36	
m-ClC_6H_4	H	H	54	143	pale yellow	$C_{15}H_{12}ClNO$	69.80 70.10	4.66 4.96	5.43 5.44	13.78 13.63
p-ClC_6H_4	H	H	39	170	white	$C_{15}H_{12}ClNO$	69.80 69.77	4.66 4.69	5.43 5.14	
m-BrC_6H_4	H	H	54	138	pale yellow	$C_{15}H_{12}BrNO$	59.62 59.47	3.98 4.22	4.64 4.73	26.40 26.30
p-FC_6H_4	H	H	43	141	white	$C_{15}H_{12}FNO$			5.81 5.63	
2,4-$Cl_2C_6H_3$	H	H	58	195	white	$C_{15}H_{11}Cl_2NO$			4.78 4.55	23.90 23.45
p-$CH_3C_6H_4$	H	H	46	139	white	$C_{16}H_{15}NO$	81.00 80.88	6.38 6.41	5.90 6.13	
C_5H_4N	H	H	52	187	pale yellow	$C_{14}H_{12}N_2O$	75.00 75.04	5.35 5.64	12.50 12.83	
C_6H_5	5-CH_3	H	55	177	yellow	$C_{16}H_{15}NO$	81.00 81.22	6.38 6.26	5.90 5.80	
C_6H_5	8-CH_3	H	45	142	yellow	$C_{16}H_{15}NO$	81.00 81.20	6.38 6.20	5.90 5.81	
C_6H_5	7-CH_3	H	63	179	white	$C_{16}H_{15}NO$	81.00 81.10	6.38 6.24	5.90 5.79	
C_6H_5	7-OCH_3	OCH_3	50	198	pale yellow	$C_{17}H_{17}NO_3$	72.10 71.89	6.06 6.12	4.95 5.00	

* All melting points reported are uncorrected

dimethoxy- or the 7,8-dimethoxy derivative, and *m*-methylbenzyl cyanide may give the 6-methyl or 8-methyl derivative.

Taking into account the electron-releasing effect of the methoxy and methyl groups, there is equal probability for the formation of both types of products. If steric factors are also considered, the formation of the 6,7-dimethoxy isomer and the 6-methyl derivative, respectively, is to be expected. The yields and melting points indicated that the products obtained were actually homogeneous. The elucidation of their structures did not require the chemical methods regularly used in quinoline and isoquinoline syntheses, as the problem could be solved by a study of the infrared spectra. The bands appearing in the region between 900 and 700 cm^{-1}, arising from the out-of-plane deformation vibrations of the hydrogen atoms attached to the aromatic nucleus, constituted the basis for the determination of the sites of substitution. These bands are known to be characteristic of the pattern of substitution. The spectrum of the dimethoxy derivative possessed three bands in the above region, at 860 (*m*), 750 (*s*) and 700 cm^{-1} (*s*). Since it had been determined earlier that the bands at 750 and 700 cm^{-1} arise from the monosubstituted aromatic ring attached to C-1 of the isoquinolinone skeleton, the pattern of substitution of the fused aromatic ring was deduced from the band at 860 cm^{-1}, which is characteristic of a 1,2,4,5-tetrasubstituted benzene ring. Therefore, the product obtained from 3,4-dimethoxybenzyl cyanide is the expected 1-phenyl-1,4-dihydro-6,7-dimethoxy-3(2*H*)-isoquinolinone.

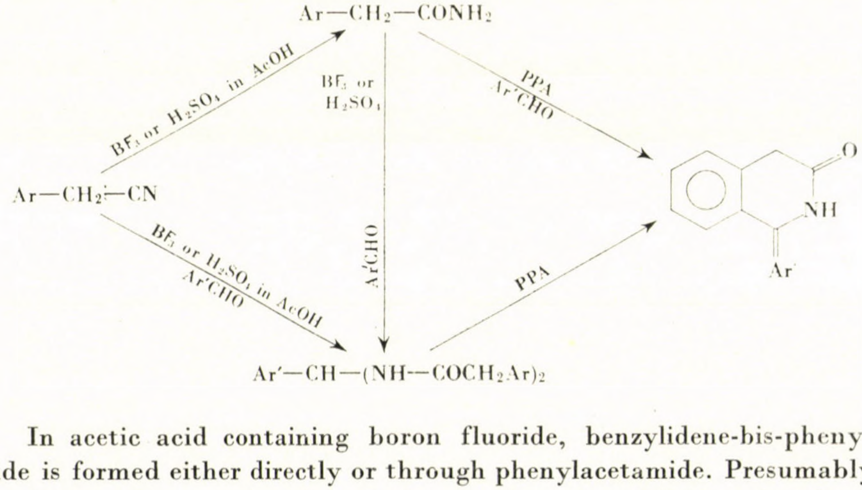
The structure of the product obtained from *m*-methylbenzyl cyanide was elucidated analogously, by comparison of its infrared spectrum with that of the products obtained from *o*- and *p*-methylbenzyl cyanide. The characteristic bands in the spectra of the three methyl derivatives were as follows:

1-phenyl-1,4-dihydro-5-methyl-3(2*H*)-isoquinolinone	795 cm^{-1} (*m*) 760 cm^{-1} (*s*) 705 cm^{-1} (*s*) 700 cm^{-1} (*s*)
1-phenyl-1,4-dihydro-6(or 8)-methyl-3(2*H*)-isoquinolinone	790 cm^{-1} (*m*) 750 cm^{-1} (*s*) 710 cm^{-1} (*s*) 695 cm^{-1} (*s*)
1-phenyl-1,4-dihydro-7-methyl-3(2*H*)-isoquinolinone	820 cm^{-1} (*m*) 755 cm^{-1} (*s*) 700 cm^{-1} (*s*)

It can be stated that the bands at 700–695 and 760–750 cm^{-1} in the spectrum of the methyl derivatives are to be assigned to the phenyl group attached to the C-1 atom. In the spectrum of the product obtained from *o*-methylbenzyl cyanide, the bands at 795 and 705 cm^{-1} indicate a 1,2,3-trisubstituted aromatic ring (5-methylisoquinolinone derivative), while the band at 820 cm^{-1} in that obtained from *p*-methylbenzyl cyanide shows the presence of a 1,2,4-trisubstituted aromatic ring. The spectrum of the product, whose structure was to be elucidated and which originated from *m*-methylbenzyl cyanide, had two bands at 790 and 710 cm^{-1}, and thus it was very similar to that of 1-phenyl-1,4-dihydro-5-methyl-3(2*H*)-isoquinolinone, unequivocally indicating the presence of a 1,2,3-trisubstituted aromatic ring in the compound. This, again, means that instead of the isomer expected on the basis of steric considerations, *m*-methylbenzyl cyanide gave 1-phenyl-1,4-dihydro-8-methyl-3(2*H*)-isoquinolinone.

Since, as it has been mentioned, benzylidene-bis-phenylacetamide can also be prepared from phenylacetamide, the assumption seems reasonable that as far as it is possible for the phenylacetamide by-product, formed in the reaction of benzaldehyde and benzyl cyanide in the presence of polyphosphoric acid, to transform again to benzylidene-bis-phenylacetamide, in principle the same yield as obtained under the above conditions will also be attainable when benzaldehyde and benzyl cyanide are used in 1 : 1 molar ratio. Under appropriate reaction conditions this expectation could actually be realized: the modification may have advantage particularly in the cases when more expensive benzyl cyanide derivatives are used.

On the basis of our experiments it is assumed that the reactions which may occur between benzaldehyde and benzyl cyanide in the presence of strong acids are the following:



In acetic acid containing boron fluoride, benzylidene-bis-phenylacetamide is formed either directly or through phenylacetamide. Presumably this is the intermediary product in polyphosphoric acid, and it immediately undergoes cyclization. However, it can also be supposed that in the first step a carboxamide is formed from the nitrile, and this latter is converted through the bis-amide to give the isoquinolinone derivative. Further experiments are in progress to clarify this problem, and kinetic measurements are intended to obtain further information about the reaction.

Experimental

1. 1-phenyl-1,4-dihydro-3(2H)-isoquinolinone

(a) From benzyl cyanide

In a four-necked round-bottomed flask equipped with a mechanical stirrer, a thermometer, a dropping funnel and a gas-outlet tube, was placed 100 g of 1 : 1 polyphosphoric acid. 23 g (0.196 mole) of benzyl cyanide was added in portions, with continuous stirring. The temperature of the mixture rose to 60 °C. It was then heated to 95 °C and stirred at this temperature for 30 min. 10 g (0.09 mole) of benzaldehyde was added in portions at such a rate (during about 20 min) that the temperature rose to 110—120 °C. The mixture was stirred at 120—125 °C for a further 3 hrs, allowed to cool to 60 °C and poured into 1 l of water, with thorough stirring. The product separated as yellow semi-solid clots. The supernatant was decanted, the product suspensed in 1 l of water, the suspension made alkaline with ammonium hydroxide and heated to boiling, when the product transformed to a yellow powder-like precipitate. It was filtered off, washed with water until neutral and dried at 60 °C to obtain 29.6 g, m.p. 150—157 °C. The washing contained the main portion of phenylacetamide formed in the reaction, and also this compound was the main contamination of the product. Recrystallization of the crude product from 200 ml of abs. ethanol afforded 11 g (52%) of the pure substance, m.p. 164 °C.

All derivatives of the parent compound listed in Table II were synthesized analogously. The compounds were soluble in warm alcohol and benzene, or in acetone at room temperature.

(b) From phenylacetamide

0.8 g (0.0075 mole) of benzaldehyde and 2.04 g (0.015 mole) of phenylacetamide were reacted with 6.0 g of polyphosphoric acid. The reaction mixture was worked up as described under (*a*) to obtain 1.4 g of a crude product, m.p. 155—160 °C, which on recrystallization from seven parts of alcohol yielded 0.76 g (45%) of the pure compound, m.p. 164—165 °C.

(c) From equivalent amounts of benzaldehyde and benzyl cyanide

In the apparatus described above, 100 g of 1 : 1 polyphosphoric acid was mixed with 19.0 g of benzyl cyanide at room temperature. The mixture was heated to 80 °C, and 8.0 g of benzaldehyde was added dropwise with stirring at this temperature. The temperature was raised to 100 °C, which was maintained for 1 hr. A further 8.0 g of benzaldehyde was added in three portions over a period of 30 min, the mixture stirred for 1 hr., and worked up as above to yield 27.6 g (84%) of 1-phenyl-1,4-dihydro-3(2*H*)-isoquinolinone, m.p. 162—163 °C.

2. 1-Phenyl-1,4-dihydro-4,4-dimethyl-3(2H)-isoquinolinone

3.3 g (0.0224 mole) of 2-phenylisobutyronitrile [8], 20 g of polyphosphoric acid, and 1.2 g (0.0113 mole) of benzaldehyde were reacted at 100 °C for 2 hrs as described under 1 (*a*). The reaction mixture was worked up as usual, and the 2.3 g of crude product, m.p. 160—165 °C, was recrystallized from ten parts of benzene to yield 1.2 g (42%) of 1-phenyl-1,4-dihydro-4,4-dimethyl-3(2*H*)-isoquinolinone, m.p. 168.5—169.5 °C.

$C_{17}H_{17}NO$ (251.32). Calcd. C 81.30; H 6.78; N 5.75. Found: C 81.26; H 7.01; N 5.67%.

3. cis-1-Phenylcinnamide

(a) trans-α-Phenylcinnamic acid

The compound was prepared according to BUCKLES and HAUSMAN [9] by the condensation of benzaldehyde and phenylacetic acid in the presence of acetic anhydride and triethylamine catalyst.

(b) cis-α-Phenylcinnamic acid [2]

3 g of *trans*-α-phenylcinnamic acid was heated at 400—450 °C for 1 min. The melt which solidified on cooling was dissolved in 50 ml of 5% ammonium hydroxide, the solution was decolourized with charcoal, filtered, and the unchanged *trans* isomer was precipitated by acidification with 50% aqueous acetic acid to pH 4.5. The filtered solution was then treated with 1 : 1 aqueous HCl to precipitate the *cis* isomer in crystalline form (0.5 g), m.p. 134—135 °C.

(c) cis-α-Phenylcinnamide [2]

0.3 g of *cis*-α-phenylcinnamic acid was refluxed with 0.4 g of phosphorus pentachloride in 5 ml of abs. ether for 1 hr. 100 ml conc. ammonium hydroxide solution was added, and the product which precipitated was filtered off, washed until neutral, and dried to give 0.2 g (67%) of *cis*-α-phenylcinnamamide, m.p. 165—166 °C (lit. m.p. 167—168 °C).

4. 1,2,3,4-Tetrahydro-3-oxo-1-phenylisoquinolinium chloride

1.0 g of 1-phenyl-1,4-dihydro-3(2*H*)-isoquinolinone was dissolved in a mixture of benzene (35 ml) and methanol (5 ml), and dry hydrogen chloride gas was passed through the solution at 25—30 °C for 2 hrs. The solution was evaporated to dryness in vacuum at 30 °C bath temperature. An oily product was obtained, which solidified to white crystals when rubbed with 10 ml of dry petroleum ether. After drying in vacuum 0.8 g (70%) of 1,2,3,4-tetrahydro-3-oxo-1-phenylisoquinolinium chloride was obtained, m.p. 129—131 °C.

$C_{15}H_{14}ClNO$ (259.72). Calcd. HCl 14.05%. Found: HCl 13.90%.

Under the effect of water or alcohol, or simply on exposure to air, the hydrochloride salt decomposed to the yellow starting material.

5. Reduction of 1-phenyl-1,4-dihydro-3(2H)-isoquinolinone to 1-phenyltetrahydroisoquinoline [5]

In a three-necked round-bottomed flask equipped with a mechanical stirrer, a reflux condenser and a stopper, 10 g of 1-phenyl-1,4-dihydro-3(2*H*)-isoquinolinone was dissolved, with stirring, in 600 ml of abs. ethanol, and then 70 g of sodium metal, cut to small pieces, was added in portions to the boiling solution over a period of 45 min. The mixture was refluxed for a further 30 min with stirring; during this period the Na reacted completely. Then 300 ml of water was added, with stirring, in small portions under cooling, and the solution was concentrated in vacuum until the alcohol was completely removed. The white, crystalline precipitate was collected, dissolved in 100 ml of 5% HCl, and the solution was filtered and treated with 10% aqueous ammonium hydroxide to precipitate the base. After filtration and drying 7.5 g (80%) of the crude product was obtained, m.p. 96—97 °C. Recrystallization from 20 parts of petroleum ether raised the m.p. to 97 °C (lit. m.p. 97 °C).

*

The authors wish to express their thanks to Dr. M. VAJDA for his valuable suggestions concerning the structural elucidation of the parent compound. The microanalyses were performed in the Microanalytical Laboratory (head: Mrs. M. KÁLOVITS-SÁRI) of Gedeon Richter Pharmaceutical Works, Budapest.

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FROUDE NUMBER, AND POWER CONSUMPTION OF MIXING I

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1. Measurements were made with paddle-, centrifugal-, and propeller-mixers in concave bottomed vessels with liquids of various viscosities, for the determination of the power consumption of mixers. These measurements were carried out in the turbulent range of flow, $Re = 300$ to $4 \cdot 10^5$. We have found that, irrespective of Fr number, measured data fall on the same Eu *vs.* Re curve until the vortex does not reach the impeller blades, *i.e.* until dispersion of air into the liquid does not begin. This "standard curve" is defined by the correlation $Eu = A \cdot Re^{-a}$, where the constant A is a function of the type of mixer and of the geometrical dimensions of the vessel, and the exponent a of the Re number is an empirical value that varies with the Re number.

2. Within one series of experiments, *i.e.* with d, H, h, D, b, further μ, and ϱ severally the same, at a certain n_{crit} number of revolutions the vortex generated on the surface of the liquid sinks down to the level of the impeller blades and dispersion of air into the liquid begins. From this point on, characterized by a Re_{crit}, further increase of n causes the Eu *vs.* $Re_{(\nu\ const)}$ curve to deviate from the former standard curve. In this two-phase mixing domain the $\nu =$ same curves run about parallel to each other, $Eu_{disp} = B_{(\nu)} \cdot Re^{-a}$, where $a = 0.7$ to 1.2.

3. We repeated one of the experiments of Rushton, Costich, and Everett, and have found that

a) the data given by Rushton *et al.* lead to Eu numbers too high, probably because of a systematic error due to frictional losses in their instrument;

b) it may be also due to systematic error that Rushton *et al.* report differentiation according to Fr numbers from $Re = 300$ on;

c) contrary to findings of Rushton *et al.*, with none of the liquids and with none of the impellers used could different Eu *vs.* Re curves be distinguished on the grounds of differences in *iso-Fr* values till the impeller did not disperse air into the liquid. Thus *iso-Fr* lines have, in principle, no meaning at all;

d) according to our experimental finding, and in contrast to those of Rushton *et al.*, after dispersion of air into the liquid, power consumption does increase even if not in a proportion to n^3, yet in a proportion to about n^2.

4. In our opinion the *Eu-Re-iso-Fr* method of presentation adopted by Rushton *et al.* is better discarded. It seems more correct to use, besides the Eu *vs.* Re standard curve characteristic of mono-phase mixing, the plotting of Eu *vs.* $Re_{(\nu\ const)}$ curves for the characterization of the two-phase domain.

Introduction

According to experience, the power to be supplied to agitators is a function of the dimensions of the vessel and of the impeller, further of the number of revolutions, and of the density and the viscosity of the liquid to be stirred.

$$N = f(d,\ b,\ D,\ H,\ h,\ n\ \varrho,\ \mu) \quad \dots\dots\dots \quad (1)$$

where N = the power consumption, kg · m²/sec³ = watt
d = the diameter of the impeller, m
b = the width of the impeller blade, m
D = the diameter of the vessel, m
H = the height of the liquid level at rest in the vessel, m
h = the distance between the impeller and the bottom of the vessel, m
n = the number of revolutions, $\sec^{-1}$
ϱ = the density of the liquid, kg/m³
μ = the dynamic viscosity of the liquid, kg/m · sec
$\nu = \mu/\varrho$, the kinematic viscosity of the liquid, m²/sec

By dimensional analysis, WHITE and BRENNER solved this problem [1] in 1934, and arrived to the following correlation.

$$N = A \cdot d^5 \cdot n^3 \cdot \varrho \cdot \left(\frac{d^2 \cdot n \cdot \varrho}{\mu}\right)^{-a} \left(\frac{b}{d}\right)^c \left(\frac{D}{d}\right)^e \left(\frac{H}{d}\right)^f \left(\frac{h}{d}\right)^j \tag{2}$$

The values for the constant A, and for the exponents were determined experimentally.

If the full-scale equipment is geometrically similar to the experimental apparatus, *i.e.* the ratios $\left(\frac{b}{d}\right)$, $\left(\frac{D}{d}\right)$, $\left(\frac{H}{d}\right)$ and $\left(\frac{h}{d}\right)$, the so-called "internal scale factors" or dimensionless "length ratios" are the same for both, Eq. (2) presents a more simple form

$$\frac{N}{d^5 \cdot n^3 \cdot \varrho} = A \cdot \left(\frac{d^2 \cdot n \cdot \varrho}{\mu}\right)^{-a} \tag{3}$$

where

$$\frac{d^2 \cdot n \cdot \varrho}{\mu} = Re_{\text{mix}} \tag{4}$$

= the mixing *Reynolds number* abbreviated as *Re*.

$$\frac{N}{d^5 \cdot n^3 \cdot \varrho} = Eu \tag{5}$$

= power number, or mixing *Euler number*

or

$$Eu = A \cdot Re^{-a} \tag{6}$$

Effects of the Froude number upon power consumption of mixing

If the vessel is not provided with baffles that would brake the rotation of the liquid then therein a vortex is generated of which depth and surface shape are functions of the gravitational and centrifugal forces acting upon the liquid in rotation. Thus the dynamics of the flow is a function also of gravitational force.

Hixson and **Baum** [2], in the course of their experiments with turbine impellers, in 1942, pointed to the fact that when the vortex reaches down to the impeller blades the power number curve branches away, steeply downward, from the "standard" *Eu vs. Re* curve. The above authors did not study this phenomenon in details and did not mention its correlation with the *Fr*-number. (According to them the standard curve is defined by the $H = D$ geometrical criterion.)

In the literature, it is only **Kafarov** [3, Fig. 32] who published a diagram for the linear correlation between *Fr*-number and surge of liquid level (Δh), but he did not study the question at which operational parameters (n, *i.e.* Re, or Fr) does the vortex extend down to the impeller blades or to the depth $(H - h)$.

Rushton *et al.* [4, 5] were the first to account also for gravitational acceleration in a calculation of the power consumption of mixers. By dimensional analysis they worked out the following correlation

$$Eu = A \cdot Re^{-a} \cdot Fr^{-b} \tag{7}$$

where

$$Fr = \frac{d \cdot n^2}{g}, \text{ the mixing } \textit{Froude number} \tag{8}$$

and since the peripheral speed, $v = d \cdot \pi \cdot n$, and the centrifugal acceleration produced by it,

$$a_c = \frac{v^2}{r} = \frac{d^2 \cdot \pi^2 \cdot n^2}{r} = 2d \cdot \pi^2 \cdot n^2$$

the physical sense of the mixing *Froude number* is

$$Fr = \frac{1}{2 \cdot \pi^2} \cdot \frac{a_c}{g} \tag{9}$$

where a_c = centrifugal acceleration, $\mathrm{m \cdot sec^{-2}}$
g = gravitational acceleration, $\mathrm{m \cdot sec^{-2}}$

Thus in the dynamics of mixers the *Froude number* expresses the ratio of the centrifugal force to the gravitational force acting upon a unit mass of liquid.

In their experiments, **Rushton** used various types of mixer-impellers of which one [4, Fig. 12] is shown in Fig. 1, and another [4, Fig. 14, Curve 4 complemented with the same ν values] in Fig. 7.

In the course of their experiments, **Rushton** noted that at $Re < 300$ the vortex of the liquid in the vessel is small and that *Eu numbers*, calculated on the basis of measured power consumption values, describe one curve. They found that the *Fr* number does not affect power consumption but from $Re > 300$ onwards. Also in this $Re > 300$ domain the points measured for one certain substance (thus: ν = const.) fall upon one *Eu vs.* $Re_{(\nu=const.)}$ straight line, but results of measurements on various liquids do not align themselves on a common *Eu vs. Re* curve (*cf.* Fig. 1) even if *Re* numbers are severally the same. RUSHTON *et al.* joined the points assignable to the same *Fr* number, thus they got *iso-Fr* lines.

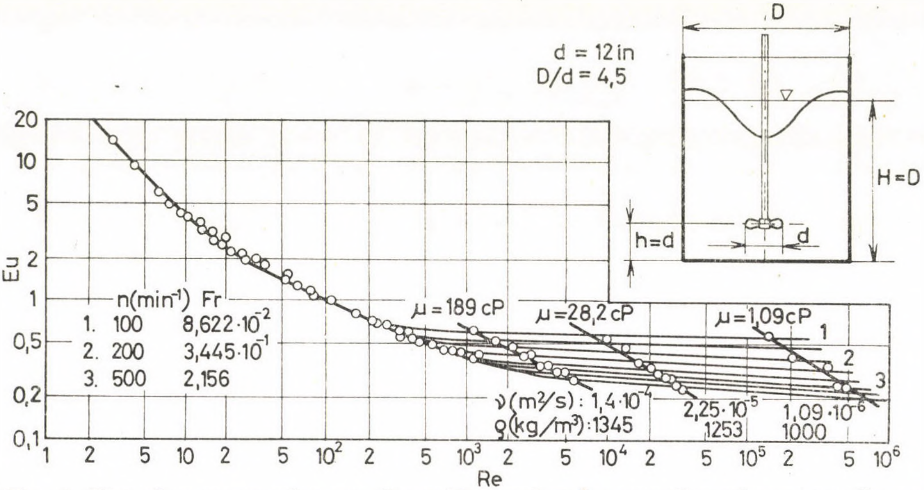

Fig. 1. Plot of power number *vs.* Reynolds number for propeller mixer, according to RUSHTON [4]

In this domain they applied Eq. (7) to the *Eu vs.* $Re_{(Fr\ const)}$ lines. According to data measured by them, the exponent of the *Fr* number was a function also of *Re*, the value of *b* varied between 0 and $\frac{1}{3}$! However, while each *Eu vs.* $Re_{(\nu\ const)}$ curve describes an operation carried out with one specific substance, the presentation of such an *iso-Fr* curve as if it were that of the main parameter is misleading since every point on it is assigned to a different liquid, thus it is not an operating line.

Our other objection to this diagram consists in that, though the correlation between *Fr* number and vortex is a well-known fact, data and diagrams published by RUSHTON unfortunately do not indicate at which point admixture of air into the liquid begins, *i.e.* at which critical *Re* or *Fr* number the vortex sinks down to the critical depth of the impeller (critical depth, h_{crit}, is the distance between the impeller and the level of liquid at rest, *i.e.* $H - h$, *cf.* Fig. 1).

Further, we think it advisable to study more closely the statement made by RUSHTON *et al.*, purporting that the point of admixture of air is also the extreme limit of the power capable to be imparted to the liquid: "The maximum power that can be impressed on the fluid is reached when vortex depth is equal to propeller depth . . ." [4, p. 404].

Our aim was to settle our doubts in connexion with the data and interpretation of RUSHTON, further, to clarify the interaction between experimental parameters and admixture of air (Re_{crit} or Fr_{crit} values), in order to propose a graphical presentation more suitable from an operational point of view.

Experimental apparatus

The axis of the driving motor is arranged perpendicularly, its speed infinitely variable. The housing of the motor is allowed freely to rotate on minimum friction ball bearings attached to its upper and lower ends. The electrical terminals of the motor dip into channels filled with mercury thus do not hinder the movement of the motor housing.

During the mixing the torque generated on the housing of the motor is balanced by a measurable opposing torque of the same magnitude, from this the power consumption of the mixer can be calculated

$$N = 2\pi \cdot P \cdot k \cdot n \left(\frac{\text{kg weight} \cdot \text{m}}{\text{sec}}\right) \tag{10}$$

where P = weight measured by the balance
(kg weight = 9.80665 newtons)
k = arm of force P, (m)
(in our apparatus 0.494 m)
n = revolutions, sec^{-1}

Note. Power input N was measured in $\frac{\text{kg weight} \cdot \text{m}}{\text{sec}}$ units,

1 unit = 9.80665 abs.watts

The maximum power of the motor was 600 watts, that is about 60 kg weight · m · sec^{-1}. Accuracy of measurements was between 1 and 2 gramme weight, thus between 0.5 and $1 \cdot 10^{-3}$ kg weight · metre torque; by taking the mean of several readings the accuracy can be improved. The maximum revolution of the motor was $n = 900\ \text{min}^{-1}$, or 15 sec^{-1}.

Experiments were carried out in a vessel of $D = 0.380$ m diameter, at liquid levels $H = 0.440$ m, with impeller blades of radial diameters from $d = 0.130$ to $d = 0.160$ m, with water and with aqueous glycerol solutions, in a concave bottomed vessel (*cf.* Figs 3, 4). In a separate experiment in a flat bottomed vessel one of the experiments of RUSHTON was reproduced under perfectly similar conditions (*cf.* Fig. 5), with water and aqueous solutions of sugar.

With the dimensions of the vessel and the impeller as mentioned, measurements only in the turbulent domain ($Re > 300$) were feasible, this being appropriate to our aim since significant vortex formation cannot be expected but in the turbulent zone (thus we worked mainly between $Re = 5 \cdot 10^3$ and $3 \cdot 10^5$).

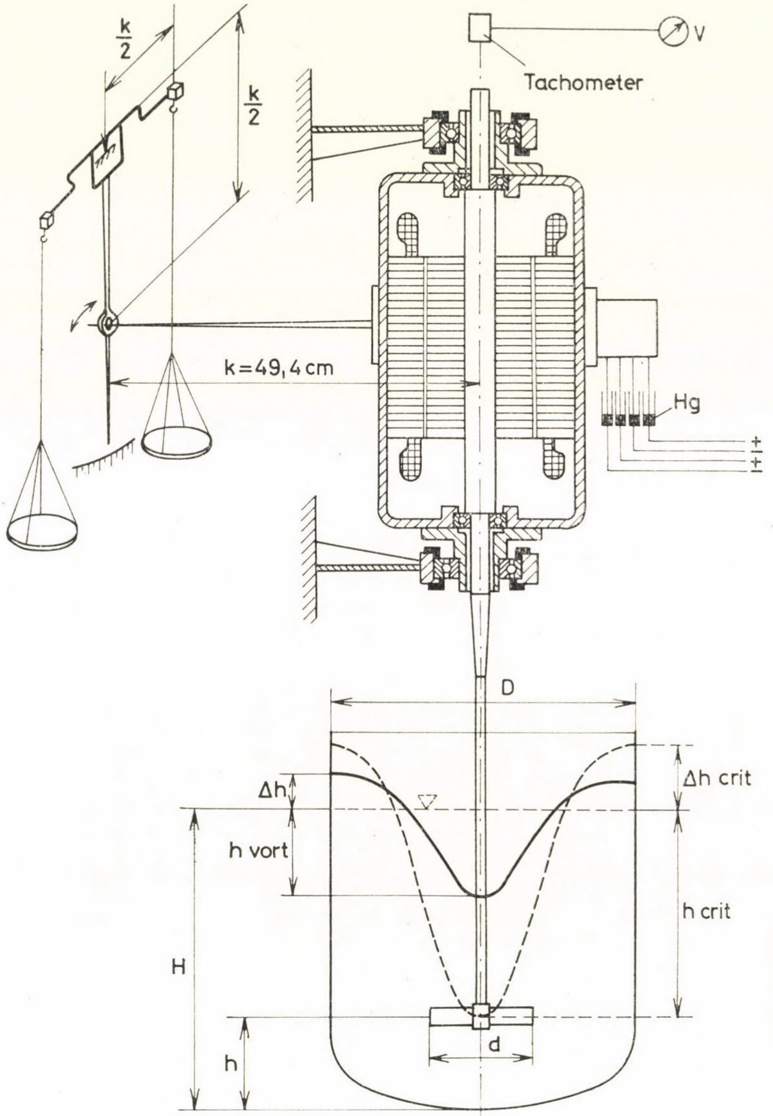

Fig. 2. Experimental apparatus used in this work

Results

Experiments were carried out with 10 different types of impellers. Experiments with two of these, with 3 liquids each, are shown in Tables I and II, and Figs 3 and 4, respectively.

Table I (*cf.* Fig. 3)

Measured data for a three-blade propeller mixer working in a concave bottomed vessel without baffles

$d = 1.554 \cdot 10^{-1}$ m

n (sec^{-1})	P (g · weight)	μ (cP)	ϱ $\left(\frac{\text{g}}{\text{cm}^3}\right)$	N $\left(\frac{\text{kg weight} \cdot \text{m}}{\text{sec}}\right)$	Eu	Re	Fr
3.05	13	13.03	1.16	$1.24 \cdot 10^{-1}$	$3.83 \cdot 10^{-1}$	$6.55 \cdot 10^{3}$	0.1474
10	90	12.74	1.16	2.83	$2.64 \cdot 10^{-1}$	$2.2 \cdot 10^{4}$	1.585
15	140	12.64	1.16	6.59	$1.83 \cdot 10^{-1}$	$3.22 \cdot 10^{4}$	3.565
3	8	2.4	1.048	$7.54 \cdot 10^{-2}$	$2.88 \cdot 10^{-1}$	$3.16 \cdot 10^{4}$	0.1426
9	51	2.4	1.048	1.43	$2.02 \cdot 10^{-1}$	$9.47 \cdot 10^{4}$	1.283
12	72	2.39	1.048	2.71	$1.61 \cdot 10^{-1}$	$1.26 \cdot 10^{5}$	2.28
6	22	1.08	1.0	$4.14 \cdot 10^{-1}$	$2.07 \cdot 10^{-1}$	$1.34 \cdot 10^{5}$	0.571
9	42	1.05	1.0	1.19	$1.76 \cdot 10^{-1}$	$2.09 \cdot 10^{5}$	1.283
12	60	1.03	1.0	2.26	$1.41 \cdot 10^{-1}$	$2.81 \cdot 10^{5}$	2.28

Note. In the course of these experiments we recorded data of 10 to 12 measurements at $n = 2$ to 15 revolutions per second. From this series of data, Tables I and II include only 3 values, one is the point on the standard curve, the other two are the two extreme values of the two-phase mixing (admixture of air). Figs 3 and 4 show all the measured values.

In contrast to results of RUSHTON, in preliminary experiments in a concave bottomed vessel we found that if the liquid vortex did not yet reach down to the impeller of the mixing vessel and thus the impeller did not disperse air into the liquid, the same Eu number appertains to the same Re number in

Table II (*cf.* Fig. 4)

Measured data for a centrifugal mixer (on top suction) in a concave bottomed vessel without baffles

$d = 1.600 \cdot 10^{-1}$ m

n (sec^{-1})	P (g · weight)	μ (cP)	ϱ $\left(\frac{\text{g}}{\text{cm}^3}\right)$	N $\left(\frac{\text{kg weight} \cdot \text{m}}{\text{sec}}\right)$	Eu	Re	Fr
2	6	12.74	1.16	$3.77 \cdot 10^{-2}$	$3.80 \cdot 10^{-1}$	$4.65 \cdot 10^{3}$	0.0653
8	65	12.07	1.16	$1.63 \cdot 10^{-1}$	$2.57 \cdot 10^{-1}$	$1.97 \cdot 10^{4}$	1.043
15	140	12.07	1.16	6.59	$1.57 \cdot 10^{-1}$	$3.69 \cdot 10^{4}$	3.67
3	10	2.38	1.048	$9.42 \cdot 10^{-2}$	$3.11 \cdot 10^{-1}$	$3.37 \cdot 10^{4}$	0.1468
6	28	2.38	1.048	$5.28 \cdot 10^{-1}$	$2.18 \cdot 10^{-1}$	$6.74 \cdot 10^{4}$	0.587
14	82	2.38	1.048	3.60	$1.17 \cdot 10^{-1}$	$1.57 \cdot 10^{5}$	3.20
2	4	0.936	1.0	$2.51 \cdot 10^{-2}$	$2.93 \cdot 10^{-1}$	$5.47 \cdot 10^{4}$	0.0653
6	28	0.932	1.0	$5.28 \cdot 10^{-1}$	$2.29 \cdot 10^{-1}$	$1.65 \cdot 10^{4}$	0.587
12	58	0.932	1.0	2.18	$1.18 \cdot 10^{-1}$	$3.30 \cdot 10^{5}$	2.35

every case, also when the revolutions per second, thus the *Fr* numbers, are not the same. Accordingly, within errors of measurement, points fall on a common curve, on the so-called "*standard curve*", as long as dispersion of air into the liquid does not occur. In other words, within the domain of the standard curve the exponent of the *Fr* number is zero ($b = 0$), or, instead of Eq. (7), Eq. (6) is valid.

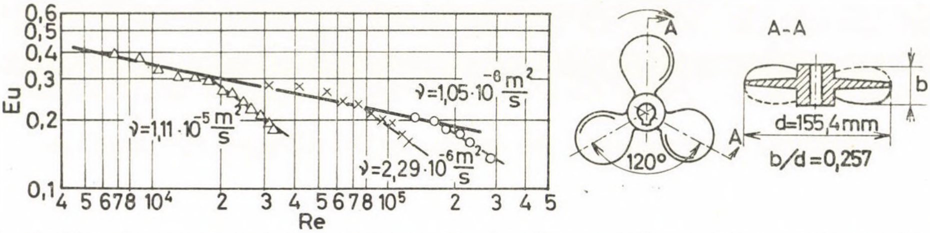

Fig. 3. Plot of power number *vs.* Reynolds number for propellers in tanks without baffles. $D = 0.380$ m; $H = 0.440$ m; $h = d$

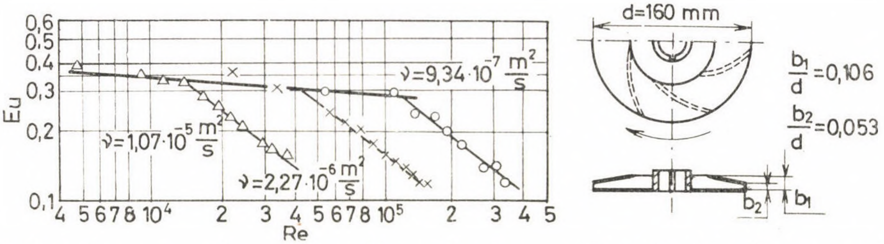

Fig. 4. Plot of power number *vs.* Reynolds number for centrifugal impellers (on top suction) in tanks without baffles. $D = 0.380$ m; $H = 0.440$ m; $h = d$

In the case of any stirred liquid (ν being the same), at a value n_{crit} (Re_{crit} or Fr_{crit}, respectively) the depth of the vortex reaches the impeller ($h_{crit} = H - h$), *i. e.* admixture of air begins (domain of two-phase stirring). From this point on a further increase of n causes the *Eu vs. Re* curve to branch off the slightly sloping standard curve ("break point").

According to our measurements, in the case of the two stirrers shown in Figs 3 and 4, the exponent of *Re* is in the two-phase mixing domain, $a = -0.7$ to -0.8 (also after the dispersion of air into it, we calculated the values of the *Re* numbers from the parameters of the till now mono-phase liquid).

This break point appears at lower *Re* numbers when the liquids have a high ν value, liquids of lower ν values continue to follow the standard curve and it is but later that points begin to branch away.

The n_{crit} critical number of revolutions assignable to the beginning of dispersion of air into the liquid can be determined on the basis of the following dimensional correlation

$$h_{crit} = f(d^{\alpha}, g^{\beta}, n_{crit}^{\gamma}, \nu^{\delta}) \tag{11}$$

When writing this equation, geometrical similarity was assumed to hold, *i.e.* it was assumed that the dimensions b, H, D, h are always proportional to the diameter of the impeller ("internal scale factors" are the same).

By dimensional analysis, Eq. (11) leads to the following solution

$$\frac{h_{crit}}{d} = A \cdot Re_{crit}^{-\delta} \cdot Fr_{crit}^{-\beta} \tag{12}$$

where h_{crit} = the distance between the impeller and the liquid level at rest ($h_{crit} = H - h$, *cf.* Fig. 2).

The constant A, further the exponents δ and β have values that depend on the type of impeller. Since in the course of experiments carried out with 10 types of impellers in a concave bottomed mixing vessel we never found that Eu numbers were functions of Fr numbers, we reproduced an experiment of Rushton (Chem. Eng. Progress, 46, 468, Fig. 14, Curve 4) under the same conditions. For this experiment we took a $d = 6$ inch (0.1524 m) diameter 6-straight-blade turbine impeller, and a $D = 18$ inch ($= 0.4572$ m) diameter flat bottomed cylindrical vessel. The impeller reached down to $h = 6$ inches above the bottom, and the liquid level was $H = 18$ inches in the vessel. No baffles were mounted. Measurements were made at various temperatures, with water and with aqueous solutions of sugar in various concentrations ($\mu = 0.643 - 255$ cP; $\varrho = 993 - 1335$ kg/m^3). Results are shown in Table III, and Fig. 5. (For comments, *cf.* Tables I and II.)

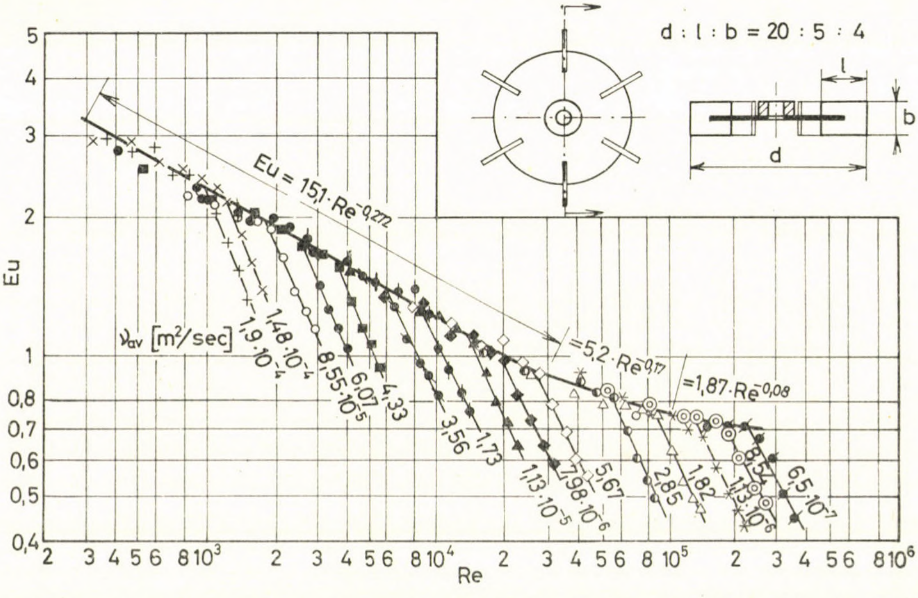

Fig. 5. Plot of power number *vs.* Reynolds number for turbine impellers with six straight blades in tanks without baffles. Dimensions: $D = 18$ in., d = 6 in., $H = D$, h = d

Table III (*cf.* Fig. 5)

Measured data for a six-straight-blade turbine impeller working in a flat bottomed vessel without baffles

$d = 1.524 \cdot 10^{-1}$ m

n (sec^{-1})	P (g · weight)	μ (c P)	ϱ $\left(\frac{\mathrm{g}}{\mathrm{cm}^3}\right)$	N $\left(\frac{\mathrm{kg\ weight \cdot m}}{\mathrm{sec}}\right)$	*Eu*	*Re*	*Fr*
3	96	261	1.335	$8.934 \cdot 10^{-1}$	2.95	$3.56 \cdot 10^{2}$	0.14
9	590	251	1.335	$1.647 \cdot 10$	2.02	$1.11 \cdot 10^{3}$	1.25
12	695	246	1.335	$2.587 \cdot 10$	1.34	$1.51 \cdot 10^{3}$	2.24
3	94	199	1.333	$8.748 \cdot 10^{-1}$	2.899	$4.67 \cdot 10^{2}$	0.14
8	502	198	1.333	$1.246 \cdot 10$	2.18	$1.25 \cdot 10^{3}$	0.995
11	610	195	1.333	$2.081 \cdot 10$	1.40	$1.75 \cdot 10^{3}$	1.88
4	122	113.2	1.328	1.514	2.12	$1.09 \cdot 10^{3}$	0.249
8	372	113.8	1.328	9.232	1.62	$2.17 \cdot 10^{3}$	0.995
11	495	114.4	1.328	$1.689 \cdot 10$	1.14	$2.97 \cdot 10^{3}$	1.88
4	112	79.5	1.326	1.39	1.96	$1.55 \cdot 10^{3}$	0.249
8	325	81	1.326	8.07	1.419	$3.05 \cdot 10^{3}$	0.995
11	450	83.5	1.326	$1.54 \cdot 10$	1.04	$4.07 \cdot 10^{3}$	1.88
3	65	57.1	1.315	$6.049 \cdot 10^{-1}$	2.03	$1.61 \cdot 10^{3}$	0.14
8	297	58	1.315	7.370	1.31	$4.21 \cdot 10^{3}$	0.995
11	405	59.8	1.315	$1.382 \cdot 10$	$9.42 \cdot 10^{-1}$	$5.62 \cdot 10^{3}$	1.88
2	26	31.4	1.273	$1.613 \cdot 10^{-1}$	1.89	$1.88 \cdot 10^{3}$	0.0622
7	216	31.6	1.273	4.690	1.28	$6.55 \cdot 10^{3}$	0.762
11	340	31.7	1.273	$1.160 \cdot 10$	$8.17 \cdot 10^{-1}$	$1.03 \cdot 10^{4}$	1.88
3	50	22.05	1.287	$4.653 \cdot 10^{-1}$	1.59	$4.07 \cdot 10^{3}$	0.14
8	230	22.8	1.287	5.708	1.04	$1.05 \cdot 10^{4}$	0.995
11	320	23.2	1.287	$1.092 \cdot 10$	$7.60 \cdot 10^{-1}$	$1.42 \cdot 10^{4}$	1.88
2	20	13.8	1.224	$1.241 \cdot 10^{-1}$	1.51	$4.12 \cdot 10^{3}$	0.0622
7	172	13.8	1.224	3.735	1.06	$1.44 \cdot 10^{4}$	0.762
11	260	13.8	1.224	8.872	$6.49 \cdot 10^{-1}$	$2.27 \cdot 10^{4}$	1.88
2	18	9.75	1.224	$1.117 \cdot 10^{-1}$	1.36	$5.83 \cdot 10^{3}$	0.0622
8	175	9.8	1.224	4.343	$8.26 \cdot 10^{-1}$	$2.32 \cdot 10^{4}$	0.995
11	238	9.82	1.224	8.121	$5.94 \cdot 10^{-1}$	$3.18 \cdot 10^{4}$	1.88
3	34	6.97	1.187	$3.160 \cdot 10^{-1}$	1.178	$1.19 \cdot 10^{4}$	0.14
8	162	6.97	1.187	4.020	0.79	$3.16 \cdot 10^{4}$	0.995
11	216	6.97	1.187	7.370	0.56	$4.35 \cdot 10^{4}$	1.88
2	13	3.32	1.187	$8.065 \cdot 10^{-2}$	1.01	$1.66 \cdot 10^{4}$	0.0622
6	97	3.38	1.187	1.805	$8.40 \cdot 10^{-1}$	$4.89 \cdot 10^{4}$	0.559
8	142	3.41	1.187	3.524	$6.92 \cdot 10^{-1}$	$6.47 \cdot 10^{4}$	0.995
11	194	3.45	1.187	6.62	$5.00 \cdot 10^{-1}$	$8.79 \cdot 10^{4}$	1.88
2	11	2.045	1.123	$6.824 \cdot 10^{-2}$	$9.07 \cdot 10^{-1}$	$2.55 \cdot 10^{4}$	0.0622

n (sec^{-1})	P (g · weight)	μ (cP)	ϱ $\left(\frac{\text{g}}{\text{cm}^3}\right)$	N $\left(\frac{\text{kg weight}\cdot\text{m}}{\text{sec}}\right)$	Eu	Re	Fr
5	61	2.05	1.123	$9.461 \cdot 10^{-1}$	$7.80 \cdot 10^{-1}$	$6.36 \cdot 10^{4}$	0.388
8	122	2.055	1.123	3.028	$6.29 \cdot 10^{-1}$	$1.01 \cdot 10^{5}$	0.995
11	171	2.06	1.123	5.835	$4.66 \cdot 10^{-1}$	$1.39 \cdot 10^{5}$	1.88
4	33	1.13	1.009	$4.095 \cdot 10^{-1}$	$7.57 \cdot 10^{-1}$	$8.29 \cdot 10^{4}$	0.249
7	91	1.13	1.009	1.976	$6.81 \cdot 10^{-1}$	$1.45 \cdot 10^{5}$	0.762
11	140	1.13	1.009	4.777	$4.25 \cdot 10^{-1}$	$2.28 \cdot 10^{5}$	1.88
4	32	0.852	0.9985	$3.97 \cdot 10^{-1}$	0.74	$1.09 \cdot 10^{5}$	0.249
7	92	0.855	0.9985	1.99	0.69	$1.90 \cdot 10^{5}$	0.762
10	131	0.856	0.9985	4.063	0.48	$2.77 \cdot 10^{5}$	1.554
5	47	0.642	0.9928	$7.28 \cdot 10^{-1}$	0.70	$1.80 \cdot 10^{5}$	0.388
7	88	0.645	0.9928	1.91	0.67	$2.51 \cdot 10^{5}$	0.762
10	119	0.649	0.9928	3.47	0.444	$3.56 \cdot 10^{5}$	1.554

Similar to our previous measurements carried out in a concave bottomed vessel with paddle-, centrifugal-, and propeller mixers, also in this control experiment we found that as long as the mixer did not disperse air into the liquid the points measured fell on the same *Eu vs. Re* curve (the "standard curve"), thus no differentiation according to *Fr* numbers was possible up to this state though of course with a change of *n*, respectively of the *Re* number, also the *Fr* number changed so that each point of the standard curve corresponded to a different *Fr* number. This finding was in complete accord with those noted by HIXSON and BAUM [2]. The conclusion to be drawn is that the standard curve is defined by Eq. (6), the corresponding constants being those in Table IV. As soon as the impeller disperses air into the liquid (Re_{crit}) the experimental data show a change of direction and take a course that is directed more steeply downward off the hitherto common standard curve. The slope of each of these downward curves — at least in the case of one and the same impeller — is nearly the same. (In these experiments the slope varied between —1.0 and —1.2.) The abrupt fall of *Eu* values is easily explained if account is taken of the fact that air dispersed in a liquid abruptly changes the viscosity as well as the density of the stirred liquid.

Thus, according to our experiments, subsequently to the "break" or "critical" point, in the "two-phase mixing domain", *Eu* numbers can again be described by an equation of type (6), that is independently of the *Fr* number, where the exponent of the *Re* number has values between —0.7 and —1.2 according to the type of impeller and according to material constants of the liquid.

$$Eu_{disp} = B_{(v)} \cdot Re^{-a} \tag{6a}$$

Table IV

Constants of the Eu vs. Re curve, measured with a 6-straight-blade turbine impeller
(so-called standard curve; no admixture of air)
$(Eu = A \cdot Re^{-a})$
(For experiments in this laboratory, *cf.* also Fig. 6)

Re	domain	*Eu*	*A*	*a*
$3 \cdot 10^2$		3.2	—	—
$3 \cdot 10^2$	$\ldots 3.2 \cdot 10^4$	—	15.1	0.272
$3.2 \cdot 10^4$		0.9	—	—
$3.2 \cdot 10^4$	$\ldots 1 \cdot 10^5$	—	5.2	0.170
$1 \cdot 10^5$		0.73	—	—
$1 \cdot 10^5$	$\ldots 2.5 \cdot 10^5$	—	1.87	0.08
$2.5 \cdot 10^5$		0.69	—	—

The constant $B_{(\nu)}$ of this equation is the function of the locus of the inflexion point (Re_{crit}, Fr_{crit}), thus it can be determined on the basis of Eq. (12). The discussion of this we reserve for a next communication.

From the course taken by the *Eu vs. Re* function of the two-phase mixing it follows that in this domain the power consumption of mixing is the function

$$N = B_{(\nu)} \cdot \varrho \cdot d^5 \cdot n^3 \cdot Re^{-a} \tag{2a}$$

or that this power, in a given vessel and with a given liquid to be stirred, is proportional to the 2.3 to 1.8th power of the process parameter n revolutions per second, *i.e.* when air is dispersed into the liquid a further increase of n results in a further increase, by about the second power of n, of power consumption, like in the viscous domain (*cf.* Fig. 6). Also this our statement contradicts that of Rushton who suggested that for a given apparatus and liquid a higher value of power consumption than that needed for the beginning of the dispersion of air into the liquid cannot be attained.

Rushton described his above-mentioned experiments by an $Eu \cdot Fr^{-b}$ *vs. Re* diagram only; on the basis of this curve and using Eq. (7) and the corresponding b powers we calculated the *Eu vs. Re* curve with constant *iso-Fr* lines and completed the original Figure with several ν = constant curves (Fig. 7).

Into Fig. 7 we have drawn the curve that represents our measurements (*cf.* Table IV). This Figure shows that the curves drawn by Rushton *et al.* run above that drawn according to our data. The deviation is particularly discernible at high *Re* numbers ($Re > 10^4$). This seems to allow the conclusion that in the instrument used by Rushton for the measurement of torque

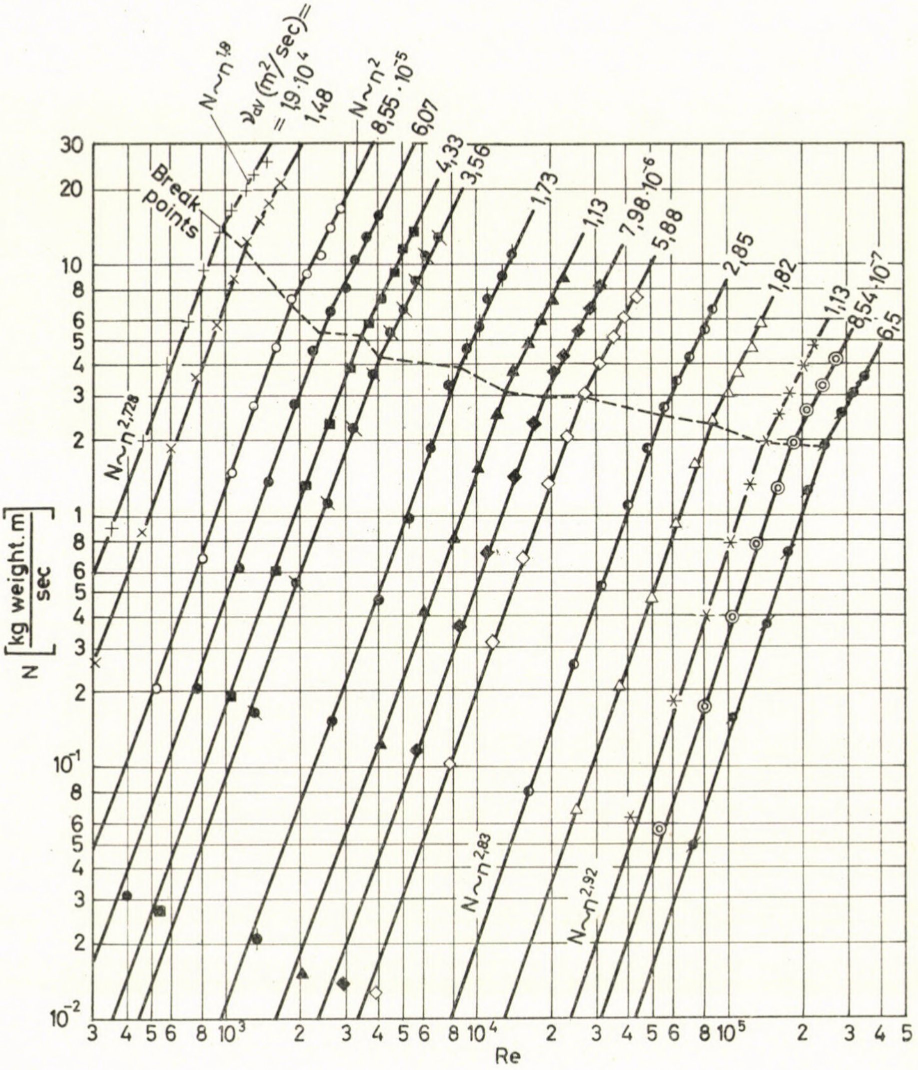

Fig. 6. Plot of power input *vs.* Reynolds number for turbine impellers with six straight blades in tanks without baffles. Dimensions: $D = 18$ in., $d = 6$ in., $H = D$, $h = d$

(differential gear dynamometer) friction was considerable because of the series of linked transmissions and caused percentually significant inaccuracies in two domains, *i.e.* at low power consumptions or revolutions per second, and in measurements on liquids of low viscosity (high *Re*-numbers). We think it highly probable that this was the cause why the *Eu vs. Re* curve took an, according to "Froude number", premature turn, *i.e.* one previous to dispersion of air into the liquid ($h_{vort} < h_{crit}$).

Thus, *e.g.* in Fig. 7, according to RUSHTON the Eu numbers of a liquid with the viscosity $\nu = 1.73 \cdot 10^{-5}$ m$^2 \cdot$ sec^{-1} become sharply differentiated according to the Fr number, in the domain of $Re = 2 \cdot 10^3$ to 10^4, whereas our measurements seem to indicate that the points of a liquid of this viscosity continue on the standard curve irrespective of Fr numbers up to $Re_{crit} \simeq 8 \cdot 10^3$ (*cf.* Fig. 5).

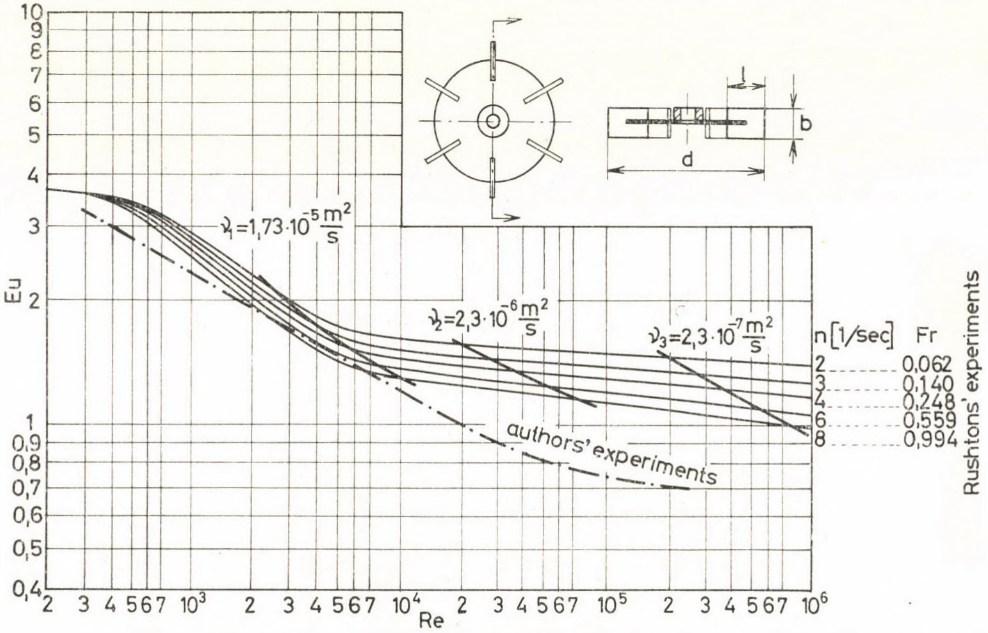

Fig. 7. Plot of power number *vs.* Reynolds number for six straight-blade turbines in tanks without baffles. (Comparison of experiments of RUSHTON with those of the authors of this paper)

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РЕЗЮМЕ

Изучение адсорбции шестифтористого урана, IV

Л. МЮЛЛЕР и Л. ФАЙ

С точки зрения изучения неконвекционных процессов диффузии-адсорбции UF_6, важно знать нестационарное решение уравнения транспорта.

Для определения переходных функций неконвекционного диффузионно-адсорбционного аппарата используется математическая модель с учетом изотермы адсорбции типа Фрайндлиха, при условии быстрой кинетики реакций.

Дается функция решений и приводятся значения функции $f(C, l, t)$ для модели с заданными параметрами.

Приблизительное определение молекулярных весов и полидисперсности кремнеорганических полимеров с помощью бумажной хроматографии

А. МЕСТИЦКИ и Т. ХАЛМОШ

Был разработан метод бумажной хроматографии для быстрого серийного определения молекулярного веса и распределения по молекулярным весам полидиметилсилоксанов. Для измерений использовались узкие фракции, а также искусственные полидисперсные образцы полученные их смешиванием. Согласно нашим исследованиям, разделение по молекулярным весам в интервале $100.10^3 + 300.10^3$ может быть осуществлено с помощью смеси растворителей следующего состава: толуол/этилацетат/ацетон/уксусная кислота/ = 1,5 : 6 : 0,5 : 0,27. Из позиции пятна на бумаге можно судить о молекулярном весе нанесенного вещества, а из формы пятна — о полидисперсности образца. Были разработаны такие экспериментальные условия, которые позволяют устранить помехи, возникающие за счет влияния края бумаги и взаимодействия пятен.

О гидратах сульфатов алюминия

И. НАРАИ-САБО

Обыкновенный (высший) гидрат сульфата алюминия содержит 17 молекул рикстализационной воды. Этот гидрат является триклинным: $a = 7{,}420 \pm 0{,}004$ Å, $b = 26{,}900 + 0{,}04$ Å, $c = 6{,}105 \pm 0{,}004$ Å, $\alpha = 90{,}00 \pm 0{,}03°$, $\beta = 97{,}30 \pm 0{,}13°$, $\gamma = 91{,}80 \pm 0{,}04°$; $Z = 2$, $d_x = 1{,}782$ г · см$^{-3}$, $d_{\text{эксп.}} = 1{,}771 \pm 0{,}002$ п · см$^{-3}$. Путем дегидратации 17-гидрата получаются 14- и 12-гидраты, которые характеризуются диффрактограммами. Первому можно приписать ромбические индексы. Получение 16-гидрата оказалось невозможным; соединение, которое соответствует такому составу, содержит, главным образом, линии 17-гидрата, а также некоторые линии 14-гидрата. При дегидратации наблюдается резкий перелом на термогравиметрической кривой, который соответствует 3-гидрату. Этот продукт, однако, дает аморфную диффрактограмму. Приводится дериватограмма 17-гидрата.

Одновременное определение структурных изомеров аллиламида камфарной кислоты, I

Р. Г. ХЕНЕИН и Й. Ч. ХОРВАИ

Был разработан простой и быстрый метод определения бинарных смесей, содержащих два структурных изомера и-аллиламида dc-камфарной кислоты. Точность метода вполне высока, принимая во внимание сложность данной проблемы.

Сорбция ионов металлов из водно-органических растворителей на целлюлозоионитах

А. ЛАСТИТИ, Ж. РЕМПОРТ-ХОРВАТ, И. ПОЖОНИ и К. ВЕРЕШ

На основе изучения сорбции металлических ионов (Cu^{+2}, Co^{+2}) на целлюлозных ионнообменниках из различных растворителей было установлено, что при сорбции ионов тяжелых металлов оказалось благоприятным использование, наряду с водой, метанола, этанола, ацетона и формамида, в качестве растворителей, т. к. металлические ионы из этих растворителей сорбируются относительно хорошо на целлюлозоионитах. Среди ионообменников наиболее подходящими для этий растворителей являются ФЦ (фосфоцеллюлоза) и КЦ (карбоксицеллюлоза), а в некоторых случаях могут успешно испола, зоваться и целлюлозоаниониты. Как степень сорбции, так и скорость ионного обмена понижаются с уменьшением диэлектрической постоянной растворителя. Этот еффект можно хорошо наблюдать в ряду метанол-етанол-пропанол-бутанол.

Применение метода осциллометрической индикации конечной точки титрования в аскорбинометрии, III

Определение ионов ртути(II)

М. Т. ВАНДОРФИ и Л. ЭРДЕИ

Метод осциллометрической индикации конечной точки использовался в аскорбинометрическом определении ионов ртути(II) при малых концентрациях. Определение может быть произведено двумя путями: 1) восстановление ионов ртути до металлической ртути, титруя измерительным раствором аскорбиновой кислоты; 2) восстановление ионов ртути(II) до ионов ртути(I), титруя измерительным раствором аскорбиновой кислоты, содержащей хлористые ионы. Концентрация ионов ртути(II) при измерениях находилась в пределах 10^{-3}—10^{-2} н. Точность измерений равна 1—2%.

Реакция электронного обмена между железом(II) и железом(III) в формамиде

И. РУФФ и Э. РЕНДЕК

Изучалась кинетика реакции электронного обмена между железом(II) и железом(III) в формамиде. Реакция имеет первый порядок по обоим реагентам и показывает слабую зависимость от pH. В формамиде реакция протекает значительно медленнее, нежели в воде. Энергия активации — $5{,}8 \pm 1{,}4$ ккал/моль, а энтропия активации равна -41 ± 5 кал/моль · град. Результаты находятся в противоречии с электростатической поляризационной теорией реакций перехода электронов, согласно которой скорость реакции в формамиде должна быть больше, чем в воде. Зависимость от pH объяснялась с помощью полосной модели, что дает для расстояния между реагентами в активированном комплексе значение 13 Å, которое является вполне приемлимым.

Расчет влияния сопротивления ячейки в полярографии с переменным током в случае обратимого электродного процесса

Й. ДЕВАИ, Л. МЕСАРОШ и Т. ГАРАИ

Теоретические зависимости для первого и второго гармонического составляющих переменного тока, возникающего в обратимых полярографических процессах под влиянием синусоидного переменного напряжения с небольшой амплитудой, наложенного на постоянное напряжение, были дополнены факторами поправки, принимая во внимание омическое сопротивление ячейки. Из расчетов, проведенных на основе этих зависимостей, было установлено, что под влиянием омического сопротивления R_0 (рис. 2) амплитуды первого и второго гармонического уменьшаются по сравнению со случаем, когда $R_0 = 0$, в мере увеличивания круговой частоты переменного тока, концентрации компонентов, принимающих участие в электродной реакции, а также изменения элементарного заряда. Величины потенциалов, соответствующих максимальной амплитуде второго гармонического, с увеличением R_0 удаляются от потенциала полуволны, и в тем большей степени, чем больше круговая частота переменного тока, концентрация компонентов электродной реакции и изменение элементарного заряда.

Кинетический анализ некоторых последовательных реакций, IV

Системы последовательно-параллельных реакций A → C, A + C → E и
A + B → C, A + C → E

Т. КЕЛЕН

Проведен кинетический анализ систем A → C, A + C → E и A + B → C, A + C → → E. Установлено, что в случае системы A → C, A + C → E точное решение системы дифференциальных уравнений получается с помощью неполной гамма-функции, а в случае системы A + B → C, A + C → E с помощью неполной бета-функции.

Параметрическое определение F-матрицы силовых постоянных, IX

О связи между нормальными и симметричными координатами

Ф. ТЁРЁК

На основе изучения связи между симметричными и нормальными координатами было заключено, что область силовых постоянных, относящаяся к заданной классификации (определение которой было приведено в предыдущем сообщении) может быть далее сужена. Тот факт, что знак перед столбцами матрицы, трансформирующими симметричные и нормальные координаты друг в друга, не определен, приводит к тому, что величины угловых параметров, из которых получают все возможные ряды силовых постоянных, изменяется лишь в пределах $-\pi/_2$ и $\pi/_2$. Приводятся методы получения параметров, характерных для заданной связи между симметричными и нормальными координатами.

Метод приближения для кинетического анализа последовательных реакций

Т. КЕЛЕН

Изложен простой метод приближения для кинетического анализа системы, состоящей из двух последовательных моно- и/или бимолекулярных реакций. Этот метод проиллюстрирован на примере реакционной системы A + B → C, C + D → E, для которой имеется также и точное решение. Оценивается также погрешность приближения.

Программы для счетной машины типа УРАЛ-2 с целью рентгенодифракционного исследования структуры, II

Определение плоскости, наиболее хорошо соприкасающейся к данной группе атомов, с помощью итерационного метода Шомакера

Д. МЕНЦЕЛЬ

Была разработана программа для счетной машины УРАЛ—2, с помощью которой определяется плоскость, наиболее хорошо соприкасающаяся к данной группе атомов. Для расчетов использовался итерационный метод Шомакера. Программа описывается в машинном коде и пригодна для расчетов веществ с моноклинной и более высокой симметрией. Количество атомов, определяющих плоскость, не более чем 10. С помощью данной программы могут быть определены расстояния еще 10 других атомов от рассчитанной плоскости.

Гидантоины, тиогидантоины и гликоциамидины, XXVII

Перегруппировки типа ретробензиловой кислоты под влиянием кислот Льюиса, IV. Область действительности реакции дитиогидантоинов и аренов, вызванной хлористым алюминием

Й. НИТРАИ, Р. МАРКОВИЧ-КОРНИШ и К. ЛЕМПЕРТ

5,5-Диарил-дитиогидантоины (где арил = фенил и п-хлор-фенил) при кипячении в бензольном растворе с хлористым алюминием, перегруппируются и одновременно, десульфурилуются в соответствующие 4,5-диарил-4-имидазолин-2-тионы. 5,5-Диметил- и 5,5-дибензил-дитиогидантоины не дают аналогичный продукт, в то время как 5-арил-5-метил-дитиогидантоины (где арил = фенил, п-толил и п-хлорфенил), десульфурилуются с одновременным перемещением арильной группы.

Гетероциклические спиро-соединения, VI

К. КЁРМЕНДИ, П. ШОХАР, А. ПФИСТНЕР-ФРАЙД и Ф. РУФФ

В таутомерии спироксазона могут принимать участие шесть таутомерных форм (две спирановые, и четыре открытые формы). Среди таутомеров две формы являются стабильными: *α-спироксазон* спиранового строения Ia и открытый *β-спироксазон* со строением Ic, содержащий эндо-циклическую C=N связь. Эти в изолированном состоянии, при комнатной температуре продолжительно сохраняют свою структуру.

Стабильность двух дезмотропов вызвана относительно высоким потенциальным барьером экзо-эндо перегруппировки связи C=N в открытой форме спироксазона, повышенной стабильностью полу-иминогидринового таутомера с точки зрения циклических гидразидных групп, а также избирательностью присоединения в зависимости от экзо- или эндо-положения двойной связи C=N. Положение связи C=N доказалось с помощью спектров ямр и реакцией присоединения спирта.

N-Гликозиды, XIV

Изучение β—D-глюкопиранозил-морфолина

Р. БОГНАР, Х. ФРЕНЦЕЛЬ и И. ФАРКАШ

Описываются получение и свойства 2,3,4,6-тетра-O-ацетил-β-D-глюкопиранозилморфолина (I) и β-D-глюкопиранозилморфолина. С ацетатом натрия последнее соединение образует кристаллический продукт присоединения (II), имеющий сложную стехиометрию. I имеет две модификации. Путем деацетилирования I может быть превращен в известную I-дезокси-I-морфолино-D-фруктозу (III).

Получение и реакции литиевых солей ароматических сульфеновых кислот

Э. ВИНКЛЕР, Ф. КЛИВЕНИ, Й. ЛАЗАР и И. КОЗАКЕВИЧ

На основе реакции взаимодействия фениллития с эфирами тиолсульфиновой кислоты были изолированы, до сих пор мало исследованные, литиевые соли сульфеновой кислоты простого строения. Было установлено, что эти соединения образуются и могут сохраняться лишь в отсутствии воздуха. Изучались гидролитические и автоокислительные реакции литий-сульфенатов, а также их диспропорционирования и взаимодействия с различными галогенидами. Под влиянием воды они превращаются в тиолсульфинаты, воздуха — литий-сульфинаты и нагрева — сульфиновую кислоту и дисульфид. Взаимодействуя с органическими соединениями, содержащими подвижный атом галогена, в токе азота превращаются в сульфоксид, а в присутствии воздуха — в сульфон. При реакции взаимодействия с галогенидами кислот, содержащих серу, с хлоридом сульфиновой кислоты они дают тиолсульфонат, а с хлоридом сульфокислоты — «триокись дисульфида».

Изучение реакций катализированных сильными кислотами, в неводных средах, III

Синтез 1-фенил-1,4-дигидро-3(2*H*)-изохинолинона и его производных на основе реакции ароматических альдегидов и арил-ацетонитрилов, катализированной полифосфорной кислотой

З. ЧЮРЁШ, Д. ДЕАК, Й. ХОФФМАНН и А. ТЁРЁК-КАЛМАР

Был разработан метод получения 1-фенил-1,4-дигидро-3(2*H*)-изохинолинена и его замещенных производных из ароматических альдегидов и арил-ацетонитрилов в полифосфорной кислоте. С помощью данного метода было получено четырнадцать новых производных основного соединения. Структура продуктов, образующихся при взаимодействии *м*-метил-бензил-цианида и гомовератронитрила (3,4-диметокси-бензилцианид), определялась на основе ик-спектров. Было доказано, что промежуточным продуктом является бензилиден-бис-фенилацетамид, который может быть приготовлен и другим путем. Этот промежуточный продукт циклизуется быстро в полифосфорной кислоте с отщеплением фенил-ацетамида в 1-фенил-1,4-дигидро-3(2*H*)-изохинолинон.

Влияние числа Фруда на потребляемую мощность мешалок

К. ТЕТТАМАНТИ, Г. ХАВАШ и Й. ШАВИНСКИЙ

1. Изучалась потребляемая мощность лопатных, центрифугальных и пропеллерных мешалок в круглодонных сосудах, в турбулентной зоне при значениях Re = 300 — $4 \cdot 10^5$. Пока глубина воронки не достигает лопаты мешалки, т. наз. *стандартная кривая* потребляемой мощности не зависит от числа Фруда и описывается следующим уравнением:

$$Eu = A \cdot Re^{-a}$$

где a также зависит от числа Рейнольдса.

2. Если воронка достигла лопаты мешалки (n_{krit}, Re_{krit}), то кривая потребляемой мощности отделяется от стандартной кривой, и в этой области «двухфазового перемешивания» кривые $v = idem$ лежат почти параллельно и описываются следующим уравнением:

$$Eu_{disp} = B(v) \cdot Re^{-a}$$

где $a = 0{,}7 - 1{,}2$ в зависимости от v, но не зависит от числа Re.

3. Критически обсуждались исследования *Раштона*, *Костича* и *Эверетта* и было найдено, что число Fr не оказывает влияния на потребляемую мощность в области однофазного перемешивания (стандартная кривая). Также было установлено, что после подмешивания воздуха — хотя и в пониженной степени — потребляемая мощность перемешивания продолжает возрастать.

4. Вместо изображения, типа *Раштона*, кривых Eu—Re по *изо-Фруд*-параметрам, согласно нашим измерениям, кажется более правильным изображение кривых Eu—Re при параметрах $v = idem$.

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JÁNOS PROSZT

(1892—1968)

On July 6, 1968, at the age of 76 died JÁNOS PROSZT, Corresponding Member of the Hungarian Academy of Sciences, emeritus professor, Kossuth-Prize winner, an outstanding scientist in the field of physical and inorganic chemistry.

János Proszt was born on February 6, 1892, in Budapest. He studied at the Universities of Budapest and Berlin. He spent the years preceding World War I in Berlin, a prominent center of exact sciences with an influence reaching far beyond the borders of Germany. A number of Nobel-Prize winners, among them EINSTEIN, PLANCK, NERNST, and VAN'T HOFF, were active in the universities and research institutes of the country. This atmosphere apprehended the students, among them János Proszt, who all his life proudly confessed himself a pupil of NERNST, whose suggestive personality obviously played a decisive part in shaping Proszt's future career.

After his return to Hungary in 1913, he was appointed an assistant at the No. III Institute of Chemistry, University of Budapest, where he later became a senior assistant. The director of the Institute, Gusztáv BUCHBÖCK, was a pioneer of physico-chemical research in Hungary. His profound knowledge, critical approach, experimental skill, and last but not least his readiness to help younger associates directed Proszt's interest finally towards physical chemistry. He completed his Ph. D. thesis at this Institute, but his activity was interrupted for a longer period by four years of military service and the post-war conditions hardly favourable for scientific research.

In 1924 he was appointed Professor of Chemistry at the Sopron College of Forestry Engineering. After moving to Sopron, he began his enthusiastic efforts to develop the Department. His appointment occurred only a few years after the College had been transferred from Selmecbánya to Sopron. The financial means were very limited, therefore, the organization of the teaching and research activities required much energy and persistence. Proszt was glad to take this work upon himself. He worked in Sopron for full 24 years and kept his Department after the College had been reorganized to become the Faculty of Mining, Metallurgical and Forestry Engineering of the "József

Nádor" Polytechnical University. In 1940 and 1946 he was elected Dean of the Faculty.

The year 1948 marked a turning-point in his life: he was offered a professorship at the Department of Inorganic Chemistry, Technical University of Budapest. He took office on November 1, 1948, and this date was the beginning of a new period of creative activity in his life. The new conditions offered greater possibilities and, surrounded by a team of young assistants, he markedly extended his field of research. To meet the increased requirements, he accomplished very much in raising the level of teaching in chemical education.

The Hungarian Academy of Sciences recognized his merits by electing him a Corresponding Member in 1956. The Hungarian Government awarded him the Kossuth-Prize in 1953, and the Order of Labour in 1962.

His retirement in 1963 did not break his activity. Up to his death, he took active part in the work of numerous committees of the Academy and the Hungarian Chemical Society.

His life-work primarily concerns pure and applied physical chemistry. In his Ph. D. thesis dealing with the chemistry of variously coloured iodine solutions he showed that the colour changes were not due to the varying degree of association of iodine molecules as assumed earlier, but are to be ascribed to addition compounds formed with the solvent. The brown solutions contain the largest amounts of these compounds, the shift of the colour towards violet being due to a gradual decrease in the concentration of the addition compounds.

During his Sopron period, as a consequence of the specialized educational objective of the College, he became interested in the flotation process widely used for the concentration of ores. Though there were several hypotheses attempting to explain the mechanism of flotation, the actual process was almost exclusively based on practical experience because of the complexity and individual character of the systems. Proszt recognized that flotation is essentially a special kind of coagulation, *i.e.* a complex surface interaction between suspended solid particles, droplets and fine bubbles. Since the medium contains electrolytes, ion adsorption and the electrokinetic potential at the solid/liquid interface play an important part in the processes.

His systematic studies were carried out on simple models, using galenite and quartzite suspensions and emulsions in paraffin oil/water. His first objective was to study the phenomenon of coagulation of coarse dispersions under the influence of ions. Proszt confirmed that, similarly to sols, the strongest coagulating effect on coarse dispersions occurred at the isoelectric point. Further, he showed that the electric condition of the slurry could be specifically influenced by ion adsorption; this fact is important in connection with selectivity problems.

Later his interest gradually turned towards electrokinetic phenomena in general. First of all, he wanted to elucidate the dependence of electrophoretic mobility on the particle size. This dependence was known in an implicit form, since the constants of the Smoluchowski or Hückel equation for electrokinetic mobility differ for spherical and cylindrical particles. However, it was not yet recognized that the different behaviour of these two models was not caused by the shape itself but rather by the curvature, which can be formulated as a general particle-size effect, regardless of the actual shape. Proszt deserved credit for making this clear and confirming it experimentally in two independent ways. In one of his two studies on this subject, he showed that the electrophoretic mobility of microscopic paraffin oil droplets emulsified in water increased with the size of the droplets. Though the experimental method seems to be overly simplified according to standards of today, and no correct particle size determination could be performed due to the lack of a suitable technique, the qualitative observation is of considerable value.

In the second study, Proszt made further generalizations and experimentally compared the displacement caused by the electrokinetic potential of a surface having finite curvature, *i.e.* a particle, with that of a plane having zero curvature, using a simple but ingenious method. In an open microelectrophoretic chamber he measured the mobility of glass and mica suspensions between horizontal plates made of the same materials. He established that at a given chamber-depth the direction of migration changed. The reason is that the speed of the electroosmotic migration of the liquid due to the electrokinetic potential at the surface of a wall with an infinite radius of curvature is higher (but has, of course, reversed sign) than that around the particle. Unfortunately, this second paper does not contain any numerical data but is restricted to a description of the observation, which is an experimental verification of the interesting assumption made in the introduction.

Another important field of Proszt's investigations was the study of vapor–liquid equilibria in binary systems. In connection with earlier efforts to increase the efficiency of separation of components of liquid mixtures by distillation, among other attempts, certain solids were dissolved to effect favourable shifts of the equilibrium. In order to throw more light on the nature of these effects, Proszt determined the vapor–liquid equilibrium curves for a number of binary mixtures (methanol–benzene, ethanol–water, methanol–acetone, carbon disulfide–acetone) containing dissolved electrolytes (lithium chloride, lithium iodide, sodium iodide, calcium chloride). He established that the azeotropic point can, in general, be shifted by adding a salt and, in some cases, the azeotropic property can even be eliminated. Substances which cannot undergo dissociation (sulphur, naphthalene) do not have any effect. On the basis of his observations he concluded that added salts make the component with the smaller dielectric constant more volatile.

Studying the reason for this salt effect, he performed ebullioscopic measurements. He found that the boiling point rise curves of the salt solutions in all cases showed flat minima or maxima. In systems that form azeotropes, sharp maxima or minima were observed in addition to this. The sharp maxima and minima appear at the azeotropic composition, while the flat ones are at the composition where the experimental vapor–liquid equilibrium curves intersect with those calculated from Raoult's law, *i.e.* where the real mixture behaves ideally.

This special point was named the Raoultpoint by Proszt. The solvation of ions responsible for the salt effect is the strongest and most selective at this point. As a consequence of solvation, the composition may shift so as to cause a boiling point depression. This effect, if strong enough, may exceed the extent of the "classical" ebullioscopic effect resulting in boiling point depression actually observed in some cases ("ebullioscopic paradox").

As a result of ebullioscopic measurements on systems containing dissolved salts, one can determine both the azeotropic and the Raoult point, the two most important points on the vapor–liquid equilibrium curve, which emphasizes the practical usefulness of these studies.

Polarography is one of the most significant electrochemical methods of the last decades. Its theory and application have reached a very high level as a result of Nobel-Prize winner HEYROVSKY's outstanding work. Since the first publication by Heyrovsky in 1922, more than 15,000 papers have been published and now the yearly production is over 1000 papers.

Proszt's interest turned towards this subject about 15 years ago. By concentrating on various aspects of the technique and its practical application, he solved a number of problems from which the following should be mentioned.

He established the exact conditions for producing aluminum waves that are the best for evaluation, and increased the sensitivity of Al analysis so that several tenths of a per cent of aluminum could be determined in steel with satisfactory precision. In order to increase the selectivity of the Al analysis, he used the known method of derivation, but improved it by leading the polarographic current to the primary coil of a transformer and recording the secondary current.

In connection with the polarography of ammonia, Proszt recognized the effect of the pH on the height of the NH_4^+ wave and worked out the conditions for maximum sensitivity. Proper adjustment of the pH is especially important when only a small volume of the solution is available. This case occurs, for example, in the analysis of the very small nitrogen contents of "nitride steels", where polarographic determination is preceded by converting nitrogen into ammonia by the Kjeldahl method. Proszt also applied this method to the determination of small amounts of nitrogen (a few tenths of a per cent) in petroleum.

Proszt's methodological innovation, called polarocoulometry, consists of measuring the amount of charge carried by the diffusion current of a given component by coulometry at a fixed potential. This technique is suitable for performing serial quantitative determinations for practical purposes.

In addition to original papers, the wide range of his activities in the field of polarography is reflected by his bulky textbook "Polarography" written with co-authors, which has been published both in Hungarian and German.

His studies concerning the preparation of organosilicon polymers (silicones) were aimed at purely practical problems. The results are described in several patents but have not been used in actual technology.

The scientific activity of Proszt was decorously complemented by his achievements in chemical education during his career as a professor. His carefully prepared and colourful lectures always attracted the attention of his audience. To increase the efficiency of teaching, he wrote two chemical textbooks with co-authors. The "Practical Physical Chemistry" ran into ten, the "General and Inorganic Chemistry" into five editions. By revising and enlarging the subsequent editions, he was able to keep these books up to date.

Professor János Proszt's life-work produced imperishable results and influence; his memory is cherished with the tribute of respect in Hungarian science and higher education.

B. Lengyel

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ANALYSIS OF MIXTURES OF THE STRUCTURAL ISOMERS OF N-ALLYL-*dl*-CAMPHORAMIC ACID, II

X-RAY ANALYSIS

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A quantitative analytical method has been developed which is based on the measurement of the peak intensities in the X-ray diffractogram, for the determination of the structural isomers α- and β-N-allyl-*dl*-camphoramic acids in the presence of each other. The average square error is 2.1%.

Introduction

Quantitative phase analysis performed by the X-ray method has been known for many years [1]. Gordon and Harris [2] applied the X-ray diffractogram peaks for the determination of two components of a mixture. They chose two proper peaks and determined the intensity ratio which was connected with the relative amounts of the components. In this way a calibration curve was constructed by which the composition of the mixture could be determined. We investigated the application of this procedure for the case of α- and β-N-allyl-*dl*-camphoramic acids (**I** and **II**), in the hope that the method will be more accurate than thermal analysis [3].

The intensity of a reflection *hkl* which is characteristic of the α-component in a binary mixture is the following:

$$I_{hkl\alpha} = \frac{K_{hkl\alpha}}{\mu_M} \cdot W_\alpha$$

where $K_{hkl\alpha}$ contains the diffraction and other constants characteristic of the X-ray technique, μ_M is the resulting linear absorption constant of the mixture, and W_α is the weight ratio. Let us select a characteristic peak for **I** and **II**, respectively, and let us denote them, for the sake of simplicity, by A and B. The intensity ratio mentioned above will be:

$$\frac{I_{A\alpha}}{I_{A\alpha} + I_{B\beta}} = \frac{\dfrac{K_{A\alpha}}{\mu_M} \cdot W_\alpha}{\dfrac{K_{A\alpha}}{\mu_M} \cdot W_\alpha + \dfrac{K_{B\beta}}{\mu_M} \cdot W_\beta} .$$

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In our case the constants $K_A\,\alpha/\mu_M$ and $K_B\,\beta/\mu_M$ are approximately equal, because the two structural isomers differ only very slightly from each other. So we can write

$$\frac{I_{A\alpha}}{I_{A\alpha}+I_{B\beta}}=\frac{W_\alpha}{W_\alpha+W_\beta}=W_\alpha\,. \qquad (1)$$

If the two components of the mixture do not interact at all, Eq. (1) holds for all weight ratios and is applicable for the accurate determination of the composition of the system.

Experimental

In order to construct a calibration curve, we obtained the diffractograms of mixtures containing 5, 10, ..., 90, 95% of **I**. The samples were prepared using pure **I** and **II** homogenized by dissolving them in acetone and evaporating to dryness. The samples were very

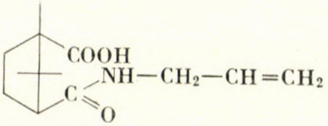
Table I

α-isomer		β-isomer	
d_{hkl}	I/I_o	d_{hkl}	I/I_o
9.31	1.08	7.81	0.78
7.51	10.00	7.01	0.85
6.35	0.78	6.05	5.52
5.95	1.79	5.55	10.00
5.52	0.25	5.12	7.32
5.40	0.50	4.71	0.79
4.77	5.72	4.48	2.43
4.59	2.23	4.04	0.59
4.48	1.07	3.91	1.94
4.00	0.20	3.81	1.58
3.91	0.20	3.74	0.31
3.81	0.20	3.69	0.35
3.73	0.45	3.32	0.82
3.57	0.48	3.22	1.47
3.50	0.28	3.16	0.54
3.39	1.15	2.99	0.25
3.27	0.50	2.91	0.49
3.18	0.40	2.82	—
3.13	0.13	2.80	—
2.96	0.16	2.79	—
2.85	0.40		
2.71	1.35		
2.67	0.58		
2.54	0.26		

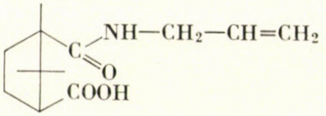
carefully pulverized, and great care was taken in their preparation in order to ensure standard experimental conditions. The diffractograms were obtained with a MÜLLER MICRO 111 apparatus with Cu/Ni tube (voltage: 36 kV; stream intensity: 18 mA; sensitivity: $4 \cdot 10^2$; needle sensitivity 8; paper speed 800 mm/hr).

Results and discussion

The most intense peaks of **I** and **II** are given in Table I. The $d_{hkl} = 9.31$ Å and the $d_{hkl} = 3.81$ Å peaks are the most convenient for the analysis (peak *A* of **I** and peak *B* of **II**, respectively). The former is completely absent from the diffractogram of **II**, but the latter occurs with a slight intensity in the diffractogram of **I**. Therefore, we made a correction of peak *B* so that we took, instead of $I_{B\beta}$, $I_{B\beta} - 0.1851\ I_{A\alpha}$ in Eq. (1). So in the case of pure **II**, $W_\alpha = 0$, and in that of pure **I**, $W_\alpha = 1$.



I



II

Fig. 1 shows the theoretical curve corrected according to Eq. (1) in full line. The points of measurement are along this line up to $W_\alpha = 0.5$, but here the curve has a break, and there is another break at $W_\alpha = 0.95$ (dashed line). This is in good agreement with the breakpoints of the melting temperature curve (see Part I of this series) and confirms the fact that an interaction occurs between **I** and **II**.

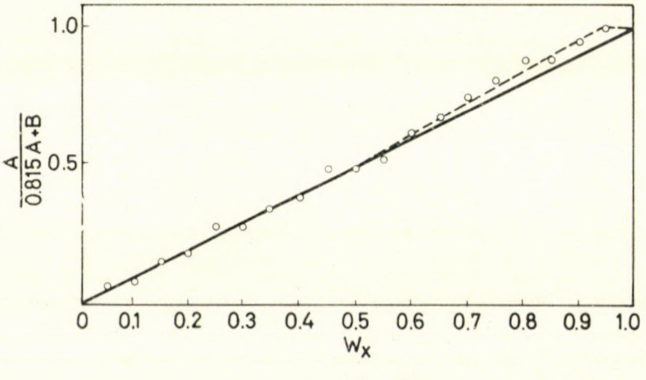


Fig. 1

Using the calibration curve, the average square error of the method is 2.1%, while the greatest absolute errors are +3.6% and —4.4%. The accuracy

is greatly influenced by the preparation of the samples and the measurement of the intensities. If the samples are not pulverized satisfactorily, there is an intense background, and accurate measurement of the intensities is impossible.

*

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OSZILLOMETRISCHE ENDPUNKTSANZEIGE BEI DER BESTIMMUNG VON ORTHOPHOSPHATIONEN MIT EISEN(III)CHLORID

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Bei der Bestimmung von Orthophosphationen mit Eisen(III)chlorid-Maßlösung wurde der Endpunkt oszillometrisch angezeigt. Die Bestimmung der Orthophosphationen kann innerhalb der Konzentrationsgrenzen von 3 und 25 mg pro 15 ml selbst bei dreißigfachem Fremdionenüberschuß mit einer Genauigkeit von 1—2% durchgeführt werden. Die Methode wurde zur Bestimmung des Gesamtphosphatgehalts von Waschmitteln angewendet.

Es ist seit langem bekannt, daß Orthophosphationen in saurer Lösung mit Eisen(III)-Ionen Komplexe bilden. Schon im Jahre 1878 erwähnte Erlenmeyer [1] einen Eisen(III)phosphat-Komplex. Weinland und Ensgraber [2] konnten die Existenz von Eisen(III)phosphat-Komplexen experimentell-preparativ nachweisen. Dede [3] sowie auch Ricca und Meduri [4] untersuchten die Leitfähigkeit von verschiedenen Eisen(III) und Orthophosphat enthaltenden Lösungen. Aufgrund der berechneten und gemessenen Leitfähigkeiten nahmen sie an, daß in saurer Lösung ein 1 : 1-Komplex gebildet wird. Diese Zusammensetzung wurde auch von Lanford und Kiehl [5] bestätigt und die Stabilitätskonstante des Komplexes bestimmt. Der Stabilitätsexponent des Komplexes $[Fe(HPO_4)]^+$ beträgt nach ihren Messungen 9,35. Banerjee [6] titrierte eine Eisen(III)chloridlösung mit Phosphorsäure und beobachtete dabei die Änderung verschiedener physikalischer Eigenschaften der Lösung, u. a. Temperatur-, Leitfähigkeits-, Farb- und Ionenwanderungsänderungen. Durch Messung der Temperaturänderungen konnte die Bildung von drei Komplexen nachgewiesen werden und zwar bei Verhältnissen von Eisen(III)-Ionen zu Orthophosphationen von 1 : 1, 2 : 3 und 1 : 2. Durch Leitfähigkeitsmessungen konnten 1 : 1- und 1 : 2-Komplexe, durch die optische Messung der Änderung der gelben Farbe des Eisen(III)chlorids im Laufe der Phosphorsäurezugabe die Bildung des 1 : 1-Komplexes nachgewiesen werden. Bei der Untersuchung der Ionenwanderung zeigten die Versuche, daß bei einem Verhältnis des Eisen(III)chlorids und der Phosphorsäure von 1 : 1 die Phosphationen in der Umgebung der Kathode auffindbar sind, daß sie also mit den Eisen(III)-Ionen ein komplexes Kation bilden. Ist jedoch die Phosphorsäure auf die Eisen(III)-Ionen bezogen im Überschuß vorhanden, so wandern die Phosphationen in Form eines komplexen Anions zur Anode. Aufgrund der mit viererlei Methoden durchgeführten Versuche nimmt Banerjee die Existenz von $[Fe(HPO_4)]^+$ und $[Fe(HPO_4)_2]^-$ an. D'Amore [7] konnte auf spektrophotometrischem Weg nur die Existenz des 1 : 1-Komplexes bestätigen. Mehrere Verfasser [8–12] führten polarographische Untersuchungen der Komplexe durch, wobei die Existenz des komplexen Anions $[Fe(HPO_4)_2]^-$ bestätigt wurde. Faucherre und Msika [13] berichten über potentiometrische Untersuchungen und folgern auf Grund ihrer Ergebnisse, daß 1 : 1-Komplexe dann gebildet werden, wenn die Menge der Phosphationen gering und die Lösung schwach sauer ist, während der 1 : 2-Komplex bei höheren Phosphatmengen und in stark saurer Lösung entsteht.

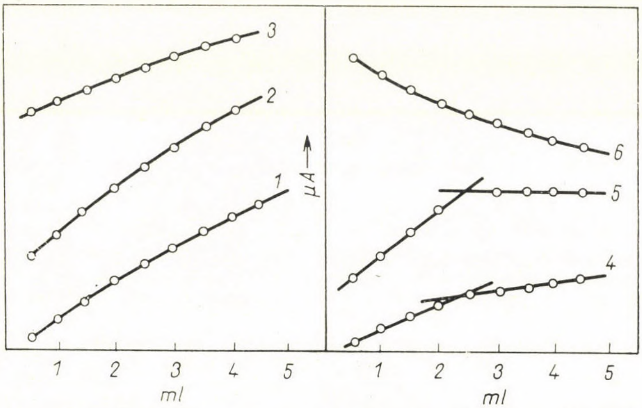

Abb. 1. Titration von Orthosphosphationen in Lösungen mit verschiedenen pH-Werten, mit 0,1 *m* Eisen(III)chlorid-Maßlösung. 1 — pH 5; 2 — pH 4; 3 — pH 3; 4 — pH 2; 5 — pH 1; 6 — pH 0,5

Das Ziel unserer Versuche war, festzustellen, mit welchem Komplex bei der quantitativen Bestimmung von Phosphationen mit einer Eisen(III)-Maßlösung, unter Anwendung der oszillometrischen Endpunktsanzeige, zu rechnen ist. Die Orthophosphationen wurden in Lösungen mit verschiedenem pH mit einer Eisen(III)chlorid-Maßlösung titriert. Die oszillometrischen Titrationskurven zeigten bei pH = 1–2 einen Knickpunkt bei dem Verhältnis Phosphat : Fe(III)-Ion = 1 : 1 (Abb. 1). Der Verlauf der Titrationskurve kann folgend gedeutet werden:

Bei der Grundreaktion

$$Fe^{3+} + H_2PO_4^- \rightleftharpoons [FeHPO_4]^+ + H^+ \quad \text{Stab. exp. } 9{,}35$$

werden Wasserstoffionen frei, folglich nimmt die Leitfähigkeit zu. Letztere wird auch durch die mit der salzsauren Eisen(III)chlorid-Maßlösung in die Lösung gelangenden sonstigen Ionen erhöht. Bis zum Endpunkt der Titration erfolgt also ein wesentlicher Anstieg der Leitfähigkeit. Die Form der oszillometrischen Titrationskurve nach dem Endpunkt wird durch die Empfindlichkeitskurve einer der Gesamtionenkonzentration entsprechenden Maßlösung bestimmt.

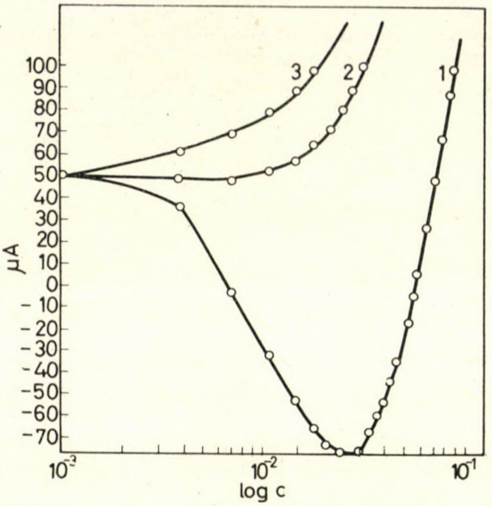

Abb. 2. Empfindlichkeitskurven von Salzsäure. 1 — in der Gegenwart von 0,1 *m* Natriumnitrat, 2 — in der Gegenwart von 0,2 *m* Natriumnitrat, 3 — in der Gegenwart von 0,25 *m* Natriumnitrat

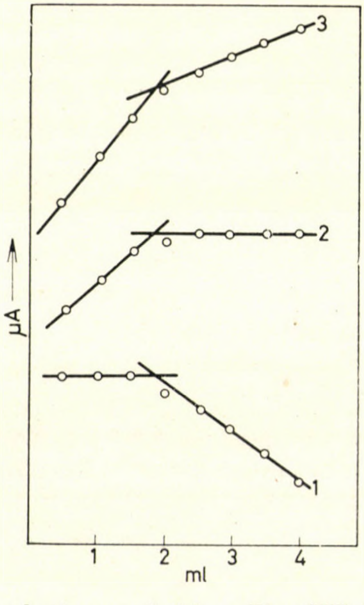

Abb. 3. Titration von Phosphationen mit 0,1 *m* Eisen(III)chlorid-Maßlösung. 1 — pH 1; 2 — pH 1,2; 3 — pH 1,5

Da während der Titration — gemäß der Reaktionsgleichung — Wasserstoffionen frei werden, und die Änderung der Leitfähigkeit hauptsächlich durch diese Wasserstoffionen beeinflußt wird, übt der pH-Wert der Ausgangslösung eine Wirkung auf die Titrationskurve und auf die Bestimmbarkeit aus. In Abb. 2 sind Salzsäureempfindlichkeitskurven dargestellt, die in Gegenwart von verschiedenen Fremdionenkonzentrationen aufgenommen wurden. Das Minimum der Kurven, d. h. das für die Titration unempfindliche Gebiet, liegt zwischen pH 1 und 2 bzw. bei höherer Fremdionenkonzentration unter pH 2.

Der pH der Ausgangslösung muß also — der Fremdionenkonzentration entsprechend — zwischen 1 und 2 liegen, damit die Titration mit unserem Gerät überhaupt durchführbar wird. Dies wird auch durch Abb. 1 bestätigt. Ist also die zu untersuchende Ausgangslösung stärker sauer, so muß ihre Wasserstoffionenkonzentration mit Natriumhydroxyd oder Natriumacetat herabgesetzt werden. Die in Abb. 3 gezeigten Titrationskurven wurden mit einer Orthophosphatlösung erhalten, deren pH ursprünglich 0,5 war und mit Natriumhydroxyd auf 1, 1,2 bzw. 1,5 abgestumpft wurde. Die so erhaltenen Lösungen wurden dann mit der Eisen(III)chlorid-Maßlösung titriert.

Durch die Einstellung der geeigneten Ionenstärke und pH-Werte kann also erreicht werden, daß die Titrationskurve einen gut auswertbaren Knickpunkt aufweist (Abb. 3, Kurve 2).

Experimenteller Teil

Lösungen und Gerät

1. 0,1 *m* KH_2PO_4-Lösung. P_2O_5-Gehalt 7,09 mg/ml. Die entsprechende Menge von analytisch reinem kristallinem KH_2PO_4 wurde in dest. Wasser gelöst. Der Wirkungswert der Lösung wurde gravimetrisch (in Form von Magnesiumpyrophosphat) bestimmt.
2. 0,1 *m* $FeCl_3$-Maßlösung. Die Fe^{3+}-Konzentration der Lösung wurde gravimetrisch bestimmt (Abscheidung mit Ammoniumhydroxyd in Form von $Fe(OH)_3$, Wägung in Form von Fe_2O_3).
3. 3 *n* Salpetersäurelösung
4. 1 *m* NaOH-Lösung
5. 1 *m* Natriumacetatlösung
6. 1 *m* Natriumnitratlösung.

Die Bestimmungen wurden mit dem Oszillotitrator Typ OK-302 (Hersteller: Radelkisz, Budapest) ausgeführt.

Es wurden 20 ml-Meßzellen verwendet.

Ausführung der Bestimmungen

Aus der 0,1 *m* KH_2PO_4-Lösung wurde soviel in die 20-ml-Meßzelle eingeführt, daß die Orthophosphationenkonzentration zwischen 3 und 25 mg pro 15 ml lag. Der pH-Wert der Lösung wurde mit Salpetersäure oder Salzsäure auf einen Wert zwischen 1 und 1,5 eingestellt. Die dazu nötige Säuremenge wurde durch die pH-Titration einer anderen Probe der Lösung bestimmt. Der Magnetrührer wurde in Gang gesetzt und es wurde so lange gewartet, bis der Zeiger des Gerätes zur Ruhe kam. Die Titration wurde dann mit der 0,1 *m* Eisen(III)chlorid-Maßlösung durchgeführt, die aus einer Mikrobürette in Portionen von 0,1—0,2 ml zugegeben wurde. Die bei der Titration von Orthophosphatlösungen verschiedener Konzentrationen erhaltenen Titrationskurven sind in Abb. 4 dargestellt. Die Fremdionenkonzentration wurde mit Natriumnitratlösung verändert. Dabei wurde festgestellt, daß die Bestimmung selbst bei dreißigfacher Fremdionenkonzentration durchführbar ist. Die Ergebnisse sind in Tabelle I

Tabelle I

Einwaage P_2O_5, mg	Gefunden P_2O_5, mg	Abweichung	
		mg	%
3,54	3,61	+0,07	+1,9
7,09	7,18	+0,09	+1,3
10,63	10,55	—0,09	—0,75
14,18	14,30	+0,12	+0,85
17,73	17,60	—0,13	—0,73
21,27	21,15	—0,12	—0,56

Konzentration der Lösungen: 10^{-3} — 10^{-2} *m* P_2O_5

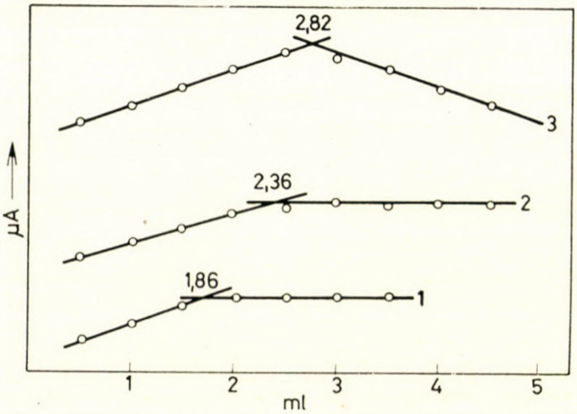

Abb. 4. Bestimmung von Phosphationen mit 0,1 *m* Eisen(III)chlorid-Maßlösung. 1 — 14,18 mg P_2O_5; 2 — 17,73 mg P_2O_5; 3 — 21,27 mg P_2O_5

enthalten. Um die Genauigkeit der Bestimmung zu berechnen, wurden 12 Parallelmessungen mit einer 10^{-3} *m* Orthophosphatlösung durchgeführt. Die Streuung σ betrug $\pm 6,17\%$, die Streuung des Mittelwerts $\sigma_k \pm 1,8\%$ (Tabelle II).

Tabelle II

Einwaage P_2O_5, mg	Gefunden P_2O_5, mg	Gefunden P_2O_5, mg
10,63	10,55	10,60
	10,55	10,66
	10,55	10,66
	10,55	10,66
	10,55	10,70
	10,60	10,70

Mittelwert: 10,61 mg P_2O_5

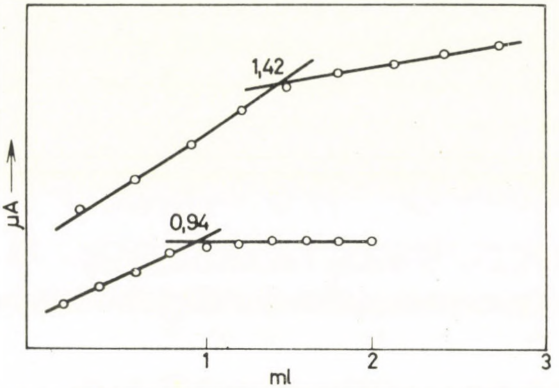

Abb. 5. Bestimmung des Gesamtphosphatgehalts von Waschmitteln mit 0,1 *m* Eisen(III)chlorid-Maßlösung

$$\sigma = \sqrt{\frac{\Sigma \varepsilon_i^2}{n-1}} = \pm 0{,}062 \quad \sigma\% = \pm 6{,}2\%$$

$$\sigma_k = \frac{\sigma}{\sqrt{n}} = \pm 0{,}018 \quad \sigma_k\% = \pm 1{,}8\%$$

Die Bestimmungsmethode wurde zur Untersuchung des Gesamtphosphatgehalts von Waschmitteln angewendet. Der Vorteil der Methode zeigte sich darin, daß der Gesamtphosphatgehalt nach der Hydrolyse der kondensierten Phosphate unmittelbar titriert werden konnte. Die Bestimmung wird durch die in der Probe enthaltenen Trübungen und durch ihren Ölemulsionscharakter nicht gestört, so daß die bei sonstigen Bestimmungen notwendige Zerstörung der organischen Stoffe überflüssig war. Die Dauer der Bestimmung wurde gegenüber den früher angewendeten Methoden auf die Hälfte herabgesetzt.

Die Bestimmung des Gesamtphosphatgehalts von Waschmitteln wurde wie folgt durchgeführt: je nach dem zu erwartenden Phosphatgehalt wurden 2—3 g Waschmittel eingewogen und in einem Becher mit 25 ml 3 *n* Salpetersäure eine halbe Stunde lang gekocht, um die kondensierten Phosphate zu hydrolysieren. Aus dem Hydrolysat wurde in einem 100-ml-Meßkolben eine Stammlösung bereitet. 5 ml dieser Stammlösung wurden in die Meßzelle des Geräts pipettiert und mit dest. Wasser auf 15 ml verdünnt, wobei der gewünschte pH-Wert mit Natriumhydroxyd- oder Natriumacetatlösung eingestellt wurde. Die Oberfläche der Lösung lag über den Kondensatorringen. Nachdem der Magnetrührer in Gang gesetzt worden war und das Gleichgewicht sich eingestellt hatte, wurde mit der 0,1 *m* Eisen(III)chlorid-Maßlösung titriert. Nach der Zugabe der Maßlösung stellt sich das Gleichgewicht jeweils nach 10—20 Sekunden ein. Die erhaltenen Titrationskurven sind in Abb. 5 dargestellt. Die Versuchsergebnisse sind in Tabelle III zusammengefaßt.

Tabelle III

Bestimmung des Gesamtphosphatgehalts von Waschmitteln mit 0,1 m Eisen(III)chlorid-Maßlösung

Einwaage P_2O_5, mg	Gefunden P_2O_5, mg	Abweichung %	Gefunden P_2O_5, mg	Abweichung %
17,61	17,50	—0,63	17,68	+0,40
	17,55	—0,34	17,68	+0,40
	17,55	—0,34	17,80	+1,07
	17,68	+0,40	17,90	+1,6

Mittelwert: 17,63 mg P_2O_5; Abweichung: +0,11%

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INVESTIGATIONS ON ION EXCHANGE EQUILIBRIA WITH RADIOACTIVE TRACER METHOD, XIV

COMPARISON OF STABILITY CONSTANTS AND THERMODYNAMIC FUNCTIONS OF 1 : 1 EUROPIUM-TRICARBALLATE AND EUROPIUM-CITRATE COMPLEXES

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With the aid of the temperature coefficient method the enthalpy and entropy changes accompanying complex formation were determined in the systems europium–tricarballylic acid and europium–citric acid, using liquid ion exchange technique. The comparison of the results implied the chelating effect of the hydroxy group of the citric acid, while the tricarballylic acid, functioning as a monodentate ligand in the concentration region investigated, gave evidence of simple complex formation only.

Introduction

In the previous paper of this series [1] it was shown that the temperature coefficient method can be used for the determination of enthalpy and entropy changes accompanying complex formation. However, this statement may be generalized only with the assumption that the temperature dependence of the formation constants is high enough to obtain reliable data, as it is to be expected *e.g.* when chelate complexes are formed.

The principle aim of the present work was in fact the comparison of the effect of chelation, so the two ligands chosen as models differed only in the ring-forming hydroxy group from each other.

Since the first homologues of simple carboxylic acids are soluble both in organic solvents and aqueous solutions, the two ligands investigated were the tribasic tricarballylic and citric acids, the latter having an additional hydroxy group as compared with the former.

In order to avoid the difficulties in interpreting the data when — due to the stepwise dissociation of the acids — more than one species are formed, only the 1 : 1 complexes have been investigated maintaining the free ligand concentrations fairly low, partly by working in the low pH region.

Experimental

The conventional thermostated static equilibration technique described in detail previously [1] was used. Distribution measurements were carried out using 0.1 F di-2-ethylhexyl phosphoric acid dissolved in toluene, as liquid ion exchanger.

Europium concentration was set to 10^{-6} *M*; the $^{152-154}$Eu tracer of high specific activity assured considerable precision of the measurements.

Ionic strength was adjusted to 0.75 *M* with perchloric acid and sodium perchlorate. Careful pre-equilibration of the aqueous and organic phases rendered possible to keep the pH at constant values, being 1.65 ± 0.02 in the europium–citrate and 1.75 ± 0.02 in the europium–tricarballate systems, respectively.

The free ligand concentrations were calculated after having determined the dissociation constants at the same ionic strength for the first step of deprotonation. The pK_d values (3.59 for tricarballylic acid and 2.91 for citric acid, respectively) proved to be in good agreement with literature data [2]. In the region 12—38 °C no temperature dependence exceeding limits of error was observed.

Results and discussion

The results of equilibrium measurements performed at 12.5, 25.0 and 37.5 °C are presented in Figs 1 and 2. As it has been shown [3], if the free ligand concentration is kept low enough to restrict formation of higher complexes, from a plot of $1/D$ *vs.* $[L]$ the first stability constant K_{13} can be easily calculated, according to the relation

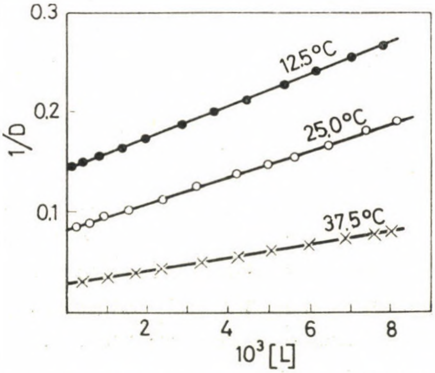

Fig. 1. 1/*D* as a function of free ligand concentration at 12.5, 25.0 and 37.5 °C in the system europium—tricarballylic acid

$$\frac{D^\circ}{D} = 1 + K_{13}[L] \tag{1}$$

where K_{13} denotes the stability constant of the 1 : 1 complex of the central ion and the ligand, formed by the first step of deprotonation, D and D° are the distribution ratios of the metal between the organic and aqueous phases, in the presence and absence of the complexing agent, respectively.

The perturbing effects due to the loss of the second and third protons from the carboxylic groups can be excluded as the corresponding dissociation constants are considerably lower.

According to the values presented in Figs 1 and 2, the temperature dependence of the stability constants shown in Fig. 3 can be represented as follows:

Europium–tricarballate

$$\log K_{13} = -9.28\times10^{-1} + 7.34\times10^{-3}T + 1.05\times10^{-5}T^2 \tag{2}$$

Europium–citrate

$$\log K_{13} = 2.03\times10^{-2} + 8.51\times10^{-3}T + 2.25\times10^{-7}T^2 \tag{3}$$

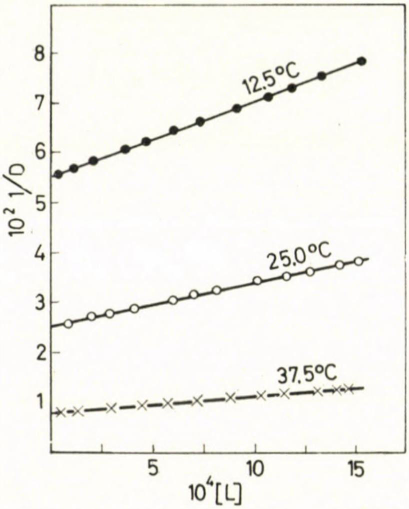

Fig. 2. $1/D$ as a function of free ligand concentration at 12.5, 25.0 and 37.5 °C in the system europium—citric acid

In the previous paper [1] it has been shown that in the knowledge of the constants b and c of the

$$\log K_{13} = a + bT + cT^2 \tag{4}$$

equation the enthalpy change can be calculated from the relation

$$\Delta H_{13} = 2.303\,RT^2(b+2cT), \tag{5}$$

whence the entropy change accompanying complex formation may be obtained with the aid of Eq. (6):

$$\Delta S_{13} = \frac{\Delta H_{13} + 2.303\,RT\log K_{13}}{T} \tag{6}$$

The results of the calculations performed are summarized in Table I. As the error of the determination of the stability constants does not exceed 0.02 units on logarithmic scale, the values of the thermodynamic constants calculated on the basis of temperature dependence can be considered as reliable ones.

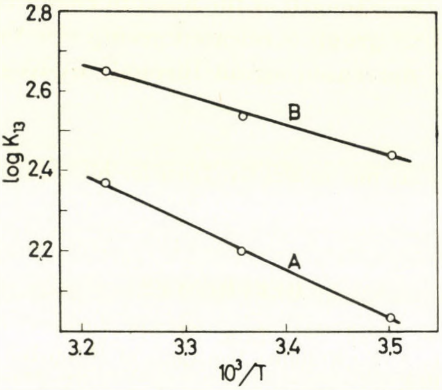

Fig. 3. Stability constants of 1 : 1 complexes as a function of $1/T$. A: europium–tricarballate, B: europium–citrate

Table I

Stability constants and thermodynamic functions in the system europium—tricarballylic acid (A) and europium—citric acid (B) at 12.5, 25.0 and 37.5 °C

	12.5 °C		25.0 °C		37.5 °C	
	A	*B*	*A*	*B*	*A*	*B*
log K_{13}	2.03	2.44	2.19	2.54	2.37	2.65
ΔG_{13} kcal/mole	—2.65	—3.19	—2.99	—3.46	—3.37	—3.77
ΔH_{13} kcal/mole	4.97	3.13	5.52	3.41	6.11	3.70
ΔS_{13} e. u.	26.7	22.1	28.6	23.0	30.5	24.1

The figures of Table I indicate that, in spite of the higher proton affinity of tricarballylic acid (as it is obvious from the corresponding dissociation constants) the citrate complex is of considerably higher stability. This fact can be a consequence of chelate formation only. At the same time it is to be mentioned that the values refer to ionic strength of 0.75 *M*; no extrapolation to infinite dilution was attempted and therefore the corresponding stability constants are lower than it might be expected from literature data available for similar systems [2].

It is striking that — in accordance with Eq. (6) — the formation constant of the chelate complex is higher than that of the non-chelated tricarballate complex, while the value of enthalpy change is higher in the formation of the latter.

On the contrary, the entropy contribution to complex formation is relatively more pronounced in the chelated citrate system, as it is associated with ring closure; this phenomenon was observed also earlier [1, 4], and is in good agreement with configurational considerations. As the central ion is rather electropositive, the strength of the bond between the oxygen and hydrogen atoms in the hydroxy group is released giving rise to the formation of the five-membered ring of decreased strain through hydrogen bonding.

*

The author's thanks are due to Mr. Gy. Tóth for his valuable help in performing the measurements.

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FURTHER REFINEMENT OF THE ELECTRON DIFFRACTION DATA ON $SOCl_2$ AND SO_2Cl_2 VAPORS

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The structural analysis of $SOCl_2$ and SO_2Cl_2 based on electron diffraction data was repeated using complex scattering factors in the theoretical molecular intensity expression. In a previous study a constant scattering function was used. There was no significant difference in the results obtained in the two refinements.

Molecular structure studies on $SOCl_2$ and SO_2Cl_2 by sector-microphotometer electron diffraction method were recently carried out in this Laboratory [1, 2]. In both cases a least-squares refinement based on the experimental molecular intensities (modified by the experimental background) was performed using constant values for the scattering functions in the corresponding theoretical molecular intensity expression.

Visiting the Oslo Electron Diffraction Group it was decided to repeat the structural analysis using partial waves atomic scattering factors. The results of this reinvestigation are reported in this paper.

The experimental molecular intensities referred to as curve *M* in [1] for $SOCl_2$ and curve *M* 1 in [2] for SO_2Cl_2, respectively, were used.

Since there was a possibility to calculate complex scattering amplitudes, the following scattering functions were used in the present work:

$$g_{ij/B}(s) = \frac{n_{ij}|f_i(s)|\,|f_j(s)|}{I_b^T(s)} \cos\left[\eta_i(s) - \eta_j(s)\right]$$

where $|f(s)|$ and $\eta(s)$ are the absolute value and phase of the atomic complex electron scattering amplitude, and $I_b^T(s)$ denotes the theoretical background function. A description of the theory might be found in the literature [3]. (It should be mentioned that instead of the theoretical background the experimental one could not be used as a modification function for the theoretical molecular intensities because it was unknown after averaging the experimental molecular intensities.)

The partial waves electron scattering factors for chlorine, sulphur and

oxygen at 50 kV accelerating voltage as well as the scattering functions were calculated using STRAND's programs [4, 5]. Fig. 1 shows the $g_{ij/B}(s)$ functions a) for $SOCl_2$ and b) for SO_2Cl_2.

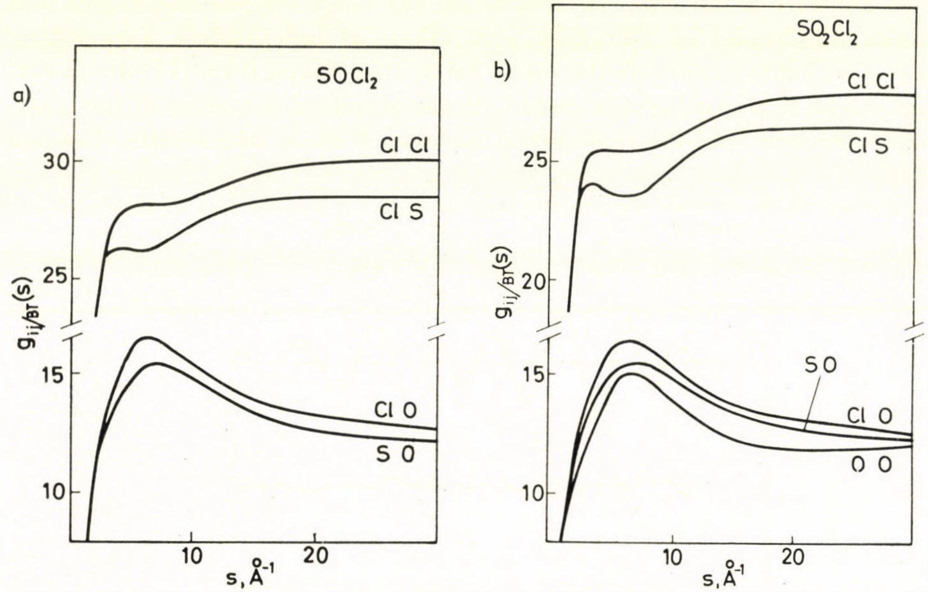

Fig. 1. $g_{ij/B}(s)$ functions; a) for $SOCl_2$; b) for SO_2Cl_2

Table I

Results of the least-squares refinement for $SOCl_2$
(see text)

	A	*B*	*C*
r(S—O), Å	1.444 (±0.007)	1.4429±0.0045	1.4425±0.0032
r(Cl—S), Å	2.076 (±0.006)	2.0755±0.0021	2.0755±0.0015
Cl—S—Cl°	96.2 (±1.0)	96.11 ±0.66	96.10 ±0.48
Cl—S—O°	107.3 (±0.6)	106.28 ±0.60	106.28 ±0.41
r(Cl . . . Cl), Å	3.091 (±0.014)	3.0875±0.0157	3.0871±0.0112
r(Cl . . . O), Å	2.860 (±0.010)	2.8405±0.0096	2.8402±0.0068
l(S—O), Å	0.031 (±0.010)	0.0239±0.0114	0.0243±0.0080
l(Cl—S), Å	0.052 (±0.004)	0.0512±0.0035	0.0512±0.0025
l(Cl . . . Cl), Å	0.102 (±0.012)	0.1009±0.0118	0.1013±0.0085
l(Cl . . . O), Å	0.075 (±0.008)	0.0758±0.0087	0.0760±0.0062

Thionyl chloride

In this reinvestigation both for $SOCl_2$ and SO_2Cl_2 SEIP's least-squares program [6] was used with an approparite weight function.

In the case of the thionyl chloride all the bond lengths and angles and the mean amplitudes of vibration were taken as independent parameters. Column *A* in Table I contains the input parameters taken from [1] (the uncertainties shown in parentheses include both the standard deviation of the least-squares refinement and the scale error). Column *B* shows the results obtained

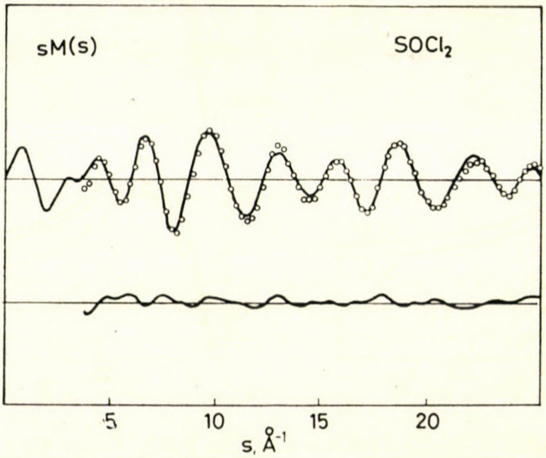

Fig. 2. Molecular intensities for $SOCl_2$, circles — experimental. Full line — theoretical (computed from the parameter values of Column *C*, Table I); below — their difference

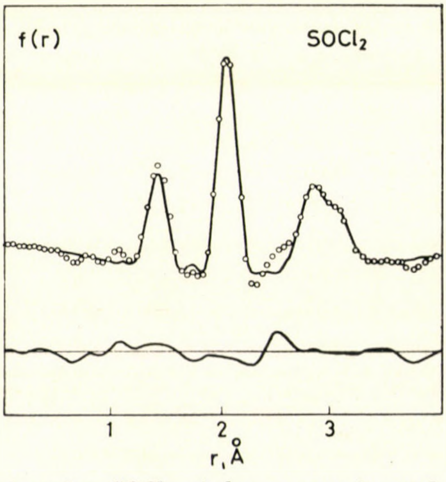

Fig. 3. Radial distributions for $SOCl_2$, circles — experimental. Full line — theoretical; below — their difference

in this reinvestigation. The results obtained after a modification of the background (eliminating the trend of the difference curve between the experimental and theoretical intensities) are shown in Column *C*. In Columns *B* and *C* the standard deviation of the least-squares refinement is presented too. Fig. 2 shows the experimental molecular intensities after the modification of the background (circles) and the theoretical molecular intensities corresponding to the parameters of Column *C*, Table I. The corresponding radial distributions are shown in Fig. 3.

The results of Column *C*, Table I served for comparison in a spectroscopic analysis of the mean amplitudes of vibration [7].

Sulfuryl chloride

The unpublished results obtained in a least-squares refinement based on the experimental molecular intensities referred to as *M* 1 in [2] using constant scattering functions are shown in Column *A*, Table II. These parameters were used as input data for the present reinvestigation, the results of which are shown in Column *B*, Table II. At first the bond lengths and angles and all the mean amplitudes were taken as independent parameters. Then, because of its improbably small value of *l*(O . . . O) obtained in the refinement (similarly to that in [2]) it was decided to keep *l*(O . . . O) unvaried, a value taken from VENKATESWARLU *et al.* [8] quoted in CYVIN's book [9].

It was the parameters of this Column which served for comparison in a spectroscopic analysis of the mean amplitudes of vibration ([7], following paper).

Table II

Results of the least-squares refinement for SO_2Cl_2
(see text)

	A	*B*	*C*
r(S—O), Å	1.407 (±0.009)	1.4069±0.0033	1.4038±0.0015
r(Cl—S), Å	2.011 (±0.008)	2.0100±0.0028	2.0111±0.0013
∢ Cl—S—Cl°	100 ±2	100.3 ±1.2	100.0 ±0.5
∢ Cl—S—O°	108.3 ±0.6	107.8 ±0.4	107.7 ±0.2
∢ O—S—O°	121.4 ±2	122.3 ±1.6	123.45 ±0.7
r(Cl . . . Cl), Å	3.085	3.0873±0.0238	3.0815±0.0109
r(Cl . . . O), Å	2.784 (±0.010)	2.7840±0.0058	2.7810±0.0026
r(O . . . O), Å	2.478 (±0.023)	2.4717±0.0200	2.4727±0.0089
l(S—O), Å	0.035 (±0.003)	0.0350±0,0069	0.0342±0.0032
l(Cl—S), Å	0.047 (±0.003)	0.0464±0.0044	0.0461±0.0020
l(Cl . . . Cl), Å	0.108 (±0.021)	0.1012±0.0182	0.1019±0.0083
l(Cl . . . O), Å	0.072 (±0.006)	0.0716±0.0063	0.0693±0.0028
l(O . . . O), Å	0.070 (ass.)	0.0612 (ass.)	0.0612 (ass.)

The parameters obtained after a modification of the experimental background are shown in Column *C*, Table II.

Figs 4 and 5, respectively show molecular intensities and radial distributions for SO_2Cl_2 in a similar way as it was for $SOCl_2$ in Figs 2 and 3, respectively.

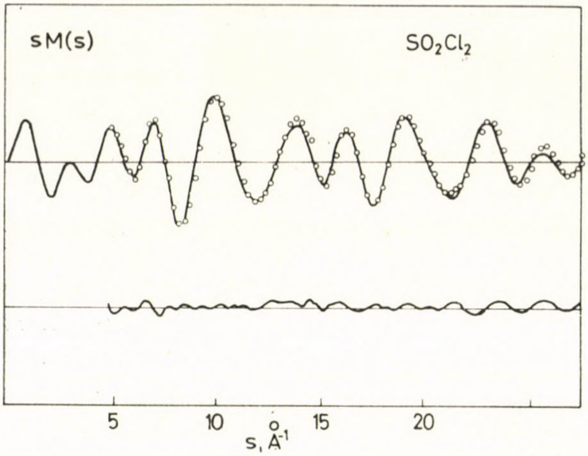

Fig. 4. Molecular intensities for SO_2Cl_2, circles — experimental. Full line — theoretica (computed from the parameter values of Column *C*, Table II); below — their difference

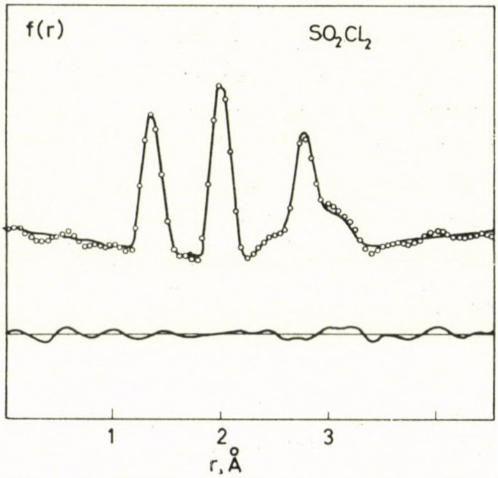

Fig. 5. Radial distributions for SO_2Cl_2, circles — experimental. Full line — theoretical; below — their difference

Conclusions

There was no significant difference in the results obtained in the two refinements using the expressions (1) and (2), respectively, for $g_{ij/B}$ (*cf.* the data presented in Columns *A* and *B* in Tables I and II).

Only one of the parameters [*r*(*S*—O) in thionyl chloride] was significantly influenced by the modification of the background which in general reduced the standard deviation.

The final values of bond lengths and angles and the mean amplitudes of vibration (with their uncertainties including the scale error for the former) are presented in Table III.

Table III

Final results

	$SOCl_2$	SO_2Cl_2
r(S—O), Å	1.443 ± 0.006	1.404 ± 0.004
r(Cl—S), Å	2.076 ± 0.006	2.011 ± 0.005
∢ Cl—S—Cl°	96.1 ± 0.7	100.0 ± 0.7
∢ Cl—S—O°	106.3 ± 0.6	107.7 ± 0.4
∢ O—S—O°		123.5 ± 0.8
l(S—O), Å	0.024 ± 0.008	0.034 ± 0.003
l(Cl—S), Å	0.051 ± 0.003	0.046 ± 0.002
l(Cl . . . Cl), Å	0.101 ± 0.009	0.102 ± 0.008
l(Cl . . . O), Å	0.076 ± 0.006	0.069 ± 0.003
l(O . . . O), Å		0.061 (ass.)

The good agreement between the mean amplitude values obtained by electron diffraction and calculated from spectroscopic data (see next paper, [7]) indicated an appropriate choice of some of the conditions (*e.g.* the geometry of the nozzle and the electron beam) of the electron diffraction experiment [10].

Since there was no significant change in the structural parameters, all conclusions made for sulphur bond lengths in [1] can be considered as valid.

*

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TENTATIVE KINETIC INTERPRETATION OF ADSORPTION ISOTHERMS OF BINARY MIXTURES OF NON-ELECTROLYTES

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Attention is called to the fact that current thermodynamic theories of monolayer adsorption seem not to be able to account satisfactorily for the behaviour of surface activity coefficients, because in many instances ideality or non-ideality of the bulk liquid does not involve a parallel behaviour in the adsorption layer. Using a simplified liquid model and assuming a hole mechanism to be operative in the elementary acts of desorption and adsorption at the interface, energetic considerations lead to the derivation of a basically linear relationship between the logarithm of the separation factor and the equilibrium mole fraction of any of the components in the bulk of a binary mixture. Actual experimental examples of such behaviour are shown, and deviations met with in other cases discussed in the light of some possible refinements of the crude theory.

Some years ago, together with L. G. Nagy [1], the study of the adsorption isotherms of binary liquid mixtures of non-electrolytes on solid adsorbents led us to distinguish five fundamental types of experimental isotherms in cases of physical adsorption. Expressed in terms of directly measurable quantities, the adsorption isotherm of species *i* is defined by the function:

$$f(x_i) = \frac{n^0(x_i^0 - x_i)}{m} \qquad (i = 1, 2) \tag{1}$$

where n^0 is the number of moles of the mixture brought into contact with m grams of the adsorbent, in which the original mole fraction of the species in question was x_i, this fraction changing to the final value x_i in the bulk of the liquid in adsorption equilibrium. The five types just mentioned are shown on Fig. 1. Three of them (II—IV) exhibit a more or less long section which is practically linear, within the limits of experimental error. Such portions may be represented algebraically:

$$f(x_1) = a - bx_1,\ f(x_2) = -f(x_1) = (b - a) - bx_2 \tag{2}$$

a and b being constants, respectively.

It is well known, on the other hand, that an expression for $f(x_1)$ can be derived on the basis of a simple material balance if the liquid in contact with the adsorbent is mentally divided into two parts, one of them being within

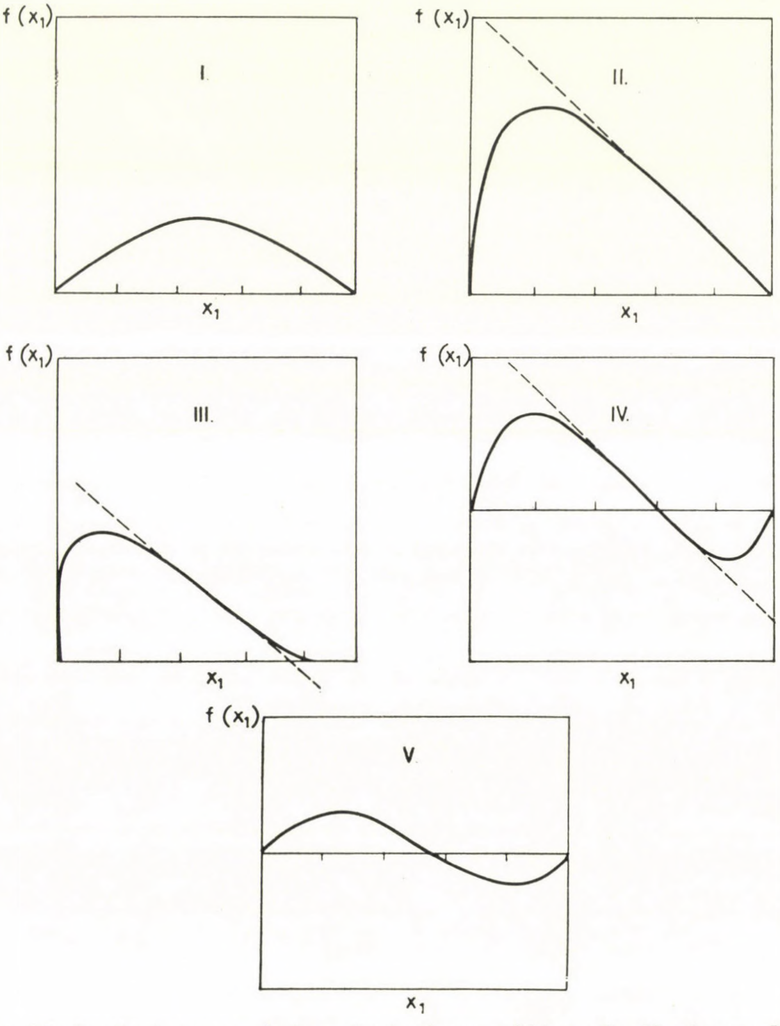

Fig. 1. The five basic types of adsorption isotherms of binary liquid mixtures [1, 2]

the reach of the adsorption forces emanating from the solid and containing n_1^a and n_2^a moles per gram of adsorbent, respectively, of the two species, whereas the remaining "free" liquid is characterized by the equilibrium mole fractions x_1 and x_2, respectively:

$$f(x_1) = n_1^a(1 - x_1) - n_2^a x_1 = n_1^a - (n_1^a + n_2^a)x_1 \tag{3}$$

By a comparison with (2), one feels induced to postulate for the linear section of an isotherm the relations:

$$n_1^a = a \qquad \text{and} \qquad (n_1^a + n_2^a) = b \tag{4}$$

Such a conclusion is fallacious, however, as long as one does not have a definite notion about the extent of the adsorption layer (*i.e.* the number of moles contained in it), since any algebraic difference remains unchanged if its two terms are altered by identical quantities, respectively.

L. G. NAGY and SCHAY (l.c.) could show that the numbers of moles computed according to (4) are practically equivalent with a complete monolayer whenever adsorption is of the purely physical type, the molecules of the mixture are not too different in size and the entire adsorbent surface is equally accessible to both kinds of molecules. The authors could show that this equivalence proves to be so good as to make specific surface area determinations possible with an accuracy not worse than that of other usual methods.

The notion of monolayer adsorption has been familiar for long in connexion with the liquid/vapour interface and since the first attempt of BUTLER in 1932 [2], many authors were concerned with the elaboration of an adequate thermodynamic theory. Without entering into details, the essential features of the theory in its present status can be outlined as follows. First of all, it is derived that the chemical potential of any component appears augmented in the adsorption layer by a term which is the product of the surface tension γ and of the surface area A_i occupied by one mole of component *i*:

$$\mu_i^\sigma = \gamma A_i + \mu_i \tag{5}$$

This basic relation is then developed in more detail by introduction of activities and activity coefficients, with the result:

$$lg\, a_i^\sigma = lg f_i^\sigma + lg\, x_i^\sigma = (\gamma - \gamma_i)A_i/RT + lg\, a_i\,, \tag{6}$$

where upper index σ refers to the monolayer (f_i^σ being the surface activity coefficient, x_i^σ the mole fraction in the adsorption layer), and γ_i is the surface tension of pure *i*.

In the case of liquid/vapour interfaces, the surface tension can be directly measured as the function of x_i, and if the activity coefficients f_i of the bulk liquid are known, γ can be represented as a function of a_i. By graphical differentiation of the latter function, and by making use of Gibbs's well-known adsorption equation on the one hand, and of the algebraic relations valid for the model of a compact monolayer, on the other hand, the x_i^σ pertaining to any x_i can be computed, and then also f_i^σ by Eq. (6).

If the notion of the adsorption monolayer is transferred, as done by us, to the solid/liquid interface, Eq. (6) is still applicable to the calculation of surface activity coefficients, in principle at least. It is not possible in this case, however, to measure the surface tension, the correct interpretation of this quantity becoming even problematic since originally it is defined for smooth surfaces only. An alternative interpretation of γ is, on the other hand, that of a free energy excess, and this latter definition may be extended without ambiguity to rough surfaces also as those of real adsorbents. It can be shown then that Gibbs's fundamental equation remains valid for this case also. It is the concentration shift $x_i^0 - x_i$, caused by adsorption, which can be measured directly now, and x_i^σ can be computed without difficulty by relying on the model of the adsorption monolayer. By introducing these surface concentrations into the Gibbs relation, a graphical integration enables us to determine the difference $\gamma - \gamma_i$ (not the absolute value of any γ), and then surface activity coefficients can be computed by Eq. (6). An alternative method for finding these coefficients without recurring in an explicit way to the surface tension has been proposed by EVERETT [3].

As the forces acting between the molecules of the mixture are certainly the same within the adsorption layer as in the bulk liquid, one would expect to find more or less simple relations between the f_i and f_i^σ, respectively, such as the f_i^σ assuming values practically equal to unity, whenever the mixture behaves ideally, or the deviations from ideality are showing some parallelism. In fact, any attempts at the theoretical prediction of surface activity coefficients are based on such ideas. In our opinion, however, existing experimental evidence is rather disillusioning in this respect.

Although sets of really exact data are very seldom available for a quite reassuringly reliable determination of the course of the surface activity coefficients, the general impression is nevertheless that it would be difficult if not impossible to find any clear correlations between the f_i^σ and the corresponding f_i, respectively. This view may be illustrated by a few examples. The f_i^σ of mixtures of water and alcohol are scarcely different from unity, although the behaviour of these mixtures is far from being ideal in the bulk; this statement is true for the case of the liquid/vapour interface (where there is no foreign matter, as an adsorbent, present) as well as for the adsorption on charcoal, the isotherm (of Type III) being even of a very similar character in both cases. Mixtures of benzene and 1,2-dichloroethane, on the other hand, which behave practically ideally, give on charcoal an isotherm of Type V from which values of f_i^σ can be derived, beginning below 0.5 at the lowest concentrations and increasing steadily up to 1 at the limits $x_i^\sigma = x_i = 1$.

Examples of such contradictions could be multiplied, so that one is led to the conclusion that the existing thermodynamic theory of monolayer adsorption is too formalistic and not very fruitful. In fact, such a monolayer cannot be regarded as an autonomous phase, and it may be doubtful whether one is justified to treat adsorption equilibrium by thermodynamic methods which were developed and are fundamentally valid for equilibria between autonomous phases. Formally correct relations can be established without doubt by the introduction of surface activity coefficients, but it may be questioned whether these coefficients will ever be accessible to any intuitive interpretation. We think especially that it is fallacious to treat the excess free energy at the interface and the activities in the adsorption layer as two separate parameters, both of them being manifestations of the same intermolecular forces.

The following is the outline of a tentative theory, based on kinetical-statistical considerations, taking account of the dynamic character of adsorption equilibrium. From this latter point of view, an eventual difference between the composition of the interfacial layer and that of the bulk liquid has to be a consequence of the mean residence times of the components at the surface being different. Let us suppose, for the sake of simplifying the argumentation, that the portions of surface area occupied by the single molecules are about equal for the two species of the mixture, so that the total concentration in the monolayer is constant, independent of the composition:

$$\Gamma = \Gamma_1 + \Gamma_2 = \text{const.} \tag{7}$$

Any molecule of the monolayer cannot get desorbed but by a jump into a neighbouring hole present in the next layer of the liquid, leaving now a hole in the adsorption layer which, however, will be filled in automatically, in order to ensure the constant total surface concentration (at the liquid/vapour interface, holes in the surface layer can and will be produced by evaporation also, but they will be filled up decisively from the liquid side, as long as the vapour density is low enough).

Let τ_1 and τ_2 be the respective mean residence times of the two kinds of molecules at the interface. Generally, these times will be different as a consequence of the adsorption energies being different, on the one hand, but also because the activation energies necessary for the jump into a neighbouring hole may be different for the two kinds of molecules. As will be seen presently, this latter point is a vital one in the theory, but not important for the moment, because by simply accepting that τ_1 and τ_2 are not identical, one can write for the respective rates of desorption:

$$\left(\frac{d\Gamma_1}{dt}\right)_{-} = \Gamma_1 \tau_1^{-1}, \quad \left(\frac{d\Gamma_2}{dt}\right)_{-} = \Gamma_2 \tau_2^{-1} \tag{8}$$

and for the total rate of production of holes in the interfacial monolayer:

$$\left(\frac{d\Gamma}{dt}\right)_{-} = \Gamma_1 \tau_1^{-1} + \Gamma_2 \tau_2^{-1} \tag{9}$$

According to our model, these holes are refilled automatically by molecules coming from the neighbouring first layer of the liquid, and that in proportion of their mole fractions $x_1^{(1)}$ and $x_2^{(1)}$ in that layer. The resulting adsorption rates will be accordingly:

$$\frac{d\Gamma_1}{dt} = x_1^{(1)}(\Gamma_1\tau_1^{-1} + \Gamma_2\tau_2^{-1}) - \Gamma_1\tau_1^{-1} = x_1^{(1)}\Gamma_2\tau_2^{-1} - x_2^{(1)}\Gamma_1\tau_1^{-1} \tag{10}$$

and naturally:

$$\frac{d\Gamma_2}{dt} = -\frac{d\Gamma_1}{dt} \tag{11}$$

satisfying the requirement of the adsorption layer remaining complete, so that an accumulation of one of the components cannot occur but at the expense of the other one.

The above resulting rates have to vanish in equilibrium, and at the same time, according to the monolayer model, the composition of the next first layer has to become equal to that of the bulk liquid. By introducing surface mole fractions, one can then write for the adsorption equilibrium:

$$\alpha \equiv \frac{x_2 x_1^\sigma}{x_1 x_2^\sigma} = \frac{\tau_1}{\tau_2} \tag{12}$$

α being the enrichment factor, defined at the analogy of other separation processes, such as distillation, etc. By this analogy, the result (12) seems almost trivial, indeed.

Relation (12) is an implicit equation of the adsorption isotherm. To make it explicit, particulars have to be stated as to the dependence of the mean residence times on the composition of the mixture. Since the sizes of the two kinds of molecules have been assumed to be similar, it is the energetic conditions only which have to be considered. For this purpose, the simplest possible model shall be used here, that of regularly arranged molecular cubes, with the admission of the presence of holes, however, in order to account for transport processes. Any molecule in a complete layer has eight, or more generally z neighbours in the same layer. Fig. 2 is a schematic picture of a single desorption act according to this crude model.

Let ε_1 and ε_2 be the fundamental values of the respective desorption energies of the two kinds of molecules, which represent their direct interaction with the solid surface, and ε_{11}, ε_{12}, ε_{22} the energies necessary for severing the respective contacts between two molecules of the liquid. The total potential energy of a molecule of species 1 will then be:

$\varepsilon_1 + z(x_1^\sigma\,\varepsilon_{11} + x_2^\sigma\,\varepsilon_{12}) + z(x_1\,\varepsilon_{11} + x_2\,\varepsilon_{12})$ before desorption and:

$z(x_1^\sigma\,\varepsilon_{11} + x_2^\sigma\,\varepsilon_{12}) + (2\,z + 1)\,(x_1\,\varepsilon_{11} + x_2\,\varepsilon_{12})$ after desorption, and similar expressions can be written for species 2. The energy changes accompanied with the elementary acts of desorption are the differences of the above expressions, *i.e.*:

$$\varepsilon_1 - (z + 1)\,(x_1\,\varepsilon_{11} + x_2\,\varepsilon_{12}) = \varepsilon_1 - (z + 1)\,\varepsilon_{12} - (z + 1\,(\varepsilon_{11} - \varepsilon_{12})\,x_1$$

and (13)

$$\varepsilon_2 - (z + 1)\,(x_1\,\varepsilon_{12} + x_2\,\varepsilon_{22}) = \varepsilon_2 - (z + 1)\,\varepsilon_{22} - (z + 1)\,(\varepsilon_{12} - \varepsilon_{22})\,x_1$$

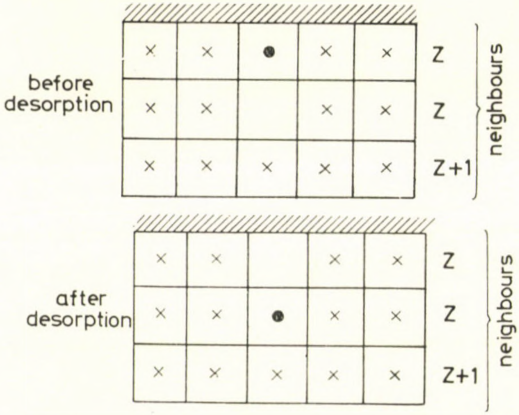

Fig. 2. Schematic model of an elementary desorption act

It is remarkable and at the same time characteristic of the treatment adopted here that these differences do not contain any explicit dependence on the x_i^σ, *i.e.* on the composition of the adsorption layer. An implicit dependence may be anticipated, however, through the values ε_1 and ε_2, respectively, which will probably not remain strictly constant.

The mean times τ_1 and τ_2 are determined by the activation energies needed for the desorption acts to occur. Let us suppose that these activation energies are not solely governed by the interaction energies with the surface but that they contain also an accessory term characteristic of the jump into a neighbouring hole, an idea familiar in connexion with all transport processes in the liquid phase. With allusion to the Polányi rule, it may be supposed that these accessory terms are proportional with the respective energy differences, so that one can write for the mean residence times, with β_1 and β_2 as the respective proportionality factors:

$$\tau_1 = \tau_1^0 \exp\left\{\frac{1}{kT}\left[\varepsilon_1 - \beta_1(z + 1)\,\varepsilon_{12} - \beta_1(z + 1)\,(\varepsilon_{11} - \varepsilon_{12})x_1\right]\right\}$$

$$\tau_2 = \tau_2^0 \exp\left\{\frac{1}{kT}\left[\varepsilon_2 - \beta_2(z + 1)\,\varepsilon_{22} - \beta_2(z + 1)\,(\varepsilon_{12} - \varepsilon_{22})x_1\right]\right\} \qquad (14)$$

and for their quotient, *i.e.* the enrichment factor:

$$\alpha = \frac{\tau_1}{\tau_2} = \frac{\tau_1^0}{\tau_2^0} \exp \left\{ \frac{1}{kT} \left[(\varepsilon_1 - \varepsilon_2) + (z+1)(\beta_2 \varepsilon_{22} - \beta_1 \varepsilon_{12}) - \right. \right. \\ \left. \left. - (z+1)(\beta_1 \varepsilon_{11} - \beta_1 \varepsilon_{12} - \beta_2 \varepsilon_{12} + \beta_2 \varepsilon_{22}) x_1 \right] \right\} \qquad (15)$$

That last one has to be regarded as the fundamental relation of our theory. It can be given the general form:

$$\lg \alpha = A - Bx_1 , \qquad (16)$$

where B has to be a constant, while A will be constant only when constancy of ε_1 and ε_2 is supposed. It can be predicted that the second term on the right hand side has normally to be negative, as indicated in (16). Indeed, by the assumption:

$$\beta_1 = \beta_2 = \beta \qquad (17)$$

which will probably not fall far from truth, the last term of (15) becomes:

$$(z+1)\,\beta(\varepsilon_{11} - 2\,\varepsilon_{12} + \varepsilon_{22})\,x_1 \qquad (18)$$

and if the theory of regular solutions can be applied, one has:

$$\varepsilon_{11} - 2\varepsilon_{12} + \varepsilon_{22} = (\sqrt{\varepsilon_{11}} - (\sqrt{\varepsilon_{22}})^2 \geqslant 0 \qquad (19)$$

This latter reasoning suggests also the probability of the second term of (16), linear in x_1, becoming the decisive one, whenever the mixture in question is far from behaving ideally. As a matter of fact, this latter conclusion seems to be corroborated by experience. Fig. 3 (this and all the following figures consist of three parts, showing: the course of $\gamma_2 - \gamma$, in cal/m^2, as determined by the graphical method outlined above; the equilibrium diagram of the system in question, *i.e.* x_1^σ as the function of x_1; and finally, $\lg \alpha$ as the function of x_1) shows the behaviour of mixtures of acetic acid and benzene on a charcoal of 620 m^2/g, and Fig. 4 that of mixtures of ethanol and benzene on another charcoal of 615 m^2/g. Evidently, the dependence of $\lg \alpha$ on x_1 is surprisingly linear in both cases and the slope is negative, as predicted.

It has to be admitted, however, that the linearity is not always so good. Figs 5 and 6 show the behaviour of the same pair, ethanol—benzene, on a

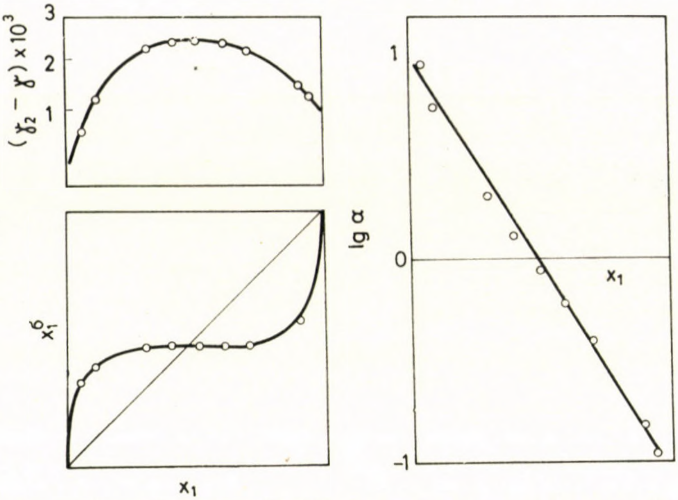

Fig. 3. Adsorption of acetic acid—benzene mixtures on charcoal, 620 m^2/g [4]

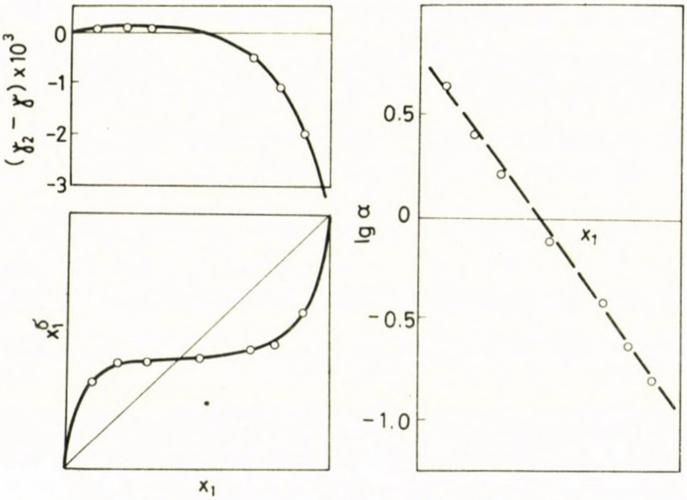

Fig. 4. Adsorption of ethanol—benzene on charcoal, 615 m^2/g [6]

different charcoal with a greater specific surface area of 720 m^2/g and on an alumina gel of 274 m^2/g, respectively. In these examples, the graphs of lg α are visibly curved, but not to a decisive extent, and what is important, their mean slopes are more or less identical with those in Figs 3 and 4, showing thus the preponderant role of the factor B. This latter factor proved to be the same in the case of the pair methanol—benzene, too, on the same kind of charcoal of 720 m^2/g (Fig. 7). A more pronounced heterogeneity of the adsorbent

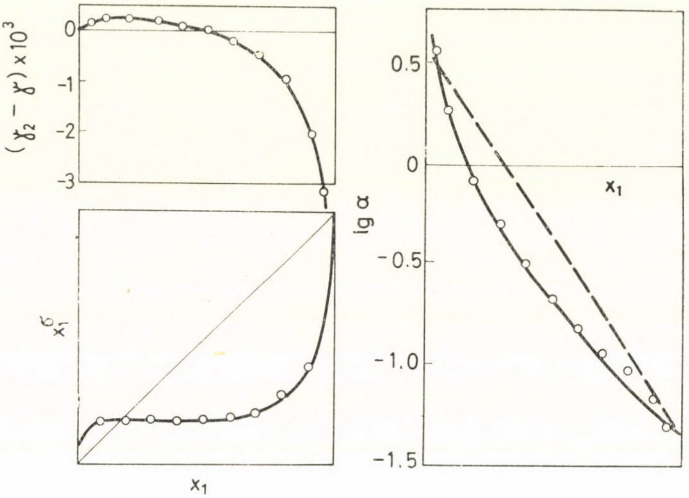

Fig. 5. Adsorption of ethanol—benzene on charcoal, 720 m²/g [5]

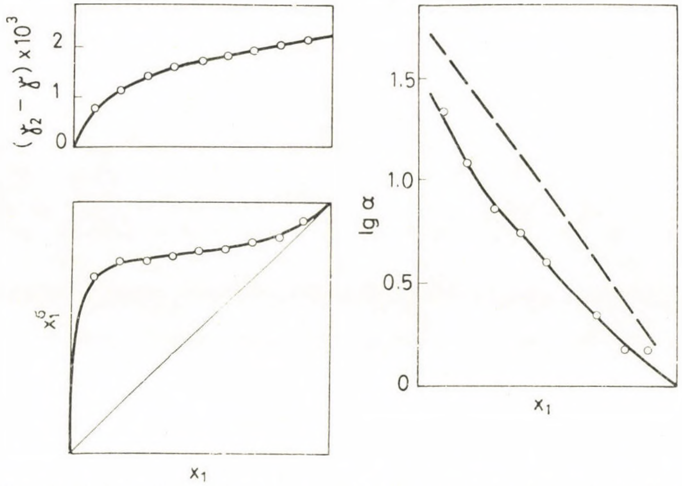

Fig. 6. Adsorption of ethanol—benzene on alumina gel, 274 m²/g [7]

surface may be suspected to be responsible for the marked curvature in the latter cases, for it is quite possible that an increased heterogeneity causes a variation of the values of ε_1 and ε_2 with the composition of the mixture.

The pair methylacetate—benzene had given, with the same charcoal as that of Fig. 4, an isotherm from which a very satisfactory straight plot could be derived for lg α (Fig. 8), the slope of the straight line being, however, markedly less steep, this being in good agreement with the fact that the departure of this system from ideality is far less pronounced.

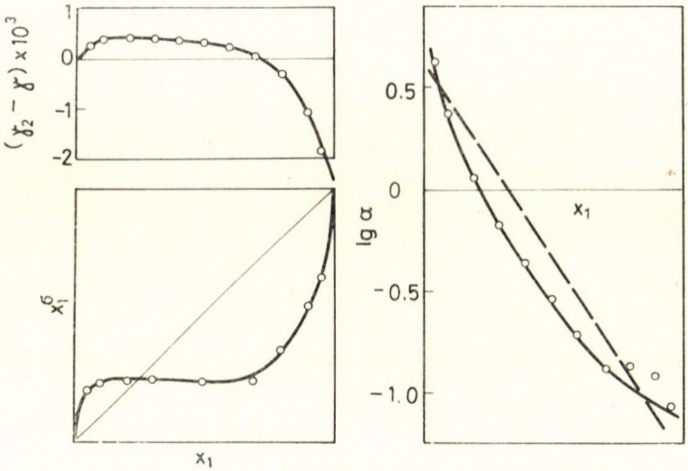

Fig. 7. Adsorption of methanol—benzene on charcoal, 720 m^2/g [5]

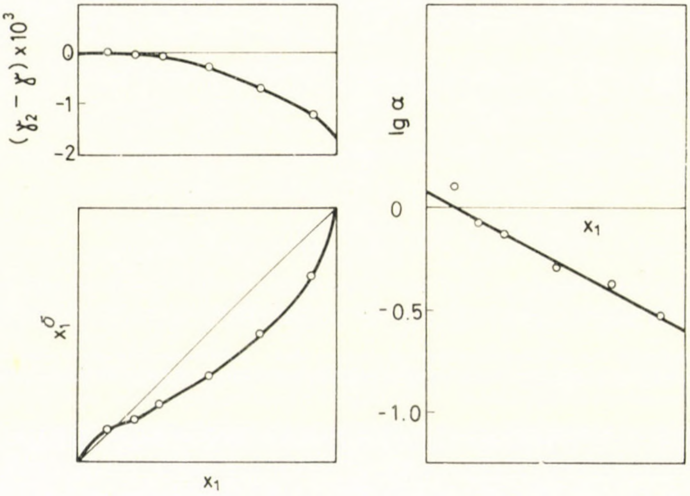

Fig. 8. Adsorption of methylacetate—benzene on charcoal, 615 m^2/g [6]

In the systems quoted so far, one of the components was polar, while the other one (benzene) is, if not polar, but easily polarisable. It is of interest to examine the situation arising when benzene is coupled with an apolar and scarcely polarisable liquid, such as *e.g.* cyclohexane. Although this system is far enough from behaving ideally, not more than a tendency of a linear dependence of lg α on x_1 can be detected, as illustrated by Figs 9—12. Three of the shown curves are decidedly sigmoidal, and their average slopes are markedly different. This behaviour shows clearly that in this case the factor

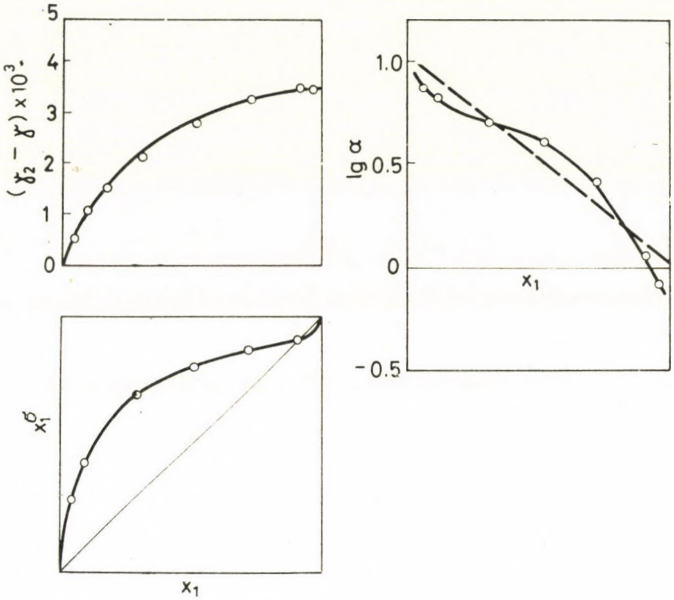

Fig. 9. Adsorption of benzene—cyclohexane on charcoal, 615 m^2/g [6]

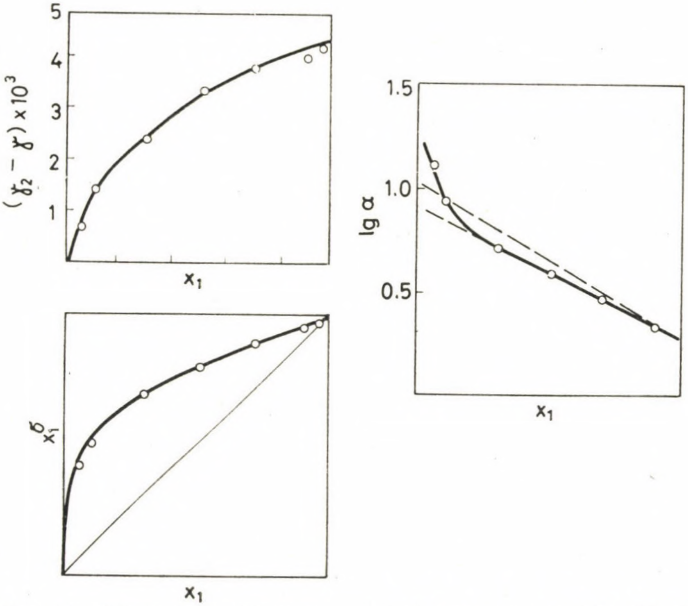

Fig. 10. Adsorption of benzene—cyclohexane on graphite, 88 m^2/g [6]

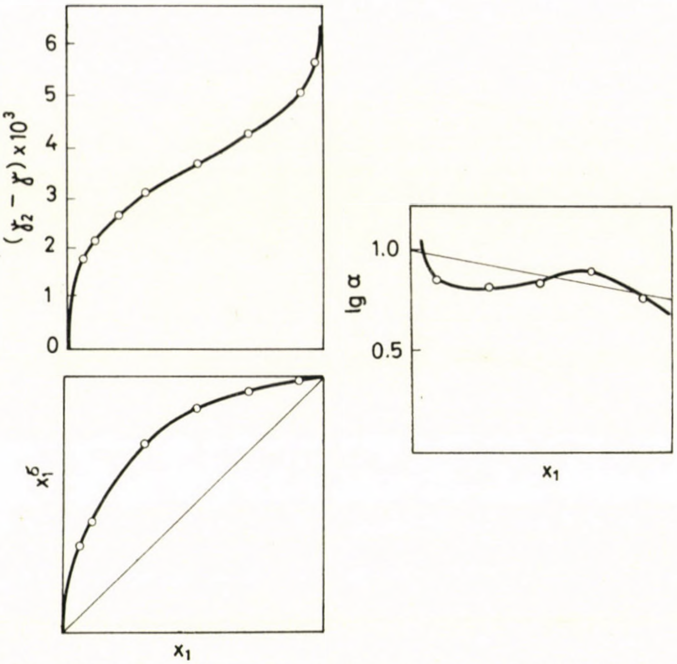

Fig. 11. Adsorption of benzene—cyclohexane on carbon black, 80 m²/g [6]

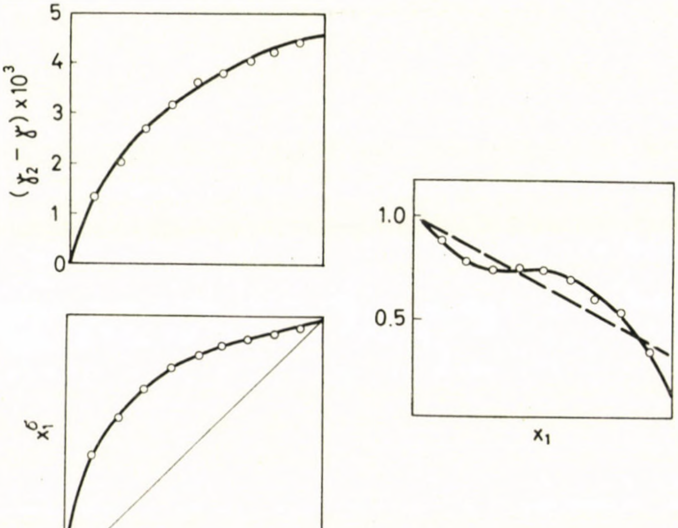

Fig. 12. Adsorption of benzene—cyclohexane on alumina gel, 274 m²/g [7]

B in Eq. (16) is not the only main decisive one, but that the factor A is more or less far from being constant and that in addition this latter term has a strong influence on the average slope of the curve. In the case of carbon black (Fig. 11), where the variation of the surface free energy is not only greater but also of a character different from that in the other systems, the term A seems to have even a compensating effect, with the result that α does not more than oscillate around an almost constant value.

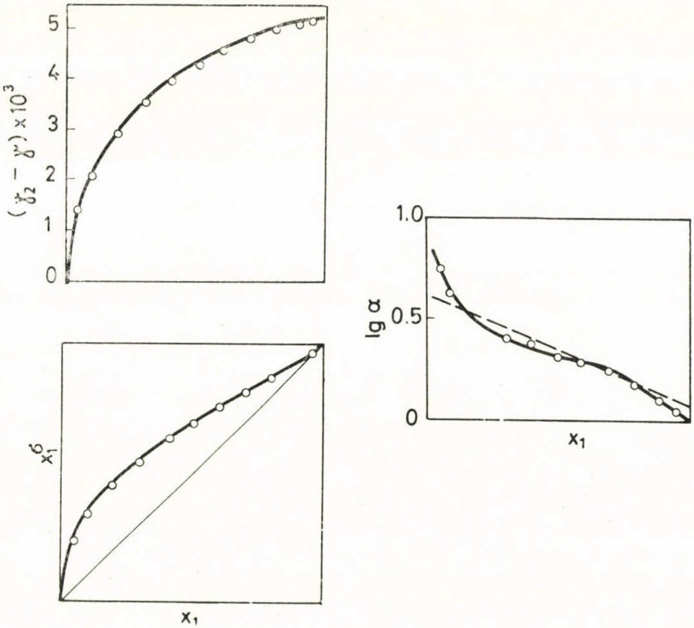

Fig. 13. Adsorption of pyridine—ethanol on charcoal, 615 m^2/g [6]

Of further interest are systems with liquid mixtures behaving ideally in the thermodynamic sense, *i.e.* characterized by activity coefficients practically not different from unity. From the energetic point of view, such mixtures satisfy the relation:

$$\varepsilon_{11} - 2\,\varepsilon_{12} + \varepsilon_{22} \approx 0 \tag{20}$$

so that the factor B should be expected to be zero, provided assumption (17) is valid. Figs 13 and 14 show the separations obtained in the systems pyridine—ethanol and 1,2-dichloroethane—benzene, respectively, with the same kind of charcoal of 615 m^2/g which figured already in some of the previous examples. Evidently, lg α is far from being constant so that the assumption $\beta_1 = \beta_2$ does not seem to be valid, while the linearity postulated in our fundamental equa-

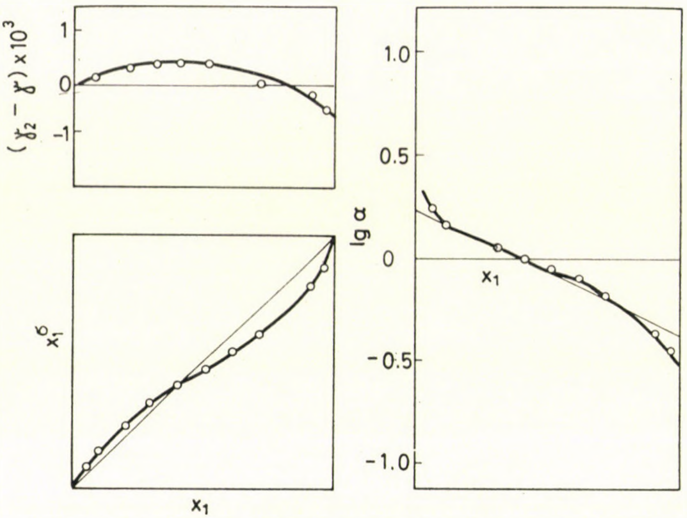

Fig. 14. Adsorption of 1,2-dichloroethane—benzene on charcoal, 615 m^2/g [6]

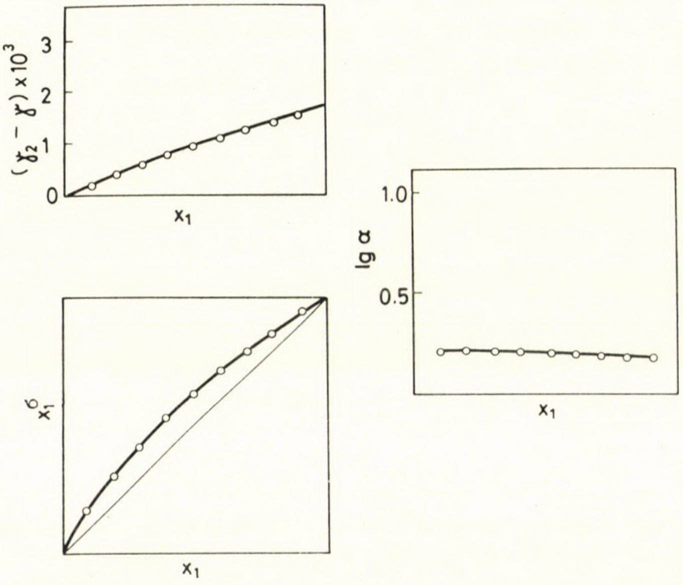

Fig. 15. Adsorption of 1,2-dichloroethane—benzene on silica gel, 580 m^2/g [7]

tion is approximately fulfilled (except at the two ends of the composition intervals where, however, experimental determinations are always much less exact). Independent of any theoretical interpretation, these examples are instructive by demonstrating that ideal behaviour of a mixture is by no means a guarantee for adsorption being "ideal", in the sense of the thermodynamic theory of the monolayer, *i.e.* for the surface activity coefficients being equal with unity. Figs 15 and 16 show, however, that there are cases, in which this latter claim is fulfilled: the separation factor proved to remain practically constant in the case of mixtures of 1,2-dichloroethane and benzene, on silica and alumina gel, respectively. Within the frame of our theory, this result may be explained by the compensating effect of term A, as mentioned previously.

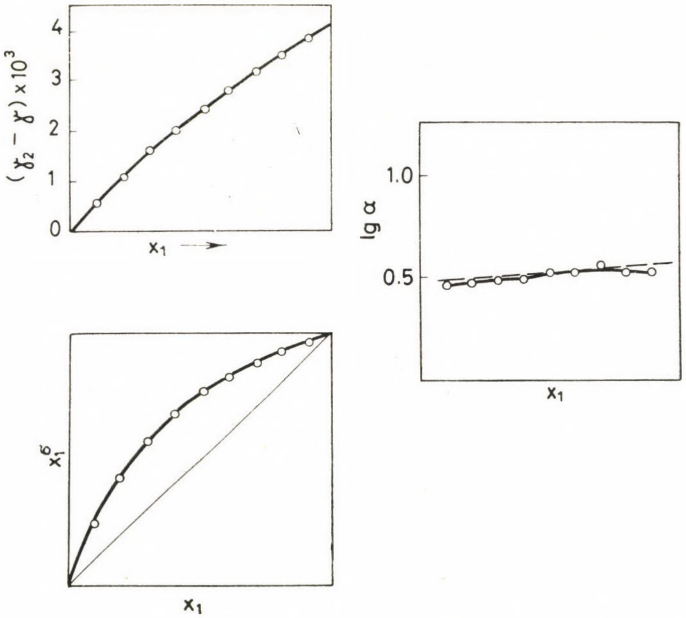

Fig. 16. Adsorption of 1,2-dichloroethane—benzene on alumina gel, 274 m^2/g [7]

The theory outlined in this paper is certainly far from being quantitatively correct, and we are aware that there is not much more to be hoped for as long as we do not dispose of a more detailed knowledge about the intervening molecular interactions. Within the frame of the theory, the type of isotherm to be met with, *i.e.* preferential adsorption of the same component throughout or appearance of an adsorption azeotrope, depends on the relative magnitudes of A and B, respectively, which occur in the fundamental Eq. (16). The examples shown in the figures prove that the approximate linearity of lg α as a function of the composition may be fulfilled irrespective of the actual type of the isotherm, and we think that it is just this common feature which may be of interest and which has not been noticed until now.

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STEREOCHEMICAL STUDIES, IV* QUATERNIZATION OF 1,2-DISUBSTITUTED 1,2,3,4-TETRAHYDROISOQUINOLINES, II*

QUATERNIZATION OF 1-PHENYL-, 1-ISOPROPYL- AND 1-(3',4'-DIMETHOXYBENZYL)-2-ALKYL-6,7-DIMETHOXY-1,2,3,4-TETRAHYDROISOQUINOLINES AND EXAMINATION OF THE STEREOSELECTIVITY OF THE QUATERNIZATION REACTION

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Several 1,2-disubstituted-6,7-dimethoxy-3,4-dihydro- and 1,2,3,4-tetrahydroisoquinoline derivatives were prepared. The stereoselectivity of the quaternization reactions of 1-substituted-2-methyl-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinolines (where the substituent in the 1-position was isopropyl, phenyl or 3,4-dimethoxybenzyl) with ethyl and benzyl iodides, as well as of the corresponding 2-ethyl and 2-benzyl derivatives with methyl iodide, were examined. It was demonstrated by means of proton resonance spectroscopic and chromatographic analyses, and by fractional crystallization of the crude products that quaternizations of N-ethyl and N-benzyl bases with methyl iodide, as well as of the N-methyl bases with ethyl iodide took place with only moderate selectivity. On the contrary, the quaternization of N-methyl bases with benzyl iodide afforded, within the limits of proton resonance spectroscopic evaluation (5%), only one quaternary product. The main component of the equilibration of isomeric N-benzyl quaternary salts in chloroform solution is identical with the product obtained in the quaternization of N-alkyl bases with benzyl iodide.

In our previous publication [1] the quaternization reaction of 1-methyl-2-alkyl-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline bases was reported. It was shown by means of proton resonance spectroscopic analysis and by the preparative work up of the crude products that both "direct" and "reverse" quaternizations of the examined tertiary bases proceeded with moderate stereoselectivity. On the contrary, full stereoselectivity was found in the quaternization reaction of 1,2-dimethyl-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline (carnegine) with benzyl iodide, at least within the limits of proton resonance spectroscopic evaluation, while quaternization of 1-methyl-2-benzyl-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline with methyl iodide resulted in a practically 1 : 1 mixture of the two isomeric quaternary salts. In the examined 1-methyl-tetrahydroisoquinoline series and in the case of methyl, ethyl, *n*-propyl and *n*-butyl substituents attached to the nitrogen atom, "direct" quaternization (N-methyl base + alkyl iodide) proved to be always more selective than "reverse" quaternization (N-alkyl base + methyl iodide). In these reaction series the main products of "direct" and "reverse" quaterni-

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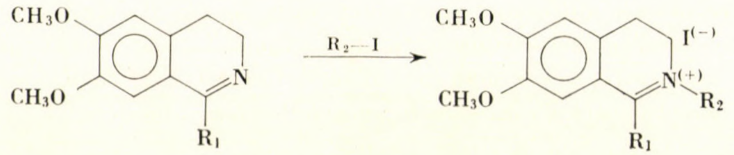
* Parts III and I: Bernáth, G., Koczka, K., Kóbor, J., Radics, L., Kajtár, M.: Acta Chim. Acad. Sci. Hung. **55**, 331 (1968).

zations were always different quaternary salts being diastereomeric to one another, but the stereoselectivity of the quaternization reaction of the N-alkyl derivatives was always lower than that observed in the reaction of the N-methyl base with benzyl iodide. From the changes in the dependence of stereoselectivity upon the relative spatial requirements of the substituents attached to the tertiary nitrogen atom, and those entering in the quaternization reaction, moreover on the basis of proton resonance spectra of the diastereomeric quaternary salts, assumptions have been made concerning the steric course of quaternization, as well as the configuration of the quaternary salts obtained.

The experiments have been extended to the quaternization of tertiary tetrahydroisoquinoline bases containing rather bulky substituents attached to the C_1 carbon atom. The purpose of these experiments was a study of the effect of substituents upon the stereoselectivity of quaternization, and the determination of the configuration of the diastereomeric quaternary salts obtained, as well as examination of the conformational relationships of 1,2-disubstituted-1,2,3,4-tetrahydroisoquinoline derivatives. Namely, it appeared evident that the steric course of the quaternization reaction of 1,2-disubstituted tetrahydroisoquinoline derivatives is subjected to the influence of the substituents attached to the C_1 and nitrogen atoms, and of the entering alkyl group. It was assumed that an interpretation of the courses of the reactions accomplished with a systematic variation of the relative space requirements of these substituents would afford data concerning the conformational relations of the 1,2,3,4-tetrahydroisoquinoline skeleton, which had been little studied earlier from a conformational point of view [2–4].

In the present communication the first part of our investigations, the quaternization of 6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline tertiary bases (**IIId—l**) containing phenyl, isopropyl, or 3,4-dimethoxybenzyl groups attached to the C_1 carbon atom, is reported. An interpretation of the stereoselectivity data to be shown below, as well as our further results concerning the steric structures of the stereoisomeric quaternary salts will be described in detail in our next publication. In the "direct" and "reverse" quaternization processes the methyl, ethyl and benzyl groups were varied.

Several procedures have been tried in the course of preparation of 1,2-disubstituted tetrahydroisoquinoline bases (**IIIa—l**). In connection with the processes listed in Figs 1 and 2, and concerning the data given in detail in the experimental part, the following general remarks may be made. The synthesis of the isoquinoline skeleton followed the generally applied BISCHLER–NAPIERALSKI [5] procedure. The starting material was homoveratrylamine, except in the case of the derivative containing a 3,4-dimethoxybenzyl moiety in the 1-position, when 3,4-dihydropapaverine was accessible. The cyclodehydratation of the N-acyl-homoveratrylamines was effected with phosphorus oxychloride in chloroform [1, 6, 7].



I a—d

a) $R_1 = H$
b) $R_1 = (CH_3)_2CH—$
c) $R_1 = C_6H_5—$
d) $R_1 = 3,4\text{-}(CH_3O)_2C_6H_3—CH_2—$

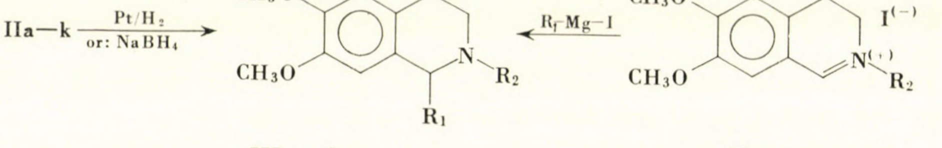
II a—k

a) $R_1 = H$, $R_2 = CH_3—$
b) $R_1 = H$, $R_2 = CH_3—CH_2—$
c) $R_1 = H$, $R_2 = C_6H_5—CH_2—$
d) $R_1 = (CH_3)_2CH—$, $R_2 = CH_3—$
e) $R_1 = (CH_3)_2CH—$, $R_2 = CH_3—CH_2—$
f) $R_1 = C_6H_5—$, $R_2 = CH_3—$
g) $R_1 = C_6H_5—$, $R_2 = CH_3—CH_2—$
h) $R_1 = C_6H_5—$, $R_2 = C_6H_5—CH_2—$
i) $R_1 = 3,4\text{-}(CH_3O)_2C_6H_3—CH_2—$, $R_2 = CH_3—$
j) $R_1 = 3,4\text{-}(CH_3O)_2C_6H_3—CH_2—$, $R_2 = CH_3—CH_2—$
k) $R_1 = 3,4\text{-}(CH_3O)_2C_6H_3—CH_2—$, -
$R_2 = C_6H_5—CH_2—$

Fig. 1

The 3,4-dihydroisoquinoline bases (**Ia—Id**) obtained this way were treated with the corresponding alkyl iodides (benzy iodide) to afford the 6,7-dimethoxy-3,4-dihydroisoquinolinium iodides (**IIa—k**), which were then reduced in the presence of Adams (PtO_2) catalyst at room temperature and atmospheric pressure. In a few cases the reduction of the above quaternary 3,4-dihydroisoquinolinium salts (**IIc, IIh—k**) was also accomplished with sodium borohydride [8, 9], and the products obtained by these two independent methods were identical and formed in nearly equal yields.

The synthesis of 1-isopropyl-2-alkyl- and 1-isopropyl-2-benzyl-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline derivatives was also achieved in



III a—l

a) $R_1 = H$, $R_2 = CH_3—$
b) $R_1 = H$, $R_2 = CH_3—CH_2—$
c) $R_1 = H$, $R_2 = C_6H_5—CH_2—$
d) $R_1 = (CH_3)_2CH—$, $R_2 = CH_3—$
e) $R_1 = (CH_3)_2CH—$, $R_2 = CH_3—CH_2—$
f) $R_1 = C_6H_5—$, $R_2 = CH_3—$
g) $R_1 = C_6H_5—$, $R_2 = CH_3—CH_2—$
h) $R_1 = C_6H_5—$, $R_2 = C_6H_5—CH_2—$
i) $R_1 = 3,4\text{-}(CH_3O)_2C_6H_3—CH_2—$, $R_2 = CH_3—$
j) $R_1 = 3,4\text{-}(CH_3O)_2C_6H_3—CH_2—$, $R_2 = CH_3—CH_2—$
k) $R_1 = 3,4\text{-}(CH_3O)_2C_6H_3—CH_2—$, $R_2 = C_6H_5—CH_2—$
l) $R_1 = (CH_3)_2CH—$, $R_2 = C_6H_5—CH_2—$

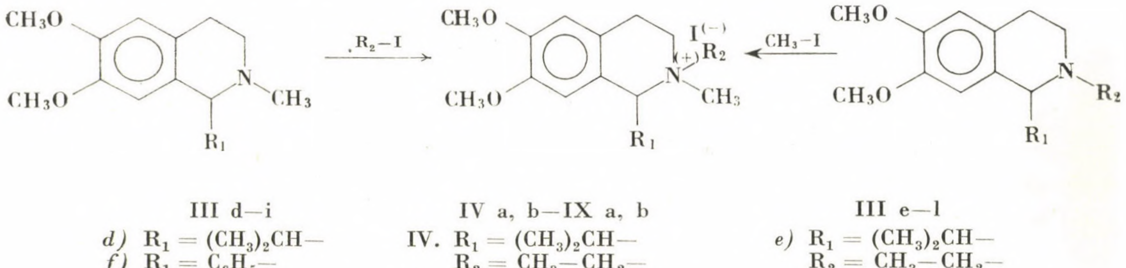
II a—c

a) $R_2 = CH_3—$
b) $R_2 = CH_3—CH_2—$
c) $R_2 = C_6H_5—CH_2—$

Fig. 2

another way. It is known [10] that the azomethine group of quaternary 3,4-dihydroisoquinolinium salts reacts with Grignard reagents. Thus the reaction of N-substituted-6,7-dimethoxy-3,4-dihydroisoquinolinium iodide (**IIa—c**) and isopropyl magnesium iodide gave directly the corresponding 1-isopropyl-tetrahydroisoquinoline derivative (**IIId, e, l**). The products obtained by Grignard-addition and by catalytic reduction of the corresponding N-substituted-1-isopropyl-3,4-dihydro-6,7-dimethoxyisoquinolinium salts proved to be identical both on the basis of melting points and chromatographic behaviour.

The "direct" ($R_2 = CH_3—CH_2$, or $C_6H_5—CH_2$) and "reverse" (methyl iodide) quaternizations of the 1,2-disubstituted-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline bases (**IIId—l**), obtained as outlined above, were effected with an excess of the appropriate alkyl iodide (benzyl iodide) in acetone at room temperature (Fig. 3). The time necessary for the completion of the quaternization reaction varied from a few minutes up to 1—2 days. In a few cases, for the sake of comparison, the alkylations were also accomplished in methanol, ethanol, or acetone at reflux temperature. According to proton resonance spectroscopic data, the stereoselectivity of the quaternization reaction was not affected fundamentally by these varying experimental conditions.



III d—i

d) $R_1 = (CH_3)_2CH—$
f) $R_1 = C_6H_5—$
i) $R_1 =$ $3,4\text{-}(CH_3O)_2C_6H_3—CH_2$

IV a, b—IX a, b

IV. $R_1 = (CH_3)_2CH—$
$R_2 = CH_3—CH_2—$
V. $R_1 = (CH_3)_2CH—$
$R_2 = C_6H_5—CH_2—$
VI. $R_1 = C_6H_5—$
$R_2 = CH_3—CH_2—$
VII. $R_1 = C_6H_5—$
$R_2 = C_6H_5—CH_2—$
VIII. $R_1 =$ $3,4\text{-}(CH_3O)_2C_6H_3—CH_2$
$R_2 = CH_3—CH_2—$
IX. $R_1 =$ $3,4\text{-}(CH_3O)_2C_6H_3—CH_2$
$R_2 = C_6H_5—CH_2—$

III e—l

e) $R_1 = (CH_3)_2CH—$
$R_2 = CH_3—CH_2—$
g) $R_1 = C_6H_5—$
$R_2 = CH_3—CH_2—$
h) $R_1 = C_6H_5—$
$R_2 = C_6H_5—CH_2—$
j) $R_1 =$ $3,4\text{-}(CH_3O)_2C_6H_3—CH_2$
$R_2 = CH_3—CH_2—$
k) $R_1 =$ $3,4\text{-}(CH_3O)_2C_6H_3—CH_2$
$R_2 = C_6H_5—CH_2—$
l) $R_1 = (CH_3)_2CH—$
$R_2 = C_6H_5—CH_2—$

Fig. 3. Within the isomeric pairs, designation *a* indicates the diastereomeric salt formed as the main product in the "direct" quaternization reaction, and *b* the other diastereomeric salt formed as a by-product, while in case of the "reverse" quaternization *b* indicates the main product

In accordance with our earlier observations [1], attempted quaternizations with secondary and tertiary alkyl iodides did not lead to the desired result. Attempted quaternization with tertiary butyl iodide yielded the hydriodides of the tertiary bases as the only product, while in the case of isopropyl iodide the product consisted of a mixture of the N-isopropyl quaternary salt and the hydriodide of the tertiary base.

The stereoselectivity of the quaternization reaction of the examined 1,2-disubstituted tetrahydroisoquinoline bases was determined by means of proton resonance spectroscopic analysis of the crude reaction product. The separation of the pure isomeric quaternary ammonium salts was also attempted by fractional crystallization of the reaction products. Conclusions were drawn concerning the steric structures of the diastereomeric quaternary salts from proton resonance spectroscopic, isomerization and chromatographic data.

As we have already pointed out [1], the stereochemistry of the quaternization reaction of 1,2-disubstituted-1,2,3,4-tetrahydroisoquinoline derivatives had only been studied [11—13] in a few classical investigations, which are difficult to evaluate. Of the 1,2-disubstituted tetrahydroisoquinolines examined by us, *e.g.* the quaternary salts of 1-(3',4'-dimethoxybenzyl)-2-methyl-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline (*dl*-laudanosine) (**IIIi**) and a few related derivatives are known [14—16]. However, the stereoisomeric quaternary salts, which evidently formed together, were not separated or subjected to any stereochemical investigation. PICTET [17] prepared laudanosine ethiodide, but no reference was made to the formation of isomeric salts. We found that laudanosine ethiodide (m.p. 202—3 °C) described by PICTET was not stereohomogeneous, but the main product laudanosine ethiodide (**VIIIa**) was contaminated with 2-ethyltetrahydropapaverine methiodide (**VIIIb**).

The stereochemically bi-directional character of the quaternization reaction could be demonstrated in the majority of cases simply by fractional crystallization of the crude reaction products [see Experimental, quaternization of laudanosine (**IIIi**) and 2-ethyltetrahydropapaverine (**IIIj**)]. In the case of 1-phenyl- and 1-(3',4'-dimethoxybenzyl)-tetrahydroisoquinoline derivatives, the diastereomeric salts were successfully isolated from the reaction products (**VIa** + **VIb** and **VIIIa** + **VIIIb**) of the "direct" and "reverse" quaternizations effected by varying the methyl and ethyl groups attached to the nitrogen. In all cases, the main product of the "direct" quaternization reaction was the by-product in the "reverse" reaction and *vica versa.* With the 1-isopropyl derivative, when the above groups at the nitrogen were varied, repeated crystallization of the crude reaction product (**IVa** + **IVb**) resulted in the enrichment of the same diastereomeric salt, 1-isopropyl-2-ethyl-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline methiodide (**IVb**), due to its special solubility and tendency for crystallization, while the other diastereomeric salt (**IVa**) could be obtained from the mother liquor only, and it was contaminated with **IVb.**

When methyl and benzyl groups were varied at the nitrogen atom, only one of the diastereomeric salts (**Va, VIIa, IXa**) could be separated from the reaction products of the "direct" quaternizations of each 1-substituted tetrahydroisoquinoline derivative examined. Fractional crystallization of the quaternization product (**IXa** + **IXb**) of 1-(3',4'-dimethoxybenzyl)-2-benzyl-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline with methyl iodide gave the main product (**IXa**) of the "direct" reaction. The preparative work up of the products of "direct" and "reverse" quaternization reactions are illustrated in detail on the examples of laudanosine (**IIIi**) and 2-ethyltetrahydropapaverine (**IIIj**). The quaternization reactions examined, and the physical constants and analysis data of the isolated quaternary salts are summarized in Table IV.

Though no satisfactory results have been obtained previously [18], we attempted the separation of the diastereomeric salts and the determination of the stereoselectivity of the reaction by chromatographic technique. Though in the case of salt-pairs containing methyl and ethyl groups at the nitrogen atom there were some slight differences in the R_f values of the pure diastereomers applied separately beside one another, this proved insufficient for a separation of mixtures, according to experiments in a great number of paper and thin-layer chromatographic systems. On the contrary, easily observable characteristic differences appear in the paper and, even more, in the thin-layer chromatography of the isomeric quaternary iodides containing methyl and benzyl groups (Figs 4 and 5).

Each examined iodide salt, obtained by the quaternization of C_1-substituted tetrahydroisoquinoline tertiary N-methyl bases with benzyl iodide, proved to be chromatographically homogeneous even in the crude state, *i.e.* prior to purification. On the contrary, chromatographic analysis of the crude reaction products from the quaternization with methyl iodide of 2-benzyl-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline bases containing the same substituent at the C_1-carbon atom ("reverse" quaternization) showed in each case the presence of two distinctly separating spots of comparable intensity, with differences in the R_f values of about 0.05—0.07. Of the two spots, the one with the lower R_f value had the same R_f as the product of the "direct" quaternization reaction. Repeated recrystallizations of the crude product of the "reverse" quaternization reaction gave the main product of the reaction, with the exception of the 1-methyl- and 1-(3',4'-dimethoxybenzyl) derivatives, where fractionation failed; these main products proved to be homogeneous, and their R_f values were higher by 0.05—0.07 than those of the corresponding quaternary products obtained in the "direct" quaternization reaction.

The above procedure represents the first successful paper chromatographic separation of diastereomeric quaternary ammonium salts, and apparently it is a suitable method for the determination of the degree of stereoselectivity in the quaternization reactions of tertiary amines.

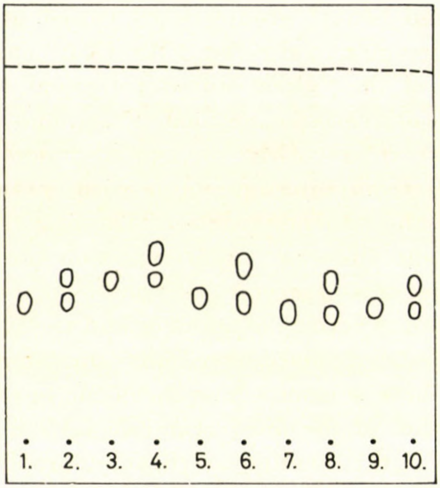


Fig. 4. Thin-layer chromatogram of the crude products of quaternizations (*cf.* Fig. 2) of 1-substituted-2-methyl-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinolines with benzyl iodide, and 1-substituted-2-benzyl-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinolines with methyl iodide, respectively

1.: **IIId** + $C_6H_5CH_2I$; 2.: **IIIl** + CH_3I; 3.: **IIIf** + $C_6H_5CH_2I$; 4.: **IIIh** + CH_3I; 5.: **IIIi** + $C_6H_5CH_2I$; 6.: **IIIk** + CH_3I; 7.: 1,2-dimethyl-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline + $C_6H_5CH_2I$ (**X**) [1]; 8.: 1-methyl-2-benzyl-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline + CH_3 (**X**) [1]; 9.: 1-ethyl-2-methyl-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline + $C_6H_5CH_2I$ (**XI**)*] 10.: 1-ethyl-2-benzyl-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline + CH_3I (**XI**)*.

Method: thin-layer chromatography according to STAHL [19]; adsorbent: silicagel; solvent: *n*-butanol–water–acetic acid (7 : 2 : 1); detection: in iodine vapour, or with Dragendorff reagent [20]

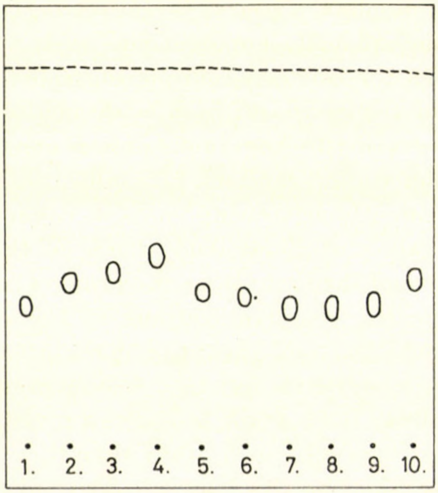


Fig. 5. Thin-layer chromatogram of diastereomeric 1-substituted-2-methyl-2-benzyl-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinolinium iodides separated by fractional crystallization.

1.: **Va**; 2.: **Vb**; 3.: **VIIa**; 4.: **VIIb**; 5.: **IXa**; 6.: **IXb**; 7.: **Xa**; 8.: **Xb**; 9.: **XIa**; 10.: **XIb**. Method: the same as with Fig. 4

* Results to be published later.

Evaluation of these preparative and chromatographic findings led to the conclusion that the reaction of the examined 1-substituted-2-methyl-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline bases with benzyl iodide gives rise to practically one quaternary salt, while both the "direct" and "reverse" quaternizations of the other 1,2-disubstituted-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline bases studied occur only with moderate stereoselectivity. In accordance with experiments of similar character carried out with other substrates [18, 21, 22], the main product of "reverse" quaternization was identical with the diastereomeric salt formed in inferior amount in the "direct" quaternization process.

Though these examinations do not yield exact information about the actual steric structures of the diastereomeric salts, some stereochemical conclusions may be drawn from the chromatographic behaviour of the diastereomeric 1-substituted tetrahydroisoquinolinium iodide derivatives containing a methyl or benzyl group attached to the nitrogen. Namely, the fact that the almost homogeneous main product (isomer *a*) of the benzylation of each 1-substituted-2-methyl-1,2,3,4-tetrahydroisoquinoline ("direct" quaternization) examined by us has lower R_f values than the corresponding diastereomeric salts (isomers *b*) isolated from the product of the "reverse" quaternization reaction, leads to the conclusion that all isomers *a* correspond to one of the two possible steric structures and similarly, isomers *b* to the other.

In order to obtain further information about the steric structures of these derivatives, the equilibration reaction of the diastereomeric salts containing methyl and benzyl groups attached to the nitrogen was carried out, the reaction being characteristic of quaternary ammonium salts containing a benzyl substitutent [21]. The isomer-equilibrium was established in boiling chloroform solution of stereohomogeneous salt pairs containing isopropyl and phenyl substituents at C_1 (**Va, Vb** and **VIIa, VIIb**). It was found that those diastereomeric salts (**Va** and **VIIa**) were prevailing which had been the main products of the "direct" quaternization reaction. The isomerization experiments thus revealed a difference in the stability of isomers *a* and *b*. On the basis of general stability considerations, the greater stability of the diastereomeric salts *a* supports the assumption that in these derivatives the relative spatial orientation of the substituent attached to C_1 and of the larger group (*e.g.* benzyl) linked to the nitrogen atom is *trans*. Hence the direction *trans* to the substituent at C_1 seems to be preferred for the quaternizing agent. These stereochemical conclusions of the chromatographic and isomerization studies are also supported by the proton resonance spectroscopic analysis of the diastereomeric salts.

For an exact quantitative determination of the stereoselectivity of the examined quaternization reactions, and in order to elucidate more exactly the configurational and conformational relationships in the diastereomeric salt-pairs obtained, the crude products of both the "direct" and "reverse" quaternization reactions, as well as the quaternary salts obtained therefrom by means of fractional crystallization were subjected to proton resonance spectroscopic analysis. The distribution of the diastereomers in the crude products and the assignment of the relative configurations to the diastereomers on the basis of proton resonance spectroscopy are shown in Table III; the purity and steric structures of the purified products are given in Table IV.

The proton resonance spectroscopic data of the diastereomeric salts described in the present communication, a detailed analysis of the spectra, and a discussion of the specific properties appearing in the quaternization reaction of 1,2-disubstituted-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline bases carried out so far will constitute the subject matter of our next publication [24].

Experimental

1. Preparation of 1-substituted-3,4-dihydro-6,7-dimethoxyisoquinoline derivatives (Ia – d)

The 1-substituted-3,4-dihydro-6,7-dimethoxyisoquinoline derivatives (**Ia – d**) were prepared from the corresponding N-acyl-homoveratrylamine with phosphorus oxychloride in chloroform [1]. The dihydroisoquinoline base was purified by distillation in vacuum, or by crystallization.

(a) **6,7-Dimethoxy-3,4-dihydroisoquinoline (Ia).** It was prepared from homoveratrylamine and 92% formic acid in 80% yield, b.p. 143 °C at 1.5–2 mm. Pale yellow oil. The picrate had m.p. 203–205 °C (lit. [25] m.p. 201–203 °C).

(b) **1-Isopropyl-6,7-dimethoxy-3,4-dihydroisoquinoline (Ib).** It was obtained from homoveratrylamine and isobutyric acid in 84% yield, as a pale yellow oil. The hydrochloride had m.p. 192—193 °C (from ethanol).

$C_{14}H_{20}NO_2Cl$ (269.76). Calcd. C 63.33; H 7.47; Cl^- 13.14. Found: C 63.56; H 7.20; Cl^- 13.42%.

The methiodide had m.p. 199—201 °C (lit. [9] m.p. 200—202 °C).

(c) **1-Phenyl-6,7-dimethoxy-3,4-dihydroisoquinoline (Ic).** It was obtained by Schotten—Baumann acylation of homoveratrylamine with benzoyl chloride and subsequent ring closure as above, in 84% overall yield. M.p. 121–122 °C (lit. [26] m.p. 120.5–121.5 °C).

2. 2-Alkyl-3,4-dihydro-6,7-dimethoxyisoquinolinium iodide derivatives (IIa – c)

(a) **2-Benzyl-6,7-dimethoxy-3,4-dihydroisoquinolinium iodide (IIc).** A solution of 6 g (0.0313 mole) of 6,7-dimethoxy-3,4-dihydroisoquinoline in 30 ml of benzene was refluxed with 10 g (0.0458 mole) of benzyl iodide for 30 min. The crystals which separated were collected and washed with benzene to obtain 11.1 g (86.4%) of a pale yellow powder. Repeated crystallization from ethanol (70 ml) gave pale yellow prisms, m.p. 180 °C.

$C_{18}H_{20}NO_2I$ (409.22). Calcd. C 52.82; H 4.92; I^- 31.00. Found: C 52.89; H 4.98; I^- 31.24%.

The 2-alkyl-6,7-dimethoxy-3,4-dihydroisoquinolinium iodides (**IIa, IIb**) were prepared analogously with the corresponding alkyl iodides.

(b) **2-Methyl-6,7-dimethoxy-3,4-dihydroisoquinolinium iodide (IIa).** 9.55 g of base **Ia** afforded 15.6 g (94%) of the product as orange crystals, m.p. 201–203 °C (from methanol) (lit. [27] m.p. 202 °C).

(c) **2-Ethyl-6,7-dimethoxy-3,4-dihydroisoquinolinium iodide (IIb).** The yield was 93%. Yellow crystals, m.p. 183—184 °C (from ethanol) (lit. [28] m.p. 186.5 °C).

3. 1-Substituted-2-alkyl-6,7-dimethoxy-3,4-dihydroisoquinolinium iodides (IId – k)

These derivatives were prepared from the corresponding tertiary dihydroisoquinoline bases (**Ib – d**) with excess quaternizing alkyl iodide (benzyl iodide) at the boiling temperature

Table I

Yields, melting points and analyses of 1,2-disubstituted-6,7-dimethoxy-3,4-dihydroisoquinoline iodides (IId—k)

Compound	R_1	R_2	Solvent, reaction time, yield	M.p., °C (solvent)	Empirical formula (Molecular weight)	Analysis, Calcd./Found			Remarks
						C	H	I^-	
IId	$(CH_3)_2CH$	CH_3	benzene, 5 hrs, 92%	199—201 (methanol)	$C_{15}H_{22}NO_2I$ (375.24)	48.00 47.73	5.91 5.78	33.81 33.40	a)
IIe	$(CH_3)_2CH$	CH_2CH_2	ethanol, 12 hrs, 94%	183—185 (ethanol)	$C_{16}H_{24}NO_2I$ (389.26)	49.36 48.94	6.21 5.84	32.60 32.92	
IIf	C_6H_5	CH_3	acetone, 2 hrs, 98%	194—195 (ethanol)	$C_{18}H_{20}NO_2I$ (409.25)	52.69 52.82	5.06 4.92	31.23 31.00	b)
IIg	C_6H_5	CH_3CH_2	benzene, 8 hrs, 96%	196—197 (ethanol)	$C_{19}H_{22}NO_2I$ (423.27)	53.91 53.56	5.39 5.45	29.98 29.88	
IIh	C_6H_5	$C_6H_5CH_2$	benzene, 30 min, 98%	161—163 (acetone)	$C_{24}H_{24}NO_2I$ (485.34)	59.38 59.75	4.98 5.22	26.14 25.83	
IIi	$3,4\text{-}(CH_3O)_2C_6H_3CH_2$	CH_3	benzene, 30 min, 90%	185—186 (ethanol)	$C_{21}H_{26}NO_4I$ (483.33)	52.18 52.29	5.42 5.00	26.25 26.18	
IIj	$3,4\text{-}(CH_3O)_2C_6H_3CH_2$	CH_3CH_2	benzene, 2 hrs, 78%	177—178 (ethanol)	$C_{22}H_{28}NO_4I$ (497.35)	53.12 53.37	5.67 5.84	25.51 25.25	
IIk	$3,4\text{-}(CH_3O)_2C_6H_3CH_2$	$C_6H_5CH_2$	acetone, 2 hrs, 88%	184—185 (ethanol)	$C_{27}H_{30}NO_4I$ (559.42)	57.96 57.61	5.40 5.26	22.68 22.89	

Remarks: a) Lit. [9] m.p.: 200—202 °C;
b) Lit. [23] m.p.: 188—190 °C.

Table II

Melting points and analyses of 1,2-disubstituted-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinolines[a)]

Compound	R_1	R_2	M.p. °C (solvent)	Empirical formula (Molecular weight)	Analysis Calcd. Found			Remarks
					C	H	I⁻	
IIIa.HI	H	CH_3	162—163 (ethanol)	$C_{12}H_{18}NO_2I$ (335.19)	43.00 43.08	5.41 5.48	37.85 37.80	b)
IIIb.HI	H	CH_3CH_2	169—171 (ethanol)	$C_{13}H_{20}NO_2I$ (349.20)	44.71 44.52	5.77 5.65	36.34 36.55	
IIIc.HI	H	$C_6H_5CH_2$	216—217 (ethanol)	$C_{18}H_{22}NO_2I$ (411.27)	52.56 52.88	5.39 5.33	30.85 31.02	c)
IIId.HI	$(CH_3)_2CH$	CH_3	220—221 (methanol)	$C_{15}H_{24}NO_2I$ (377.25)	47.75 47.54	6.41 6.35	33.63 33.87	d), e)
IIIe.HCl	$(CH_3)_2CH$	CH_3CH_2	182—183 (ethanol–ether)	$C_{16}H_{26}NO_2Cl$ (299.83)	64.08 63.42	8.74 8.00		f)
IIIf.HI	C_6H_5	CH_3	206—208 (ethanol)	$C_{18}H_{22}NO_2I$ (411.27)	52.56 52.92	5.39 5.57	30.85 30.70	g)
IIIg.HI	C_6H_5	CH_3CH_2	198—199 (ethanol)	$C_{19}H_{24}NO_2I$ (425.29)	53.65 53.89	5.68 5.75	29.83 29.64	h)
IIIh	C_6H_5	$C_6H_5CH_2$	double m. p. 125—126 and 131—132	$C_{24}H_{25}O_2N$ (359.47)	80.18 79.85	7.01 7.26		i)

Remarks: a) The compounds have been prepared by catalytic hydrogenation. For the experimental conditions, see 4 (*a*). b) Base **IIIa** m.p. 84—85 °C (lit. [30] m.p. 83—84 °C). Picrate, m.p. 160—161 °C (MeOH) (lit. [30, 31] m.p. 159—160 °C). c) Base **IIIc** m.p. 97 °C (ether). d) **IIId**.HCl, m.p. 215—216 °C. e) 1-Isopropyl-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline base [**III**, $R_1 = (CH_3)_2CH$; $R_2 = H$], m.p. 94—95 °C (ether); $C_{14}H_{21}NO_2$ (235.32). Calcd. C 71.45; H 8.99. Found C 71.30; H 8.71%. Hydrochloride, m.p. 247—248 °C (MeOH) (lit. [32] m.p. 243 °C). $C_{14}H_{22}NO_2Cl$ (271.78). Calcd. C 61.86; H 8.16; Cl⁻ 13.043. Found C 61.87; H 8.00; Cl⁻ 13.02%. f) Cl⁻ calcd. 11.82; found 11.90%. g) Base **IIIf**, m.p. 82—83 °C (lit. [34] m.p. 81—82 °C). h) Base **IIIg**, m.p. 76—78 °C (petroleum ether). i) N calcd. 3.89; found 3.95%.

of the solvents used. The experimental conditions, melting points and analyses of the obtained quaternary 1,2-substituted-6,7-dimethoxy-3,4-dihydroisoquinolinium iodides are summarized in Table I.

4. Preparation of 2-alkyl-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinolines (IIIa–c) and the 1-substituted derivatives (IIId—l)

(a) By catalytic reduction

The catalytic hydrogenation of 1,2-disubstituted-6,7-dimethoxy-3,4-dihydroisoquinolinium iodide homologues (**IIa–k**) was carried out in methanol solution in the presence of pre-hydrogenated Adams PtO_2 catalyst [29] at room temperature and atmospheric pressure. After the absorption of the theoretical amount of hydrogen, the reaction mixture was shaken for 30 min, filtered to remove the catalyst, and the filtrate was concentrated in vacuum until crystallization commenced. The crude tetrahydro derivative was purified by repeated recrystallizations. The yields were almost quantitative. The m.p. and analysis data of the products are summarized in Table II.

(b) By reduction with sodium borohydride

1-(3',4'-Dimethoxybenzyl)-2-methyl-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline (laudanosine) (IIIi). 11 g (0.0227 mole) of 2-methyl-3,4-dihydropapaverinium iodide (**IIi**) was dissolved in a mixture of 200 ml of methanol and 20 ml of water, 3.5 g (0.0927 mole) of sodium borohydride was added, and the mixture heated on a water bath for 15 min. After cooling, the mixture was diluted with 600 ml of water, the crystalline precipitate collected and thoroughly washed with water. The crude laudanosine (7.95 g; 97.7%) was recrystallized from methanol several times to obtain m.p. 115—116 °C (lit. [17] m.p. 115 °C).

The following derivatives were prepared analogously:

2-Ethyl-1,2,3,4-tetrahydropapaverine (IIIj). From 2-ethyl-3,4-dihydropapaverinium iodide (**IIj**) in 98% yield, m.p. 89—91 °C (from ether) (lit. [30] m.p. 89 °C).

2-Benzyl-1,2,3,4-tetrahydropapaverine (IIIk). From 2-benzyl-3,4-dihydropapaverinium iodide (**IIk**) in 95% yield. White needles (from ether), m.p. 91—92 °C.

$C_{27}H_{31}NO_4$ (433.53). Calcd. C 74.49; H 7.20; N 3.28. Found: C 74.80; H 7.20; N 3.42%.

1-Phenyl-2-methyl-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline (IIIh). From 1-phenyl-2-benzyl-6,7-dimethoxy-3,4-dihydroisoquinolinium iodide (**IIh**) in quantitative yield. White needles, showing double melting point: the substance melts first at 125—126 °C, then re-solidifies and melts again at 131—132 °C (*cf.* Table II).

$C_{24}H_{25}NO_2$ (359.45). Calcd. C 80.18; H 7.01; N 3.89. Found: C 79.85; H 7.26; N 3.95%.

1-Phenyl-2-methyl-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline (IIIf). From 1-phenyl-2-methyl-6,7-dimethoxy-3,4-dihydroisoquinolinium iodide (**IIf**) in quantitative yield, m.p. 85—86 °C (from ether). The product was identical with that obtained by catalytic hydrogenation (see Table II).

2-Benzyl-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline (IIIc). From 2-benzyl-6,7-dimethoxy-3,4-dihydroisoquinolinium iodide (**IIc**). White needles, m.p. 97 °C (from ether). The product was identical with that obtained in the catalytic hydrogenation of **IIc** (see Table II).

(c) By Grignard reaction

1-Isopropyl-2-methyl-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline (IIId). 9.9 g (0.03 mole) of thoroughly dried and finely powdered 2-methyl-6,7-dimethoxy-3,4-dihydroisoquinolinium iodide (**IIa**) was added in portions, with stirring, to 0.1 mole of isopropyl magnesium iodide in 30 ml of ether. The mixture was stirred for 90 min, and the complex was decomposed by adding a solution of ammonium chloride in ammonium hydroxide, while cooling in ice-water. The ethereal phase was separated, and the aqueous phase extracted four times with 60 ml ether each. The combined ethereal fractions were dried over anhydrous Na_2SO_4, decolorized with charcoal, and concentrated in vacuum to give 7.35 g (98.4%) of a colourless oil. The hydrochloride had m.p. 215—216 °C (from ethanol–ether).

$C_{15}H_{24}NO_2Cl$ (285.80) Calcd. C 63.03; H 8.46; Cl^- 12.40. Found: C 62.94; H 8.41; Cl^- 12.32%.

The hydriodide melted at 220—221 °C after crystallization from methanol. No depression was observed in the mixed m.p. determination with the product obtained from 1-isopropyl-2-methyl-6,7-dimethoxy-3,4-dihydroisoquinolinium iodide by catalytic hydrogenation (see Table II).

The following tetrahydroisoquinoline derivatives were synthesized analogously from the corresponding 2-alkyl-dihydroisoquinolinium salts (1 mole) and alkyl magnesium halide (3 moles):

1-Isopropyl-2-ethyl-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline (IIIe). From 2-ethyl-6,7-dimethoxy-3,4-dihydroisoquinolinium iodide (**IIb**) in 96% yield. Colourless oil, the hydrochloride melted at 182—183 °C (from methanol–ether).

$C_{16}H_{26}NO_2Cl$ (299.83). Calcd. Cl^- 11.82. Found: Cl^- 11.90%.

1-Isopropyl-2-benzyl-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline (III l). From 2-benzyl-6,7-dimethoxy-3,4-dihydroisoquinolinium iodide (**IIc**) in 98% yield. The hydrochloride had m.p. 207—208 °C (from ethanol–ether).

$C_{21}H_{27}NO_2Cl$ (361.89). Calcd. Cl^- 9.79. Found: Cl^- 9.60%.

1-Phenyl-2-methyl-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline (IIIf). From 2-methyl-6,7-dimethoxy-3,4-dihydroisoquinolinium iodide (**IIa**) with phenyl magnesium bromide in 85% yield, m.p. 82—83 °C. No melting point depression was observed with either of the products obtained by catalytic hydrogenation and sodium borohydride reduction.

5. Quaternization of 1,2-disubstituted-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline bases (IIId—l).

The quaternizations (see Table II) were carried out with 1—5 g of the corresponding base in 20% acetone, methanol or ethanol solution, with 30—50% excess of alkyl iodide (benzyl iodide), either at room temperature (1—5 days), or at the boiling temperature of the solution (1—10 hours). The reaction mixture was evaporated to dryness in vacuum, the residue was washed with a little ether and 1—2 ml of acetone. The yields varied between 92 and 100%. The isomeric composition of the crude reaction products was determined by proton resonance spectroscopy (see Table III). The crude products were subjected to repeated recrystallizations from the solvents shown in Table IV. The stereochemical purity and steric structures of the crystallized substances, determined by proton resonance spectroscopy, are given in Table IV.

6. "Direct" and "reverse" quaternizations of laudanosine (IIIi) and 2-ethyltetrahydropapaverine (IIIj) and working up of the crude products

a) Laudanosine ethiodide (VIIIa)

A solution of 11.0 g (0.0308 mole) of laudanosine (**IIIi**) in 200 ml of acetone was mixed with 7.0 g (0.045 mole) of ethyl iodide and allowed to stand at room temperature for a week. The solvent and excess ethyl iodide were removed in vacuum and the residue was crystallized from 80% ethanol to give 10.6 g (65.9%) of greenish-yellow lentiform crystals, m.p. 161—162 °C (1st fraction). On repeated crystallizations from 80% alcohol the m.p. raised to 163 °C.

$C_{23}H_{32}O_4NI \cdot 1/2\ H_2O$ (522.43). Calcd. C 52.88; H 6.38; I^- 24.29. Found: C 52.98; H 6.30; I^- 24.56%.

The substance was kept in an exsiccator over P_2O_5 for 12 hrs, and then dried at 117 °C and 25 mm pressure.

$C_{23}H_{32}O_4NI$ (513.43). Calcd. C 53.80; H 6.28; I^- 24.72. Found: C 53.49; H 6.08; I^- 24.60%.

After recrystallization from abs. ethanol the m.p. was 208—209 °C. On subsequent recrystallization from aqueous ethanol the m.p. was 162—163 °C again. (Lit. [17] m.p. 202—203 °C.)

According to proton resonance spectroscopy, the substance was stereohomogeneous, and free from the diastereomeric 2-ethyltetrahydropapaverine methiodide (**VIIIb**).

The picrate derivative prepared from laudanosine ethiodide (**VIIIa**) in the usual way only slowly solidified in water. Crystallization from 80% ethanol gave lentiform crystals, which, after three crystallizations, melted at 118 °C.

$C_{29}H_{34}O_{11}N_4$ (614.63). Calcd. C 56.67; H 5.70; N 9.12. Found: 56.95; H 5.86; N 9.00%.

Evaporation of the mother liquor of the 1st fraction to dryness gave 3.7 g (23.4%) of white, rosette-like crystals (2nd fraction), m.p. 194—195 °C. After two recrystallizations from ethanol, the m.p. increased to 196—197 °C. No m.p. depression was observed with 2-ethyltetrahydropapaverine methiodide (**VIIIb**) obtained from 2-ethyltetrahydropapaverine (**IIIj**) with methyl iodide as the main product. The picrate separated from 90% ethanol in the form of well-crystallized needles, m.p. 157 °C. Two recrystallizations raised the m.p. to 162—163 °C. No m.p. depression was observed with the picrate prepared from 2-ethyltetrahydropapaverine methiodide.

A further 0.8 g (5%) of crystalline material, m.p. 180—195 °C, could be isolated from the mother liquor of the 2nd fraction.

(b) 2-Ethyltetrahydropapaverine methiodide (VIIIb)

A solution of 7.0 g (0.019 mole) of 2-ethyltetrahydropapaverine (**IIIj**) and 4.0 g (0.028 mole) of methyl iodide in 200 ml of acetone was allowed to stand at room temperature (23 ± 2 °C) for a week. The reaction mixture was concentrated in vacuum and the residue crystallized from 80% ethanol to yield 8.1 g (83.7%) of almost homogeneous 2-ethyltetrahydropapaverine methiodide (**VIIIb**) (1st fraction), m.p. 196—197 °C. Two recrystallizations from 80% ethanol yielded 5.15 g of the product, white needles, m.p. 200 °C.

$C_{23}H_{32}O_4NI$ (513.43). Calcd. C 53.80; H 6.28; I^- 24.72. Found: C 53.65; H 6.11; I^- 25.15%.

According to proton resonance spectroscopy, the product was stereohomogeneous, and free from the diastereomeric ethiodide (**VIIIa**). The picrate crystallized from ethanol, the well developed needles had m.p. 162—163 °C.

$C_{29}H_{34}O_{11}N_4$ (614.63). Calcd. C 56.67; H 5.70; N 9.12. Found: C 56.84; H 5.50; N 9.29%.

The 1 : 4 and 4 : 1 mixtures of 2-ethyltetrahydropapaverine methiodide (**VIIIb**) (m.p. 200 °C) and of laudanosine ethiodide (**VIIIa**) (m.p. 208 °C) melted at 194—203 °C and 184—192 °C, respectively.

The mother liquor of the 1st fraction was concentrated in vacuum to deposit 0.7 g of a substance (2nd fraction), m.p. 162 °C, which consisted mainly of laudanosine ethiodide · 1/2 H_2O (**VIIIa**). The product was recrystallized and converted into the picrate, lentiform crystals, m.p. 117—119 °C (from ethanol), which did not give m.p. depression with the picrate of laudanosine ethiodide · 1/2 H_2O (m.p. 118 °C).

A further 1.0 g of a substance could be isolated from the mother liquor of the 2nd fraction, which consisted mainly of laudanosine ethiodide · 1/2 H_2O, m.p. 150—154 °C.

7. Proton resonance spectroscopic examinations

The proton resonance spectra were taken at 60 MHz with an AEI RS-2 instrument. The solvent used was deuterochloroform, with tetramethylsilane internal reference. Calibration of the spectra was done by the usual side-band technique. The error limit in the determination of the percentage distribution of the isomers is less than 5%.

8. Isomerization experiments

(a) 100 mg of 1-phenyl-2-methyl-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline N-benzyl iodide (**VIIa**) was dissolved in 120 ml of abs. $CHCl_3$ and heated in a sealed tube at 80 °C for 20 hrs. The solution was evaporated to dryness and the homogenized residue subjected to proton resonance spectroscopic analysis, which showed it to consist of a 70 : 30% mixture of 1-phenyl-2-methyl-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline N-benzyl iodide (**VIIa**) and 1-phenyl-2-benzyl-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline methiodide (**VIIb**).

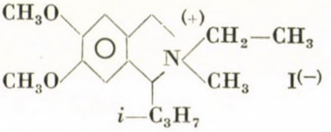
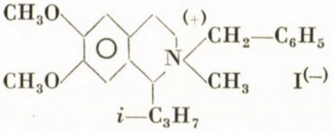
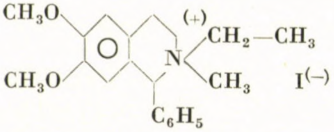
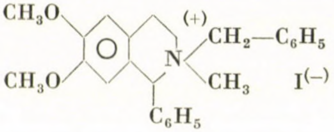
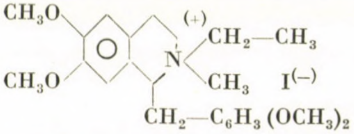
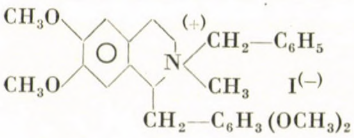
(b) Analogous treatment of 100 mg of 1-phenyl-2-benzyl-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline methiodide (**VIIb**) gave again the same 70 : 30 mixture of **VIIa** and **VIIb.** Isomerization of the **Va–Vb** diastereomeric salt pair gave, in accordance with the foregoing, an about 70 : 30 mixture of the *trans* and *cis* modifications.

*

The authors express their thanks to Dr. K. Koczka for his kind interest in the early phase of this work, to Dr. K. L. Láng and Mrs. G. Bartók for the microanalyses, and to Mr. L. Földházi for his technical assistance.

Table III

Isomer distribution and steric structures of the crude products of the "direct" and "reverse" quaternization reactions of 1,2-disubstituted-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline derivatives (IIId—l)[a]

Compound	Isomer distribution, % "direct"	"reverse" quaternization[b]	Relative spatial orientation of the substituents attached to C_1 and the N (in the latter case the larger substituent is meant)	
	60±5	17±5	*trans*	**IVa**
	40±5	83±5	*cis*	**IVb**
	95±5	40±5	*trans*	**Va**
	5±5	60±5	*cis*	**Vb**
	76±5	14±5	*trans*	**VIa**
	24±5	86±5	*cis*	**VIb**
	95±5	35±5	*trans*	**VIIa**
	5±5	65±5	*cis*	**VIIb**
	65±5	30±5	*trans*	**VIIIa**
	35±5	70±5	*cis*	**VIIIb**
	95±5	40±5	*trans*	**IXa**
	5±5	60±5	*cis*	**IXb**

[a] *Cf.* Fig. 3.

[b] "Direct" quaternization: N-methyl compound + ethyl iodide or benzyl iodide; "reverse" quaternization: N-ethyl or N-benzyl derivative + methyl iodide.

Table IV

Stereohomogeneity, melting points and analysis data[a] of the quaternary salts (IVa, b—IXa, b) obtained by fractional crystallization from the reaction products of "direct" and "reverse" quaternizations of 1,2-disubstituted-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline derivatives (IIId—l)

Reaction[c]	Substituents[c]			M.p.; °C; yield, % (solvent, number of crystals)	Empirical formula (molecular weight)	Analysis Calcd. Found			Stereochemical purity, %; configuration[b]	Remarks
	R$_1$	R$_2$	R$_3$			C	H	I$^-$		
IIId + EtI	*i*-Pr	Me	Et	193—194; 40; (ethanol, 4)	$C_{17}H_{23}NO_2I$ (405.30)	50.37 50.63	6.96 6.98	31.31 31.54	>90 *cis* **IVb**	d)
IIIe + MeI	*i*-Pr	Et	Me	194; 53; (ethanol, 4)	$C_{17}H_{23}NO_2I$ (405.30)	50.37 50.46	6.96 6.85	31.31 31.35	>95 *cis* **IVb**	d)
IIId + BzI	*i*-Pr	Me	Bz	174—175; 90; (ethanol, 3)	$C_{22}H_{30}NO_2I$ (467.37)	56.53 56.70	6.47 6.62	27.15 27.40	>95 *trans* **Va**	e)
IIIf + MeI	*i*-Pr	Bz	Me	177—178; 42; (ethanol, 3)	$C_{22}H_{30}NO_2I$ (467.37)	56.53 56.60	6.47 6.41	27.15 27.25	>95 *cis* **Vb**	f)
IIIg + EtI	Ph	Me	Et	191—192; 35; (acetone, 4)	$C_{20}H_{26}NO_2I$ (439.32)	54.67 54.82	5.96 5.98	28.88 28.97	>95 *trans* **VIa**	g)
IIIh + MeI	Ph	Et	Me	199—200; 39; (ethanol, 5)	$C_{20}H_{26}NO_2I$ (439.32)	54.67 54.75	5.96 5.85	28.88 29.08	>95 *cis* **VIb**	h)
IIIg + BzI	Ph	Me	Bz	178—179; 70; (ethanol, 3)	$C_{25}H_{28}NO_2I$ (501.38)	59.88 59.77	5.63 5.68	25.31 25.23	>95 *trans* **VIIa**	i)
IIIi + MeI	Ph	Bz	Me	194—195; 48; (ethanol, 4)	$C_{25}H_{28}NO_2I$ (501.38)	59.88 59.51	5.63 6.01	25.31 24.98	>95 *cis* **VIIb**	j)
IIIj + EtI	(MeO)$_2$Bz	Me	Et	207—208; 42; (ethanol, 5)	$C_{23}H_{32}NO_4I$ (513.40)	53.80 53.49	6.28 6.08	24.71 24.60	>95 *trans* **VIIIa**	k)
IIIk + MeI	(MeO)$_2$Bz	Et	Me	198—200; 45; (ethanol, 4)	$C_{23}H_{32}NO_4I$ (513.40)	53.80 53.65	6.28 6.11	24.71 25.15	>95 *cis* **VIIIb**	l)

IIIj + BzI	$(MeO)_2Bz$	Me	Bz	178; 82; (ethanol, 2)	$C_{28}H_{34}NO_4I$ (575.46)	58.43 58.43	5.95 5.90	22.05 22.12	> 95 *trans* **IXa**	m)
IIIl + MeI	$(MeO)_2Bz$	Bz	Me	179—180; 20; (ethanol, 3)	$C_{28}H_{34}NO_4I$ (575.46)	58.43 58.27	5.95 5.86	22.05 22.26	> 90 *trans* **IXa**	m)

Remarks: a) *Cf.* Remarks a) and b) in Table III.

b) The designations *cis* and *trans* refer to the relative steric position of the substituent attached to C_1 (R_1) and the bulkier substituent at the nitrogen atom.

c) Me = CH_3; Et = CH_3CH_2; *i*-Pr = $(CH_3)_2CH$; Ph = C_6H_5; Bz = $C_6H_5CH_2$; $(MeO)_2Bz$ = 3,4-$(CH_3O)_2C_6H_3CH_2$.

d) Though considerable differences were observed in the solubilities of the crude quaternary salts obtained by "direct" and "reverse" quaternization, repeated recrystallizations resulted the same diastereomer salt (**IVb**) from both reaction products. A mixture (**IVa, b**) consisting mainly of the diastereomeric *trans* quaternary salt (**IVa**) could be isolated from the mother liquors of the "direct" and "reverse" quaternizations in 40 and 10% yields, the m.p. being 185—6 °C and 188—9 °C, respectively.

e) Colourless needles. According to proton resonance spectroscopy, the product is practically pure *trans* isomer.

f) Large, colourless tables. Needles (m.p. 173—5 °C) can be isolated from the mother liquor (**Va**).

g) Well developed tables. Glittering plates (m.p. 198—9 °C) can be isolated from the mother liquor.

h) Glittering plates. The solubility of **VIa,** obtained from the direct quaternization is lower. From the mother liquor further crystals, m.p. 193—4 °C, consisting mainly of the trans (**VIa**) isomer, could be isolated.

i) Colourless needles.

j) Well developed light-yellow plates. **VIIa,** m.p. 178—80 °C, could be isolated from the mother liquor in 17% yield.

k—l) *Cf.* Experimental.

m) Repeated recrystallizations from ethanol gave the *trans* isomer (**IXa**) as the only product from the reaction products of either "direct" or "reverse" quaternization.

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HETEROCYCLIC SPIRO COMPOUNDS, VII

STRUCTURE OF ACYLSPIROXAZONES AND ALKYL(ARYL)-SPIROXAZONES

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As a result of an elucidation [1] of the tautomeric equilibria of spiroxazone, the structural formulas of the acyl and N-alkyl (aryl) derivatives had to be modified. Using IR and NMR spectroscopic as well as synthetic methods, it has been shown that the structures of monoacyl derivatives (**VIII**) must uniformly be deduced from the open-chain endocyclic amidrazon tautomers (**III**). The N,O-diacylspiroxazones prepared with an acid anhydride have also been shown to be open amidrazon derivatives (**XVIII**), while acylation of spiroxazone in pyridine produces O,O-diacyl derivatives, **XV**.

Some mixed O,O-diacylspiroxazones may undergo O $\rightleftarrows$ N acyl migration; this is accompanied by an endo → exo migration of the C=N bond. Thus molecules with structure **XIV** are formed beside those of structure **XV**.

The exo or endo position of the C=N bonds of the various acylates has been determined by acid hydrolysis. The exocyclic tautomer yields α-spiroxazone, the endocyclic gives β-spiroxazone.

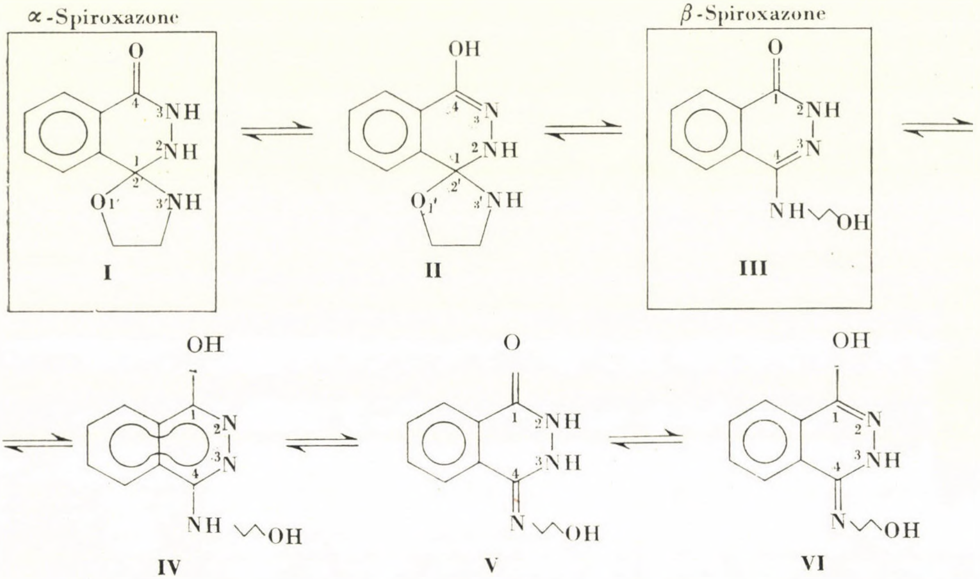
Some alkyl(aryl)-spiroxazones described earlier have now been shown to be N(2)-substituted spiroxazones (**XXV**). Their monoacyl derivatives are open ω-O-acyl compounds containing an endocyclic C=N bond, while the diacyl derivatives obtainable by treatment with an acid anhydride, have structure **XXVIII**, where R_2 and R_3 are acyl groups.

I. Structure of acylspiroxazones

Introduction

Spiroxazone may exist in six tautomeric forms (**I—VI**). The preparation of desmotropic α- and β-spiroxazone [1] and their interconversion have shown that at least two (**I** and **III**) of the tautomers do actually exist, therefore it is not sufficient to consider only structures **I** and **II** as formerly supposed [2—6]. Of course, it is possible that when derivatives are synthesized, compounds corresponding to other tautomers may also be formed.

In view of this, it seemed appropriate to revise our former suggestions about the structures of spiroxazone derivatives and to correct them if necessary on the basis of the new results.



A. Structure of monoacylspiroxazones

Since the IR spectra indicated the presence of ester groups in monoacylspiroxazones [3] (*cf.* Figs 1 and 2: IR spectra of monoacetyl- and mono-

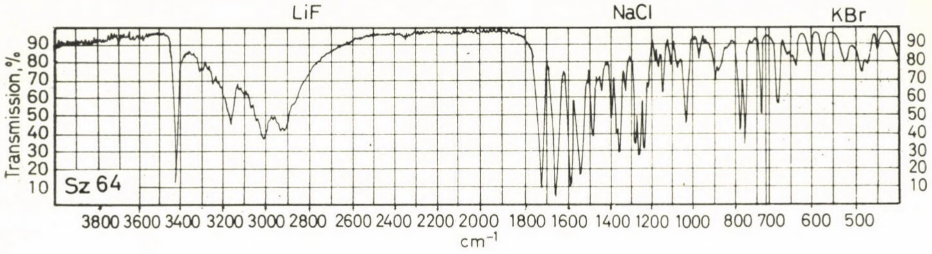


Fig. 1

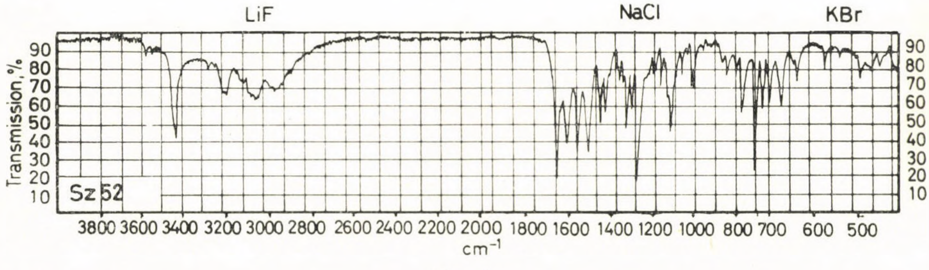
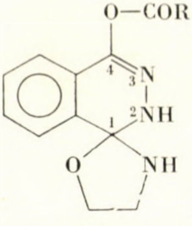


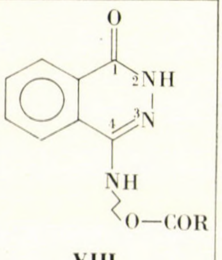
Fig. 2

benzoylspiroxazone), on the basis of structures **I** and **II** we had to suppose that esterification of the iminohydrin tautomer **II** occurred, to give O(4)-monoacyl derivatives **(VII)**.

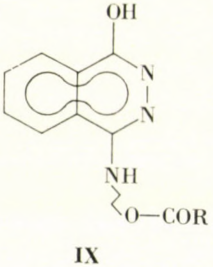


VII

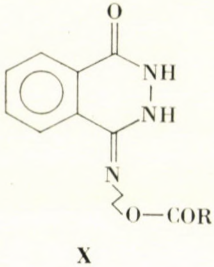
The carbonyl frequencies were not greater than those characteristic of simple esters (*cf.* Figs 1 and 2), in spite of the fact that the $-I$ effect of the C=N double bond adjacent to the ether oxygen should have increased the frequency of the νC=O band like in the case of phenolic esters [7—10]. However, we did not consider this enough to justify the exclusion of structure **VII**, because association, conjugation with the aromatic ring, and the $+T$ effect of the two nitrogen atoms in the hetero ring might cause a frequency change in the opposite sense, and thus the νC=O band may not be shifted towards higher wave numbers.



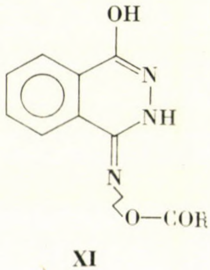
VIII



IX



X



XI

If tautomers **III—VI** are also taken into consideration, acylation of their primary hydroxyl groups may give rise again to ester derivatives **(VIII—XI)** whose structures are fully compatible with the carbonyl frequencies and with the presence of ester bands.* Thus, for a definite elucidation of the monoacylspiroxazone structures, a study of NMR spectra became necessary.

Since the band at about $\delta = 11.6$ ppm characteristic of the CONH group at the 3 position appeared in the NMR spectra of both the monoacetyl

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* Altogether 18 monoacyl compounds can be deduced from the six spiroxazone tautomers.

and the monobenzoyl derivatives (*cf.*, *e.g.*, Fig. 3) — in addition to structure **VII** suggested previously — also tautomers **IX** and **XI** had to be excluded; thus, the monoacetyl and monobenzoyl spiroxazones and all other monoacylates of spiroxazone must have structure **VIII** or **X.** The signal appearing at about 6.9 ppm — which can either be due to the exocyclic NH (structure **VIII**) or the N(3)-H (structure **X**) — is a triplet in the spectrum of the benzoyl derivative and probably also in the acetyl derivative (the signal around 6.7 ppm is very diffuse in the spectrum of this latter compound and the triplet pattern is not discernible, *cf.* Fig. 3); on the basis of this evidence, structure **X** may also be eliminated. Consequently, at least in dimethyl sulfoxide solution, tautomer **VIII** must be present, and esterification occurs at the primary alcoholic hydroxyl which becomes available by the fission of the spiro-ring, and not at hydroxyl groups of the iminohydrine tautomers. So *the structure of monoacylspiroxazones is not* **VII** *as formerly supposed, but* **VIII.**

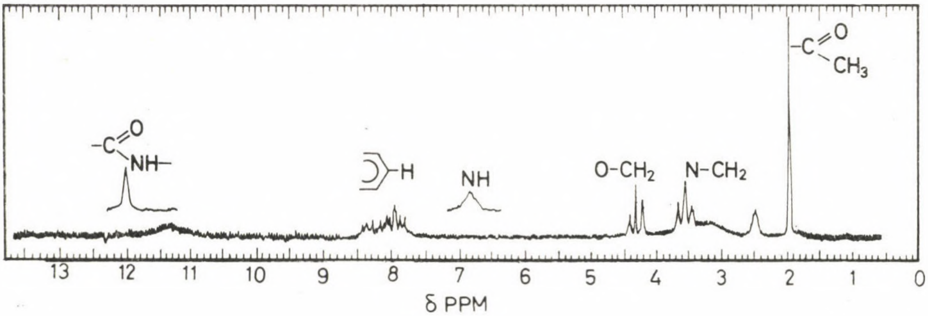
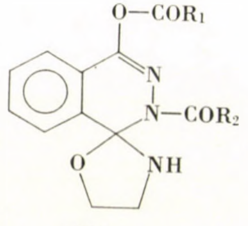


Fig. 3

Support from preparative work for the structure **VIII** of the monoacyl derivative containing an endocyclic C=N bond is furnished by an earlier observation [1] according to which α- and β-spiroxazone are not interconvertible in acid medium; thus in the acid hydrolysis of monoacylspiroxazones of structure **VIII**, the formation of β-spiroxazone is to be expected. The experimental results agree with this expectation, thus confirming the deductions from spectroscopic studies concerning the structure of monoacylspiroxazones.

B. Structure of diacylspiroxazones

The reasons discussed above made it necessary to modify our views about the structures of the diacyl compounds. At the same time, light was shed on the causes of some deviations found in the pattern of IR spectra which we previously attempted to explain by postulating different association structures and electron configurations in the various modifications of the diacyl deriva-



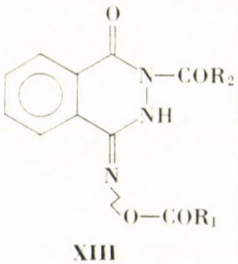
XII

tives. If the opening of the spiro ring did not occur, as we formerly supposed to be the case, most of the diacyl compounds would have one chemical structure **(XII)** only, deducible from the iminohydrin spirane-ring tautomer **(II)**, since this is the only one that could account for the presence of the βNH band at about 1550 cm^{-1} [originally assigned to the spirane N(3')-H group and the ester bands] in the IR spectrum. In the case of a spirane structure, only acylation of the iminohydrin tautomer **II** can give rise to an ester derivative.

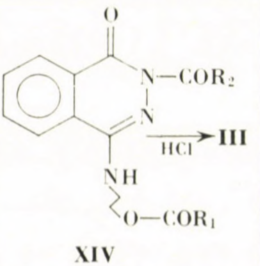
However, the situation is quite different if the open amidrazon tautomers **III—VI** of spiroxazone are also taken into account. Then the appearance of ester bands can be ascribed to the ester groups formed by acylation of the primary alcoholic hydroxyl groups. The fact that the ω-O-acyl group is always present also in diacylspiroxazones is supported by our earlier observation [2] that partial alcoholysis of the diacyl derivative always leads to the compounds having the same structure as the corresponding monoacylspiroxazones.

B.1. Diacyl derivatives with the two identical acyl groups

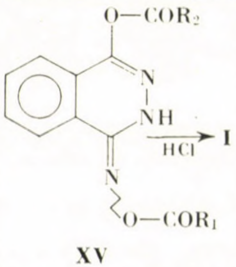
Supposing the formation of an ω-O-acyl group, there are eight possible alternatives for the diacyl compounds if the acyl groups are the same: in three of them **(XIII—XV)**, the appearance of the βNH band at about 1550 cm^{-1} can be expected. According to our observations [12], similarly to the βNH band of the NH group of the oxazolidine ring, the analogous band of amidines (—N=C—NH—) is also very intense, representing another exception among secondary amines. This is not surprising, since amidines are compounds related



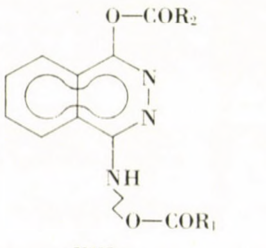
XIII



XIV



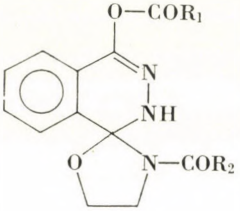
XV



XVI

to amides in which the group-vibrational (amide-II) band of βNH character is generally intense [7—10].

The appearance in the IR spectrum of the intense βNH band (together with the ester bands) is thus in agreement with structures XIII—XVI besides that of structure XII. In the case of the few compounds whose spectra have the ester bands, but the βNH band is absent, instead of the O(4)-N(3')-diacyl structure formerly proposed (XVII), the possibility of structures XVIII—XXI



XVII

must be considered. All in all, the following statements can be made concerning the structures of diacylspiroxazones.

Acetylation of spiroxazone with acid anhydrides yields diacyl compounds, whose IR spectra contain (*cf.*, *e.g.*, Spectrum 4 of the diacetyl compound, or Spectrum 5 of the dibenzoyl derivative) ester, amide and νNH bands (the latter being characteristic of cyclic dimers), but the intense βNH band is absent. The diffuse νNH band split into sub-maxima and appearing at low wave

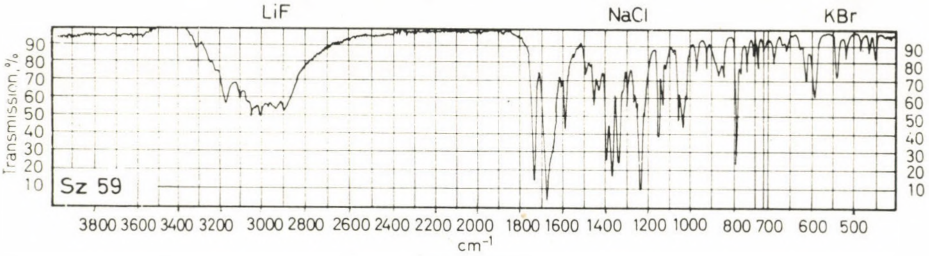


Fig. 4

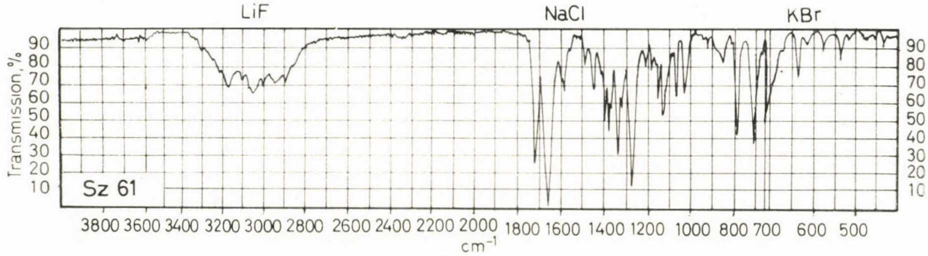


Fig. 5

numbers (between 3300 and 2800 cm^{-1}) [11—13] suggests that the lactam group has remained unchanged in these compounds. This is also supported by the NMR spectra, the signal due to the lactam NH proton appearing at 11.2 ppm for the benzoyl and at 12.8 ppm for the acetyl derivative. This shows that structure **XVII** formerly proposed cannot be correct. The NMR spectra also prove the presence of the two acyl groups. The signals of the $COCH_3$ protons are at 1.9 ppm and 2.1 ppm (Fig. 6), whereas in the spectrum of the dibenzoyl derivative the relative overall integrated intensity of the signals of the aromatic protons between 420 and 480 cps increases, compared with the value observed with spiroxazone, by the 1 : 3.5 proportion, as expected. Thus, only isomer **XVIII** or **XX** can be considered for these diacyl derivatives, and no certain choice between them seems possible on the basis of spectroscopic evidence.

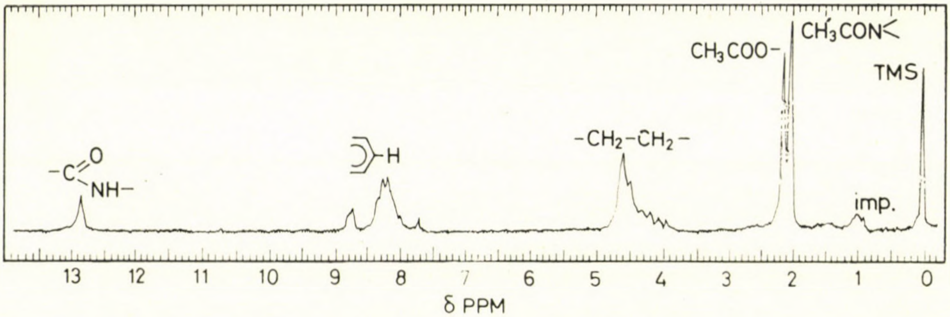
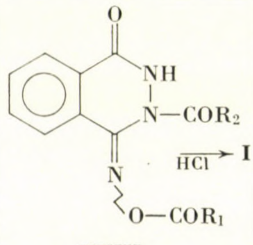
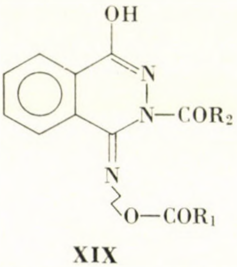


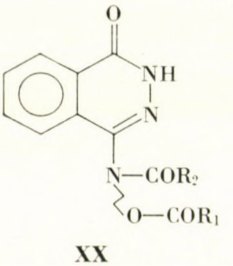
Fig. 6



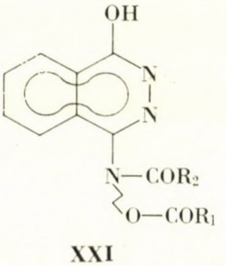
XVIII



XIX



XX



XXI

In the isomers **XVIII** and **XX**, the position of the C=N groups is exo and endo, respectively. As no exo—endo migration of this bond is possible during acid treatment of the nonacylated spiroxazone [1], decision between these two structures can be readily made on the basis of preparative evidence. Acid hydrolysis of the N,O-diacylspiroxazones yields *α-spiroxazone*. This is evidence for structure **XVIII** (*cf.* [1] the hydrolysis of trityl-spiroxazone, containing exocyclic C=N bond), because the **XX** diacyl derivative should give *β-spiroxazone* under such conditions.* According to this, ***the correct structure of the N,O-diacyl derivatives produced by an acid anhydride is* XVIII *and not* XVII.** (The singlet structure of the NH signal in the NMR spectrum makes the exo position of the C=N group likely, too.)

Acylation with an acid chloride or acid anhydride in pyridine produces diacyl compounds of other structures, as it is also shown by deviations in the IR spectra (*cf.* spectra of the diacetyl and dibenzoyl compounds, Figs 7 and 8).

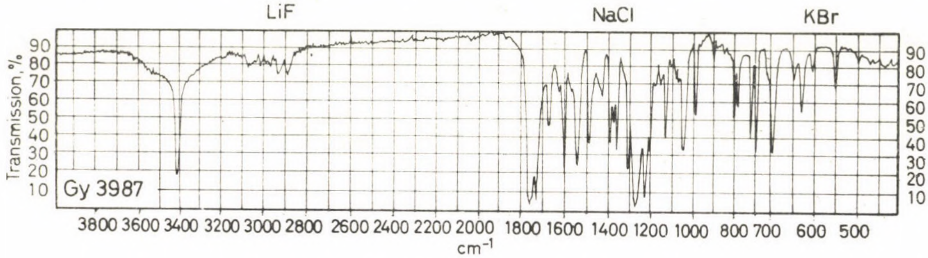


Fig. 7

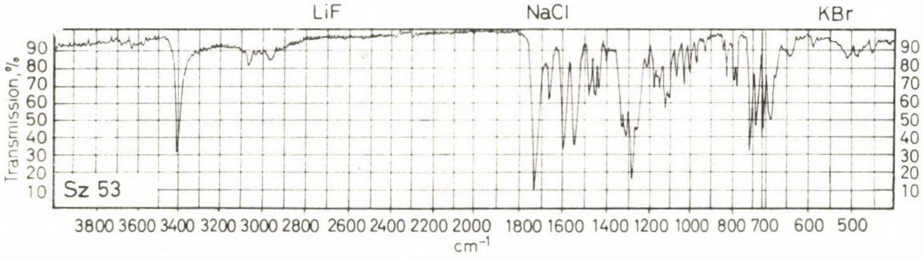


Fig. 8

The IR spectra (Figs 7** and 8) of both the diacetyl and dibenzoyl derivatives have the ester bands and also the intense βNH band, while the absence of the νNH band (characteristic of a cyclic dimeric association) and of the signal due to the N(3)-H group at 11.5 ppm in the NMR spectrum, indicate that the exocyclic NH group (or the endocyclic NH group of the open-chain exocyclic tautomers) carries no substituent. Therefore, structures **XIII—XVI** ($R_1 = R_2 =$ Ph, or Me) come into consideration.

Since the frequency of the ester carbonyl band is 1695 cm^{-1} in the IR spectrum (Fig. 2) of monobenzoylspiroxazone, and no such band is found in the IR spectrum (Fig. 8) of the dibenzoyl compound, the possibility might be

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* It is an exception of the "semi-iminohydrin rule"; shortly we shall give more statements about this problem.

** Recent spectroscopic studies revealed that our former samples of diacetylspiroxazone [2, 3] had been somewhat contaminated, mainly by monoacetylspiroxazone, as a result of recrystallization from alcohol. Fig. 7 is the IR spectrum of a recently prepared homogeneous sample (m.p. 166 °C; recrystallized from a mixture of chloroform and ether).

considered that the benzoyl group is not connected to the terminal oxygen atom in the former case. However, in dilute chloroform solution the νC=O band appears at 1725 cm^{-1}, at the same frequency as in the case of dibenzoylspiroxazone. The low frequency (at 1695 cm^{-1}) in the spectrum of a solid sample of the monobenzoyl derivative is thus due to association.

Both the increase in relative intensity of the ester band at about 1280 cm^{-1} and the frequencies and intensities of the bands in the double-bond region suggest that diacetyl or dibenzoylspiroxazones contain an enol ester group beside the ω-O-acyl group, thus pointing to structure **XV**, or possibly to **XVI**. If structures **XIII** or **XIV** were present, three carbonyl bands ought to appear in the IR spectra, at about 1770, 1740 and 1710 cm^{-1} for the diacetyl derivative, and at somewhat lower wave numbers, owing to conjugation (*i.e.*, at 1750, 1715 and 1685 cm^{-1}) for the dibenzoyl compound, as shown by spectral data of acyl derivatives of phthalic hydrazide, 1(2H)-phthalazinone, and 4(3H)-quinazolinone [11, 14].

Thus only structures **XV** and **XVI** can be present of which the latter is unlikely, as shown by preparative evidence (the formation of *α-spiroxazone* by hydrolysis with hydrochloric acid points to an exocyclic position of the C=N group [1]), chemical evidence (greater stability of the semi-iminohydrin tautomer [1, 15]), and spectroscopic evidence (the νC=N band appears at 1660 or 1670 cm^{-1} in the IR spectrum, further, the signal of the NH group is a singlet in the NMR spectrum, while it ought to be a triplet for structure **XVI** in dimethyl sulphoxide, because of the adjacent methylene group). Thus we may state that both *diacetyl- and dibenzoylspiroxazone* prepared in pyridine *have structure* **XV** *($R_1 = R_2 =$ Me, and Ph, respectively) and not structure* **XII** *as hitherto supposed.*

B.2. Mixed diacyl derivatives

The situation is still more complicated in mixed diacyl derivatives since, in principle, here 36 isomers are possible. However, the mixed diacyl derivatives have been synthesized in two steps *via* monoacyl compounds of uniform structure [3], so the number of actually possible compounds is substantially lower. From the four tautomers **(VIII—XI)** of ω-O-acylspiroxazone eight isomers can be deduced, because in either case there are two possibilities for the entry of the second acyl group. Of course, since structure **VIII** of the monoacyl derivatives is other than supposed originally **(VII)**, the mixed diacyl compounds cannot have structure **XII**, either.

As it has been reported [3, 4], when monoacetylspiroxazone is benzoylated in pyridine, two reversibly interconvertible substances, the α- and β-modifications are formed, which considerably differ in physical properties, such as colour and crystal form, and in the IR spectra (Figs 9 and 10). The intense

βNH band is present in the IR spectra, thus the exocyclic NH group, or in the tautomers that correspond to structures **V** and **VI**, the N(3)-H group, is certainly not substituted either in the α or in the β modification. The ester bands, appearing at the same wave numbers as in monoacetylspiroxazone, indicate that the acetyl group is linked to the ω-O atom. Thus, the formulas correctly representing the two substances should be selected from among the four isomeric structures **XIII—XVI** ($R_1 = Me$, $R_2 = Ph$).

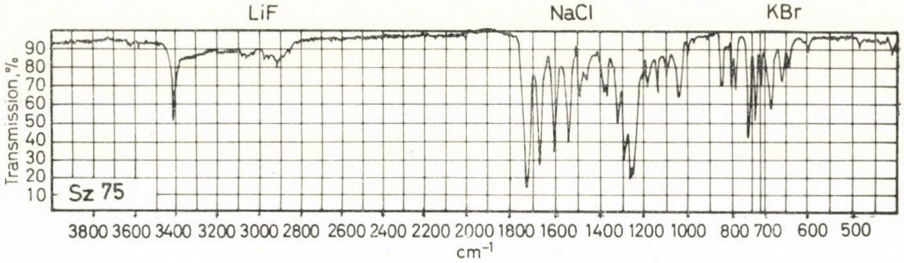

Fig. 9

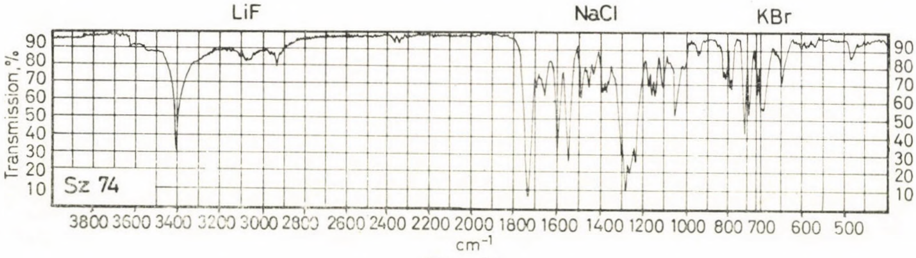

Fig. 10

The pattern of the aromatic bands is not changed either in the IR or in the NMR spectra: in the latter also the triplets of the methylenes are unchanged (*cf.* NMR spectra of the α- and β-modifications in Figs 11 and 12). This excludes structure **XVI**; the two substances are represented either by **XIII**, or **XIV** and **XV**, respectively. Since the *colourless* substance (the α-modification) has an intense band at 1675 cm^{-1} in its IR spectrum (Fig. 9), whereas the *yellow* substance (β-modification) shows a weak and broad band at about 1660 cm^{-1} (Fig. 10), obviously structure **XIII** or **XIV** belongs to the colourless, and structure **XV** (R_1=Me, R_2=Ph) to the yellow substance. The band at 1675 cm^{-1} in the spectrum shown in Fig. 9 can be assigned to the low-frequency $\nu_s C{=}O$ vibration of the imide group* (the $\nu_{as} C{=}O$ vibration absorbs, together with the ester carbonyl band, at 1730 cm^{-1}), and that at 1660 cm^{-1} in Fig. 10 to the $\nu C{=}N$ vibration.

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* In the case of imides, the stretching vibration band of the C=O bond appears instead of the amide-I band, but owing to coupling of two bands, they are shifted towards lower and higher frequencies, according to the vibration modes $\nu_{as} C{=}O$ and $\nu_s C{=}O$, respectively [9, 16].

Structures **XIII** and **XIV** cannot be directly distinguished by the spectra, but the frequency of the imide carbonyl in the spectrum of the colourless substance is the same as that of N-acetyl-1(2H)-phthalazinone [11], therefore structure **XIV** is probably the correct choice.

Our assumptions about the structures of the two modifications were confirmed by hydrolysis experiments with hydrochloric acid. As expected, the yellow β-modification identified by spectroscopy as structure **XV** was converted into *α-spiroxazone*. In a similar operation the colourless α-modification yielded *β-spiroxazone:* this constitutes evidence for structure **XIV** (R_1 = Me, R_2 = Ph). In such a treatment tautomer **XIII** ought to have given α-spiroxazone.

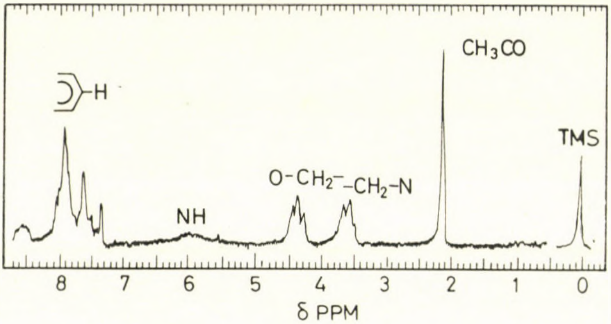

Fig. 11

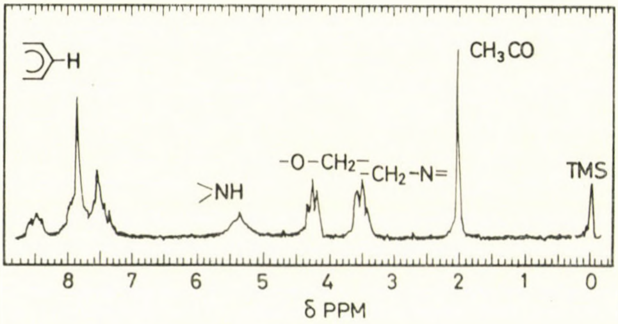

Fig. 12

Knowing that **XIV** and **XV**, respectively, are the structures of the benzoylated ω-O-acetylspiroxazone modifications, we may state that the reversible O(1) $\rightleftharpoons$ N(2) acyl migration also causes exo—endo migration of the C=N bond. This is in good agreement with the "semi-iminohydrin rule" [1] which is obeyed also in this case.*

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* The "semi-iminohydrin rule" is based on the fact that of the tautomeric forms of phthalic hydrazide, the semi-iminohydrin form is the most stable; therefore, during the formation of derivatives, simultaneous amide-iminohydrin tautomerisation (endo $\rightleftharpoons$ exo migration of the C=N bond) is also possible if this is the only way to arrive at a substance derivable from the semi-iminohydrin form

The acetylation of ω-O-benzoylspiroxazone in pyridine [3, 4] gives again a substance whose IR spectrum (Fig. 13) has an intense βNH band, while no amide-I band is present. The $\nu C{=}N$ band is at 1665 cm^{-1}, the carbonyl bands are at 1760, and 1715 cm^{-1}, respectively, the intensities of the maxima being nearly identical. All this is evident for structure **XV** ($R_1 = Ph$, $R_2 = Me$).

The splitting of the carbonyl bands may be interpreted as follows. In the presence of two equivalent acyl groups, the ester carbonyl band belonging to the iminohydrin ester group appears at somewhat higher wave numbers, because the —*I* effect of the C=N double bond raises the bond order of the carbonyl group, and thereby increases the $\nu C{=}O$ frequency (*cf.* analogous cases of enol-, phenol- and vinyl esters [7—10]).

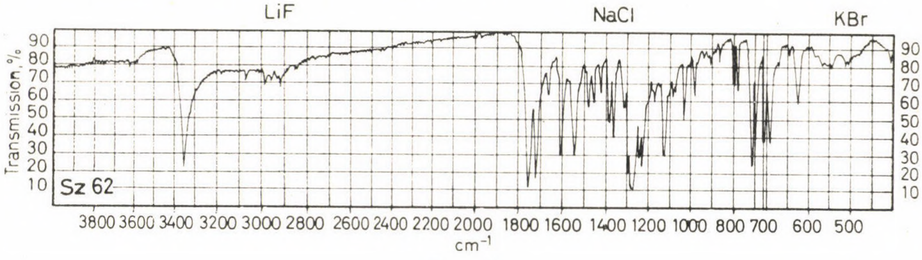

Fig. 13

In mixed esters, the structure of the acyl group also affects the $\nu C{=}O$ frequency. Owing to conjugation of the carbonyl groups, the carbonyl band in aromatic esters appears at lower wave numbers than in aliphatic esters [7—10]. Thus, if the iminohydrin group is esterified with an aromatic, and the ω-hydroxyl with an aliphatic acid, the frequencies of the two carbonyl bands will be about the same, since, in the first case, the frequency-increase due to the —*I* effect is counterbalanced by the contrary effect of conjugation. This is why the two bands coalesce if $R_1 = Me$ and $R_2 = Ph$ in the spectra of compounds of structure **XV.** However, if $R_1 = Ph$ and $R_2 = Me$, the case is reversed: compared with the simple aliphatic ester frequencies, the carbonyl band of the aliphatic (terminal) ester group is shifted towards lower, and that of the 4-group towards higher wave numbers, so that the two carbonyl bands in the spectrum become separated.

The difference in the tendency of these three substances to form associations is also connected with this. If $R_1 = Me$ and $R_2 = Ph$ in structures **XIV** and **XV**, sharp νNH bands characteristic of monomeric groups are seen in their spectra. At the same time, if $R_1 = Ph$ and $R_2 = Me$ in structure **XV**, the νNH band becomes diffuse, and the decrease of its frequency constitutes evidence for association. This can be explained as follows.

In all the three cases the NH groups can mainly associate with the terminal (aliphatic) carbonyl groups, since the tendency of the carbonyls in the iminohydrin ester and diacylamino groups to form hydrogen bonds is less pronounced. The carbonyl of aromatic esters has a more negative character owing to conjugation, therefore its role as an electron reservoir is more prominent. Thus it is understandable that in the case of structure **XV** association occurs when $R_1 = Ph$ and $R_2 = Me$. When $R_1 = Me$ and $R_2 = Ph$, the slight difference between the νNH frequencies in the cases of **XIV** and **XV** is due to the difference in the basicities of the exo- and endocyclic NH groups. In **XV**, owing to the added $-I$ effects of the iminohydrin ester group and C=N double bond, the endocyclic NH group is somewhat more acid than the exocyclic NH group adjacent to the aliphatic chain in structure **XIV** (the νNH frequency is higher, the band is sharper and less intense).

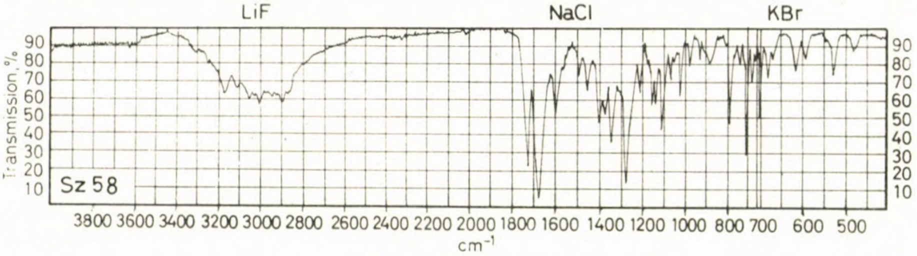

Fig. 14

Acetylation of ω-O-benzoylspiroxazone with acetic acid anhydride [3, 4] gave the derivative **XVIII** (R_1=Phe, R_2=Me). The IR spectrum of this compound is shown in Fig. 14.

B.3. Modifications of diacylspiroxazones

In our further work we examined whether there was any difference between the diacylspiroxazones formerly designated as α, β, γ_i and γ_f-modifications, that exhibited different spectra. It was known that the structures of the diacyl derivatives formerly denoted as the *α-modifications* are analogous to structure **XIV**, while to *modifications* β, γ_i, γ_f structure **XV** can be ascribed.*

Due to the electron donor substituent R_1 in γ_1*-type* substances, the tendency of the ω-ester carbonyl to form hydrogen bonds is great enough to bring about the formation of such bonds (*cf.*, *e.g.*, Spectrum 6 in [4], of di-*p*-tolyl-spiroxazone), while in the β- *and* γ_f*-types* the electron withdrawing substituent R_1 prevents any kind of association. A transition between these two limiting cases can also be observed. *E.g.* the spectrum (*cf.* Spectrum 8 in [4], of ω-O-butyroyl-O(4)-benzoylspiroxazone) shows the simultaneous presence of γ_i- and β-type (associated and monomeric) molecules.

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* The diacetylspiroxazone formerly believed, on the basis of spectra of contaminated samples, to be the α-form is, in fact, a β-modification on the basis of a spectrum of the pure substance.

If substituent R_2 of the acyl group at position 1 is electrophilic, the substances are labile, because the iminohydrin ester group is readily split off *(γ_f-modification)*. This is the reason why it is so difficult to prepare γ_f-type substances in pure form, all these products being contaminated by the monoacyl derivative (*cf.*, *e.g.*, Spectra 5, 10* and 11* in [4], of di-*p*-nitrobenzoyl-, and ω-O-cinnamoyl-O(4)-benzoylspiroxazone). This also explains the fact that the νNH band becomes more intense and more diffuse, but its frequency is not lowered (*i.e.* the N—H bond becomes polar).

If only the R_1 substituent of the ω-acyl group is electrophilic, the substance is the chemically stable *β-modification* (*cf.*, *e.g.*, Fig. 8, dibenzoylspiroxazone). Thus substances of *the types β and γ_f are identical both structurally and in their association properties.*

(A preparative distinction can be made on the basis of the greater instability of γ_f-modification.)

Structure **XIV** *(α-modification)* is formed only when R_2 in the second acyl group (linked at position 2) is not an electrophilic substituent. In this case usually there is an equilibrium between tautomers **XIV** and **XV**, and besides the α-type, molecules of the β- or γ_i types (monomeric or associated structures **XV**) are also formed. Examples are the dipropionyl- ($\alpha + \gamma_i$) and ω-O-acetyl-O(4)-benzoyl spiroxazones ($\alpha + \beta$) (see Spectrum 7 in [4] for the former mixture, and Figs 9 and 10 for the spectra of the separated components of the latter).

It follows that the statements concerning *the correlation between the chemical character of acylspiroxazones and the alternation of their modifications are correct as described earlier, though the structures of the modifications are not those formerly supposed.*

II. 2-N-alkyl- and arylspiroxazones and their acyl derivatives

If tautomers **III—VI** of spiroxazone are considered, our earlier ideas about the structures of the alkyl and aryl derivatives must be modified. Whereas from tautomers **I** and **II** only 6-monoalkyl (aryl) derivatives could be deduced, 18 types of monosubstituted alkylspiroxazones can be derived from forms **I—VI.**

It has been shown on the basis of preparative examinations [5] that alkyl (aryl) substitution can only occur on one of the N atoms in the six-membered heterocyclic ring. If only tautomers **I** and **II** are taken into account, only structures **XXII** and **XXIII** can be formed. On the basis of the UV spectra, structure **XXIII** could be excluded.

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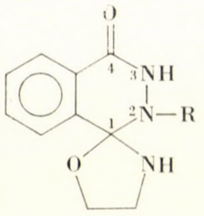
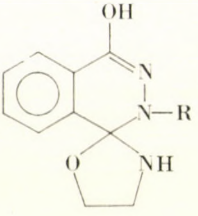
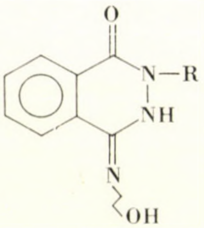
* These two spectra were obtained with a more and a less contaminated sample.



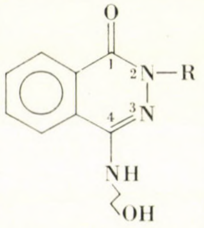
XXII



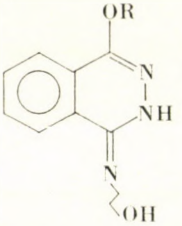
XXIII



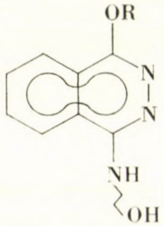
XXIV



XXV



XXVI



XXVII

If the spiroxazone tautomers **III—VI** are also taken into consideration, esterification can occur at the ω-O-atom, and consequently structures **XXIV—XXVII** (R = alkyl or aryl) become possible. From these **XXVI** and **XXVII** can be excluded in view of preparative evidence [5]. Choice between the remaining structures is facilitated by the IR spectrum (Fig. 15) of the trityl derivative of methylspiroxazone, where the intense βNH band can be seen unchanged at 1540 cm^{-1}.* The presence of the trityl group is proved by the appearance of the very intense γ(=CH) and γCC bands in the 800 and 670 cm^{-1} region, characteristic of a monosubstituted aromatic ring. Since the trityl ether group can only form at a primary hydroxyl, structures **XXII** and **XXIII** can also be excluded.

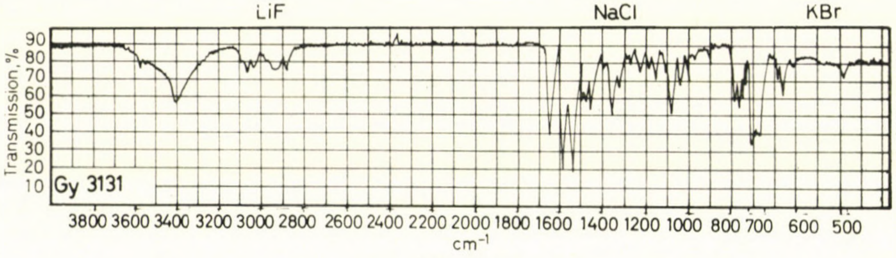


Fig. 15

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* The appearance of the unaltered βNH band at 1540 cm^{-1} means that our modified assignment of the βNH band to the amidine group, is correct (*cf.* page 277).

Thus the structure of alkyl- and arylspiroxazones is not **XXII** *but either* **XXIV** *or* **XXV**, *the latter being more probable on the basis of chemical evidence and the UV spectra* [6]. *In dimethyl sulphoxide solution structure* **XXV** *is present,* as evidenced by the triplet pattern (J = 8 cps) of the signals (δ = 6.7 and 4.7 ppm) assignable to the OH and NH groups in the NMR spectrum of methylspiroxazone (Fig. 16). The correctness of this assignment was also checked by the addition of heavy water when both signals disappear in consequence of rapid exchange reactions.

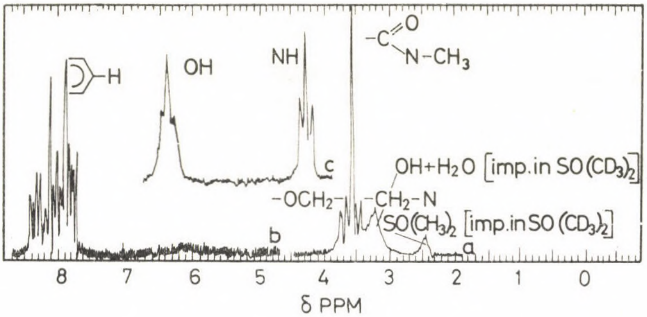
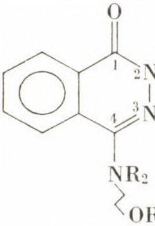


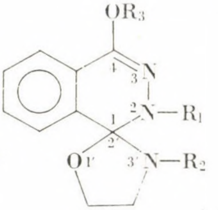
Fig. 16

Thus, **XXVIIIa, XXVIIIc** and **XXVIIIf** are the structures of the mono- and diacetyl derivatives, and of the trityl ether of methylspiroxazone, respectively.* The acyl substituent and the nature of the substituent on the N(2)-H group do not affect the structures of the acyl derivatives. For instance, **XXVIIId** (Spectrum 16 in [6]) represents the structure of diacetyl-N(2)-n-propyl-, and **XXVIIIe** (Spectrum 8 in [2]) that of diacetyl-N(2)-phenylspiroxazone. **XXVIIIb** (Spectrum 6 in [6]) corresponds to benzoyl-N(2)-methylspiroxazone.



XXVIII

a	R_1 = Me	R_2 = H	R_3 = Ac
b	Me	H	Bz
c	Me	Ac	Ac
d	n-Pr	Ac	Ac
e	Ph	Ac	Ac
f	Me	H	CPh$_3$
g	$-(CH_2)_4Br$	H	Ac
h	$-(CH_2)_4OAc$	H	Ac



XXIX

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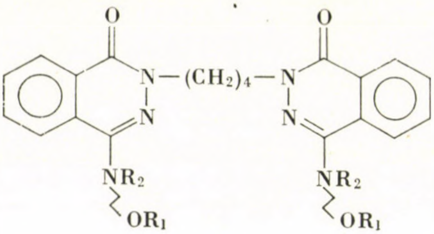
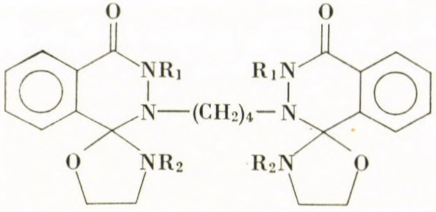
* Formulas **XXIXa—h** are former variants of **XXVIIIa—h**; the trityl compound **XXVIIIf** is an exception, since this was synthesized recently and formulated originally in this way.

From these considerations, the structure of ω-substituted butyl derivatives is evident. The structure of N(2)-(ω-bromobutyl)-, and of N(2)-(ω-acetoxybutyl)-spiroxazone (Spectra 9 and 11, in [5]) is **XXV** (R = $(CH_2)_4Br$, and $(CH_2)_4OOC \cdot CH_3$, respectively). The structure of the monoacyl derivatives of these two substances is **XXVIIIg** and **XXVIIIh**, respectively (Spectra 10 and 12 in [6]). **XXXa, XXXb** and **XXXc** (which were formerly erroneously thought to be **XXXIa, XXXIIb** and **XXXIIc**) present the structure of the bromine-free derivative obtained with tetramethylene dibromide (Spectrum 13 in [6]), and of its mono- and diacetate (Spectra 14 and 15 in [6]), respectively.

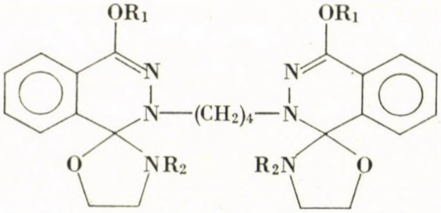


a $R_1 = R_2 = H$
b $R_1 = Ac$ $R_2 = H$
c $R_1 = R_2 = Ac$

XXX



XXXI



XXXII

According to earlier investigations [6], the νNH band of some ν-O-acyl-N(2)-substituted spiroxazones is split owing to the simultaneous presence of monomeric and associated molecules, while the νNH band of other spiroxazones is attributable to uniformly associated or to uniformly monomeric groups. This can be connected with the electronegativity of the acyl and alkyl (aryl) substituents of spiroxazone. The amide-I band changes parallel to the νNH band: if the latter is split, the amide-I band also shows a doublet pattern; if the νNH band is sharp (monomeric molecules) the amide-I band is also sharp and is found at higher frequencies; if the νNH band becomes diffuse and appears at lower frequencies due to association, the amide-I band behaves similarly.

This phenomenon can be interpreted on the basis of structures **XXVIIIa** and its analogues, by assuming the possibility of an intermolecular association between the amide carbonyl and exocyclic NH groups. Association is favoured when the amide carbonyl is negatively polarized, therefore if substituent R_1

is an electron donor, association is more probable. If a series of models is studied wherein substituents R_1 with gradually increased electronegativity are bound to the N(2) atom, the spectra of the substances first show the characteristics of uniformly associated molecules and change gradually through monomeric and associated molecules to uniformly monomeric molecules.

Accordingly, the correlation found earlier between the properties of the substituents and types of association is satisfactorily explained. This is well illustrated by Table I, which shows the correlation between the electron affinity of alkyl or aryl substituents at position 2 and the association structures formed.

Table I

Association forms of N(2)-alkyl(aryl)acylspiroxazones

XXVIII

R_1	R_2	R_3	Type of association	IR spectrum*
Methyl	H	Benzoyl	intermolecrlarly associated molecules	6
***i*-Propyl**	H	Acetyl	the same	18
***p*-Tolyl**	H	Acetyl	the same	21
Phenyl	H	Acetyl	monomeric and intermolecularly associated molecules	19
p-Nitrophenyl	H	Acetyl	monomeric molecules	20
p-Nitrophenyl	H	Benzoyl	the same	22

* In the last column the serial numbers used in this paper for formerly published spectra [6] of the compounds are given.

Experimental

Hydrolysis of acylspiroxazones with hydrochloric acid

200—300 mg samples of the monoacyl- **(VIII)** and diacylspiroxazones **(XIV, XV, XVIII)** were boiled in 5—7 ml of conc. HCl for 3 hrs. After cooling, the solution was filtered and the solid washed with water. The combined filtrate and washing was evaporated three or four times to dryness in vacuum, with water added each time. The residue was taken up in 5—10 ml of water and the separated spiroxazone base recrystallized from water to obtain colourless needles, m.p. 254—6 °C. The product was identified by the IR spectrum.

ω-O-Trityl-N(2)-methylspiroxazone (4-[2-trityloxyethylamino]-2-methyl-1(2H)-phthalazinone)

XXVIIIf

Methylspiroxazone (2.19 g; 10 mmoles) dissolved in abs. pyridine (40 ml) was allowed to react with trityl chloride (5.58 g; 20 mmoles) at room temperature. Next day the product was separated by the addition of water, and the air-dry substance recrystallized from alcohol to obtain 3.68 g (79.9%) of colourless needles, m.p. 207—208.5 °C. Prior to analysis, the substance was dried in vacuum over phosphorus pentoxide at 100 °C for 10 hrs.

$C_{30}H_{27}N_3O_2$ (461.6). Calcd. C 78.1; H 5.9; N 9.1%. Found C 78.2; H 5.8; N 9.2%.

All melting points were determined using a Boëtius apparatus. The IR spectra were obtained with a UR-10 (Zeiss, Jena) spectrometer, in KBr pellets or in chloroform solution, using sodium chloride cells of 1 mm, at concentrations of about 10^{-1} *M*. The NMR spectra were recorded with a 60 MHz JNM-C-60 (JEOL) spectrometer, using TMS internal standard, and concentrated solutions of the compounds in carbon tetrachloride, deuterochloroform, dimethyl sulphoxide or deutero-dimethyl sulphoxide.

Table II

Hydrolysis of acylspiroxazones with hydrochloric acid

$$\text{Acylspiroxazone} \xrightarrow{\text{HCl}} \text{Spiroxazone tautomer}$$

ω-O-acetyl **(VIII)**	β
ω-O-benzoyl **(VIII)**	β
ω-O,O(4)-diacetyl **(XV)**	α
ω-O,O(4)-dibenzoyl **(XV)**	α
N(3)-ω-O-diacetyl **(XVIII)**	α
N(3)-ω-O-dibenzoyl **(XVIII)**	α
O(4)-benzoyl-ω-O-acetyl **(XV)**	α
O(4)-acetyl-ω-O-benzoyl **(XV)**	α
N(2)-benzoyl-ω-O-acetyl **(XIV)**	β

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TRANSACYLATION REACTIONS IN THE FLAVONOID SERIES, IV*

NEW SYNTHESES OF 5-METHYLGENISTEIN, PRUNETIN, BIOCHANIN-A AND SISSOTRIN

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Genistein-7-benzoate was transformed into the 4'-benzoate by treatment with Ag_2CO_3 in pyridine. An equimolecular mixture of genistein and its 4',7-dibenzoate gave under the same conditions 2 moles of genistein-4'-benzoate. From these intermediates new syntheses of the natural isoflavones 5-methylgenistein, prunetin. biochanin-A and sissotrin have been achieved.

In preceding papers of this series [1—3] we have reported about a novel base-catalyzed isomerization of partially benzoylated flavones, that can be depicted by the following general equation:

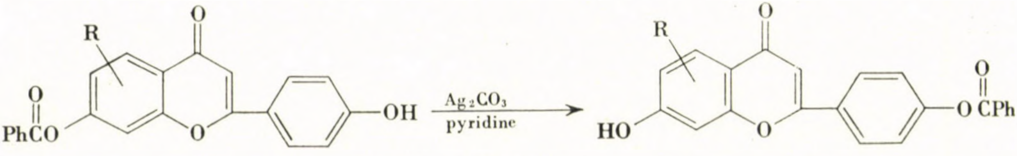

Fig. 1

The driving force of this transacylation reaction is the difference in acidity of the various hydroxyl groups attached to the flavone nucleus; thus acyl groups are transferred from the more acidic oxygen at C_7 to that on C_4.

A similar gradient in the acidities of the hydroxyl groups, shown by the enhanced reactivity of C_7-OH, has been observed several times also with isoflavones (*e g.* [4]); therefore, it could be anticipated that the scope of these transacylation reactions may also be extended to this class of flavonoids.

In this paper we report about transacylation reactions of the partial benzoates of 4',5,7-trihydroxyisoflavone, genistein **(1)**. The model compounds and some of their derivatives were prepared as follows.

The C_5-OH group is deactivated owing to chelation with the adjacent carbonyl, therefore, 4',7-dibenzoylgenistein **(2)** can be conveniently prepared by acylating genistein **(1)** with two equivalents of benzoyl chloride.

The structure of **2** was supported by its positive ferric chloride colour

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* Preceding paper in this series: Farkas, L., Wolfner, A., Nógrádi, M., Wagner, H., Hörhammer, L.: Chem. Ber. **101**, 1630 (1968).

reaction, and by methylation to 5-methoxy-4',7-dibenzoyloxyisoflavone **(3)**. Saponification of **3** afforded 5-methylgenistein **(4)**, a compound isolated from *Cytisus laburnum* by Chopin *et al.* [5] and, preceding its isolation from plant material, prepared in another way by Heitz and Mentzer [6].

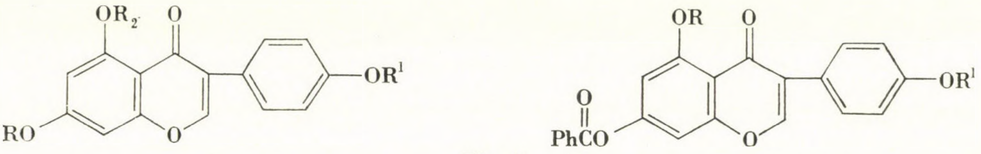


Fig. 2

1: $R=R^1=R^2=H$
4: $R=R^1=H$, $R^2=CH_3$
6: $R=R^2=H$, $R^1=$-β-D-glucosyl
9: $R=R^2=H$, $R^1=CH_3$
10: $R=$-β-D-glucosyl, $R^1=CH_3$, $R^2=H$
11: $R=R^2=H$, $R^1=PhCO$
12: $R=PhCH_2$, $R^1=R^2=H$
13: $R=PhCH_2$, $R^1=PhCO$, $R^2=H$
14: $R=CH_3$, $R^1=R^2=H$

2: $R=H$, $R^1=PhCO$
3: $R=CH_3$, $R^1=PhCO$
5: $R=R^1=H$
7: $R=H$, $R^1=$-β-D-glucosyl
8: $R=H$, $R^1=CH_3$

On benzoylating genistein **(1)** with one equivalent of benzoyl chloride, preferential attack on the C_7-OH group was observed, and genistein-7-benzoate **(5)** was isolated as the main product. Pure **5** can be prepared more conveniently by careful benzoylation of genistein-4'-β-D-glucoside, sophoricoside **(6)**, in aqueous alkali and subsequent cleavage of the sugar by treating the product **(7)** for a short time with a mixture of acetic acid and hydrochloric acid.

The position of the benzoyl group has been further supported by careful methylation yielding the monomethyl ether **8**, that was saponified to 4'-methylgenistein **(9)**, *i.e.* biochanin-A, a substance found, among other plants, in *Cicer arietinum* by Siddiqui [7]. The first synthesis of **9** has been accomplished by Baker and Ollis [8].

Recently the 7-glucoside of biochanin-A, **10**, named sissotrin has been isolated from *Dalbergia sissoo* [9] and its structure proved by coupling **9** with acetobromoglucose [10]. Now sissotrin has been prepared by partial methylation of genistin (genistein-7-glucoside) [4].

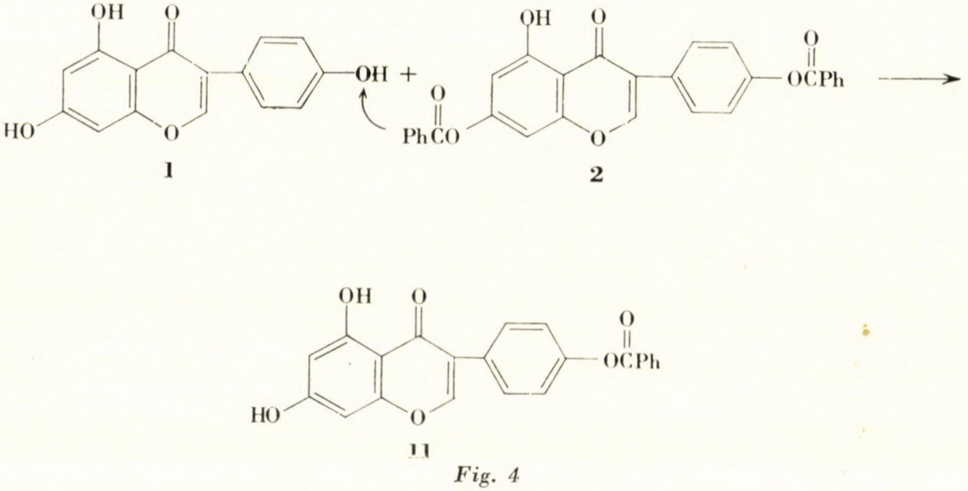
In order to obtain genistein-4'-benzoate **(11)**, 7-benzylgenistein **(12)** [11] was transformed to its monobenzoate (13). Short boiling with a 20% solution of hydrogen bromide in acetic acid effected selective elimination of the more sensitive benzyl group affording **11.** Cautious methylation with diazomethane and saponification of the product gave 4',5-dihydroxy-7-methoxyisoflavone, prunetin **(14)**, a constituent of *Prunus puddum* L. [12], first prepared by Iyer *et al.* [13].

As partially acylated derivatives of flavonoids are liable to thermal rearrangement during m.p. determination [2], **2, 5** and **11** were further characterized as the acetates.

Similarly to the corresponding flavone analogue, when treated in pyridine at room temperature with silver carbonate, genistein-7-benzoate (5) was smoothly converted to an isomeric compound, that proved to be identical with genistein-4'-benzoate (11). It gave a positive ferric chloride colour reaction indicating the presence of free C_5-OH, and its acetate was clearly different from that of **5**. Thus the benzoyl group on C_7-OH, rendered more acidic by the electron attraction of the carbonyl group in *para* position, was transferred to the less acidic C_4-OH. Participation of the C_5-OH group in this reaction was prevented by chelation.

5 **11**

Fig. 3



1 **2** **11**

Fig. 4

Benzoyl transfer between different molecules can also be realized. If an equimolecular mixture of genistein (**1**) and its 4',7-dibenzoate (**2**) is treated under the above reaction conditions, about two moles of genistein-4'-benzoate (**11**) are obtained.

These experiments reveal the close analogy of flavones and isoflavones in respect of the behaviour of their partial benzoates.

Difficulties were encountered in the course of the preparation of the acetates of 4',7-dibenzoyl- and 7-benzoylgenistein (**2** and **5**, respectively). Acetic anhydride/sodium acetate at 100 °C failed to convert the deactivated C_5-OH; instead displacement of the 7-O-benzoyl group was experienced at the boiling point.

Thus short acetylation of 7-benzoylgenistein (**5**) afforded 4'-acetoxy-7-benzoyloxy-5-hydroxyisoflavone, but prolonged treatment gave genistein triacetate. The desired diacetate of **5** was finally prepared in three steps from 7-benzylgenistein (**12**) by acetylation to the diacetate, catalytic debenzylation to 4',5-diacetoxy-7-hydroxyisoflavone and benzoylation.

Similarly, 4',7-dibenzoylgenistein (**2**) was transformed by boiling acetic anhydride in the presence of sodium acetate to 4'-benzoyloxy-5,7-diacetoxyisoflavone. The monoacetate has been prepared by acid-catalyzed acetylation of **2**.

In conformity with these results, the tribenzoate [14] of genistein was transformed by prolonged boiling with acetic anhydride and sodium acetate to the diacetate of 4'-benzoylgenistein.

Experimental

Genistein-4',7-dibenzoate (5-hydroxy-4',7-dibenzoyloxyisoflavone) (2)

A solution of genistein (**1**) (1.0 g) [14] in dry pyridine (4 ml) was heated with benzoyl chloride (0.95 ml) for 3 hrs on a water bath. The reaction mixture was poured into 5% HCl, and the precipitate that separated was filtered off, giving 1.5 g of a crude product. It was recrystallized several times from acetic acid—dimethylformamide to obtain thin needles (1.1 g), m.p. 232—234 °C. $FeCl_3$ reaction in methanol: violet.

$C_{29}H_{18}O_7$ (478.4). Calcd. C 72.80; H 3.76. Found C 73.00; H 3.99%.

5-Acetoxy-4',7-dibenzoyloxyisoflavone

A solution of **2** in acetic anhydride (4 ml) containing two drops of perchloric acid was heated for 2 hrs on a water bath. Dilution with water precipitated an oil, that slowly crystallized. Repeated recrystallizations from chloroform–methanol (1 : 1) and acetic acid afforded colorless needless (190 mg), m.p. 247—250 °C.

$C_{31}H_{20}O_8$ (520.5). Calcd. C 71.53; H 3.87. Found C 71.51; H 3.93%.

5-Methylgenistein dibenzoate (4',7-dibenzoyloxy-5-methoxyisoflavone) (3)

A mixture of **2** (400 mg), dry potassium carbonate (400 mg) and dimethyl sulphate (0.4 ml) was boiled for 2.5 hrs in acetone (40 ml) with stirring. The crude product that crystallized directly from the filtered solution was recrystallized from acetone and then from dioxan to obtain **3** as colorless needles (150 mg), m.p. 237—239.5 °C.

$C_{30}H_{20}O_7$ (492.5). Calcd. C 73.16; H 4.09. Found C 73.14; H 4.01%.

5-Methylgenistein (4',7-dihydroxy-5-methoxyisoflavone) (4)

3 (130 mg) was refluxed for 30 min with 1 *N* sodium methoxide (2 ml). After evaporation, the residue was treated with aq. $NaHCO_3$ and filtered, to afford a product of m.p. 294 °C (lit. [6] m.p. 300 °C), that was directly acetylated to yield 4'-7-diacetoxy-5-methoxyisoflavone (70 mg), m.p. 163 °C (lit. [6] m.p. 173 °C).

Genistein-7-benzoate (7-benzoyloxy-4',5-dihydroxyisoflavone) (5)

(a) *From genistein.* **1** (1.0 g) in pyridine (8 ml) was treated with benzoyl chloride (0.7 ml) for 16 hrs at room temperature. The solution was poured into 5% aq. HCl, and the precipitate separated. The crude product was dissolved in hot acetone, and diluted with an equal volume of methanol, whereupon the by-product (**2**) precipitated. After having filtered off **2**, the mother liquor was concentrated, and the residue crystallized repeatedly from ethanol–acetone to obtain colorless needles (200 mg), m.p. 247—249 °C. $FeCl_3$ reaction in methanol: violet.

$C_{22}H_{14}O_6$ (374.3). Calcd. C 70.58; H 3.77. Found C 70.18; H 3.80%.

(b) *From 7-benzoylsophoricoside.* Conc. hydrochloric acid (5 ml) was added to a boiling solution of crude **7** (2.5 g) in acetic acid (20 ml). After 10 min, the solution was cooled, whereupon **5** separated. Recrystallization from acetic acid–dioxan gave pure **5** (0.9 g), identical with the above product.

7-Benzoyloxy-4',5-diacetoxyisoflavone

4',5-Diacetoxy-7-hydroxyisoflavone (200 mg) was benzoylated in cold pyridine for 24 hrs, to afford, after the usual work-up and recrystallization from acetic acid, colorless needles (180 mg), m.p. 191—192 °C.

$C_{26}H_{18}O_8$ (458.4). Calcd. C 68.12; H 3.96. Found C 67.98; H 4.05.

7-Benzoylsophoricoside (7-benzoyloxy-4',5-dihydroxyisoflavone-4'-β-D-glucoside) (7)

A solution of sophoricoside (2.5 g) in 0.4 *N* NaOH (20 ml) was mixed, with vigorous stirring, with benzoyl chloride (0.7 ml) for 10 min. After the addition of 1 *N* NaOH (4 ml), the precipitate was immediately filtered off and washed with some methanol. The crude product (2.5 g), that can be used without further purification, was recrystallized for analysis several times from acetic acid to give colorless needles, m.p. 222—224 °C.

$C_{28}H_{24}O_{11}$ (537.4). Calcd. C 62.68; H 4.51. Found C 61.28; H 4.63%.

7-Benzoyloxy-5-hydroxy-4'-methoxyisoflavone (8)

A solution of **5** (400 mg) in dry acetone (50 ml) was stirred at reflux temperature with anhydrous potassium carbonate (0.4 g) and dimethyl sulphate (0.2 ml) for 3 hrs. The filtered solution was evaporated, and the residue crystallized from methanol to obtain colorless needles (0.22 g), m.p. 205—208 °C.

$C_{23}H_{16}O_6$ (388.4). Calcd. C 71.13; H 4.14. Found C 70.82; H 4.17%.

5,7-Dihydroxy-4'-methoxyisoflavone (biochanin-A) (9)

8 (0.2 g) in methanol (3 ml) was boiled for 5 min with 10% NaOH (1 ml). The solution was acidified with 10% HCl, the precipitate filtered off, washed with water and petroleum ether. The crude product was crystallized from aq. methanol to yield **9** (50 mg), m.p. 212—214 °C (lit. [7] m.p. 212—216 °C).

5,7-Dihydroxy-4'-methoxyisoflavone-7-β-D-glucoside (sissotrin) (10)

A solution of genistin [15] (0.6 g) in dimethylformamide (10 ml) was treated for 2 hrs with dimethyl sulphate (0.15 ml) and anhydrous potassium carbonate (1.8 g) at 60 °C. The mixture was diluted with water, the precipitate separated and recrystallized from aq. methanol to obtain colorless plates (80 mg), m.p. 214—215 °C (lit. [9] m.p. 213—214 °C). $FeCl_3$ reaction in methanol: deep orange. $[\alpha]_D^{20}$ —33 °C ($c = 1.0$, pyridine), lit. [9] $[\alpha]_D^{23}$ —35.5 °C (dimethylformamide).

$C_{22}H_{22}O_{10}$ (346.4). Calcd. C 59.18; H 4.96. Found C 58.88; H 5.27%.

7-Benzyloxy-4'-benzoyloxy-5-hydroxyisoflavone (13)

A solution of **12** [11] (1.0 g) in pyridine (4 ml) was heated with benzoyl chloride (0.8 ml) for 30 min at 110 °C. After cooling, the mixture was diluted with methanol (20 ml) and the product that crystallized in a short time was filtered off. The crude product (1.1 g) was repeatedly recrystallized from acetic acid to yield colourless needles (0.8 g), m.p. 208—210 °C. $FeCl_3$ reaction in methanol: violet.

$C_{29}H_{20}O_6$ (464.48). Calcd. C 74.99; H 4.34. Found C 75.01; H 4.31%.

Genistein-4'-benzoate (4'-benzoyloxy-5,7-dihydroxyisoflavone) (11)

(a) *From 7-benzyloxy-4'-benzoyloxy-5-hydroxyisoflavone* **(13)**. A solution of **13** (200 mg) in acetic acid (6 ml) was boiled for 10 min with a 20% solution of hydrobromic acid in acetic acid (1 ml). The dark solution was poured into water, the precipitate separated, washed with methanol and recrystallized from dioxan to yield colorless needles (100 mg), m.p. 233—236 °C.

$C_{22}H_{14}O_6$ (374.3). Calcd. C 70.58; H 3.77. Found C 70.13; H 4.36%.

(b) *From genistein-7-benzoate* **(5)**. A solution of **5** (700 mg) in pyridine (7 ml) was shaken for 1 hr. at room temperature with silver carbonate (700 mg). The filtered solution was diluted with 5% aq. perchloric acid (200 ml), the precipitate was filtered off, and washed thoroughly with hot water and then with some methanol. The crude product (700 mg) was recrystallized several times from dioxan to yield a product that was identical with **11**, prepared in the foregoing experiment.

(c) *From genistein and genistein-4',7-dibenzoate* **(2)**. A solution of **1** (339 mg) and **2** (600 mg) in pyridine (6 ml) was shaken for 1 hr. at room temperature with silver carbonate (600 mg). Working up as described above gave 900 mg of essentially pure **11**, that after purification was completely identical with the above product.

4'-Benzoyloxy-5,7-diacetoxyisoflavone

11 (400 mg) was acetylated by the usual procedure to yield, after working up and repeated recrystallizations from dioxan and acetic acid, colorless needles (450 mg), m.p. 250—252 °C.

$C_{26}H_{18}O_8$ (458.43). Calcd. C 67.97; H 3.94. Found C 67.80; H 4.01%.

Prunetin (4',5-dihydroxy-7-methoxyisoflavone) (14)

A solution of **11** (200 mg) in dioxan (20 ml) was allowed to stand overnight with an excess of ethereal diazomethane solution. After evaporation, the residue was boiled for 30 min with 1 *N* sodium methoxide (2 ml), evaporated, and the residue dissolved in a small amount of water. Saturation with carbon dioxide precipitated prunetin of m.p. 234—236 °C (lit. [13] m.p. 239—240 °C), that was acetylated without further purification. After the usual work up, the crude product was repeatedly recrystallized from ethanol–chloroform. Colorless plates (40 mg), m.p. 224—226 °C (lit. [15] m.p. 224—226 °C).

4'-Acetoxy-7-benzoyloxy-5-hydroxyisoflavone

5 (200 mg) was acetylated with acetic anhydride (1 ml) containing anhydrous sodium acetate (0.2 g) at 100 °C for 1 hr. After the usual work-up and repeated recrystallizations from acetic acid, colorless needles (200 mg), m.p. 213—215 °C were obtained. $FeCl_3$ reaction: violet.

$C_{24}H_{16}O_7$ (416.4). Calcd. C 69.23; H 3.87. Found C 69.20; H 4.39.

7-Benzyloxy-4',5-diacetoxyisoflavone

12 [11] (2 g) was acetylated in the usual way to afford, after repeated recrystallizations from acetic acid, colorless crystals (2.0 g), m.p. 184—186 °C.

$C_{26}H_{20}O_7$ (444.4). Calcd. C 70.26; H 4.54. Found C 70.22; H 4.79.

4',5-Diacetoxy-7-hydroxyisoflavone

7-Benzyloxy-4',5-diacetoxyisoflavone (1.5 g) was hydrogenated in dioxan (50 ml) in the presence of palladium on charcoal until the uptake of one equivalent of hydrogen. The filtered solution was evaporated, and the residue recrystallized twice from 80% aqueous methanol to obtain colorless spears (0.6 g), m.p. 214 °C.

$C_{19}H_{14}O_7$ (354.3). Calcd. C 64.40; H 3.98. Found C 64.06; H 3.86%.

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LABELLED AMINO ACIDS AND THEIR DERIVATIVES, I

STRECKER SYNTHESES WITH α-KETOCARBOXYLIC ACIDS

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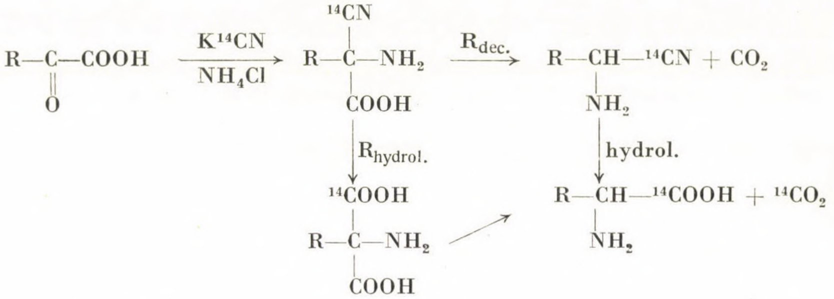
α-Ketocarboxylic acids have been used as the carbonyl components in the Strecker synthesis. The method has been found suitable for the preparation of DL-glutamic-1-^{14}C acid. The reaction mechanism of the decarboxylation and hydrolysis of α-amino-(cyano-^{14}C)acetic acid type compounds has been studied.

For the preparation of amino acids labelled with ^{14}C in the carboxyl group, the Strecker synthesis is used almost exclusively [1, 2]. Generally, the experimental methods follow the reaction routes originally developed for the syntheses of the non-labelled compounds [3—6], the only difference being reduction of the scale and the use of labelled cyanide. It may be noted that KOURIM and ZIKMUND [7], utilizing the reversibility of cyanohydrin formation, prepared the labelled amino nitrile intermediates by an exchange reaction between inactive cyanohydrins and labelled potassium cyanide, followed by treatment with ammonia. This modification, however, did not gain much ground in practice.

In a number of cases difficulties have been encountered in performing the Strecker synthesis, since the starting aldehydes are not readily available or they are unstable; in reactions carried out with small amounts, this instability may considerably lower the yields. For this reason, in the preparation of variants of glutamic acid labelled with various isotopes, instead of the Strecker synthesis, methods starting with the stable and readily available α-ketoglutaric acid are preferred. Reductive ammonolysis of α-ketoglutaric acid conveniently gives DL-glutamic acid [8]. This reaction has been used for the preparation of glutamic acids labelled with deuterium [9], ^{15}N [10] and ^{14}C [11, 12]. KÖGL *et al.* [11] prepared α-ketoglutaric-1,2-^{14}C acid for use as a starting material, from labelled sodium oxalate, in five reaction steps; HENDLER *et al.* [12] achieved the synthesis from labelled oxalic acid in three steps, in 60—65% yield. Using the various radioisomers of α-ketoglutaric acid, glutamic acids labelled at other sites can be prepared under the same conditions.

The synthesis of labelled α-ketocarboxylic acids involves many difficulties which have been studied in connection with the syntheses of the various radioisomers of pyruvic acid [13]. Recently, the micro-scale synthesis of radiochemically pure labelled α-ketocarboxylic acids has been described in detail [14]. This synthesis consists in the reaction of acid chlorides, freshly prepared from carboxylic acids, with copper cyanide, followed by careful hydrolysis. However, this method cannot be applied directly to the synthesis of α-ketodicarboxylic acids. It is not easy to accomplish the synthesis of α-ketoglutaric-1-^{14}C acid, or of DL-glutamic-1-^{14}C acid, in this way.



where:	keto acid	amino acid
R = CH_3	pyruvic acid	alanine
CH_2COOH	oxalacetic acid	aspartic acid
CH_2CH_2COOH	α-ketoglutaric acid	glutamic acid

Fig. 1. Preparation of α-amino acids labelled in the carboxyl group, from inactive α-keto acids

In view of the problems outlined above, a synthesis of labelled amino acids has been attempted starting with a non-labelled α-ketoacid that can be easily prepared. The reaction between an α-keto acid and labelled potassium cyanide has been found to be the most suitable for this purpose, when the reaction is carried out under experimental conditions similar to those of the Strecker synthesis. No report has been found in the literature for such reactions. From the theoretical point of view, such a reaction is, in essence, a combination of the Strecker and the cyanoacetic ester syntheses, because it proceeds via an intermediate of α-aminocyanoacetic acid type. The intermediary amino-(cyano-^{14}C)acetic acid allows, on the basis of a simple measurement of the specific activities, the comparison of the relative decarboxylation and hydrolysis rates of the compounds mentioned.

Results and discussion

Fig. 1 shows the Strecker type reaction of α-ketocarboxylic acids with radioactive potassium cyanide, and Table I lists the results of such reactions. The data in this Table show that though various α-keto acids undergo the reaction, the yields of the amino acid end-products are lower than those obtain-

Table I

Strecker syntheses with α-keto acids

α-Keto acid	Specific activity $\frac{\mu Ci}{mM}$			Act. %	Yield, %		Product amino acid
	$K^{14}CN$	Amino acid	$^{14}CO_2$		Chem.	Rad.	
1. Pyruvic	—	—	—	—	4	—	DL-alanine
2. Sodium pyruvate	0.205	0.172		84	14		DL-alanine-1-^{14}C
3. Oxalacetic*	0.205	0.158	0.41	77	10.7		DL-aspartic-1-^{14}C-acid
4. α-Keto-glutaric	2.27	1.92	0.31	82	32.2	25.8	DL-glutamic-1-^{14}C-acid
5. α-Keto-glutaric	2.27	1.91	0.34	84	12	10.1	DL-glutamic-1-^{14}C-acid
6. α-Keto-glutaric	0.205	0.174	0.028	84.5	13.6	—	DL-glutamic-1-^{14}C-acid

* The chemical and radiochemical purity of the DL-aspartic-1-^{14}C acid formed was only 88—92%.

able in the usual Strecker synthesis. The fact that the yields in Strecker syntheses are generally not higher than 50% is attributed mainly to the reversible formation of the intermediate α-amino nitriles. It seems probable that in reactions of α-keto acids the equilibrium reaction is shifted more in the direction of the initial components, because the carbon atom in α-position is sterically more hindered than the carbonyl carbon of aldehydes. Another explanation may be found in the connection between the stability of the initial α-keto acids (α-ketoglutaric acid > sodium pyruvate > oxalacetic acid) and the decreasing yields of the reactions. On the basis of these considerations concerning the reactivity of α-keto acids, it is also expected that the decarboxylation of the intermediate of α-aminocyanoacetic acid type proceeds faster than the hydrolysis of its nitrile group.

If the hydrolysis of the nitrile group (R_h) and decarboxylation (R_d) are competitive reactions, and the isotope effect is left out of consideration, a comparison of the molar activity of the amino acid produced with that of the initial potassium cyanide allows an approximate estimation of the ratio of the rates of the two competing reactions. If the hydrolysis and the decarboxylation of the intermediate proceed at an equal rate, 75% of the activity will be contained in the labelled amino acid produced, and 25% will be found in the carbon dioxide. However, should either of the two processes, *viz.* decarboxylation or hydrolysis, be significantly faster than the other (the ratio being a hundred, at least), then

(*a*) a 50% loss of activity is to be expected when hydrolysis is the faster, or

(*b*) decarboxylation of the intermediate occurs without loss of activity, when this is the faster process.

The latter case would result in considerable radiochemical advantages both in Strecker syntheses of this type and in syntheses starting with substituted α-acylamino(cyano-^{14}C)acetic acid derivatives.

From Table I it is to be seen that the molar activity of α-amino acids formed in the reaction is about 80 to 85% of the molar activity of the starting potassium cyanide. Consequently, decarboxylation and hydrolysis of the substituted α-amino(cyano-^{14}C)acetic acid derivatives are competing reactions of which decarboxylation is the faster. No doubt, this is favourable from the radiochemical point of view, but it is, unfortunately, associated with the disadvantage of poor chemical yields.

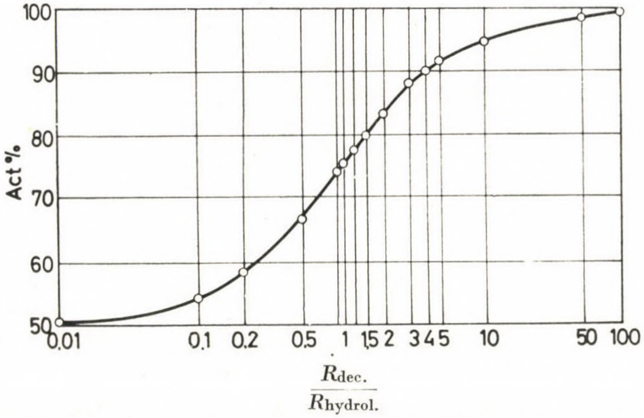


Fig. 2. The specific activity of amino acids as a function of the relative rates of the decarboxylation and hydrolysis of the intermediate formed in the Strecker reaction of α-keto acids

Fig. 2 shows the ratio of the reaction rates $\frac{R_d}{R_h}$, calculated on a theoretical basis, as a function of the percentage molar activity of the amino acid produced in the reaction. The course of this curve indicates that reaction rate ratios varying between $\frac{R_d}{R_h} = 1.4$ and 2.7, can be calculated for reactions of this type. This estimation has reality only if the molar activity of the amino acid formed in the reaction is measured after the completion of the competing reactions, since further chemical conversions are possible whose effects are not expressed in the quotient of reaction rates.

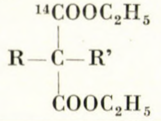
It is evident on the basis of a simple estimation of errors that, in the domain around the inflexion point, a 1% error in the determination of the molar activity of the amino acid end-product causes an error of about 5—10% in the estimation of the quotient of reaction rates. Further away from the inflexion point, however, the experimental error increases, first gradually, then for values outside the range $\frac{R_d}{R_h} = 0.3 - 4.0$, exponentially. Therefore, prior to activity measurement, any radioactive and radio-inactive impurities of the amino acid end-product should be removed very carefully, *e.g.*, by ion-exchange chromatography.

The ^{14}C-isotope effect that arises in decarboxylation practically does not affect the $\frac{R_d}{R_h}$ values. This is unequivocally shown by the fact that the experimental intramolecular isotope effects found when α-acetamidomalonic ester derivatives are hydrolyzed and decarboxylized, depend only slightly on the α-alkyl substituents (*cf.* Table II). The experimental values found by

Table II

Intramolecular ^{14}C-isotope effect in the hydrolysis and decarboxylation

of



$$R-\overset{\overset{\displaystyle ^{14}COOC_2H_5}{|}}{\underset{\underset{\displaystyle COOC_2H_5}{|}}{C}}-R'$$

derivatives

R	R'	Specific activity $10^{-2}\ \frac{\mu Ci}{mM}$			Intramolecular $\frac{k_4}{k_3}$ isotope effect		
		Starting material	Amino acid	Carbon dioxide	Found	Mean	Calc.
H	H		15.991		1.04		1.062[a]
H	NH—Ac	3.747	1.928	1.828	1.051		1.058[b]
			1.928	1.819	1.062	1.058	
			1.925	1.822	1.059	±0.007	1.040[c]
			1.927	1.820	1.062		
CH_3	NH—Ac	3.804	1.967	1.837	1.072	1.077	1.038[d]
			1.982	1.822	1.083	±0.006	
CH_3CH_2	NH—Ac	3.787	1.989	1.789	1.093	1.090	
			1.978	1.809	1.087	±0.003	
$C_6H_5CH_2$	NH—Ac	3.799	2.017	1.782	1.148	1.143	
			2.033	1.766	1.139	±0.006	

Notes

[a] Eyring—Cagle model.
[b] Zero point energy differences.
[c] Bigeleisen's approximation for heavy atoms.
[d] On the basis of Slater's coordinate.

us vary within the limits given in the literature for similar reactions [15]. In fact, the difference between our experimental values and those calculated on a theoretical basis for intramolecular isotope effect is of the same order as the experimental error in the quotients $\frac{R_d}{R_h}$ of the reaction rates. Thus the experimental determination of the decarboxylation and hydrolysis rates of α-amino(cyano-^{14}C)acetic acid derivatives can be carried out by our method within the limits of error which have been found for the intramolecular isotope effects measured in the decarboxylation of ^{14}C-labelled malonic acid derivatives.

Experimental

Synthesis of α-amino acids from α-keto acids

DL-glutamic-1-^{14}C acid

Active K^{14}CN (1.63 g; 25 mM; molar activity 2.27 mCi/mM) and NH_4Cl (1.44 g) were dissolved in a mixture of water (6 ml) and cc. NH_4OH (6 ml). To this solution α-ketoglutaric acid (3.65 g; 25 mM) was added. The reaction mixture was allowed to stand at room temperature for 1 hr, then kept at 60 °C for 4 hrs. The solution was then cooled in ice-water, acidified with cc. HCl (25 ml), and evaporated under reduced pressure. The residue was mixed with cc. HCl (25 ml) and refluxed for 6 hrs, then evaporated under reduced pressure. The residue was mixed with ethanol, and the inorganic salt was filtered off. The ethanolic solution was diluted with an equal volume of water and passed through a column of Dowex-50 (H^+) resin. The labelled amino acid was eluted with NH_4OH from the column, the solution evaporated in vacuum, and the residue dissolved in a small amount of water. The pH of this aqueous solution was adjusted to 3.1 with 6 *N* HCl. In order to complete the separation of the crude labelled DL-glutamic-1-^{14}C acid, ethanol (30 ml) was added to the mixture, and it was kept in a refrigerator for 2 hrs, then filtered, and the product was washed with ethanol to obtain 1.375 g of crude glutamic acid.

This product was dissolved in hot water (10 ml) and treated with decolourizing carbon; the filter was washed with hot water (3 ml). Ethanol (26 ml) was added to the solution and the product which separated was filtered off after standing for 2 hrs, washed with ethanol, and dried at 60 °C, to obtain 1.185 g (32.2%) of pure DL-glutamic-^{14}C acid.

Specific activity 13.05 μCi/mg.
Molar activity 1.92 μCi/mM.
Radiochemical incorporation 82%.

DL-α-alanine-1-^{14}C

Active K^{14}CN (1.63 g; 25 mM; molar activity 0.205 mCi/mM) and NH_4Cl (1. 44 g) were dissolved in a mixture of water (6 ml) and cc. NH_4OH (6 ml). Sodium pyruvate (2.75 g; 25 mM) was added, and the reaction mixture was allowed to stand at room temperature for 1 hr., then at 60 °C for 3 hrs. It was then cooled in ice-water, and acidified with cc. HCl (25 ml). Evaporation under reduced pressure gave a residue which was taken up in cc. HCl (25 ml), and refluxed for 6 hrs. The solution was evaporated in vacuum, the residue mixed with ethanol, and the inorganic salt filtered off. The ethanolic filtrate was diluted with an equal volume of water, and passed through a Dowex-50 (H^+) column. The labelled amino acid was eluted with NH_4OH, and the eluate evaporated in vacuum. The residue was dissolved in a small amount of water, and the crude labelled DL-α-alanine-1-^{14}C was precipitated with ethanol (25 ml), filtered off, and washed with ethanol.

The crude DL-α-alanine-1-^{14}C (521 mg) was dissolved in hot water (3 ml) and precipitated with ethanol (10 ml). After starting for 2 hrs in a refrigerator, filtration and washing with ethanol gave 307 mg (14%) of the pure product.

Specific activity 1.93 μCi/mg.
Molar activity 0.172 μCi/mM.
Radiochemical incorporation, 84%.

Decarboxylation of alkyl acetamidomalonic-1-^{14}C ester

Alkyl acetamidomalonic-1-^{14}C ester (10 mM) was weighed into a three-necked flask equipped with a dropping funnel, gas inlet tube, and a condenser connected to an absorption flask. The whole apparatus was flushed with nitrogen, then a 10% solution of KOH (10 ml) was placed into the absorption flask. 48% hydrogen bromide (10 ml) was added dropwise from the funnel, and the oil bath was heated to 120—140 °C. At this temperature decarboxylation took place. The labelled carbon dioxide was absorbed by the alkali, while hydrogen bromide was trapped in the condenser and flowed back into the reaction vessel.

In the absorber labelled barium carbonate was precipitated with barium hydroxide, collected by filtration, washed with anhydrous alcohol, dried, and its activity was measured.

The acid solution in the decarboxylation flask was evaporated in vacuum, then water (100 ml) was added and again evaporated. This procedure was repeated three times. After the last evaporation, the residue was diluted with water (100 ml) and passed through a Dowex-50 (H^+) resin column. The resin was washed to neutral with distilled water, and the amino acid eluted with a 1 : 1 mixture of cc. NH_4OH and water. The eluate was evaporated in vacuum, the residue stirred with dry alcohol (15 ml) and the labelled amino acid precipitate was collected by filtration, washed with dry alcohol, dried, and then its activity measured.

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ТОМ 60 — ВЫП. 3

РЕЗЮМЕ

Одновременное определение структурных изомеров аллиламида камфарной кислоты, II.

Р. Г. ХЕНЕИН, Г. НАРАИ-САБО и Ч. Й. ХОРВАИ

Был разработан количественный аналитический метод одновременного определения структурных изомеров α- и β-N-аллиламидов dl-камфарной кислоты на основе измерения интенсивностей пиков рентгенодиффрактограммы. Средняя квадратичная ошибка равна 2,1%.

Определение ортофосфатных ионов с помощью хлористого железа (III) и осциллометрической индикацией конечной точки титрования

М. Т. ВАНДОРФИ, Ф. ДЁМЁЛКИ и Л. ЭРДЕИ

Ортофосфатные ионы определялись титрованием их хлористым железом(III)с осциллометрической индикацией конечной точки. Определение ортофосфатных ионов может быть осуществлено в пределах содержания P_2O_5 в 15 мл раствора от 3 до 25 мг, причем концентрация посторонних ионов превышает концентрацию ортофосфатных ионов в 30 раз, с точностью измерения не ниже 1—2%. Метод использовался для измерения общего содержания фосфатов в стиральных порошках.

Изучение ионообменных равновесий радиоактивным методом, XIV.

Сравнение констант устойчивости и термодинамических функций для комплексов европий-трикарбаллилат и европий-цитрат, со составом 1:1

Т. ЛЕНДЬЕЛ

С помощью метода жидкого ионообменника и температурных коэффициентов определялись изменения энтальпии и энтропии, сопровождающие комплексообразование, протекающее в системах европий-трикарбаллиловая кислота и европий-лимонная кислота. При сравнении результатов было найдено, что гидроксильная группа лимонной кислоты оказывает хелатирующее влияние, в то время как трикарбаллиловая кислота, ведущая себя как монофункциональный лиганд, в изученном интервале концентраций дает лишь простой комплекс.

Дальнейшее уточнение электронографических данных для паров $SOCl_2$ и SO_2Cl_2

И. ХАРГИТТАИ

Был повторен структурный анализ электронографических данных для $SOCl_2$ и SO_2Cl_2, используя комплексные амплитуды рассеяния атомов. В предыдущей работе постоянное значение было использовано для функции рассеяния. Не была найдена существенная разница между результатами, полученными в этих двух исследованиях.

Попытки кинетической интерпретации адсорбционных изотерм бинарных смесей неэлектролитов

Г. ШАЙ

Обращается внимание на тот факт, что существующие термодинамические теории однослойной адсорбции не в состоянии удовлетворительно объяснить изменение коэффициентов поверхностной активности, т. к. во многих случаях идеальность или неидеальность жидкости не сопровождается параллельным поведением в адсорбционном слое. Используя упрощенную модель жидкости и полагая, что дырочный механизм справедлив для всех элементарных актов десорбции и адсорбции на поверхности, по энергетическим соображениям может быть выведена линейная зависимость между логарифмом фактора распределения и равновесной молярной долью любого компонента в бинарной смеси. Приводятся фактические экспериментальные примеры такого поведения, и отклонения, встречающиеся в других случаях, обсуждаются в свете уточнений к основной теории.

Стереохимические исследования, IV.
Кватернеризация 1,2-дизамещенных 1,2,3,4-тетрагидро-изохинолинов

II. Изучение кватернеризации и стереоселективности кватернеризации 1-фенил-, 1-изопропил- и 1-(3',4'-диметокси-бензил)-2-алкил-6,7-диметокси-1,2,3,4-тетрагидро-изохинолинов

Й. КОБОР, Г. БЕРНАТ, Л. РАДИЧ и М. КАЙТАР

Были приготовлены некоторые 1,2-дизамещенные производные 6,7-диметокси-3,4-дигидро- и 1,2,3,4-тетрагидро-изохинолинов. Изучалась стереоселективность реакции кватернеризации 1-замещенных 2-метил-6,7-диметокси-1,2,3,4-тетрагидро-изохинолинов (где заместителями в положении 1 являются: изопропил, фенил, 3,4-диметокси-бензил) с иодистыми этилом и бензилом, а также соответствующих 2-этил- и 2-бензил-производных с иодистым метилом. На основе исследований сырого продукта реакции ЯМР спектроскопии, хроматографическим анализом, а также дробной кристаллизацией было установлено, что кватернеризация N-этил- и N-бензил-оснований с иодистым этилом обладает лишь слабой селективностью. В противоположность этому, кватернеризация N-метил-оснований с иодистым бензилом, в пределах погрешности измерений спектров ЯМР (± 5%), дает единственный четвертичный продукт. В смеси, установившейся во время эквилибрации изомерных N-бензил-четвертичных солей в хлороформе, основным компонентом является продукт кватернеризации N-алкильных оснований иодистым бензилом.

Гетероциклические спиро-соединения, VII.

П. ШОХАР, К. КЁРМЕНДИ, А. ПФИСТНЕР-ФРАЙД и Ф. РУФФ

После выяснения сложных условий таутомерии спироксазона [1], необходимо было модифицировать строение ациловых и N-алкиловых(ариловых)-производных. С помощью ик и ямр спектроскопических и препаративных методов было установлено, что структура *моноацил-спироксазонов* (VIII) может быть однозначно выведена из открытого эндоциклического таутомера амидразона (III). Диацил-спироксазоны, получаемые с помощью ангидрида кислоты, также являются производными открытого амидразона (XVIII), в то время как ацетилирование спироксазона в пиридиновой среде приводит к образованию *диациловых соединений* со строением XV.

Отдельные смешанные O,O-диацил-спироксазоны склонны к обратимому переходу ациловой группы N $\rightleftarrows$ O, и переход ациловой группы сопровождается экзо-эндо смещением связи C$=$N. Таким образом, наряду с молекулами строения XV, образуются молекулы со строением XIV.

Экзо- и эндо-положение связи C$=$N в некоторых ацил-производных определялось с помощью солянокислого гидролиза. Из экзо-циклического таутомера был получен α-спироксазон, а из эндо-циклического — β-спироксазон.

Уже ранее описанные нами, *алкил(арил)-спироксазоны* оказались N(2)-замещенными спироксазонами (XXV). Их *моноацил-производные* (напр., XXVIIIa) представляют собой открытые ω-0-ацил-соединения, содержащие эндоциклическую C=N связь, а *диацил-производные*, получаемые с помощью ангидрида кислоты, имеют структуру XXVIII, где R_2 и R_3 — ацильные группы.

Реакции трансацилирования в серии флавоноидов, IV.

Новый синтез 5-метил-генистеина, пруметина, биоханина-А и сиссотрина

Л. ФАРКАШ, М. НОГРАДИ, Г. МЕЗЕИ-ВАНДОР и А. ГОТТЗЕГЕН

Под влиянием Ag_2CO_3 в пиридине, генистеин-7-бензоат превращается в 4'-бензоат. Эквимолекулярная смесь генистеина и его 4',7-дибензоата при тех же самых условиях дает 2 моля генистеин-4'-бензоата. На основе этих промежуточных продуктов был разработан новый синтез природных изофлавонов 5-метилгенистеина, прунетина, биоханина-А и сиссотрина.

Меченые аминокислоты и их производные, I.

Синтез Стрекера с α-кетокарбоновыми кислотами

И. ТЕПЛАН, И. МЕЗЁ, Л. БУРШИЧ и Й. МАРТОН

В качестве карбонильного компонента в синтезе Стрекера использовались α-кетокарбоновые кислоты. Данный метод пригоден для получения DL-глутаминовой-1-C^{14} кислоты. Изучались механизм реакций декарбоксилирования и гидролиза соединений типа α-амино-(циан-C^{14})-уксусной кислоты.

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THE ELECTRONIC STRUCTURE OF INORGANIC UNSATURATED CYCLIC COMPOUNDS, II

ULTRAVIOLET ABSORPTION SPECTRA OF PHOSPHONITRILIC DERIVATIVES

B. LAKATOS, Á. HESZ, ZS. VETÉSSY and G. HORVÁTH*

*(Reaction Kinetical Research Group of the Hungarian Academy of Sciences, University of Szeged and *Research Group of Chemical and Pharmaceutical Works Ltd. Chinoin, Budapest)*

Received January 2, 1968

Investigation of ultraviolet absorption spectra of several cyclic and linear phosphonitrilic derivatives led to the conclusion that in the phosphonitrilic ring there is no $p(\pi)$—$d(\pi)$ electron delocalization of high degree similar to aromatic ring systems.

The problem of the electronic structure of inorganic unsaturated cyclic compounds with bonds between different atoms only has not yet been correctly solved [1]. For solving this problem experimentally, their ultraviolet and infrared spectra, chemical behaviour and complex-forming abilities [1] were investigated.

The cyclic compounds containing no carbon atom** can be divided into two main groups: saturated and unsaturated cyclic compounds, *e.g.* hexamethyl-hexahydroborazine and borazine (in the earlier nomenclature: borazole) [2]. In our investigations the unsaturated compounds were studied to make a comparison between them and the organic, truly aromatic ones.

From the point of view of electronic structures there are three possible cases, based on the type of the orbitals of the unsaturated π-bonds:

1. So called homomorphic unsaturated rings with $p(\pi) - p(\pi)$ bonds, *e.g.* borazine and its derivatives [2].

2. Unsaturated rings with $p(\pi) - d(\pi)$, so called heteromorphic bonds, as *e.g.* disubstituted derivatives of phosphonitrilic compounds [3].

3 Unsaturated rings with $d(\pi) - d(\pi)$, homomorphic bonds as *e.g.* hexamethylcyclotrisilthiane [4].

In most cases the s^2 lone electron pair or $p(\pi)$ electron of the donor nitrogen atom and the empty $p(\pi)$ or outer $d(\pi)$ orbitals of the acceptor atom take part in the formation of the π-bonds of the ring. Thus normal and co-ordinative unsaturation can formally be considered.

The cyclic π-bonds of $p(\pi) - d(\pi)$ type promised to be the theoretically most interesting ones, so we decided to investigate them first. Since there are

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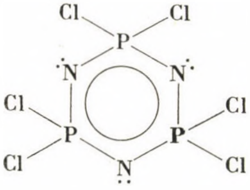
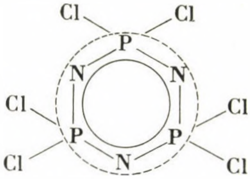
** The compounds with one or more carbon atoms in the ring skeleton are considered as organic heterocyclic ones used only for comparison.

good descriptions for the preparation of cyclic trimeric and tetrameric phosphonitrilic derivatives, we started our investigations on them. X-ray [5 a—o] and electron diffraction [6] studies on these compounds proved the cyclic structure and the equal P=N bond lengths in the ring disproved their pseudoaromatic character. For this reason, these compounds were generally considered "aromatic" like benzene, symmetrical triazine and borazole, though some experimental data seemed to be inconsistent with this picture. Therefore, an electronic structure similar to the corresponding noncyclic (monomeric) unsaturated inorganic compounds was also suggested for these compounds containing an unsaturated ring with bonds of $p(\pi) - d(\pi)$ type.

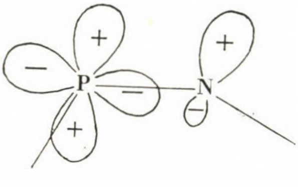
This problem could not be solved even by quantummechanical calculations. On the basis of MO-LCAO calculations CRAIG *et al.* [7 a—e] derived an aromatic, heteromorphic $p(\pi) - d(\pi)$ conjugation non-Hückel-type, expanding over the whole ring; they supposed the participation of its one single $3d_{xz}$ orbital, with lobes directed tangentially to the ring and different electronegativities for the $3d$-orbitals of the phosphorus atom:



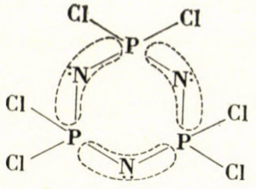
They assumed the presence of another aromatic conjugation too — it is non-Hückel-type — delocalizing over the whole ring but outside of it:



This latter should be formed between the $2s^2$ lone electron pair of nitrogen atom and the $3d_{xy}$ electrons of phosphorus atom:



However, the calculations of DEWAR *et al.* [7 f—g] resulted in nonaromatic, P—N—P three-centre bonds, so-called islands — breaking off at the phosphorus atoms — because of the orthogonality of the used — more than one — phosphorus 3*d*-orbitals of nearly equal electronegativity.



Only weak interaction was supposed to occur between the three-centre π-islands.

Later the calculations of CRAIG *et al.* [7 c—d] were extended not only over the planar but also over the most probable steric conformations of the cyclic systems, using more *d*-orbitals and considering a wider range of the values of electronegativity, resonance and overlapping parameters. They found the three-centre island π-electron model to be a special case of the perfect aromatic delocalization occurring with the nearly equal electronegativity values of the $d(\pi)$ orbitals. The approximate nature of the calculations, lack of the electron correlation, very weak approximation of the Slater-type orbitals and the absence of the actual values of important parameters make it impossible to decide definitely, which model is the better approximation.

So far, by the help of thermochemical [8 a—b] and X-ray diffraction [5 a—o] measurements, force constants calculated from infrared spectra [9], magnetic susceptibility values [7 b], nuclear magnetic resonance [10 a—b] and nuclear quadrupole resonance [10 c—e] spectra rendered possible to point out the multiple, "unsaturated" character of the P=N bonds of these rings, but could not provide an unambiguous evidence for the aromatic or nonaromatic character of the π-electron system of the ring.

After considering these results the investigation of the ultraviolet absorption spectra of the phosphonitrilic derivatives was found to be the most important step including the evaluation of the previous results given in the literature.

Among the halogen derivatives, the fluoro-derivative, hexafluorocyclotriphosphazatriene: $(NPF_2)_3$ in *n*-hexane solution, did not show significant absorption in the near ultraviolet region, between 400—180 nm [11 a]. Having no instrument suitable to measure the absorption at about 150 nm due to the excitation of the lone or rather π-bonding electrons of the fluorine atom, the data of WALSH *et al.* [11 b] have been accepted. According to these, trimeric and tetrameric cyclic phosphonitrilic fluorides begin to absorb at about 170 and 180 nm, resp., the maximum of the trimer and the tetramer were found at 149.4 ± 0.5 nm and 147.5 ± 0.5 nm, resp., with log $\varepsilon \sim 4$ intensities, and a minimum was found at 141 nm. From this wave length the intensity of the absorption rapidly increases, at 135 nm reaches a value higher than that of the maximum, and continues this increase up to the end of the measuring range, 110 nm, without showing any maximum. The first maximum can be assigned to $\pi \rightarrow \pi^*$ excitation of the fluorine atom, the second band is probably due to the excitation of the lone pair electrons of the nitrogen atoms of the ring, more exactly of those forming the exocyclic π bond out of the ring together with the phosphorus atoms.*

Several papers [12—15] mention the ultraviolet absorption spectra of cyclic phosphonitrilic chlorides, but they are quite contradictory. According to the first measurements of KRAUSE [12] in cyclohexane, cyclic trimeric and tetrameric phosphonitrilic chlorides show a sharp maximum at 217 nm with an intensity value of $\varepsilon_{\max} = 1.8 \cdot 10^3$. Nearly equal maxima were found in the spectra of the pentamer (216 nm), hexamer (217 nm) and heptamer (212 nm) with $\varepsilon_{\max} \sim 10^3$. DEWAR *et al.* [14 c] found a maximum at 199 nm of the cyclic trimer and at 203 nm of the tetramer, also in cyclohexane, with intensity values increasing with the molecular weights. According to this, the maximum of the absorption of the tetramer derivative has undergone a bathochromic shift as compared to the trimer, in contrast to the fluoro-derivatives. DE MAINE *et al.* [13 a—b] observed a single maximum between 250 and 200 nm with wave length and intensity strongly depending on the solvent, concentration and temperature, less significantly on the molecular weight. It was measured by a Bausch and Lomb Recording Spectronic 505 instrument. *E.g.* the hexachlorocyclotriphosphazatriene showed absorption maximum at 211 nm [13 b] with $\varepsilon_{\max} = 350$ intensity; in the case of the octachlorocyclotetraphosphazatetraene the obtained values were $\lambda_{\max} = 213$ nm and $\varepsilon_{\max} = 390$; both were measured in *n*-heptane at 20°. Working in different hydrocarbon and halogenated hydrocarbon solvents very different values were obtained, *e.g.* the absorption maximum of the cyclic trimer compound was found at 220 nm in *n*-pentane, at 214 nm in *n*-hexane and at 229 nm in *n*-undecane. Before measuring the solutions they were saturated with dry nitrogen.

PADDOCK's co-worker, D. R. SMITH, however, found, using a Unicam SP 500 spectrophotometer [14 a—b], that no maxima exist between 210 nm

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* This seems to be probable when comparing the ionization potential values of the cyclic phosphonitrilic fluorides and chlorides measured by a mass spectrograph:

$[NPF_2]_3$	$[NPF_2]_4$	$[NPF_2]_5$	
11.64 eV	10.86 eV	11.1 eV	
$[NPCl_2]_3$	$[NPCl_2]_4$	$[NPCl_2]_5$	$[NPCl_2]_6$
10.26 eV	9.80 eV	9.83 eV	9.81 eV

with the following ionization potentials: nitrogen atom: 14.555 eV; nitrogen molecule: 15.51 eV; methylamine: 9.8 eV; dimethylamine: 9.6 eV; trimethylamine: 9.4 eV; phosphorus trichloride: 12.2 eV; phosphorus atom: 10.43 eV; fluorine atom: 17.422 eV; tetrafluoromethane: 17.8 eV; sulphur hexafluoride: 19.3 eV.

and 350 nm, only a continuous increase could be observed in the case of the cyclic trimeric, tetrameric and higher homologues of phosphonitrilic chloride in *n*-hexane. Other solvents as cyclohexane and methanol did not alter the spectra significantly, even conc. sulphuric acid resulted in a hypsochromic shift of a few nm only. Almost no change due to increasing molecular weights was found in the spectra and no regular shift was observed. These results were supported by the measurements of **Walsh** *et al.* [11 b] recording the absorption spectrum of the hexachlorocyclotriphosphazatriene in cyclohexane solution in the 250—185 nm region by an Optica recording spectrophotometer, oxygen being excluded from the optical path. Absorption maximum did not appear, the intensity continuously increased up to 185 nm, reaching there log $\varepsilon = 3.34$ only.*

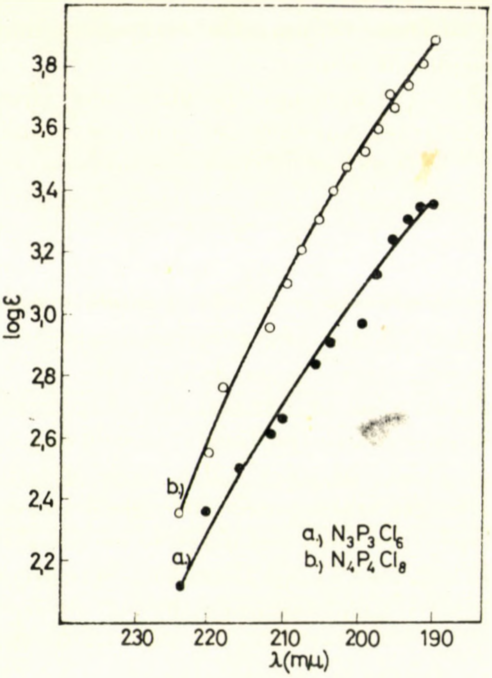

Fig. 1

Recently **Allcock** *et al.* [15] reexamined the maxima found by **De Maine** and others at about 210 nm and stated that those appeared due to scattered light. Not did these authors observe any absorption maximum above 199 nm in *n*-heptane solution of hexachlorocyclotriphosphazatriene.

We recorded the ultraviolet absorption spectra of very pure hexachlorocyclotriphosphazatriene and octachlorocyclotetraphosphazatetraene in *n*-hexane solutions between 300 nm and 190 nm by a Beckman DU spectro-

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* Nor could vacuum ultraviolet spectra be recorded in the vapour state in heated cuvettes [11 c].

photometer equipped with photomultiplier. Absorption started below 250 nm and increased gradually showing no maximum in the measured range. At every wavelengths the intensity values of the tetramer were higher than those of the trimer (Fig. 1). This is in accordance with the measurements of Walsh *et al.* [11 b—c] and Paddock *et al.* (14 a, b) that could not be explained by De Maine *et al.* [13 a]. Using solutions of different concentrations, the validity of the Lambert—Beer equation in the case of this system was proved at 200 nm. (Curve *a* in Fig. 2).

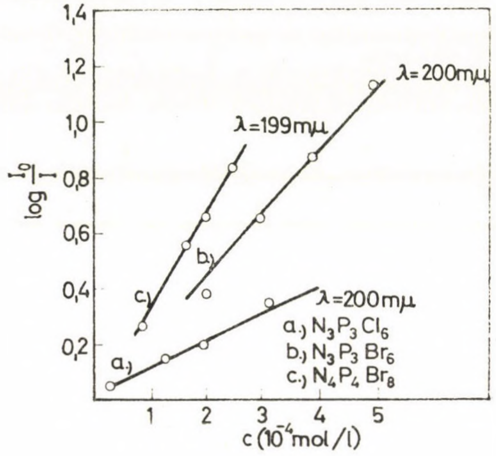

Fig. 2

To interpret the absorption of the cyclic phosphonitrilic chlorides, the knowledge of the spectra of linear polymeric phosphonitrilic chlorides with $(NPCl_2)_nPCl_5$ composition, insoluble in petroleum ether was also needed. These compounds can be obtained partly as by-products of the preparation of cyclic phosphonitrilic chlorides from phosphorus pentachloride and ammonium chloride in *sym.*-tetrachloroethane [14 b], partly by the direct heating of cyclic phosphonitrilic chlorides with phosphorus pentachloride, for a longer period at a higher temperature (350°C for 5 hours [14 b] or 200—220°C for 72 hours [16]) in a sealed tube filled with nitrogen gas. D. R. Smith [17 a, b] recorded the ultraviolet spectra of polymer oils of different molecular weights, with $(NPCl_2)_nPCl_5$ composition, insoluble in petroleum ether owing to their non-cyclic structure. A Unicam SP 500 spectrophotometer was used to measure 0.1—0.2 weight% solutions in carbon tetrachloride in the 260—450 nm region. Two sharp maxima were found at 315 nm and 365 nm and only intensity changes but not wavelength changes were found when compounds of different molecular weights were investigated [17 b]. As our assumption was that these two maxima resulted from possible contaminations of the solvent, a mixture of linear polymer oils insoluble in petroleum ether was prepared without any solvent and its spectrum was recorded by an Optica Milan CF4 recording spectrophotometer. Curve *a* in Fig. 3 shows the spectra of these linear polymeric homologues: no maximum appears in the 400—290 nm region, only a slow but continuous increase of absorption. Neither samples of the reaction mixture of phosphorus pentachloride and ammonium chloride in very carefully purified *sym.*-tetrachloroethane did show a sharp maximum between 290 and 400 nm (Curve *b* in Fig. 3).* Finally, hexachlorocyclotriphosphazatriene was heated with an excess of phosphorus pentachloride in 1 : 2 and 1 : 1 ratio at 350°C in a sealed tube for 5 hours. After dissolving the resulting oil in carbon tetrachloride its spectrum was recorded by an Optica Milan CF4 recording and a Beckman DU spectrophotometer too (curves *c* and *d* in Fig. 3). Again a slowly, continuously increasing absorption was found with no sharp maximum in the 400—290 nm region. These facts contrast with the theory of PADDOCK *et al.* concerning the π-electron structure of the linear phosphonitrilic halogenide polymers stating that it is substantially different from that of the cyclic derivatives.

Among the cyclic phosphonitrilic bromides the ultraviolet absorption spectrum of the trimeric derivative was recorded by D. R. SMITH [17 c] in *n*-hexane and in conc. sulphuric acid between 300 nm and 210 nm. Gradually increasing intensity of absorption was observed with a log ε value about 3.8 at 210 nm but no maximum was reached. The spectrum of the conc. sulphuric acid solution was similar, only a hypsochromic shift of about 8 nm was noticed. We prepared very pure hexabromocyclotriphosphazatriene and octabromocyclotetraphosphazatetraene and recorded the spectra of their solutions in *n*-hexane in the 300—190 nm region by a Beckman DU spectrophotometer [18]. Curves *a* and *b* in Fig. 4 show the ultraviolet absorption maximum of the hexabromocyclotriphosphazatriene at 200 nm (log $\varepsilon = 4.4$) and that of the tetramer at 199 nm (log $\varepsilon = 4.5$). In both cases the validity of the Lambert—Beer equation in the given system was proved at the wavelengths of the absorption maxima (curves *b* and *c* in Fig. 2). At the measurements in conc. sulphuric acid a shift of 8 nm was also observed, with the maximum appearing at 192 nm (log $\varepsilon = 4.3$).

The ultraviolet absorption spectrum of one of the cyclic trimeric mixed halogenides: tetrachlorodibromocyclotriphosphazatriene $N_3P_3Cl_4Br_2$ was also recorded (Fig. 5). The absorption maximum appeared at 192 nm (log $\varepsilon \sim 4$), near to the end of the measuring range.

Though some notes were found also on phosphonitrilic iodide derivatives in patents [19 a, b, c] dealing with phosphonitrilic halogenides, we did not succeed to prepare them up to now. The usual dry reaction of ammonium halogenide with phosphorus pentahalogenide or the methods working in sol-

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* Similar shape may be obtained by PCl_5 in *sim.* tetrachloroethane.

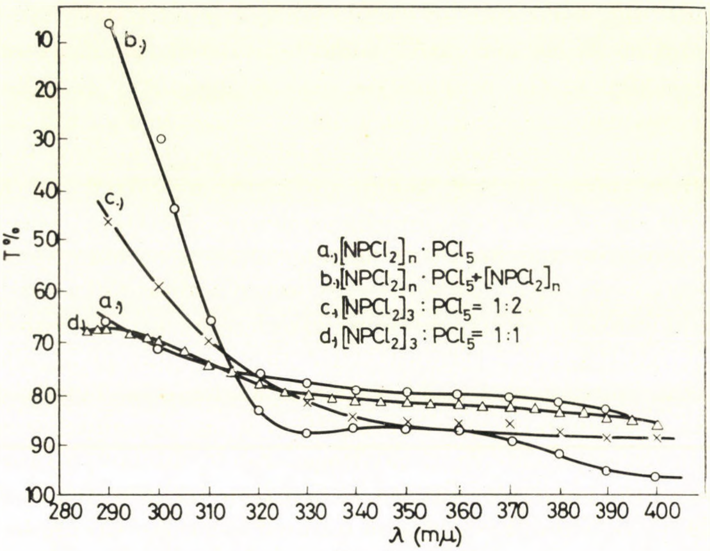


Fig. 3

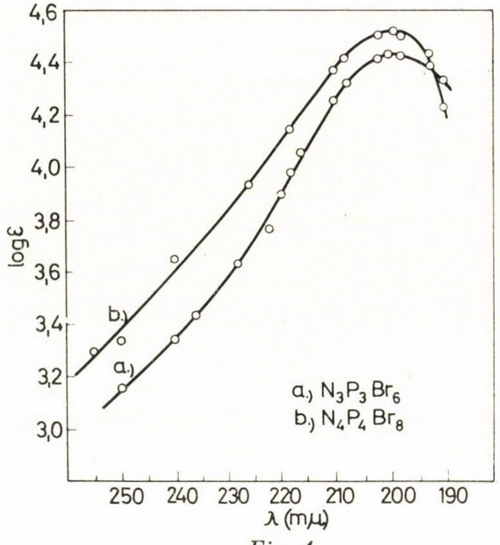


Fig. 4

vents (*sym.*-tetrachloroethane, monochlorobenzene or *o*-dichlorobenzene) could not be applied as neither phosphorus (V) iodide nor mixed phosphorus (V) iodide-halogenide derivatives are known [20 a, b]. Similarly to the preparation of fluoro-derivatives, the hexachlorocyclotriphosphazatriene was reacted with sodium iodide in acetone [21 a] and in sulphurous dioxide [21 b] medium. Though some months later the chloride was quantitatively precipitated as sodium chloride, the separation of iodine started immediately after mixing the reagents and no iodine derivative could be isolated. Similarly to diazotization reactions used in the preparative organic chemistry [22], hexamidocyclotriphosphazatriene was reacted with sodium nitrite in acetic acid medium at a low temperature, then sodium iodide was added to the mixture in the presence of a catalyst, copper(II) salt. Iodine and nitrogen evolved and the hydrolyzed product hexahydroxidocyclotriphosphazatriene $[NP(OH)_2]_3$ was obtained but no iodine derivative was found. On analogy of the reaction of phosphorus-(III)-amine derivatives with anhydrous hydrogen iodide [23 a—d] also the reaction of bisdimethylaminotetrachlorocyclotriphosphazatriene with hydrogen iodide ($N_3P_3Cl_4[N(CH_3)_2]_2 + 2\ HI$) was tried to carry out in absolute ether medium but the starting materials remained unchanged. Finally bisethylmercaptocyclotriphosphazatriene $N_3P_3Cl_4(SC_2H_5)_2$ in absolute ether was reacted with an excess of anhydrous hydrogen iodide similarly to the method of preparation of the iodine derivatives of inorganic unsaturated cyclic boron compounds [24 a—c]. The ultraviolet and infrared spectra of the products showed the presence of ethylmercaptane, ethyl-iso-thiocyanate, unreacted starting materials and unidentified substances, some iodine was formed too, but no iodine derivative of phosphorus nitride was obtained. Probably iodine derivatives of phosphorus nitride are as instable as phosphorus (V) iodide itself. Taking into consideration the Van der WAALS radii, this instability is not of steric origin. To the formation of the phosphorus (V) valence state, the empty 3*d* orbitals of the free phosphorus atom are required. However, to stabilize these by the contraction of the 3*d* orbitals [25 a, b], atoms of high electronegativity — fluorine, oxygen, nitrogen, chlorine, bromine — must be attached to the phosphorus atom. The electronegativity of the iodine atom is not high enough to produce this effect, therefore even the formed iodide compound suffers in room temperature discontinuous deformation accompanied by iodine evolution.

Table I

Data of ultraviolet absorption spectra of cyclic phosphorus nitride dihalogenides

Compound	λ_{max}	log ε_{max}
$N_3P_3F_6$	149.4	4.0
$N_4P_4F_8$	147.5	4.0
$N_3P_3Cl_6$	(175)	(4.0)
$N_4P_4Cl_8$	(173)	(4.0)
$N_3P_3Cl_5Br$	192	4.0
$N_3P_3Cl_4Br_2$	192	4.0
$N_3P_3Br_6$	200	4.4
$N_4P_4Br_8$	199	4.5

The position of the maximum of the uv. absorption spectra of the phosphonitrilic dihalogenides depend on the absorption of the halogen atom. Thus the absorption maxima of trimeric and tetrameric phosphonitrilic chlorides, not having been measured, yet can be extrapolated to $\lambda \sim 175$ nm and to $\lambda \sim 173$ nm, resp., with an intensity value of $\log \varepsilon \sim 4$ in both cases (Table I).

The order of magnitude of the absorption intensity ($\log \varepsilon \sim 4$) and the slight dependence on the polarity of the solvent (the shift produced by conc. sulphuric acid corresponds to the energy of hydrogen bonding) point to a transition of $\pi \rightarrow \pi^*$ type. Molecular weight shows only a slight effect on the spectra. They are similar to those of the corresponding inorganic linear unsaturated homologues and strictly differ from the conjugated unsaturated hydrocarbons. No bands characteristic of aromatic systems are found, as *e.g.* the *B*-band (so-called benzenoid band) between 230—270 nm.

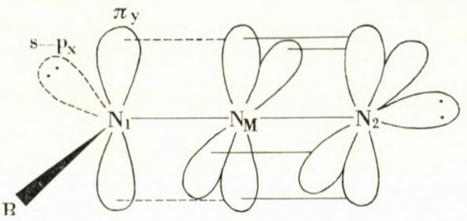
The pseudohalogenide derivatives of the cyclic phosphonitrilic compounds were represented by the azide and iso-thiocyanate as ultraviolet spectra of compounds containing these two groups suitable to comparison have already been accurately investigated [26 a—d, 27 a—d]. The data of the spectra of some organic azides, of compounds of $(CH_3)_3MN_3$ composition (M = C, Si, Ge) and of hexaazidocyclotriphosphazatriene and diethylazido-phosphate, the latter two being determined by us, are given in Table II. As can be seen

Table II

Data of ultraviolet absorption spectra of some azides

Compound	$\pi_y(2p_y\ R—N_1) \rightarrow \pi_x^*(N_M—N_2)$		$sp_x(R—N_1) \rightarrow \pi_y^*(N_M—N_2)$		$\pi_y \rightarrow \sigma_a^*$	
	λ_{max}	ε	λ_{max}	ε	λ_{max}	ε
n-butylazide	287.0	25	216.0	540		
Cyclohexylazide	287.1	26	216.7	440		
2-chloroethylazide	283.4	34	214.1	609		
Benzylazide	284.0	medium				
Phenylazide	283.0	very strong				
Cyanoazide	275.0	103	220.0	2157		
Azoimide	264.0		200			
Hydrated azide ion			230	440	188	>10000
Trimethylmethylazide	288	23	215.5	500		
Trimethylsilylazide	255.1	19	212.3	260	<180	>10000
Trimethylgermaniumazide	266.1	23	211.9	252	<180	>10000
Diethylazido-phosphate	250.0	20	208.0	316		
Hexaazidocyclotriphosphazatriene	260	20	210	(6300)	~197.0	10000

in it, the ultraviolet absorption spectra of azides contain two bands of lower intensity, and one band of high intensity is observed near to the end of the measuring range. **Closson** and **Gray** [26 a] assigned these bands to the following transitions, based on MO-LCAO calculations. The absorption of lowest energy found at 290—250 nm is of $\pi_y(2p_y,\ R-N_1) \rightarrow \pi_x^*(N_M-N_2)$ type, that of higher energy appearing between 200—235 nm corresponds to $sp_x(R-N_1) \rightarrow \pi_y^*(N_M-N_2)$ type. The $R-N_1-N_M-N_2$ bond scheme shows:



that both transitions are forbidden as a consequence that they are due to transitions between two perpendicular planes, so they are of low intensity. The third band of high intensity, appearing at the end of the measuring range is assigned to a transition of $\pi_y \rightarrow \sigma^*$ type, this is, of course an allowed transition. It can be seen in Table II that both bands of smaller intensity of the ali-

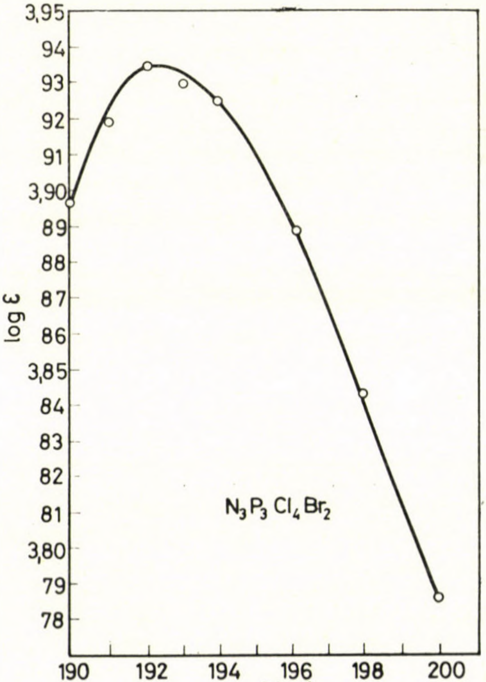


Fig. 5

phatic azides suffer a hypsochromic shift because of the inductive effect of more electronegative substituents, *e.g.* chlorine, as the energies of the sp_x and p_y orbitals are decreased. The hypsochromic shift becomes more significant when the carbon atom attached to the "first" nitrogen atom (N_1) is substituted by a silicon or germanium atom in the $(CH_3)_3MN_3$ molecule. The reason is that the acceptor effect of the empty outer *d*-orbitals of the central silicon or germanium atom produces a strong dative $\pi_y(N_1) \rightarrow d(\pi)(Si)$ bond with the neighbouring N_1 atom, which decreases most of all the energy of the $\pi_y(N_1)$ orbital and in a lesser degree that of the $sp_x(N_1)$ orbital, while only negligibly influencing the energy of the nonbonding ones. This regularity can be seen well in the spectrum of $(C_2H_5O)_2PON_3$ in hexane measured by us (Fig. 6) showing a decrease of wavelength values ($\lambda_{max} = 250$ nm, $\varepsilon = 20$ and $\lambda_{max} = 208$ nm, $\varepsilon = 316$, the third transition could not be measured) due to the stronger acceptor effect of 3*d* orbitals of phosphorus atom compared to silicon and germanium atoms. The ultraviolet absorption spectrum of hexaazidocyclotriphosphazatriene in hexane recorded by a Beckman DU spectrophotometer in the 240–190 nm region (Fig. 7 *a*) and an Optica Milan CF4 spectrophotometer too, (Fig. 7 *b*) resembles the former very much. The maximum of the band of lowest intensity is found at about 260 nm, the second band, appearing at about 210 nm

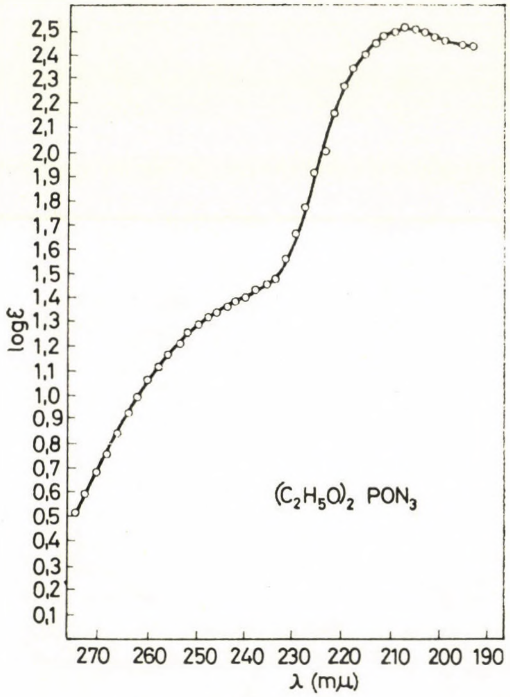


Fig. 6

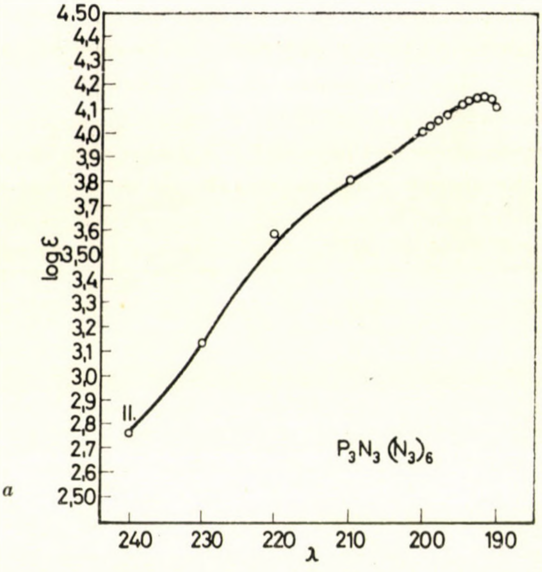


Fig. 7a

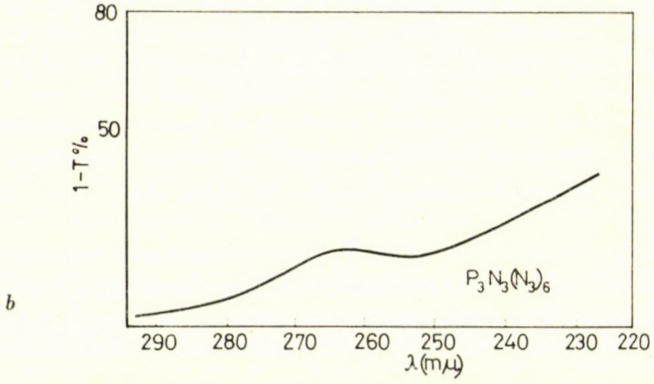


Fig. 7b

is probably overlapped by the third one of high intensity which occurs near to the end of the measuring range. The ultraviolet absorption spectrum of hexaazidocyclotriphosphazatriene is certainly similar to those of the noncyclic diethylazido phosphate and trimethylsilylazide and not to aromatic azides.

The investigation of the isothiocyanates gave similar results (Table III). Two bands were generally observed, disregarding the aromatic isothiocyanates [28]. One of them is found at about $\lambda_{\max} = 250$ nm ($\log \varepsilon \sim 3.5$), due to $\pi \rightarrow \pi^*$ excitation of the sulphur atom.*

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* This conclusion is based partly on the high intensity of the band, partly on the $\pi \rightarrow \pi^*$ transition of the sulphur atom in *n*-alkyl-mono-thiocarbamates resulting in a band at $\lambda_{\max} = 226$—236 nm ($\log \varepsilon = 4$) and on the observation that nitriles and isonitriles show no absorption between 220—770 nm.

Table III

Data of ultraviolet absorption spectra of some isothiocyanates

Compound	$N(\pi \rightarrow \pi^*)$		$S(\pi \rightarrow \pi^*)$	
	λ_{max}	log ε	λ_{max}	log ε
Methylisothiocyanate	192	4	249	3.34
Ethylisothiocyanate			250	2.94
n-butylisothiocyanate			249	3.50
Allylisothiocyanate			249	3.10
Phenylisothiocyanate	220	(4.38)	281	(4.12)
Trimethylsilylisothiocyanate	198	4.83	246	3.09
Phosphorus triisocyanate	206	4.08	230	3.96
Phosphorus oxy-isothiocyanate	213	4.00	250	3.50
Hexaisothiocyanatotriphosphazatriene	196	5.09	250	3.44

The second band (Table III) is of higher intensity (log $\varepsilon \geq 4$) and on the basis of the ultraviolet absorption spectra of azides, amides and diamine derivatives it probably belongs to the excitation of the "lone" or partly bonding electron pair of the nitrogen atom. The ultraviolet absorption spectrum of cyclic $[NP(NCS)_2]_3$ in *n*-heptane (curve *a* in Fig. 8) resembles those of $P(NCS)_3$ (curve *b* in Fig. 8) and $(CH_3)_2Si(NCS)_2$ (curve *c* in Fig. 8) in *n*-heptane solutions. Significant difference is found in the spectra of aromatic isothiocyanates *e.g.* phenylisothiocyanate in hexane (curve *d* in Fig. 8).

The weak diffuse maximum (log $\varepsilon < 1.0$), found in the 200—400 nm region in the spectra of cyclic $[NP(OCH_3)_2]_3$, and $[NP(OCH_2CF_3)_2]_3$ and the corresponding linear polymers in methanol solution is due to contaminations present in traces [15]. We recorded the spectra of very pure $[NP(OCH_3)_2]_3$ and $[NP(OCH_2CH_3)_2]_3$ in *n*-hexane (curves *a* and *b* in Fig. 9) and did not find any maxima but a continuous increase of absorption up to the end of the measuring range of the instrument. In the ultraviolet spectrum of the prepared sulphur derivative, cyclic $N_3P_3Cl_4(SC_2H_5)_2$ in *n*-heptane (Fig. 10) only a weak shoulder is found at about $\lambda \sim 240$ nm (log $\varepsilon \sim 3$) due to $\pi \rightarrow \pi^*$ excitation of the sulphur atom, followed by a gradual increase of intensity up to the measuring limit.

Investigating the nitrogen derivatives, a weak absorption band (log $\varepsilon <$ < 0.4) was observed in the spectra of the linear $[NP(NHC_2H_5)_2]_n$ and $[NP(N(CH_3)_2)_2]_n$ polymers with high molecular weights, due to the presence of contamination trace [29 a], no other absorption was found up to 200 nm. The spectra of cyclic $N_3P_3Cl_4[N(CH_3)_2]_2$, $N_3P_3Cl_2[N(CH_3)_2]_4$ and $N_3P_3[N(CH_3)_2]_6$ in hexane solutions (Curves *a*, *b* and *c* in Fig. 11) show a maximum of high intensity near to the end of the measuring range. This probably belongs to the

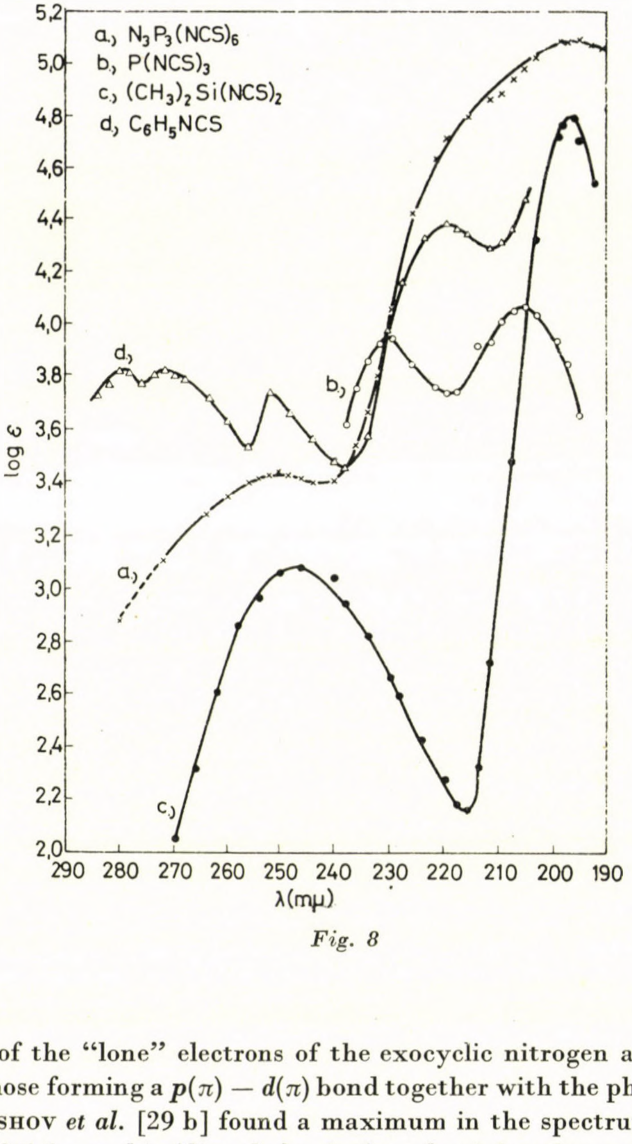
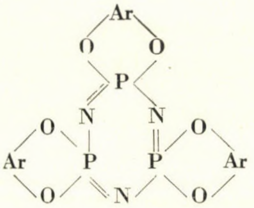


Fig. 8

excitation of the "lone" electrons of the exocyclic nitrogen atoms, more precisely, of those forming a $p(\pi) - d(\pi)$ bond together with the phosphorus atoms.

SVETSHOV *et al.* [29 b] found a maximum in the spectrum of the 1,3-bis-(amino)-1,3,5,5-tetrakis-(dimethylamino)-cyclotriphosphazatriene in *n*-hexane between 200—210 nm ($\varepsilon = 1000$). They worked on a SzF spectrophotometer. We investigated the spectrum of diaminotetrachlorocyclotriphosphazatriene in *n*-hexane and did not find any maximum up to 190 nm.

Finally, the study of the carbon derivatives showed that $[N_3P_3(CH_3)_2]_6$ in *n*-hexane has no significant absorption in the measured region. The position of the phenyl group does not affect considerably the wavelengths of the observed bands either connected directly to the phosphonitrilic ring, *e.g.* in $[NP(C_6H_5)_2]_3$ [30], or through an O, S or NH group, as in



[31 a, b], where Ar = aromatic group. So *n*-hexane solution of $[NP(C_6H_5)_2]_3$ shows a maximum at $\lambda_{max} = 260$ nm [30]. The spectrum of cyclic phosphonitrilic derivatives containing an aromatic ring connected through an O, S or NH group is almost identical to that of the compound being attached, *e.g.* in the above case to that of *o*-dimethoxybenzene [31 a, b].* All these show that no significant interaction exists between the phosphonitrilic ring and the π-electron system of the aromatic ring. The low delocalization degree of the π-electron system of phosphonitrilic ring can account for this.

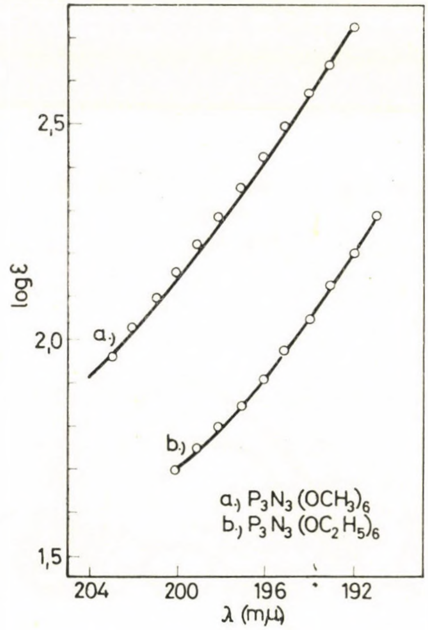


Fig. 9

Paciorek [32] obtained similar results, investigating the ultraviolet absorption spectra of linear phosphorus nitride diphenyl derivatives,

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* Nagy *et al.* [Per. Polytechnica **10**, 451 (1966) and **11**, 33 (1967)] investigated the ultraviolet absorption spectra of $[NP(OC_6H_5)_2]_3$, $P[OC_6H_5]_3$, $OP[OC_6H_5]_3$, $C_6H_5OCH_3$ and C_6H_5OH, and also established that no significant conjugation exists between the π-electron system of the aromatic phenoxy group and that of the phosphorus nitride ring. The ultraviolet spectrum of cyclic $[NP(OC_6H_5)_2]_3$ is similar to that of noncyclic $OP(OC_6H_5)_3$ ($\lambda_{max} = 262.4$ nm and 261 nm).

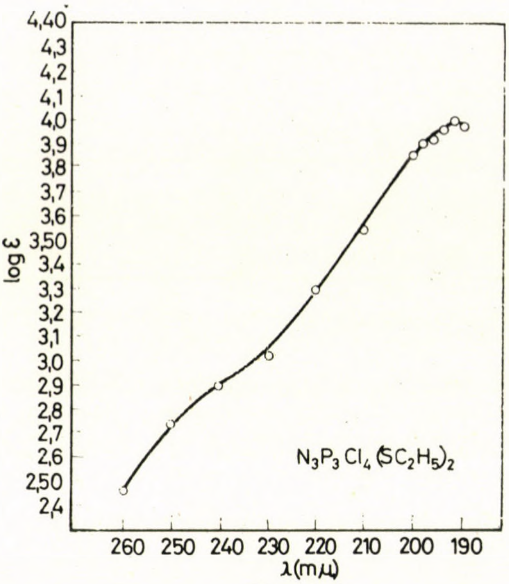

Fig. 10

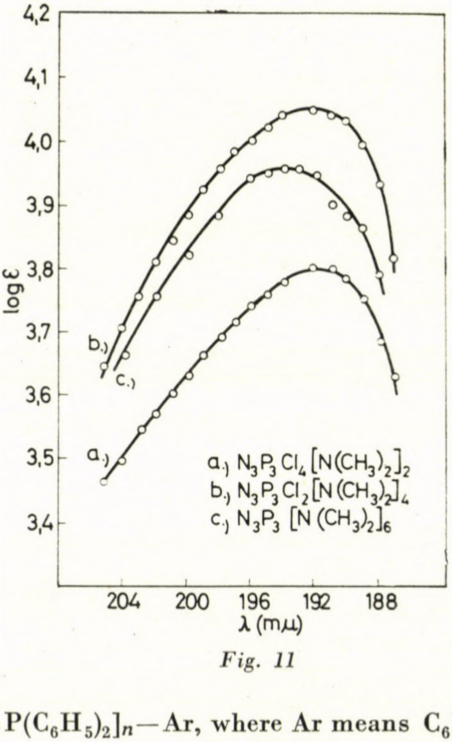

Fig. 11

$(C_6H_5)_2P(O)-[N=P(C_6H_5)_2]_n-Ar$, where Ar means C_6H_5- or $-NH-P(O)(C_6H_5)_2$ groups and $n = 1$, 2 or 4. Increasing $-P=N-$ chain length did not result in bathochromic shift.

Summing up, we can state that the ultraviolet absorption spectra of cyclic and linear polymeric phosphonitrilic disubstituted compounds primarily depend on the substituents. Cyclic derivatives do not show bands characteristic of aromatic systems; their ultraviolet absorption spectra are similar to those of noncyclic phosphorus derivatives containing the same substituents and to those of the corresponding linear polymers. Considering these facts, the conception of the "aromatic", highly delocalized structure of the π-electron system of the phosphonitrilic ring must be refused. The three-centre π-electron model suggested by Dewar seems to be more probable. This model helps to explain the failure of preparation of transition metal complexes of sandwich type with cyclic phosphonitrilic derivatives [1, 33]. Further, investigations of infrared absorption intensities proved the low delocalization degree of the π-electrons of the phosphonitrilic rings [34].

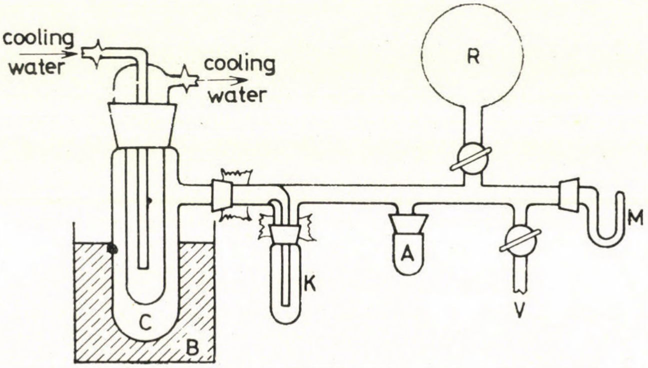

Fig. 12. A = vessel for the adsorber; B = oil bath; K = vessel for freezing; C = sublimation space; V = connection to vacuum (made by a suction engine or diffusional pump); M = manometer; R = buffer space

Experimental

Preparation of trimeric and tetrameric phosphonitrilic dichlorides

The reaction of ammonium chloride with phosphorus pentachloride was used [35, 36]. A mixture of 1.5 : 1 molar ratio of ammonium chloride and phosphorus pentachloride in monochlorobenzene was refluxed and stirred for 30—40 hours at 124—127°C. The unreacted solid residue was filtered off and the solvent was distilled. The cyclic product was extracted from the oily residue with benzene and the solution was treated with active carbon to obtain a clear liquid. After evaporating the benzene, a white crystalline product was obtained. The trimeric and tetrameric homologues were separated by repeated recrystallization from petroleum ether and by vacuum sublimation (at 124°C/10 Hgmm for the trimer and 185°C/10 Hgmm for the tetramer). The apparatus used for this separation is shown in Fig. 12. Purity test was performed by recording the infrared spectra. M.p of the trimer: 112.8°C; M.p. of the tetramer: 123.5°C.

Preparation of trimeric and tetrameric phosphonitrilic dibromide

Ammonium bromide and phosphorus tribromide was reacted with bromine [37]. Optimal yield in cyclic trimeric and tetrameric homologues (50% trimer, 8% tetramer) was obtained by the following method.

The 2/3 of the bromide needed for the reaction was added to a mixture of calculated quantities of ammonium bromide and phosphorus tribromide in *sym.*-tetrachloroethane. The reaction mixture was stirred vigorously and the temperature was raised according to the following programme:

1. day	up to	60— 70°C
2. day	”	70— 90°C
3. day	”	90—100°C
4. day	”	100—110°C
5. day	”	135°C
6.—7. day	”	135—145°C
7.—11. day	”	145°C

After the second day the second portion of bromine required was added to it. The temperature range between 110 and 135°C — less advantageous to the formation of cyclic homologues — was swiftly passed. The trimeric and tetrameric derivatives were separated by fractional recrystallization from petroleum ether and by vacuum sublimation. The purity of the products was checked by their infrared spectra. M.p. of the trimer: 188°C, M.p. of the tetramer: 197°C

Preparation of pentachloro-monobromocyclo-triphosphazatriene

Reaction of ammonium bromide and phosphorus pentachloride in *sym.*-tetrachloroethane was used [38]. Separation of the reaction product was carried out as follows: after accomplishment of the reaction the unreacted solid residue was filtered off. The filtrate was vacuum-distilled and the obtained oily residue was allowed to stand in the refrigerator over night. The crystalline product formed was filtered off by vacuum. It was extracted with petroleum ether and this solution was treated with active carbon. After evaporation of petroleum ether a colourless crystalline material was obtained. It was recrystallized from benzene and purified by vacuum-sublimation. M.p.: 122.5°C. Identification was based on the infrared spectrum published in Ref. [38].

Preparation of tetrachloro-dibromocyclotriphosphazatriene

The reaction of ammonium chloride with phosphorus pentachloride and phosphorus tribromide in *sym.*-tetrachloroethane was applied [38]. Separation of the formed products was carried out in the above described way. Colourless crystalline substance was obtained. M.p.: 134.5—135°C.

Preparation of hexamethoxy- and hexaethoxycyclotriphosphazatriene

Hexachlorocyclotriphosphazatriene was reacted with sodium methylate [39] or with ethanol [40]. Hexamethoxy derivative is a colourless crystalline substance, m.p.: 48°C; the hexaethoxy derivative is a colourless oil, b.p.: 116°C/0.1 Hgmm.

Preparation of diethylmercapto-tetrachlorocyclotriphosphazatriene

It was prepared by the reaction of hexachlorocyclotriphosphazatriene and sodium ethylmercaptide [41]. It is a pale yellow oil, b.p.: 128—130°C/0.2 Hgmm. Sodium ethylmercaptide was prepared from ethylmercaptane with metallic sodium.

Preparation of hexakis-n-isothiocyanatocyclotriphosphazatriene

Hexachlorocyclotriphosphazatriene and sodium thiocyanate was reacted [42]. It is a pale yellow crystalline substance. M.p.: 41.0—41.5°C. Identification was based on the infrared spectrum.

Preparation of hexa-azidocyclotriphosphazatriene

The reaction of hexachlorocyclotriphosphazatriene and sodium azide was carried out [43]. Colourless oily product, exploding violently on mechanical effects. It should be stored in ether or carbon tetrachloride solution.

Preparation of diethylazido phosphate

It was prepared from diethylchlorophosphate with sodium azide [44]. Colourless liquid, b.p.: 70—71°C/2—3 Hgmm. (It is a poison for nerves, inhalation of its vapours causes visual troubles.)

Preparation of diethylchlorophosphate

Diethyl phosphorous acid was chlorinated [45]. It is a colourless liquid, with a pleasant odour. B.p.: 103.0—104.5°C/20 Hgmm.

Preparation of diethyl phosphorous acid

Phosphorus trichloride was reacted with ethanol [46]. Colourless, mobile liquid, b.p.: 90—100°C/25 Hgmm.

Preparation of diamino-tetrachlorocyclotriphosphazatriene

Hexachlorocyclotriphosphazatriene was reacted with ammonia [47]. White crystalline substance, m.p.: 166.5°C.

Preparation of phosphorus tri-isothiocyanate

The reaction of phosphorus trichloride with mercury thiocyanate was used [48]. Colourless liquid, b.p.: 128°C/3 Hgmm.

Preparation of phosphorus oxy-isothiocyanate

Phosphorus oxy-chloride was reacted with potassium thiocyanate [49]. Pale yellow oil, b.p.: 170—175°C.

Preparation of dimethyl-silyl-di-isothiocyanate

It was prepared by the reaction of dimethyl-silyl dichloride and silver thiocyanate [50]. Colourless, mobile oil, it becomes yellow on air. B.p.: 92°C/9 Hgmm.

Preparation of phenyl-isothiocyanate

The reaction of aniline with carbon disulphide and ammonium hydroxide was used. The formed m-phenyl-dithiocarbamate was decomposed by lead nitrate [51]. Colourless liquid, b.p.: 121—122°C/37 Hgmm.

Preparation of methyl-isothiocyanate

Methylamine, carbon disulphide and sodium hydroxide was reacted. The formed N-methyl sodium thiocarbamate was decomposed with chlor-formic acid ethylester [52]. Colourless oily liquid, b.p.: 118—119°C.

Preparation of bis-N-dimethylamino-tetrachlorocyclotriphosphazatriene, tetrakis-N-dimethylamino-dichlorocyclotriphosphazatriene, hexakis-N-dimethylaminocyclotriphosphazatriene

They were prepared by the reaction of hexachlorocyclotriphosphazatriene and dimethylamine in absolute ether solution by proper variation of concentration and duration of the reaction [53 a, b]. Yield: 40, 74 and 80%. They are white crystalline substances, m.p.: 103.5°C, 104°C and 100°C, resp.

Purity of all substances was checked not only by m.p. or b.p. determinations and elementary analysis but by careful comparison of their infrared spectra with the published ones found in the cited papers. Their purity was found to be the same as those given in the literature.

The ultraviolet absorption spectra were recorded in *n*-hexane and *n*-heptane of "for spectroscopy" purity [made by BDH] solutions. Anhydrous solvents were prepared according to the monographs of Weissberger [54 a], Houben—Weyl [54 b] and Pestemer [54 c], just as to a private communication of Hires [54 d] and the handbook of Keil [54 e].

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THE ELECTRONIC STRUCTURE OF INORGANIC UNSATURATED CYCLIC COMPOUNDS, III

INFRARED ABSORPTION BAND INTENSITIES OF TRIMERIC PHOSPHONITRILIC PSEUDOHALOGENIDES

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Investigating the infrared absorption spectra of cyclic trimeric phosphonitrilic-azide and isothiocyanate, the integrated intensity values of the antisymmetric stretching vibrations of the azide and isothiocyanate groups were determined. These values were compared with those of several analogous aliphatic and aromatic derivatives, as well as of noncyclic silicon, phosphorus and sulphur derivatives. This comparison resulted in statement of the presence of a less delocalized PNP three-centre π-electron distribution in the phosphonitrilic ring, instead of a heteromorphic "aromatic" π-electron system.

The structure of the π-electron system of disubstituted phosphonitrilic derivatives is a long argued topic. It could not be decided by simple MO-LCAO calculations. Some authors supposed a non-Hückel-type heteromorphic $p(\pi)$—$d(\pi)$ aromatic delocalization, so-called "quasiaromatic" structure for the cyclic derivatives. Others suggested three-centre PNP π-bond units (with weak interactions), similarly to the monomers and linear polymers. Our studies on the ultraviolet absorption spectra of phosphonitrilic dihalogenides, pseudohalogenides and oxygen, sulphur, nitrogen and carbon derivatives made it very probable that no similarity exists between the aromatic π-electron systems and the phosphonitrilic rings [1]. In the present paper this was confirmed on the basis of the infrared absorption spectra of cyclic trimeric phosphonitrilic pseudohalogenides, *e.g.* azide and isothiocyanate derivatives. Integrated infrared absorption intensities of bands due to the antisymmetric stretching vibrations of the azide and isothiocyanate groups were determined.

Infrared and Raman spectra of several cyclic phosphonitrilic disubstituted derivatives have been recorded, *e.g.* those of trimeric and tetrameric difluorides [2], dichlorides [3 a—f], dibromides [4 a—c], mixed chloride bromides [5 a—d], dimethylamine derivatives [6 a—b], and di-isothiocyanate [7]. The infrared absorption spectrum of hexaazidocyclotriphosphazatriene $[NP(N_3)_2]_3$ however was not investigated. The infrared absorption spectrum of $[NP(N_3)_2]_3$ prepared by us is shown in Fig. 1. The band due to the P—N bond of the ring (ν_{as}(P—N) = 1200 cm^{-1}) and the azide bands (ν_{as} = 2165 cm^{-1},

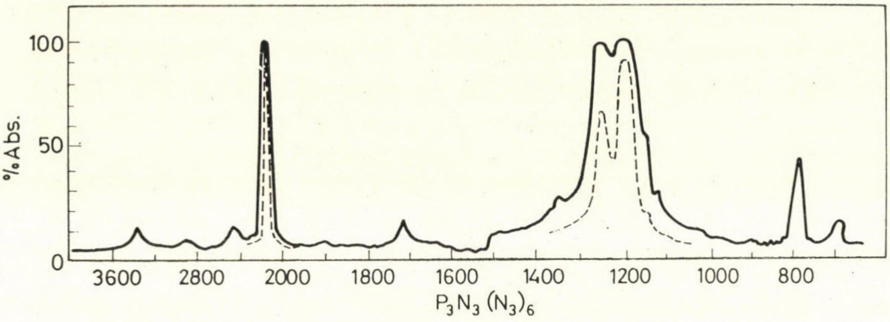


Fig. 1

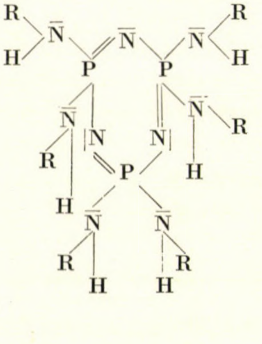
Table I

ν_{as}(P—N) frequency maxima in the infrared absorption spectra of trimeric cyclic phosphonitrilic derivatives

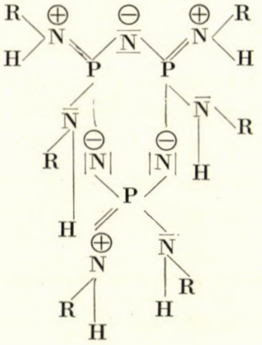
X substituents of the $[NPX_2]_3$ ring	ν_{as}(P—N) ring frequency in cm^{-1}
F_6	1297
Cl_2F_4	1283, 1276
Cl_4F_2	1246, 1226
Cl_6	1231, 1220
$(N_2H_3)_6$	1218
$(NCS)_6$	1216
Cl_5Br	1212
Cl_4Br_2	1203
Cl_3Br_3	1200
$(N_3)_6$	1200
Cl_2Br_4	1192
$ClBr_5$	1188
Br_6	1173
$[(CH_3)_2N]_6$	1195
$[CH_3(CH_2)_nNH]_6$ (n =1—5)	1192
$(CH_3)_6$	1180
$(CH_3NH)_6$	1175
$(NH_2)_6$	1170
$(CH_3CH_2)_6$	1157

ν_s = 1255 cm $^{-1}$, δ = 800 cm $^{-1}$) were easily identified. In the infrared absorption spectrum of hexaisothiocyanatocyclotriphosphazatriene $[NP(NCS)_2]_3$ the ν_{as} band of ring P—N stretching appears at 1216 cm $^{-1}$ (Table I) and the bands of the isothiocyanate group are found at ν_{as} = 1940 cm $^{-1}$, ν_s = 1060 cm $^{-1}$ and δ = 412 cm $^{-1}$ [7].

The most characteristic common feature of the infrared spectra of cyclic and also of linear phosphonitrilic disubstituted derivatives is theappearance of a strong band in the 1200—1400 cm $^{-1}$ region, assigned to the P—N stretching vibration (ν_{as}). In the case of cyclic compounds its actual value depends on n, the number of atoms of the ring, — increasing value of n results in decreasing frequency — and on the electronegativity of the substituents. The higher the values for the electronegativity, the higher the frequency, resulting in increased stability of the ring and decreased basicity of the nitrogen atoms of the ring (Table I). As seen in Table I, also a steric effect, commensurable with the inductive and mesomeric ones, may act together with those, as in the case of ethyl, propyl, etc., amino and dimethylamino derivatives (1192 cm $^{-1}$, 1195 cm $^{-1}$), in contrast to the methylamino derivative (1175 cm $^{-1}$). The structure of the latter is represented by the mesomeric formula II, while the higher homologues of the alkylamines correspond to I.



I



II

X-ray investigation of tetrameric dimethylamino derivatives showed one of the dimethylamino groups attached to phosphorus atoms to have a shorter P=N bond than the other, according to II, and they are placed into the plane of the ring. Several other deformation vibrations of phosphonitrilic ring appear in the region of lower wave numbers. These are often coupled with other vibrations, so their analysis is rather difficult.

Considering these facts, we decided to deal only with that part of the infrared spectra of cyclic trimeric phosphonitrilic derivatives, which is characteristic mainly of the substituents. As our aim was to investigate the π-electron system of the ring, substituents with significant multiple bonds and easily polarizable π-electron system were needed, being directly attached to the ring. Significant interaction was expected to occur between the substituents and the π-electron system of the ring. After theoretical and preparative considerations our choice fell on the azide and isothiocyanate derivatives.

The assignation of characteristic bands of azide and isothiocyanate groups, as being covalently bonded triatomic groups, was carried out on the analogy of free triatomic linear ions and molecules. So the two stretching vibrations are the following:

a) ν_{as} asymmetric [8 a—d] or antisymmetric [9 a—c] vibration of azides. It is a so-called pseudoantisymmetric one [9 a, b] in the case of isothiocyanates.

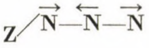
b) ν_s symmetric vibration of azides; pseudosymmetric one of isothiocyanates.

Deformation vibrations (δ) may take place in plane or perpendicularly to it.

The ν_{as} vibration, appearing at 2040—2237 cm^{-1} in the spectra of azides investigated up to now, and at 1900—2150 cm^{-1} and at 2260—2280 cm^{-1} in the spectra of isothiocyanates and isocyanates, resp., shows the following unique characteristics:

1. The above-mentioned wave number range is very suitable for measuring integrated intensities, as most of the compounds have no other fundamental vibration here.

2. The ν_{as} vibration — its approximate form is shown in the following scheme:



is very slightly coupled with the vibrations of other parts of the molecule. This is also supported by the fact that the position of ν_{as} vibration shows only a little change when studying different azide and isothiocyanate derivatives. Therefore, the more sensitive integrated absorption intensities and not the wavenumber values were used in our investigations. The low extent of the coupling can be attributed to the following facts:

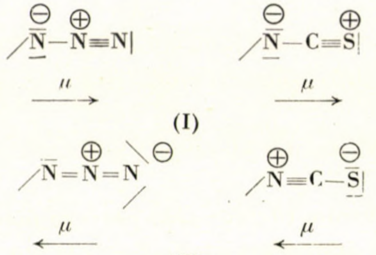
a) The mechanical coupling is not too strong, since the Z—N—N and Z—N—C angles differ from 180° (in the case of Z=CH_3 it is 117° [10]).

b) Nothing indicates the presence of considerable interaction force constants.

c) The frequency of ν_{as} vibration is far from those of the vibrations of the skeleton (in our case it is the phosphonitrilic ring).

It is well known that values of the infrared absorption intensities are very sensitive to the changes in the shape of the vibration. In this case the above-described facts promise no change in the intensities due to changes of the shape of ν_{as} vibration, especially when comparing compounds with identical Z atoms. No band split was observed in compounds with two or more N_3 or NCS groups substituted on the same atom and also this fact points to the negligible extent of coupling.

3. The values of infrared absorption intensity of this ν_{as} vibration is strikingly high. Considering the two possible limiting structures of the azide and isothiocyanate groups:



(I)

(II)

structures I and II are supposed to alternate during the ν_{as} vibration. The dipole moments of the two limiting structures are opposite in direction, therefore a considerable change in the dipole moment is resulted by the ν_{as} vibration and this explains the high intensity of this transition.

When an easily polarizable, mobile π-electron system, *e.g.* a carbon-carbon multiple bond or an aromatic system is connected with the azide or isothiocyanate group, the value of integrated absorption intensity of the ν_{as} vibration is significantly increased [11] (Tables II and III). This can be as-

Table II

Integrated intensity values of the ν_{as} band of azides

Compound	Frequency ν_{as} cm^{-1}	Intensity*/group	
		This paper	Ref. [11]
Phenylazide	2128, 2096	6.1	6.5
2,4,6-Tribromophenylazide	2147, 2112	6.1	
m-Nitrophenylazide	2132		6.2
Trimethylsilylazide	2141	6.2	
Diethoxyazide phosphate	2166	5.4	
Hexaazidocyclotriphosphazatriene	2165	4.7	
Diethoxyazido thiophosphate	2166	4.6	
Methylazido sulphate	2143		4.2
n-Butylazide	2097	4.1	
Cyclohexylazide	2093	4.6	
1-Hydroxy-2-azidoethane	2105		4.5
Azidoacetic acid ethylester	2108		4.4
Benzylazide	2097	4.4	4.5
s-Tetrafluoroazidoethane	2163		2.4

* 10^4 cm^{-2} mole^{-1} liter units

cribed to the strong dipole formed in the course of the vibration, exerting a polarizing effect on the mobile electron system thus enhancing the resulted dipole moment change and through this the intensity of the absorption band. So the high intensity of the ν_{as} band proves the existence of a mobile delocalized electron system.

Table III

Integrated intensity values of ν_{as} bands of isothiocyanates

Compound	Frequency ν_{as} cm^{-1}	Intensity*/group		
		This paper	Ref. [9b]	Ref. [14]
Methylisothiocyanate	2124	8.4	11.3	(4.0)
Allylisothiocyanate	2140		10.1	10.4
Benzylisothiocyanate	2100	11.9		
Phenylisothiocyanate	2090	17.5	15.3	15.7
p-Methoxyphenylisothiocyanate	2105		15.3	14.9
p-Chlorophenylisothiocyanate	2060		17.1	17.9
p-Bromophenylisothiocyanate	2050		18.1	
p-Nitrophenylisothiocyanate	2045			20.8
α-Naphtylisothiocyanate	2080		18.8	
3-Pyrenisothiocyanate	2120		20.2	
Dimethylsilyl-diisothiocyanate	1865	13.6		
Phosphorus tri-isothiocyanate	1940	18.3		
Phosphorus oxyisothiocyanate	1923	20.1		
Hexaisothiocyanatocyclotriphosphazatriene	1960	15.7		

* 10^4 cm^{-2} mole^{-1} liter units

According to Table II (data of azides), the intensity of the ν_{as} band decreases with increasing electronegativity of the attached Z atom (silicon $<$ phosphorus $<$ sulphur $<$ carbon); so the same Z atom should be present in both cases when comparing the intensities of cyclic (being supposed to contain a delocalized electron system) and noncyclic compounds.

The data given in Tables II and III show no increase of integrated intensity of the ν_{as} band of cyclic trimeric phosphonitrilic azide and isothiocyanate as compared to that of the corresponding noncyclic phosphorus azide and isothiocyanate* derivatives.

However, without exception, a high (50—100%) increase was observed for the aromatic derivatives as compared to the aliphatic ones. Also this fact indicates the unlikeliness of a strongly delocalized, heteromorphous $p(\pi)-d(\pi)$

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* Analysis of the infrared and Raman absorption spectra of phosphorus tri-isothiocyanate and phosphorus oxyisothiocyanate was carried out by OBA *et al.* [12].

electron system in cyclic phosphonitrilic disubstituted compounds as suggested by CRAIG and others. The frequency and intensity values of the ν_{as} (NNN) and (NCS) resp. bands of cyclic trimeric phosphonitrilic azide and isothiocyanate can well be fitted into the series of azide and isothiocyanate noncyclic derivatives containing central atoms with empty outer *d*-orbitals of low energy (*e.g.* silicon, phosphorus, sulphur). Thus similar non-aromatic, two or three-centre (see PNP π-islands suggested by DEWAR), more localized π-electron systems seem to be probable in both cases. This difference is after all due to the different symmetry properties of $2p(\pi)$-orbitals of carbon atoms and $3d(\pi)$-orbitals of phosphorus atoms.

Experimental

The investigated compounds were prepared according to methods given in our previous paper [1] and in Ref.-s [13 a—c].

Merck carbon tetrachloride with spectroscopic purity was used as solvent when recording the infrared spectra.

The spectra were recorded by a Hilger H800 (prism), a Unicam SP 100 (grating and prism) and a Perkin—Elmer 225 (grating) infrared spectrophotometer. In the 2500—1800 cm^{-1} wave number range the spectral slit width was about 2—3 cm^{-1} at the Hilger H800 spectrophotometer, using LiF prism; 1—2 cm^{-1} at the Unicam SP 100; and about 1 cm^{-1} at the Perkin—Elmer instrument. Error due to limited resolution of the instruments was not observed. The integrated intensity values spread irregularly as the function of concentration and layer thickness, since the value of half width of bands was considerable greater (especially in the case of isothiocyanates) than that of the ideal curve; so the actual value of integrated intensity of the band was determined by averaging. The line of 0% absorption was recorded before and after the spectra. At least six spectra were recorded in the case of every compound, using two different concentrations and three different layer thicknesses (usually 50, 100 and 200 μ). Most of the spectra were recorded by means of a potassium bromide micrometer cuvette, the thickness was checked by the interference method.

Calculation of intensities was carried out by the modified Wilson—Wells method; integration was performed by the Simpson approximate equation. The range of integration was about 150—200 cm^{-1} wide in most cases. The individual values of $\log \frac{T_0}{T_1}$ were read by every 10, 6.66 and 5 cm^{-1} values. As the deviation of parallel measurements was lower than 10%, the accuracy of our result is ±10%.

In every compound only the strong ν_{as} antisymmetric stretching vibration of the azide and isothiocyanate group was investigated, and its integrated intensity measured. In some compounds, as *e.g.* phenylazide, also combination bands (amplified by Fermi resonance) and overtone bands appeared together with the fundamental band. These were added to the main band when measuring integrated intensities, as their intensity was gained probably from that. Data are given together with literature data in Tables II and III [9b, 11, 14]. Our results are well consistent with those of SHEINKER *et al.* on azides [11] and of HAMM and WILLIS on isothiocyanates [9b]. There are perfectly different data of methylisothiocyanate published by CALDOW and THOMPSON [14]. Already HAMM and WILLIS stated that the methylisothiocyanate used by CALDOW and THOMPSON was strongly contaminated. Considering the higher resolution of our instruments, our results seem to be the more correct.

*

Thanks are due to Dr. S. DOBOS (Inorganic Research Group of the Hungarian Academy of Sciences) for his help in recording the spectra and to I. PINTÉR (Central Chemical Research Institute of the Hungarian Academy of Sciences) for making available for us several organic azides and trimethylsilylazide samples.

We should not miss this occasion to express our thanks to Prof. Z. SZABÓ for supporting of work and to Prof. B. LENGYEL for making possible the infrared measurements in his Institute.

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ERRATUM

Acta Chimica Academiae Scientiarum Hungaricae, Vol. 60, No. 4, p. 340

The name of Mr. Tóth (3rd row from below) has, unfortunately, been misprinted. Its correct spelling is *Gábor* (not *Géza*) Tóth.

Acta Chimica Academiae Scientiarum Hungaricae, Tomus 60 (4), pp. 341—348 (1969)

THE SORPTION OF METAL IONS FROM SOLVENT MIXTURES ON CARBOXYCELLULOSE ION EXCHANGERS

THE ADSORPTION OF COBALT(II)

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The adsorption of cobalt (II) from water–solvent and formamide–solvent mixtures on carboxycellulose (C-cellulose) ion exchanger (H-form) has been studied. The experimental results show that both the quantity of metal ion adsorbed, and the rate of ion exchange on C-cellulose in the H-form are strongly increased when a basic solvent with high dielectric constant is added to a less basic solvent with a lower dielectric constant. There is no linear relationship between the extent of adsorption and the dielectric constant of the mixture in the case of alcohol–water and alcohol–formamide mixtures. In the case of the Co(II)-hydrogen exchange, the selective swelling of carboxycellulose, the basicity of the solvent, and complex formation are much more important than the dielectric constant of the mixture.

In a previous paper [1] the adsorption of cobalt(II) ions by carboxycellulose and other cellulose ion exchangers has been described using solvents containing 0.05 mole fraction of water. The experimental results indicated that the amount of Co^{2+} retained by carboxycellulose from solvents with low dielectric constants ($\varepsilon \sim 20$) was, even after one day, very small compared with the amount taken up from water (100.0 μg Co^{2+} (20.0 ml solvent) 0.100 g C-cellulose). The studies were extended to water–solvent and formamide–solvent mixtures. Aliphatic alcohols, acetone, and dioxan were used as solvents. The objective of the experiments was to study the effect of solvents with high dielectric constants (water and formamide) on the rate and extent of Co^{2+} exchange on carboxycellulose.

The process of ion exchange in water–alcohol and water–aceton mixtures has been extensively studied. GABLE and STROBEL [2] observed that the ion exchange constant for the H^+-Na^+ exchange from methanol–water mixtures on a sulphonic acid resin had a maximum in 85% aqueous methanol (the constants differ by one order of magnitude).

A linear relationship between $1/\varepsilon$ and the logarithm of the ion exchange constant (K) has been observed by several authors [3, 4] in alcohol–water mixtures. However, the ion exchange resin used in the above studies was not in the H^+-form.

Experimental

Reagents

$CoCl_2 \cdot 6\,H_2O$, analytical grade
C-cellulose (carboxycellulose; 0.22 meq/g [5]).

Analytical grade solvents were used. The solvents, when necessary, were further purified by distillation or ion exchange on cellulose to remove metal impurities.

Method

0.1000 g of C-cellulose (in the hydrogen form) was added to 20.0 ml of a water–solvent or formamide–solvent mixture containing 100 μg of Co^{2+}. The mixture was shaken mechanically for a given time, then the two phases were separated by filtration. The amount of Co^{2+} was determined spectrophotometrically as $Co(DMG)(HDMG)I_2^-$ (DMG = dimethylglyoxime) after eluting with acid [6].

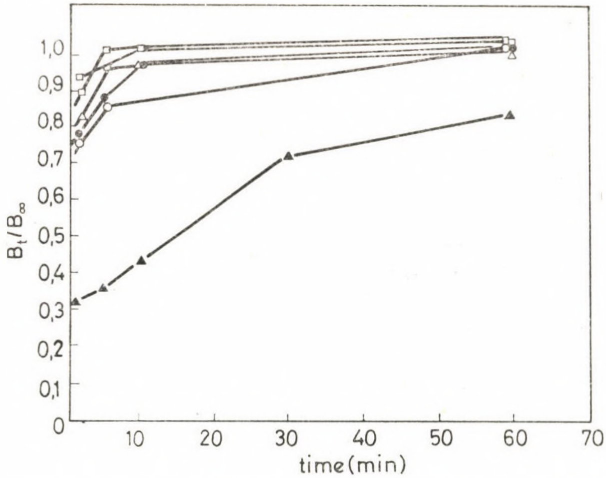

Fig. 1. Methanol–water mixtures with mole fractions of ▲: 0.05, ○: 0.17, ●: 0.31, △: 0.46, ■: 0.52, □: 0.61

Results and discussion

The extent of adsorption of Co^{2+} by C-cellulose from water–solvent mixtures was followed in time. The fraction of Co^{2+} retained by the exchanger $U = B_t/B_\infty$ (B_t = per cent of total Co^{2+} adsorbed up to time t, B_∞ = per cent of total Co^{2+} adsorbed at equilibrium), is shown as a function of time in Figs 1, 2, 3 and 4 for different water–alcohol mixtures. The water contents are given in mole fractions.

It can be seen from Figs 1—4 that the rate of ion exchange strongly increases with increasing water content. The half-time of the exchange ($t_{1/2}$) taken at $U = 0.5$ is less than 1 min. in water-rich mixtures. The equilibrium is attained within 1 min.

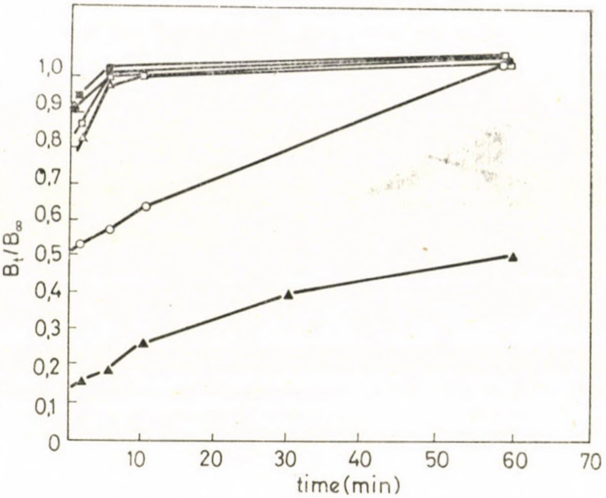

Fig. 2. Ethanol–water mixtures with mole fractions of ▲: 0.05, ○: 0.23, □: 0.36, △: 0.52, ●: 0.60, ■: 0.67

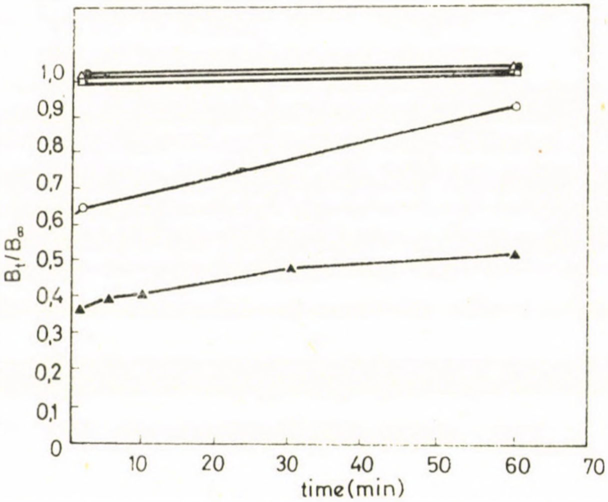

Fig. 3. *n*-Propanol–water mixtures with mole fractions of ▲: 0.05, ○: 0.30, □: 0.50, △: 0.60, ●: 0.68

The effect of increasing water content on the quantity of Co^{2+} bound at equilibrium is shown in Fig. 5. There is no direct proportionality between the quantity of Co^{2+} adsorbed and the water content of the solvent mixture. The amount of retained Co^{2+} first increases with increasing water content, but later reaches a limiting value. The per cent of metal ion retained by the exchanger at equilibrium is shown in Fig. 6 as a function of the dielectric constant of the

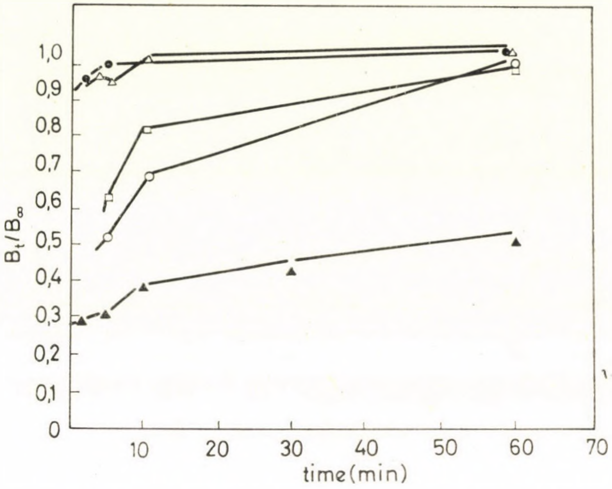

Fig. 4. *n*-Butanol–water mixtures with mole fractions of ▲: 0.05, ○: 0.10, □: 0.22, △: 0.27, ●: 0.36

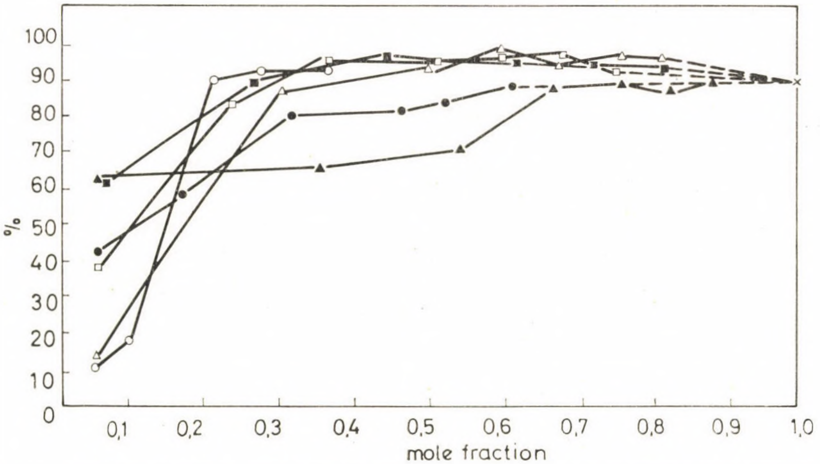

Fig. 5. Solvent–water mixtures. ○: *n*-butanol–water, △: *n*-propanol–water, □: ethanol–water, ●: methanol–water, ■: acetone-water, ▲: dioxan-water

solvent mixture. It is observed that the amount of bound Co^{2+} increases with increasing dielectric constant of the water–methanol mixture, but no further increase takes place at $\varepsilon > 40$, the limiting value being equal to that measured in water [1]. The dielectric constants at which the maxima are reached decrease in the order ethanol–*n*-propanol–acetone–*n*-butanol. The effect of the dielectric constant is different with dioxan because of the possibility of strong $CoCl_2$ adsorption [1].

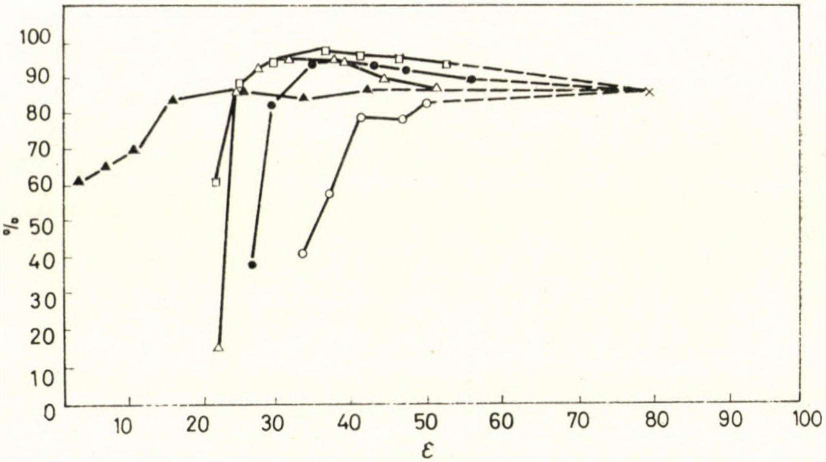

Fig. 6. ○: Methanol–water, ●: ethanol–water, △: *n*-propanol–water, □: acetone–water, ▲: dioxan–water

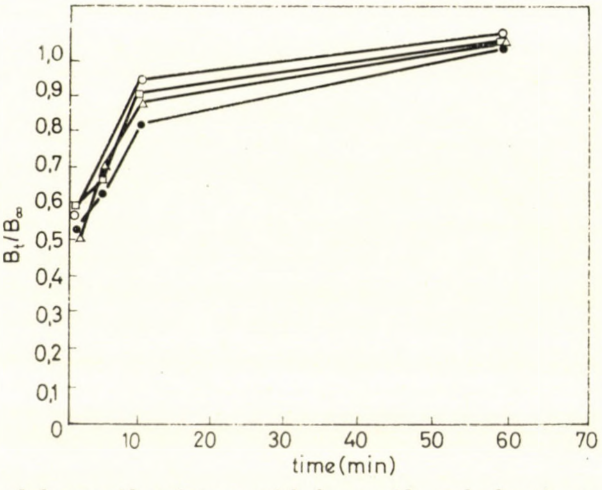

Fig. 7. Methanol–formamide mixtures with formamide mole fractions of ●: 0.05, △: 0.10, □: 0.15, ○: 0.20

Thus there is no clear-cut relationship between the dielectric constant and the quantity of adsorbed Co^{2+} ion. Since water is more basic, and causes a stronger swelling of cellulose than the rest of the solvents, selective swelling of the C-cellulose takes place in aqueous solvent mixtures, water being preferred in the process. This condition leads to the observed types of curves.

Measurement of the rates of ion exchange in formamide–alcohol mixtures gave the following results.

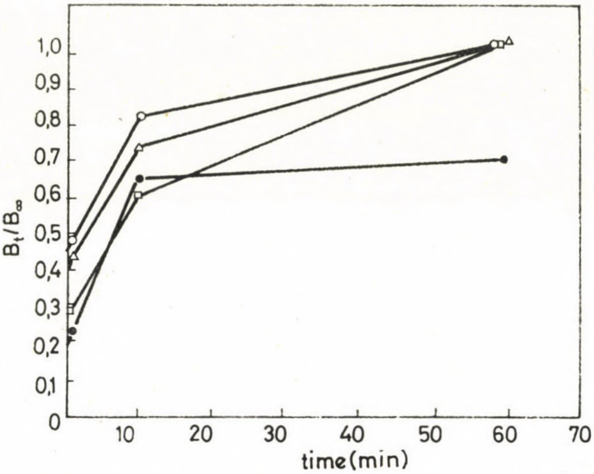

Fig. 8. Ethanol–formamide mixtures ●: 0.07, □: 0.14, ▲: 0.21, ○: 0.27

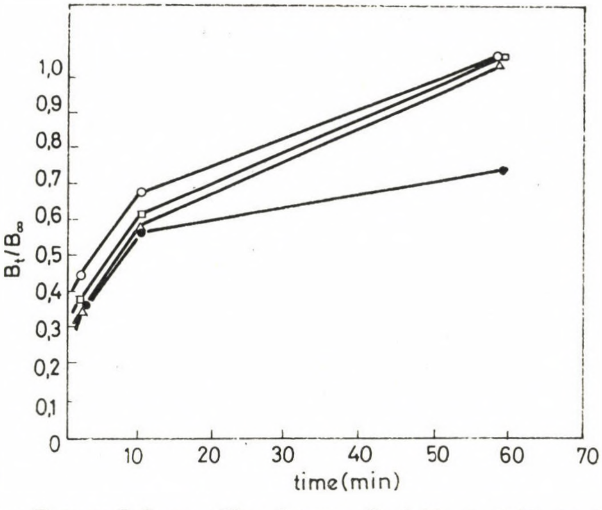

Fig. 9. *n*-Propanol–formamide mixtures ●: 0.09, △: 0.17, □: 0.26, ○: 0.31

The exchange constants obtained in different formamide–solvent mixtures are shown in Figs 7, 8, 9 and 10 as a function of time. It was observed that the value of $t_{1/2}$ decreased, *i. e.* the rate of ion exchange increased, with increasing formamide content mole fraction. The half-time of exchange increases in the direction from methanol to *n*-butanol at constant formamide mole fraction.

Fig. 11 shows the amount of metal ion bound at equilibrium plotted against the mole fraction of formamide. The amount of Co^{2+} first increases,

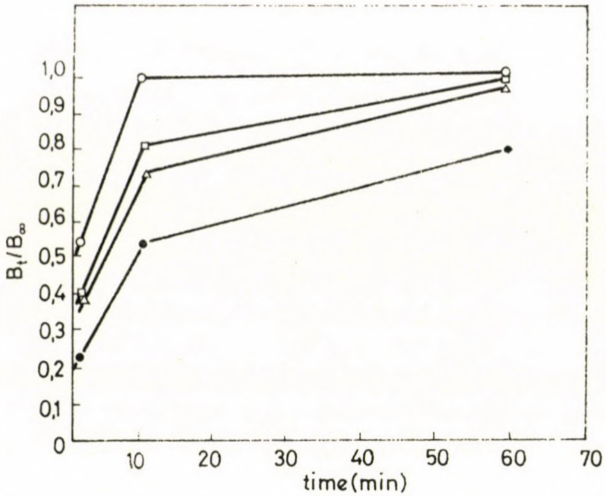

Fig. 10. *n*-Butanol–formamide mixtures ●: 0.11, ▲: 0.20, □: 0.29, ○: 0.37

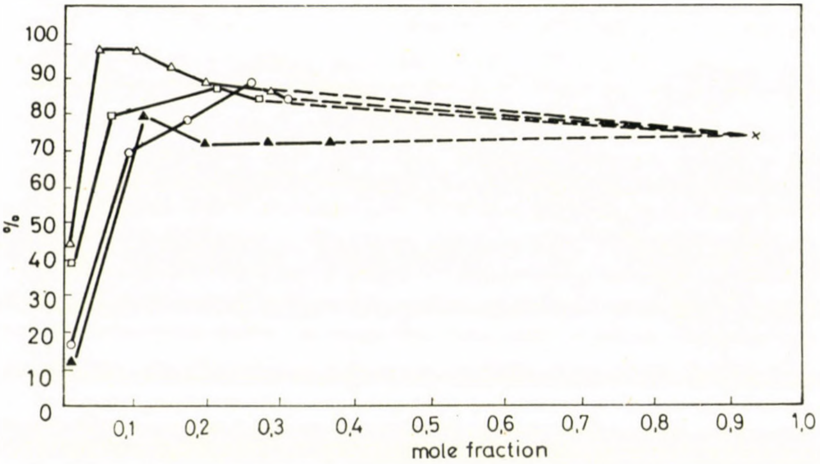

Fig. 11. Solvent–formamide mixtures ▲: *n*-butanol–formamide, ○: *n*-propanol–formamide, □: ethanol–formamide, △: methanol–formamide

then slowly decreases with increasing formamide content. As the latter increases, the adsorption of the Co(II) ion starts to be influenced by the Co-formamide complex, therefore, the effect of dielectric constant becomes less pronounced.

Comparing the results with those obtained for water–solvent mixtures it can be established that the rate and extent of exchange are strongly increased by adding a basic solvent with a high dielectric constant (*e. g.* water or formamide) to a less basic solvent with a lower dielectric constant. Water increases the rate of ion exchange stronger than formamide.

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MOLYBDÄN- UND WOLFRAMELEKTRODEN ZUR POTENTIOMETRISCHEN INDIZIERUNG DER MASSANALYTISCHEN MOLYBDAT-, WOLFRAMAT- UND BLEIBESTIMMUNG

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R. Geyer und M. Neumann

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Molybdän- und Wolframelektroden sprechen auf Bleiionen an, bei 50 °C annähernd im Sinne der Nernstschen Gleichung. Durch diese fremdionige Potentialbildung erklärt sich die schon lange bekannte Indizierbarkeit der potentiometrischen Fällungstitration von Wolframat und Molybdat mit Blei(II) in gepuffertem Medium. In nichtgepuffertem Zustand ergibt sich ein Mischpotential; es wirkt sich zusätzlich die hydrolytische pH-Änderung auf die Höhe des Potentialsprungs im Äquivalenzpunkt aus.

Der Annahme von Brinzinger und Jahn [1], daß Chrom-, Molybdän- und Wolframelektroden auf ihr Anionen CrO_4^{2-}, MoO_4^{2-} bzw. WO_4^{2-} konzentrationsrichtig ansprechen, stellten Müller und Mehlhorn [2] als Ursache für die mögliche potentiometrische Indizierung der Fällungsvorgänge dieser Ionen eine hydrolytische Änderung der Wasserstoffkonzentration entgegen, die zufolge einer pH-Funktion jener Elektrodenmetalle angezeigt wird. Zuvor hatte Bayliss [3] auf die Eignung der Wolframelektrode zur pH-Bestimmung aufmerksam gemacht, und die durch vorangehendes kurzes Glühen der Elektroden gebildete Oxidschicht schien zwanglos den Potentialgang nach positiven Werten mit sinkender Anionenkonzentration zu deuten [2]. Ganz im Gegensatz hierzu stehen jedoch Beobachtungen von Grubitzsch, Ozbil und Kluge [4], denen die potentiometrische Indizierung der $PbWO_4$-Fällung auch in gepufferter Lösung an blanker Wolframelektrode gelang. Im übrigen erzielten Klinger, Stengel und Koch [5] im Anschluß an Versuche von Dickens und Brennecke [6] bei der potentiometrischen Molybdatbestimmung mit $BaCl_2$ als Titrator nach dem Brinzingerschen Verfahren keine befriedigenden Ergebnisse. Im Hinblick auf die praktische Bedeutung, die einer fällungsanalytischen Molybdat- und Wolframattitration mit elektrochemischer Indizierung beizumessen ist, versuchten wir durch systematische Potentialmessungen zur Klärung jener Widersprüche beizutragen.

Bei den von uns durchgeführten Versuchen wurden die Potentiale nach der Poggendorfschen Kompensationsmethode gemessen. Dabei fand ein Kompensator vom Typ RFT 0145 Verwendung. Als Nullinstrument diente ein Lichtmarkengalvanometer mit einer Empfindlichkeit von $5,3 \cdot 10^{-9}$ A/Skt. Die Indikatorelektroden, deren Potentiale gegen die gesättigte

Kalomelelektrode gemessen wurden, bestanden aus W- und Mo-Draht von 0,5 cm freier Länge. Das Titrationsgefäß stand in einem Heizbecher, den zwecks Konstanthaltung der Temperatur Wasser aus einem Thermostaten kontinuierlich durchfloß. Die Lösungen wurden während der Titration mit einem Magnetrührer gerührt.

Titration von Wolframat und Molybdat

Nach erfolglosen Versuchen, die Titrationen von Molybdat und Wolframat mit Ba^{++} oder Hg_2^{++} an einer blanken oder oxydierten Mo- bzw. W-Elektrode zu indizieren, führten wir die Titration von Wolframat mit Bleinitrat an einer blanken W-Elektrode durch.

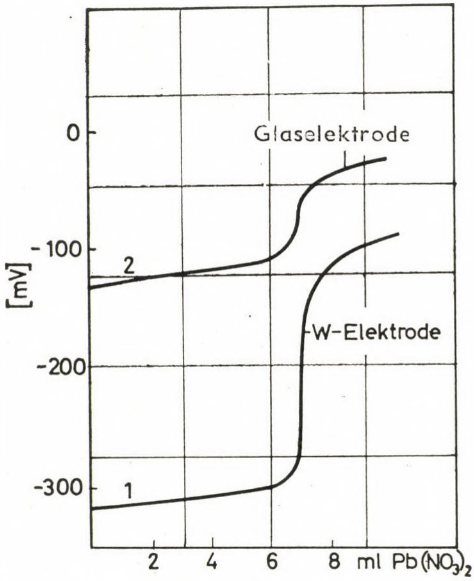

Abb. 1. Indikation der Titration von Na_2WO_4 mit 0,05 *M* $Pb(NO_3)_2$ an der Wolfram- und der Glaselektrode (50 °C)

Die Wolframat enthaltende alkalische Lösung wurde mittels HNO_3 schwach sauer gemacht, nach Zugabe von drei Tropfen 0,1% Bromthymolblau zur Austreibung des CO_2 einige Minuten gekocht und dann mit NaOH genau auf die grüne Umschlagsfarbe des Bromthymolblaus eingestellt. Die Titration erfolgte unter Rühren bei 50 °C mit 0,05 *m* $Pb(NO_3)_2$, wobei die Zugabe des Titrators tropfenweise erfolgte.

Wir konnten die Ergebnisse von GRUBITZSCH u. Mitarb. [4] bestätigen, lediglich machten sich zur Potentialeinstellung in der Nähe des Äquivalenzpunktes Wartezeiten von 2—3 min nach jedem Reagenszusatz erforderlich. Obwohl die erhaltenen Potentialkurven, wie Abb. 1 (Kurve 1) erkennen läßt, keine Symmetrie aufweisen, sind sie bei den geringen Titratorzusätzen im Äquivalenzpunkt der rechnerischen Auswertung zugänglich. Auch ist der Äquivalenzpunkt gut daran zu erkennen, daß bei kleinen Reagenszusätzen das Galvanometer im Endpunkt einen plötzlichen Ausschlag zeigt.

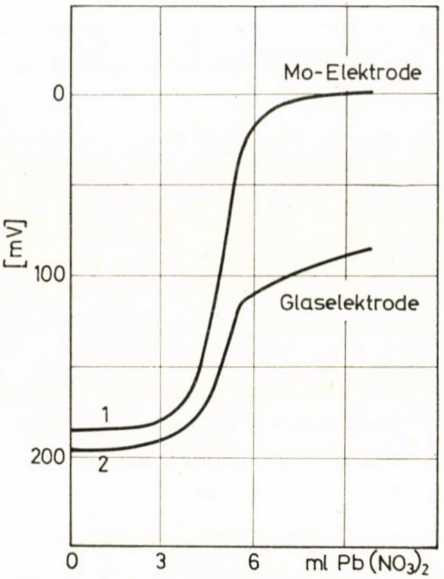

Abb. 2. Indikation der Titration von Na_2MoO_4 mit 0,05 *M* $Pb(NO_3)_2$ an der Molybdän- und der Glaselektrode (50 °C)

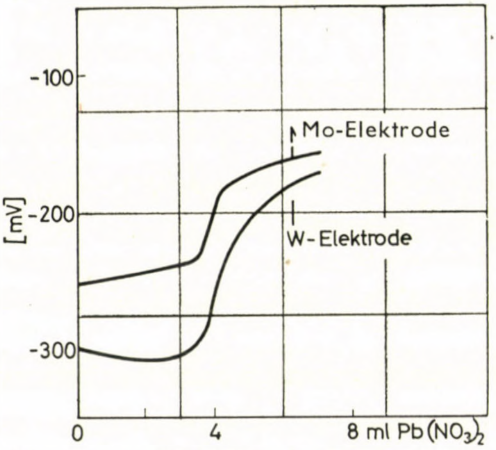

Abb. 3. Indikation der Titration von Na_2WO_4 mit 0,05 *M* $Pb(NO_3)_2$ an der W- und Mo-Elektrode in gepufferter Lösung (50 °C)

Unter den gleichen Versuchsbedingungen erfolgte die Titration von Molybdat mit Bleinitrat; zur Indizierung diente eine Mo-Elektrode. Die Molybdatlösung wurde auf die Umschlagsfarbe des Phenolrot eingestellt und bei 50 °C mit 0,05 m $Pb(NO_3)_2$ titriert (Abb. 2, Kurve 1). Der Potentialsprung war zwar nicht so scharf wie bei der Wolframattitration, ließ sich aber noch gut auswerten. Eine Temperaturerhöhung auf 85 °C erbrachte eine schnellere Potentialeinstellung und einen größeren Potentialsprung, der aber erst kurz nach dem Äquivalenzpunkt auftrat.

Um zu überprüfen, ob eine hydrolytische Indizierung der Fällungsreaktion vorliegt, wurden die Titrationen gleichzeitig mit der Glaselektrode verfolgt. Wie aus Abb. 1 und 2 (jeweils Kurven 2) hervorgeht, wird auch an der Glaselektrode im Äquivalenzpunkt ein Potentialsprung erhalten. Aber bei der Titration von Molybdat und Wolframat in gepufferter Lösung (Abb. 3 und 4) ergaben sich gleichfalls Potentialsprünge, die allerdings kleiner waren als in ungepufferter Lösung. Dieser Sachverhalt schließt eine pH-Änderung als alleinige Ursache der Indikation aus.

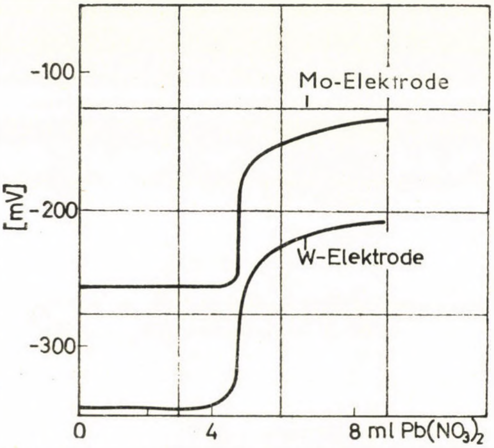

Abb. 4. Indikation der Titration von Na_2MoO_4 mit 0,05 *M* $Pb(NO_3)_2$ an der Mo- und W-Elektrode in gepufferter Lösung (50 °C)

Recht charakteristisch für die Elektrodenvorgänge sind die Ergebnisse von Versuchen, bei denen die Elektroden gegeneinander ausgetauscht wurden, so daß unter denselben Bedingungen wie vorher die Titration von Wolframat an der Mo-Elektrode und die Titration von Molybdat an der W-Elektrode erfolgte. Dabei stellte sich heraus, daß sich die Elektroden sowohl in ungepufferter als auch gepufferter Lösung gegenseitig ersetzen können. In Abb. 3 und 4 sind die Titrationskurven für Wolframat und Molybdat, jeweils erhalten mit einer Wolfram- bzw. Molybdänelektrode, wiedergegeben. An der Molybdänelektrode waren die Potentialsprünge in der Regel niedriger als unter gleichen Bedingungen an der Wolframelektrode.

Titration von Blei mit ÄDTA

Budanowa u. Platonowa [7] titrierten in schwach ammoniakalischer Lösung in Gegenwart geringer Mengen Weinsäure mit ÄDTA verschiedene Kationen, wobei der Äquivalenzpunkt mit dem Elektrodenpaar Pt—W angezeigt wurde; sie erwähnen, daß bei der Titration von Pb^{++} der Potentialsprung besonders stark ausgeprägt ist. Wir führten zunächst Vorversuche durch, in denen wir die Alkalität und die Weinsäurekonzentration der Blei-lösungen sowie die Konzentration von Titrand und Titrator variierten. In gepufferten Systemen zeigten sich sowohl im sauren (pH = 4) als auch im alkalischen Gebiet (pH = 10) gut ausgeprägte Potentialsprünge. Im alkalischen Bereich machte es sich erforderlich, Blei mittels geringer Mengen Weinsäure in Lösung zu halten. Ein zu großer Weinsäurezusatz und zu hohe Alkalität verursachten eine Verkleinerung des Potentialsprungs sowie eine geringere Steilheit der Kurve im Äquivalenzpunkt. Folgende Arbeitsweise ist am empfehlenswertesten:

Arbeitsweise: Zu einer Lösung, die 5—100 mg Pb in 200 ml H_2O enthält, werden 5—10 Tropfen 25%ige Weinsäure und tropfenweise konz. NH_3-Lösung, bis pH 8,5—9 erreicht ist,

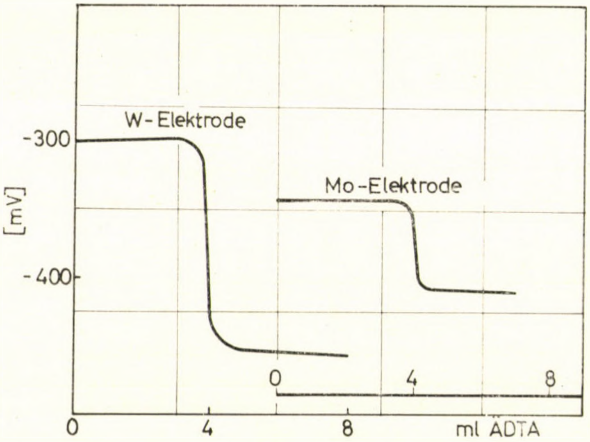

Abb. 5. Titration von Pb^{++} mit 0,05 N ÄDTA in ammoniakalischer Lösung an der Mo- und W-Elektrode (40 °C)

Tabelle I

Bleibestimmung mit ÄDTA
Indizierung mit der Wolfram- und der Molybdänelektrode

Blei vorgelegt mg	Blei gefunden	
	W-Elektrode mg	Mo-Elektrode mg
5,10	5,09	5,11
5,10	5,12	5,07
10,20	10,23	10,17
10,20	10,29	10,24
51,0	50,9	51,0
51,0	50,7	51,4
102,0	102,4	102,2
102,0	102,1	101,7

hinzugesetzt. Dann wird die Lösung bei 40 °C mit 0,05 *n* ÄDTA titriert. Die Indizierung des Äquivalenzpunktes erfolgt mit einer Wolfram- oder Molybdänelektrode. Zum Vergleich dient eine ges. Kalomelelektrode.

Abb. 5 zeigt Titrationskurven für die chelatometrische Bleibestimmung. An der Wolframelektrode wurden steile Potentialsprünge von 170—190 mV erhalten. Ebenfalls gute Ergebnisse erbrachte die Molybdänelektrode, obwohl der Potentialsprung hier nicht ganz so groß war wie an der Wolframelektrode. In Tabelle I sind einige Analysenergebnisse eingetragen.

Potentialmessungen

Es wurden die Potentiale der W- und Mo-Elektrode in Abhängigkeit von der Konzentration der einzelnen an den Reaktionen beteiligten Partner untersucht. Innerhalb des pH-Bereiches 2—10 zeigten beide Elektroden einen linearen Zusammenhang mit dem pH der Lösung, im Mittel 53 mV/pH. Zur Ausschaltung des pH-Einflusses auf die Elektroden wurden die Potentialmessungen in gepuffertem Medium vorgenommen. Dabei ergab sich überraschenderweise eine Abhängigkeit der Elektrodenpotentiale von der Pb^{++}-Konzentration, während Molybdat und Wolframat wie auch Ba^{++} bei 50 °C nur geringfügigen Einfluß ausüben. Aus Abb. 6 ist zu entnehmen, daß sich die Potentiale der W- bzw. Mo-Elektrode um 20—25 mV ändern, wenn die Pb^{++}-Konzentration um eine Zehnerpotenz steigt bzw. fällt.

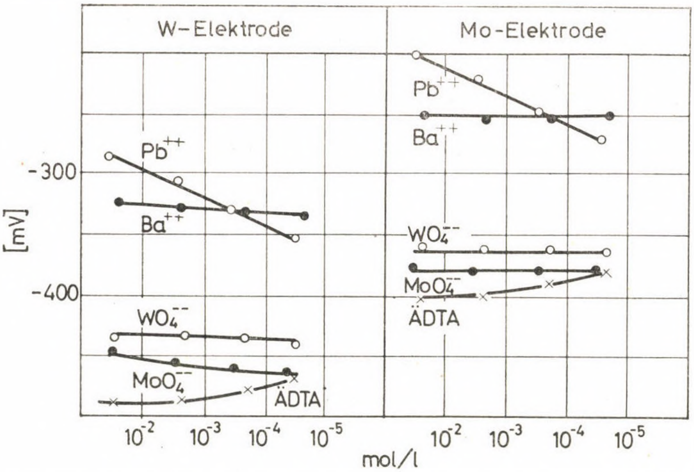

Abb. 6. Potentiale der W- und Mo-Elektrode in Abhängigkeit von der Konzentration der Reaktionspartner (50 °C)

Sofern die Wolframelektrode, wie **Brinzinger** u. Mitarb. [1] annahmen, nur auf Wolframationen ansprechen würde, müßte bei der Wolframtitration mit Pb^{++} der Potentialgang in negativer Richtung verlaufen. Tatsächlich werden die Potentiale aber positiv. Bereits MÜLLER und MEHLHORN [2] weisen auf diesen Widerspruch hin, meinen jedoch, daß der Potentialgang sich hinreichend erklären lasse durch die mit der Fällung einhergehende Änderung des pH-Wertes, bei Oxidbelag der Elektrode. Dagegen kann, wie dargelegt, in Übereinstimmung mit den Beobachtungen von GRUBITZSCH u. Mitarb. [4] die Indizierung auch in gepufferter Lösung erfolgen. Der Potentialsprung bei der Titration von Wolframat bzw. Molybdat mit Pb^{++} in ungepufferter Lösung resultiert somit vorwiegend aus der Empfindlichkeit der Wolfram- bzw. Molybdänelektrode sowohl gegenüber Wasserstoff- als auch Bleiionen. Dafür spricht, daß in gepufferten Lösungen unter vergleichbaren Bedingungen die Potentialsprünge im Äquivalenzpunkt durchweg niedriger waren als in ungepufferten Systemen.

Die Abhängigkeit der Potentiale von der Blei- sowie Wolframat- bzw. Molybdatkonzentration ist prinzipiell von ähnlicher Art wie an einer $PbWO_4$-Membran, über die an anderer Stelle [8] bereits berichtet wurde. Für das Zustandekommen der Potentiale an Wolfram- bzw. Molybdänelektroden nehmen wir an, daß das Elektrodenmetall sich mit einer Deckschicht [9] (vgl. auch [6]) oder einem Oberflächenfilm [10] überzieht, wodurch sich zwar kein Nernstsches Metallpotential bildet [10], wohl aber unter Mitwirkung von Adsorptionsvorgängen ein »Membranpotential« resultiert. Nur trennt die »Membran« hier nicht — wie üblich — zwei Lösungen, sondern anstelle der einen tritt die Metallphase. Metall/Membran-Elektroden hat bereits PUNGOR [11] hergestellt und beschrieben. Durch Gleichartigkeit der Adsorption erklärt sich das lediglich graduell unterschiedliche Verhalten beider Elektrodenmetalle. Mit steigender Temperatur geht die Adsorption der Anionen fast ganz zurück, während die Bleipotentiale nahezu unverändert bleiben. In gepufferter Lösung bei 50°C verhalten sich diese Elektroden somit annähernd wie Bleielektroden im Sinne der Nernstschen Gleichung. Diese Verhältnisse der fremdionigen Potentialbildung, W/Pb^{++} bzw. Mo/Pb^{++}, werden von uns noch weiter untersucht.

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VINYL DERIVATIVES OF THE ELEMENTS IN GROUP IV/1

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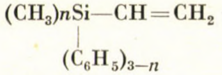
(i) The dipole moments of the trimethylvinyl derivatives of the Group IV/1 elements of the Periodic Table $(CH_3)_3ECH{=}CH_2$ where E = C, Si, Ge, Sn and of some phenylvinyl derivatives of silicon



$(CH_3)_nSi{-}CH{=}CH_2$ with $(C_6H_5)_{3-n}$ on Si

where $n = 0$ and 2

were determined by the method of ONSAGER and of HEDESTRAND, respectively.

(ii) The dipole moments of the central atom—carbon bond and of the vinyl group were calculated vectorially for trimethylvinyl derivatives. With the help of these dipole moments the resultant dipole moments of the phenylvinylsilanes were vectorially determined.

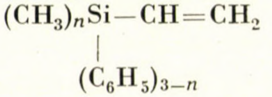
(iii) The silicon trimethylvinyl derivative was found to have the lowest dipole moment of the trimethylvinyl derivatives of this group; this was explained by the additional mesomeric (*—M*) effect of opposite direction to the inductive (*+I*) effect which appears in silicon, germanium and tin, contrary to carbon which has only an inductive effect.

(iv) This statement was supported by the results of some simplified quantum chemical calculations.

In an earlier paper [1] on silicon alkenyl derivatives we have claimed that the physical properties of trimethylvinylsilane can unequivocally be explained only by assuming a $d\pi - p\pi$ bond between the silicon and the vinyl groups. As a continuation of these studies we investigated the vinyl and phenyl derivatives of the elements in Group IV/1. In the present paper we describe our study on the molecular structure of vinyl derivatives.

These compounds are of particular interest, because they are subject to polymerization and copolymerization, their reactivity is much higher than that of the analogous carbon compounds. Various inductive and mesomeric effects have obviously a considerable influence on polymerization rate. A more thorough study of these effects necessitated the measurement of the dipole moments of the vinyl derivatives. The two groups of compounds subjected to investigation are the following:

$(CH_3)_3EH{=}CH_2$ and



$(CH_3)_nSi{-}CH{=}CH_2$ with $(C_6H_5)_{3-n}$ on Si where

$$E = C, Si, Ge, Sn \text{ and}$$
$$n = 0, 1, 2, 3.$$

With the exception of triphenylvinylsilane the dipole moments of the compounds were determined in the liquid state by ONSAGER's [2] method, while the dipole moment of crystalline triphenylvinylsilane was measured in dilute cyclohexane solutions by the method of HEDESTRAND [3].

For the calculation of the dipole moments the densities, refractive indices, dispersion values and dielectric constants of the compound (or, in the case of solid compounds, of their solutions) have to be accurately known.

The above physical parameters were measured at 25°C, the accurate temperature was ensured by means of an ultrathermostat.

Density (d) was measured with a graded dilatometer; the refractive index with reference to the sodium D-line (n_D) and the $n_F - n_C$ dispersion value were determined with an Abbé refractometer. The dielectric constant at 10,000 Hz frequency was measured with an instrument constructed in this laboratory [4].

According to ONSAGER's equation [2]:

$$\mu = 0.22123 \sqrt{P^*} \tag{1}$$

$$P^* = (\varepsilon_0 - \varepsilon_{eff}) \frac{2\varepsilon_0 + \varepsilon_{eff}}{\varepsilon_0 + (\varepsilon_{eff} + 2)^2} \cdot V \tag{2}$$

where

ε_0 is the measured dielectric constant of the compound and
V is the molar volume

$$\varepsilon_{eff} = \frac{2R + V}{V - R} \quad \text{and} \tag{3}$$

$$R = P_e + P_A \tag{4}$$

that is the sum of electronic and atomic polarization.

HEDESTRAND's equation [3] is as follows:

$$P_\infty = \frac{\varepsilon_1 - 1}{\varepsilon_1 + 2} \left(\frac{M_2}{d_1} - \frac{M_1 \beta}{d_1} \right) + \frac{3 M_1 \alpha}{(\varepsilon_1 + 2)^2 d_1} \tag{5}$$

where

d_1 is the extrapolated value for infinite dilution from the straight line density *vs.* molar fraction;

ε_1 is the extrapolated value for infinite dilution from the straight line dielectric constant *vs.* molar fraction;
β is the slope of the straight line density *vs.* molar fraction;
α is the slope of the straight line dielectric constant *vs.* molar fraction;
M_1 is the molecular weight of the solvent;
M_2 is the molecular weight of the solute.

If P_∞ is known the dipole moment can be given by the expression

$$\mu = 0.22123 \sqrt{P_\infty - R} \tag{6}$$

where R is the sum of electronic and atomic polarization.

Both methods require the accurate knowledge of the sum of electronic and atomic polarizations.

In general this sum can be calculated by multiplying the molar refraction by a factor of 1.05 to 1.1. This yields not too accurate values and has been used only in the case of trimethylvinylgermanium having no figure for its atomic polarization. For the other compounds the electronic and atomic polarizations were calculated separately according to the following method.

From the experimental results the refractive index pertaining to electronic polarization (n_∞) was calculated by using the well known interpolation formula for anomalous dispersion as described in one of our earlier paper [17].

The accurate calculation of atomic polarization is based on the method of Audsley [5] and Altshuller [6] according to which atomic polarization (P_A) is obtained additively from the bond increments (P_B) of the bonds in the molecule. We used the following bond increment values:

C—H	0.02 ml	Si—H	0.44 ml
C—C	0.03 ml	Si—O—C	0.732 ml [7]
Si—C	0.06 ml	Si—C_6H_5	2.60 ml [8]

The calculations should account for the anisotropic correction of the approximated space:

$$x = 0.21 + 0.006 \cdot C \tag{7}$$

where C is the number of carbon atoms in the molecule.

Table I contains the results obtained by measurements, according to Onsager, and by calculations in the above described manner; in Table II are given the values needed for the determination of the dipole moment of triphenylvinylsilane by Hedestrand's method.

The study of the vinyl derivatives of Group IV/1 elements with silicon, carbon, germanium or tin as the central atom seemed particularly promising. Results of the investigation of trimethylvinyltin have been reported in an

Table I

	$(CH_3)_3C—CH=CH_2$	$(CH_3)_3Si—CH=CH_2$	$(CH_3)_3Ge—CH=CH_2$	$(CH_3)_2C_6H_5SiCH=CH_2$
d	0.65044	0.68653	0.97735	0.88429
ε	1.968	2.031	2.184	2.3798
n_D	1.3732	1.3875	1.4258	1.5034
z	40.9	39.9	38.78	36.02
V	129.40	146.0	148.10	183.55
MR_D theor.	29.44	34.44	38.04	54.26
MR_D meas.	29.49	34.41	37.82	54.29
$n_F—n_C$	0.00786	0.00936	0.01128	0.01591
n_∞	1.36135	1.37339	1.4088	1.47942
P_ε	28.6434	33.2923	36.5940	52.0866
P_A	0.704	2.978	—	4.942
R	29.36	36.27	*39.82	57.029
ε_{eff}	1.8804	1.9917	2.1069	2.3523
P^*	2.2243	1.0700	2.0069	0.7954
μD	0.330	0.229	0.319	0.197

Table II

$(C_6H_5)_3Si—CH = CH_2$ *in cyclohexane*

Number of solution	1	2	3	4	5
N_2	4.5699	4.10397	3.510	2.9798	2.646
n_D	1.4443	1.4399	1.4382	1.4358	1.4350
z	40.84	40.86	41.01	41.15	41.11
d	0.80439	0.80074	0.7963	0.79416	0,79120
v	116.12	115.47	114.61	113.57	113.14
ε	2.1007	2.0892	2.0780	2.0696	2.0611
P_e	30.05	29.63	29.33	28.94	28.77

from the formula 5.

$M_1 = 84.1625$
$M_2 = 286.45246$
$\varepsilon_1 = 2.016$ from the function ε/N_2 extrapolated to
$d_1 = 0.7738$ from the function d/N_2 infinite dilution
$\alpha = 1.8182$ slope of ε/N_2
$\beta = 0.72348$ slope of d/N
$P_\infty = 104.698$
$P_A = 8.78$ ml
$P_e = 93.9670$ ml
$R = 102.7470$ $\mu = 0.22123\sqrt{P_\infty - R}$ $P_\infty - R = 0.309$ D

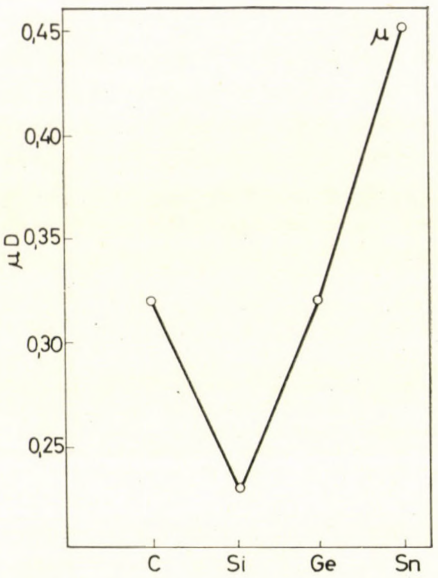


Fig. 1. The dipole moments of the members of the homologous series *vs.* the principal quantum number

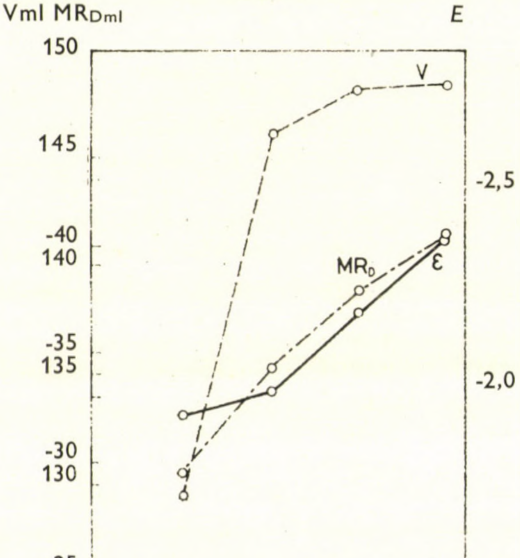


Fig. 2. Molar refractions of the members of the homologous series *vs.* the principal quantum number

earlier publication [9]. The dipole moments (Fig. 1), molar refractions, molar volumes and dielectric constants of the members of the homologous series *vs.* the principal quantum number are plotted in Fig. 2.

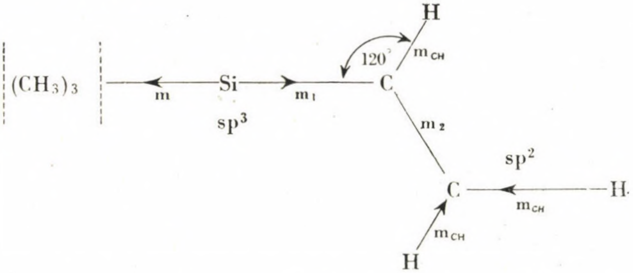
It appears from Fig. 2 that with the exception of the dielectric constant there is a very great difference between the physical properties of the carbon and silicon compounds, but a considerably less difference is observed between the properties of silicon and germanium, on the one hand, and germanium and tin compounds, on the other.

The change of the dipole moment *vs.* the principal quantum number in Fig. 1 reveals a minimum at the silicon derivatives, which can be explained only by the fact that contrary to carbon, silicon has not only an inductive ($+I$), but also a mesomeric ($-M$) effect which has a direction opposite to the first and both germanium and tin have also $+I$ and $-M$ effects.

In the case of methyl and phenyl substituted vinyl silanes the picture is not quite so unambiguous, as the dipole moment changes with the number of the different substituents in different ways.

The individual bond moments of vinyl derivatives were determined by the vectorial calculations described in one of our earlier papers [1].

The structure of trimethyl-vinyl derivatives can be illustrated by the following vectorial diagram



It is possible to calculate from this diagram the bond moments of the E—C and C=C bonds pertaining to the vinyl group, provided the dipole moments of the various vinyl derivatives, the bond moments of the C—H and C—E(aliphatic) bonds are known. The bond moment of C—H was known, 0.4 *D*, the moments of the various E—C bonds were taken from the literature [1, 16, 9] and in the case of the carbon derivative it was calculated from the dipole moment of $(CH_3)_3C—Cl$.

It follows from the sp^2 hybrid levels of the carbon atoms in the vinyl group that the valency angles around the latter are 120°.

By accounting for the $+I$ and $-M$ effects the following approximate structural formula considering the electron shift and indicating the partial charges may be written

$$\begin{array}{llcllcl} & \delta(+) & & \delta(-) & & \delta(+) & \\ (CH_3)_3 & E- & & CH & = & CH_2 & \\ & 2\varepsilon_i & & -\varepsilon_i & & -\varepsilon_i & I \text{ effect} \\ & -1/2\,\varepsilon_t & & -1/2\,\varepsilon_t & & +\varepsilon_t & M \text{ effect} \end{array}$$

where

ε_i stands for the charge fraction due to I effect
ε_t stands for the charge fraction due to M effect
δ for the resultant charge fraction.

It follows that

$$m_1 = (2\,\varepsilon_i - 1/2\,\varepsilon_t)R_{E-C}$$
$$m_2 = (\varepsilon_t - \varepsilon_i)R_{CC}$$

where R_{E-C} and R_{CC} are the pertaining bond distances.

From the vectorial diagram it follows further that if

$$m - m_1 = m_A$$

then

$$m_2 = m_B.$$

The cosine law can be written for the dipole moment of the compound as follows:

$$\mu^2 = m_A^2 + m_B^2 + 2\,m_A \cdot m_B\,\cos\Theta$$

where $\cos\Theta = -0.5$, as $\Theta = 120°$

thus

$$\mu^2 = m_A^2 + m_B^2 - m_A \cdot m_B$$

Consequently the vector moment values for the bonds E—C and the double bond C=C can be calculated for every trimethylvinyl derivative (see Table III).

The data in Table III show that the values of both vector moments

Table III

E	m_{E-C}	$m_{C=C}$
C	0.230	0.141
Si	0.338	0.157
Ge	0.351	0.242
Sn	0.488	0.323

increase from carbon to tin, due primarily to the increase of the inductive effect, the π interaction being very slight — as proved by our earlier quantum mechanical calculations. Thus the value of the dipole moment is primarily determined by the vectorial sum of the dipole moment vectors of the σ bond.

The vectorial calculations carried out for phenyldimethylvinylsilane and triphenylvinylsilane involved the supposition of free rotation in both cases.

In an analogous manner the vectorial calculation of the dipole moment of $(C_6H_5)_3SiCH{=}CH_2$ is based on the following equation:

$$\mu^2 = m_A^2 + m_B^2 - m_A m_B$$

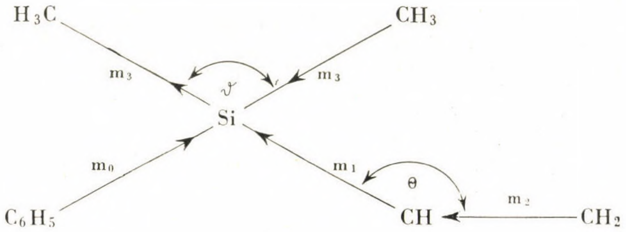
where

$$m_A = m_{Si-C_6H_5} - m_1$$
$$m_B = m_2$$
$$m_{Si-C_6H_5} = 0.16\ D\ [9]$$
$$m_1 = m_{\ Si-vin} = 0.34\ D$$
$$m_2 = m_{C-C} = 0.16\ D$$

Substituting these values into the above equation we obtain

$$\mu = 0.295\ D$$
$$\mu_{exp} = 0.309\ D$$

The dipole moment of the molecule $C_6H_5(CH_3)_2SiCH{=}CH_2$ can also be calculated vectorially by supposing free rotation:



$$\Theta = 120°$$
$$\vartheta = 110°$$
$$m_0 = 0.16\ D\ \ [9]$$
$$m_1 = 0.34\ D$$
$$m_2 = 0.16\ D$$
$$m_3 = 0.2\ D$$

$$\mu^2 = m_0^2 + m_1^2 + m_2^2 + 2m_3^2 + 2(m_0 m_1 \cos\vartheta + + m_0 m_2 \cos\vartheta \cos\Theta + m_1 m_2 \cos\Theta + 2m_0 m \cos\vartheta + + m_3^2 \cos\vartheta + 2m_1 m_3 \cos\vartheta + 2m_3 m_2 \cos\vartheta \cos\Theta)$$

Substituting the above values into this equation we get

$$\mu = 0.162\,D$$
$$\mu_{\mathrm{exp}} = 0.197\,D$$

Thus there is a very satisfactory agreement between the vectorially calculated dipole moments and the experimentally obtained values. This leads to the conclusion that in first approximation the group vectors may be considered constant independently of the substituents, thus the group vectors as given above serve for a satisfactory calculation of the dipole moments of the various derivatives.

As already mentioned in connection with Fig. 1 the dipole moment of trimethylvinylsilane is the lowest of all the vinyl derivatives. This was explained by the appearance of an additional mesomeric effect from silicon onwards, while in the case of carbon derivatives only an inductive effect prevails and the dipole moments σ and π are known to have opposite directions. To prove this assumption quantum chemical calculations were carried out for simplified conditions according to the following considerations:

The vinyl group was substituted by a pseudoatom with two electrons:

$$\mathrm{E} \underset{\sigma}{\overset{\pi}{\leftrightarrows}} \overset{\overline{\mathrm{ox}}}{\mathrm{V}}$$

Similarly to the original problem a colligative σ bond and a coordinative $d\pi - p\pi$ bond are supposed between the E(Si, Ge, Sn) atom and the pseudoatom $\overset{\mathrm{ox}}{\mathrm{V}}$.

In both cases the generalized eigenfunction (ψ_{EV}) is obtained by the linear combination of the eigenfunctions of the two atomic systems (ψ_E, ψ_V):

$$\psi_{EV} = c_E\,\psi_E + c_V\,\psi_V \tag{8}$$

The pertaining parametric matrix is:

$$\begin{vmatrix} \alpha + h_E\,\beta - \varepsilon & k\beta \\ k\beta & \alpha + h_V\,\beta - \varepsilon \end{vmatrix} = 0 \tag{9}$$

where α and β are the coulomb and interchange integrals respectively of an arbitrarily chosen basic system; h and k are variation parameters. Substituting

$$\sigma_1 = \frac{\alpha + h_E\beta - \varepsilon}{k \cdot \beta} \quad \text{and} \quad \sigma_2 = \frac{\alpha + h_V\beta - \varepsilon}{k \cdot \beta} \tag{10}$$

the following matrix is obtained:

$$\begin{vmatrix} \sigma_1 & 1 \\ 1 & \sigma_2 \end{vmatrix} = 0 \tag{11}$$

where

$$\sigma_1 = \sigma_2 + a$$

and

$$a = \frac{h_V - h_E}{k} \tag{12}$$

The ratio of the linear coefficients in Eq. (8) is:

$$\frac{c_V}{c_E} = \lambda \tag{13}$$

and from this the polarities of the colligative σ bond and the coordinative π bond are:

$$i_\sigma = \frac{\lambda_\sigma^2 - 1}{\lambda_\sigma^2 + 1} \tag{14}$$

$$i_\pi = \frac{2}{1 + \lambda_\pi^2} \tag{15}$$

According to Eqs (11) and (12) the determinant of the matrix is the following:

$$\sigma_1^2 + \sigma_1 a - 1 = 0 \tag{16}$$

from which for σ_1 two values may be obtained which at the same time determine the value of λ according to the correlation:

$$\lambda = - \sigma_1 \tag{17}$$

By substituting Eq. (17) into Eq. (16) the following correlation is obtained

$$\lambda^2 - a \cdot \lambda - 1 = 0 \tag{18}$$

so that depending on the variation parameter a various values are obtained for λ, i_σ and i_π.

Changes in i_σ and i_π vs. the variation parameter a are plotted in Fig. 3.

According to Fig. 3 i_σ increases and i_π decreases with increasing values of a, that is with the increase of the $+I$ and $-M$ (mesomeric) effects of the E atom the values of both i_σ and i_π will increase. According to MULLIKAN [15] a correlation exists between the coulomb integral and electronegativity of the ith atom:

$$(\alpha_i - \alpha_0) = B(X_i - X_0)\beta_0 \tag{19}$$

so that as an approximation a similar proportionality may be supposed between the parameter **a** and the electronegativities of the atoms E and $\overset{ox}{\mathbf{V}}$:

$$a = N \Delta X_{EV} \tag{20}$$

where

$\Delta X_{EV} = X_V - X_E,$

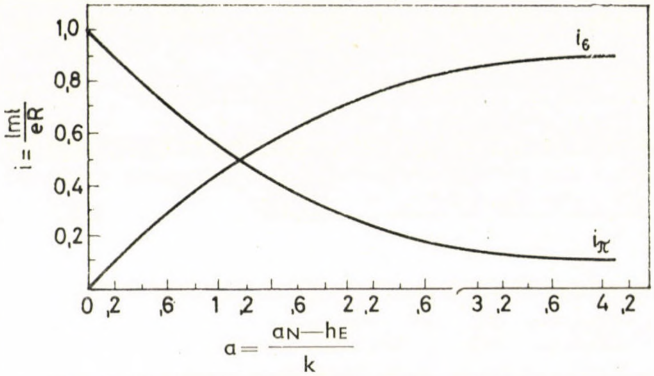


Fig. 3. Changes in i_σ and i_π *vs.* the variation parameter a

the difference between the electronegativities, N is a proportionality factor with the following values (obtained by correlation calculations):

$$N_\sigma = 0.666 \qquad N_\pi = 4.83 \tag{21}$$

The electronegativities of the E atoms (C, Si, Ge, Sn) are the following:

C	Si	Ge	Sn
2.5	1.9	1.8	1.7

With the help of these data the values of i_σ and i_π can be calculated from Eqs (18), (14) and (15). The initial data and the results of the calculation are given in Table IV. It should be mentioned here that the electronegativity value of carbon was chosen for the electronegativity of the $\overset{ox}{V}$ pseudo-atom since the carbon atom is responsible for the bond in the vinyl group.

Table IV

E	X_C	X_E	ΔX_{EC}	a_σ	a_π	i_σ	i_π	$i_\sigma - i_\pi$
C	2.55	2.45	0.1	0.066	—	0.05	—	0.05
Si	2.50	1.90	0.6	0.400	2.9	0.19	0.16	0.03
Ge	2.50	1.80	0.7	0.466	3.38	0.20	0.14	0.06
Sn	2.50	1.70	0.8	0.534	3.86	0.25	0.11	0.14

Figure 4 shows the changes in the polarities of the σ and π bonds from the values of i_σ, i_π and $i_\sigma - i_\pi$ *vs. E.*

As the difference between the coulomb integrals increases and the exchange integral decreases, the polarity of the σ bond will increase and that of the π bond decrease, consequently the difference between the electronegativities of the vinyl group, which has been replaced by a carbon-like pseudoatom, and of the Group IV/1 elements increases from carbon to tin accompanied by an increase in the difference between the coulomb integrals. The bond distance E—C is known to increase with the increase of the atomic number, so that starting from silicon the exchange integral (h_i) and the value of the related variation parameter k also decrease. These two factors together determine the value of a, so that with increasing atomic numbers i_σ increases and i_π decreases, while the difference of the two has a minimum at the Si—C bond, in agreement with the results of dipole moment measurements of compounds of the type $CH_2{=}CH{-}E(CH_3)_3$.

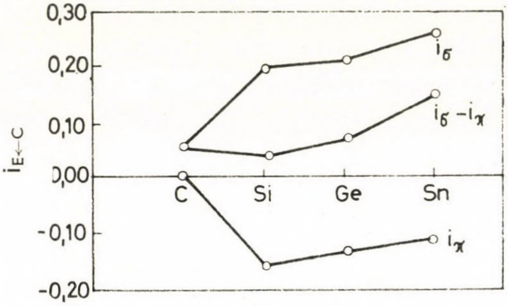
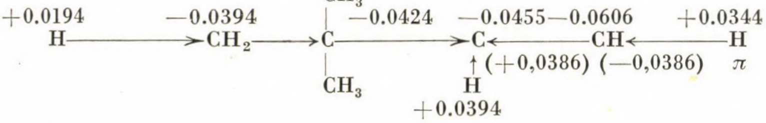


Fig. 4. The changes in the polarities of the σ and π bonds from the values of i_σ, i_π and $i_{\sigma-\pi}$

This simple quantum chemical variation method confirms that the $+I$ effect increases in the order C, Si, Ge, Sn, while the $-M$ (mesomeric) effect decreases in the order Si, Ge, Sn.

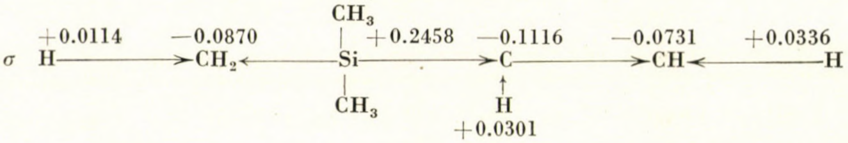
Exact quantum chemical calculations were carried out for tertiary butylethylene and the analogous trimethylvinylsilanes [10] and the following results were obtained:



$$\mu_\sigma = 0.1299\ D$$
$$\mu_\pi = 0.2480\ D$$
$$\mu_{\sigma\pi} = 0.319\ D$$
$$\mu_{\exp} = 0.330\ D$$

The case of tertiary butylethylene shows that the partial charges of the hydrogens of the methyl group are considerably lower than those of the hydrogens in the vinyl group, which may primarily be explained with the various hybrid states of the carbon atoms. While in the case of methyl groups the carbon atoms are in sp^3 state, the carbon atoms of the vinyl group are in the sp^2 hybrid state. The electron shifting effect of the tertiary butyl group also contributes to this result, causing the α carbon atom of the vinyl group to have a positive and the β carbon atom to have a negative partial charge fraction with a value of 0.0386 *e*. From the partial charge fractions a value of 0.1299 *D* is obtained for the dipole moment σ which is less than the dipole moment π with a value of 0.248 *D*. In our case the directions of the dipole moments σ and π coincide, so that from their vectorial sum 0.319 *D* is obtained for the dipole moment of the molecule. This figure is in full agreement with the experimentally determined one.

The charge distribution in trimethylvinylsilane $(CH_3)_3Si-CH=CH_2$ is the following:

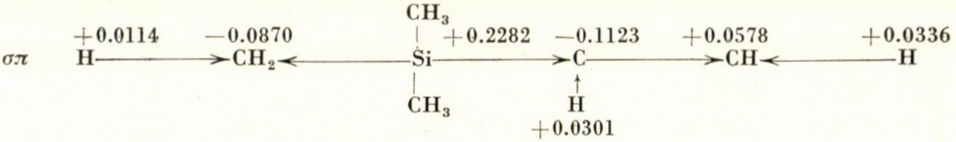


$$\sigma\quad \overset{+0.0114}{\mathrm{H}}\longrightarrow\overset{-0.0870}{\mathrm{CH_2}}\longleftarrow\underset{\underset{\mathrm{CH_3}}{|}}{\overset{\overset{\mathrm{CH_3}}{|}\ +0.2458}{\mathrm{Si}}}\longrightarrow\underset{\underset{+0.0301}{\underset{\mathrm{H}}{\uparrow}}}{\overset{-0.1116}{\mathrm{C}}}\longrightarrow\overset{-0.0731}{\mathrm{CH}}\longleftarrow\overset{+0.0336}{\mathrm{H}}$$

$$\mu_\sigma = 0.281\ D$$
$$\mu_\pi = 0.153\ D$$
$$\mu_{\sigma\pi} = 0.080\ D$$
$$\mu_{\mathrm{exp}} = 0.229\ D$$

$$\pi\quad \overset{-0.0136}{(\mathrm{CH_3})_3\mathrm{Si}}\longleftarrow\overset{-0.0017}{\mathrm{CH}}\longleftarrow\overset{+0.0153}{\mathrm{CH_2}}$$

$$\Delta m = 1.9650\,\beta$$



$$\sigma\pi\quad \overset{+0.0114}{\mathrm{H}}\longrightarrow\overset{-0.0870}{\mathrm{CH_2}}\longleftarrow\underset{\underset{\mathrm{CH_3}}{|}}{\overset{\overset{\mathrm{CH_3}}{|}\ +0.2282}{\mathrm{Si}}}\longrightarrow\underset{\underset{+0.0301}{\underset{\mathrm{H}}{\uparrow}}}{\overset{-0.1123}{\mathrm{C}}}\longrightarrow\overset{+0.0578}{\mathrm{CH}}\longleftarrow\overset{+0.0336}{\mathrm{H}}$$

$$m_{\mathrm{SiC}(\sigma)} = 0.7779\ D$$
$$m_{\mathrm{SiC}(\pi)} = 0.1210\ D$$
$$m_{\mathrm{SiC}(\sigma\pi)} = 0.6569\ D$$

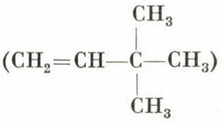
It appears from the foregoing that for partial σ charge distribution the charge fractions are higher than in the case of analogous carbon compounds, consequently the dipole moment σ is also higher, about twice the value of the first, that is, 0.281 *D*. Because of the $-M$ effect of silicon the direction of the dipole moment is the opposite of that which appears in the analogous carbon compound, and its value is lower; 0.153 *D*. From the vectorial sum of the σ and π dipole moments of opposite directions a very low value is obtained for the dipole moment of the trimethylvinylsilane molecule, namely 0.08 *D* which, however, is near to the experimentally found 0.229 Debye.

The reason for the fact that tertiary butylethylene has a higher dipole moment than the corresponding silicon compound follows unequivocally from the bond structures obtained by the above exact calculations. This explains further the finding that while tertiary butylethylene forms addition compounds with hydrogen halides according to the Markovnikov rule, addition products of trimethylvinylsilane and hydrogen halides are formed according to the anti-Markovnikov rule, since, compared to the central atom, in the case of tertiary butylethylene the α, in case of trimethylvinylsilane the β carbon atom has a more positive character.

Experimental

The investigated compounds were prepared according to the following principles:

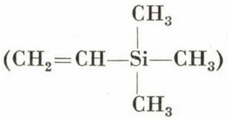
1. 3,3-Dimethylbutene-I



$$(CH_2{=}CH{-}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}{-}CH_3)$$

was prepared from 2,2-dimethylbutane by dehydrogenation in the presence of a catalyst containing aluminium, chromium and potassium [11]. Boiling point: 41.2°C at 760 mmHg.

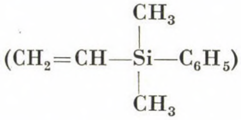
2. Vinyltrimethylsilane



$$(CH_2{=}CH{-}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{Si}}{-}CH_3)$$

was prepared from vinyltrichlorosilane and methyl magnesium bromide in a dibutylether medium [12] with a 90% yield. Boiling point: 54.4°C at 745 mmHg.

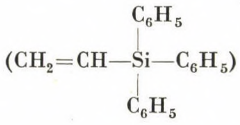
3. Vinyldimethylphenylsilane



$$(CH_2{=}CH{-}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{Si}}{-}C_6H_5)$$

was prepared from vinylphenyldichlorosilane and methyl magnesium bromide in diethylether medium. The yield was 80% [13]. Boiling point: 69°C at 4 mmHg.

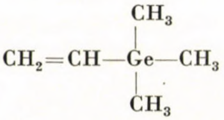
4. Vinyltriphenylsilane



$$(CH_2{=}CH{-}\overset{\displaystyle C_6H_5}{\underset{\displaystyle C_6H_5}{Si}}{-}C_6H_5)$$

was prepared from vinyltrichlorosilane and phenyl magnesium bromide in diethylether medium with a 40% yield [12]. Melting point: 58—59°C.

5. Vinyl trimethylgermane



$$CH_2{=}CH{-}\overset{CH_3}{\underset{CH_3}{Ge}}{-}CH_3$$

produced by the reaction of the Norman reagent with trimethyliodogermane contained traces of tetrahydrofurane which were difficult to remove. For this reason vinyltrimethylgermane was produced from trimethyliodogermane and vinyllithium which latter was obtained by radical rearrangement from tetravinyltin and phenyllithium. Pure vinyltrimethylgermane was obtained under these conditions in a 50% yield [14]. Boiling point: 70.6°C at 736 mmHg.

3,3-Dimethylbutene-I, vinyltrimethylsilane, vinyldimethylphenylsilane and vinyltrimethylgermane were dried over calcium chloride, sodium metal and lithium hydride, repeatedly fractionated and the fractions collected in narrow temperature intervals corresponding to their boiling points.

Since for the determination of the dipole moment substances of high purity are required, the purity of the preparations was checked by the identification of their molar refractions (Table I) and gas chromatographically by means of the W. Giede Type 18.2 gaschromatograph using nitrogen of 0.6—0.8 atmosphere pressure as a carrier gas. The 1 m long and 4 mm diameter column was packed with 80—120 mesh ceolite carrying 3% of silicone grease. The recording was of sensitivity 4 with a 200—600 mm/hour paper speed; the detector current was 125 mA. All compounds were found both optically and gaschromatographically pure.

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Acta Chimica Academiae Scientiarum Hungaricae, Tomus 60 (4), pp. 373—379 (1969)

INVESTIGATIONS ON ION EXCHANGE EQUILIBRIA WITH RADIOACTIVE TRACER METHOD, XV

LIQUID ION EXCHANGE TECHNIQUE FOR INVESTIGATING THE MIXED COMPLEX SPECIES OF ZINC WITH GLYCOLIC AND α-HYDROXYISOBUTYRIC ACID

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With the aid of liquid ion exchange technique, using di-2-ethylhexyl phosphoric acid, the formation of the mixed complex species has been studied in the system zinc – glycolic acid – α-hydroxyisobutyric acid. Based on theoretical considerations the formation constant of the mixed complex $[MLA]$ was determined using a graphical way of calculation, yielding the value $\log K_m = 0.88$.

Ion exchange and liquid—liquid partition techniques are already more or less well proved tools for the chemist for investigating the formation and stability of complex species. In the recent years a considerable amount of data determined by these techniques has been published, and the excellent compilation of Sillén and Martell [1] indicates the usefulness of these results. However, as regards complexes with mixed ligands, literature data are far from being complete and the results quoted refer first of all to spectrophotometric methods; extraction and ion exchange have been scarcely used. In this paper the attempt to extend the liquid ion exchange method, used also previously [2—5] is described, summarizing the results obtained for the system zinc—glycolic acid—α-hydroxyisobutyric acid.

Theoretical

Let us take into consideration the formation of the mixed complex of the divalent metal ion M with ligands L and A (both being bound in the same coordination sphere), according to the reaction

$$[ML_2] + [MA_2] = 2[MLA] \tag{1}$$

The formation constant of this complex can be determined as

$$K_m = \frac{[MLA]^2}{[ML_2]\,[MA_2]} \tag{2}$$

In the course of further calculations the following assumptions were made:

1. When using liquid ion exchanger only the M^{2+} species are involved in the partition process.

2. Highly coordinated complexes *e.g.* $[ML_3]^-$, $[ML_4]^{2-}$, $[M\Lambda_3]^-$, $[M\Lambda_4]^{2-}$ etc. do not form.

3. Under the given conditions polynuclear or hydroxo complexes do not exist in appreciable amount. Introducing the distribution ratios with simplified notations we have

$$D^\circ = \frac{_o[M]}{_w[M]} \tag{3}$$

$$D_L = \frac{_o[M]}{_w[M] + {}_w[ML] + {}_w[ML_2]} \tag{4}$$

$$D_\Lambda = \frac{_o[M]}{_w[M] + {}_w[M\Lambda] + {}_w[M\Lambda_2]} \tag{5}$$

$$D_m = \frac{_o[M]}{_w[M] + {}_w[ML] + {}_w[ML_2] + {}_w[M\Lambda] + {}_w[M\Lambda_2] + {}_w[ML\Lambda]} \tag{6}$$

from which the following relation is obtained

$$\frac{1}{D_m} = \frac{1}{D_L} + \frac{1}{D_\Lambda} - \frac{1}{D^\circ} + \frac{_w[ML\Lambda]}{_o[M]} \tag{7}$$

which on rearranging yields

$$_w[ML\Lambda] = {}_o[M]\left(\frac{1}{D_m} + \frac{1}{D^\circ} - \frac{1}{D_L} - \frac{1}{D_\Lambda}\right) \tag{8}$$

Taking into consideration that

$$\beta_{2L} = \frac{_w[ML_2]}{_w[M]\ {}_w[L]^2} \tag{9}$$

and

$$\beta_{2\Lambda} = \frac{_w[M\Lambda_2]}{_w[M]\,{}_w[\Lambda]^2} \tag{10}$$

Eqs (2), (8), (9) and (10) can be combined to result in

$$K_m = \frac{D^{\circ 2}\left(\dfrac{1}{D_m} + \dfrac{1}{D^\circ} - \dfrac{1}{D_L} - \dfrac{1}{D_\Lambda}\right)^2}{\beta_{2L}\,\beta_{2\Lambda}\,{}_w[L]^2\,{}_w[\Lambda]^2} \tag{11}$$

For graphic calculation, in the knowledge of D°, β_{2L} and $\beta_{2\Lambda}$, and the values D_L, D_Λ and D_m as a function of [L] and [Λ], respectively, the term

$$\Psi = \frac{D^{\circ 2}\left(\frac{1}{D_m} + \frac{1}{D^\circ} - \frac{1}{D_L} - \frac{1}{D_\Lambda}\right)^2}{\beta_{2L}\ \beta_{2\Lambda}} \tag{12}$$

is plotted against $_w[L]^2\ _w[\Lambda]^2$, yielding a linear correlation with slope K_m.

In these measurements care must be taken to keep concentrations of $_w[L]$ and $_w[\Lambda]$ in the same order of magnitude, thus to avoid any discrepancies because of formation of higher mixed complexes.

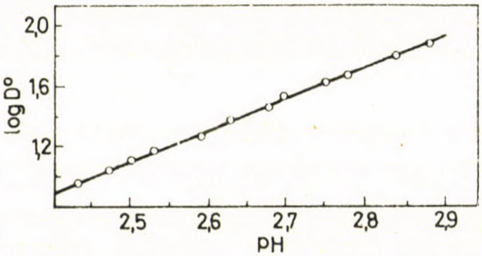

Fig. 1. Distribution ratio as a function of the pH $[Zn^{2+}] = 2 \cdot 10^{-5}$ *M*, [DEHPA] = 0.1 *F*, ionic strength: 0.75 *M* as perchlorate

Experimental

Equilibration of the aqueous and organic phases was carried out by shaking the samples filled in sealed ampoules at 25°C for 15 hours.

Distribution coefficients were determined by radiometric assay of the metal concentration in both phases, while the pH of the aqueous phase was measured by means of Radiometer PH-4. ^{65}Zn tracer of high specific activity was produced by the conventional (n, γ) reaction by irradiating specpure zinc target with a thermal neutron flux of $5 \cdot 10^{13}\ n \cdot cm^{-2}\ sec^{-1}$. The systems investigated were $2 \cdot 10^{-5}$ *M* for zinc, while the ionic strength was adjusted to 0.75 *M* with perchloric acid and sodium perchlorate. The pH of the aqueous phase was kept at about 2.4—2.8, depending on the set of measurements.

Di-2-ethylhexyl phosphoric acid (DEHPA) diluted with toluene in 0.1 *F* concentration was used as liquid ion exchanger, representing the organic phase.

Chemicals of c.p. grade and redistilled water were used all over the measurements.

The free ligand concentrations were calculated in the knowledge of the pH and the dissociation constant values of the corresponding acids.

Results and discussion

The aim of the first series of measurements was to determine the distribution ratio of zinc between the organic and aqueous phases as a function of the pH, in the absence of any complexing agent. The data obtained are shown in Fig. 1.

The second power dependence from the hydrogen ion concentration indicates the partition of the divalent zinc ions.

Table I

Results of equilibrium measurements for the system zinc—glycolate

$10^3 \cdot [L]$	$1/D_L$	pH
7.2	0.029	2.82
12.0	0.039	2.82
18.4	0.050	2.83
25.4	0.061	2.84
30.9	0.077	2.84
36.4	0.092	2.84
40.0	0.103	2.84
48.5	0.140	2.82
51.8	0.135	2.85
59.6	0.167	2.86
69.0	0.188	2.86
77.3	0.220	2.86

Table II

Results of equilibrium measurements for the system zinc—α-hydroxyisobutyrate

$10^3 \cdot [A]$	$1/D_A$	pH
3.0	0.137	2.42
6.0	0.160	2.42
9.6	0.181	2.43
12.2	0.201	2.43
16.1	0.240	2.43
19.3	0.240	2.45
22.9	0.271	2.46
26.6	0.285	2.47
30.9	0.317	2.48
35.0	0.351	2.49
39.8	0.397	2.49
42.4	0.407	2.50

Starting out from the data of Tables I and II, which refer to equilibrium measurements in the presence of the two complexing agents, the plots shown in Figs 2 and 3 were constructed. The corresponding stability constants were determined as slopes (β_2) and intercepts (K_1) of the linear correlations according to the method developed by LEDEN [6].

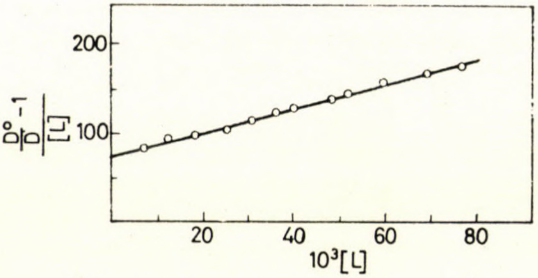

Fig. 2. $\frac{D^\circ/D-1}{[L]}$ as a function of the free glycolate ligand concentration $[L]$
$[Zn^{2+}] = 2 \cdot 10^{-5}$ M, [DEHPA] = 0.1 F, ionic strength: 0.75 M as perchlorate

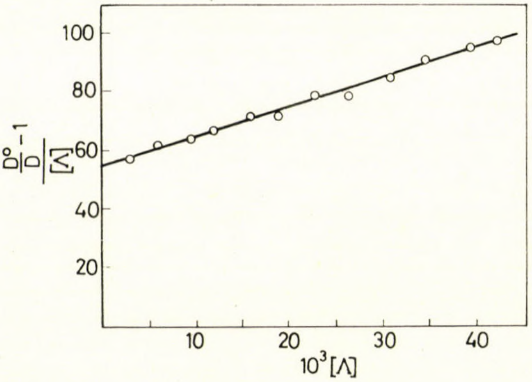

Fig. 3. $\frac{D^\circ/D-1}{[\Lambda]}$ as a function of the free α-hydroxyisobutyrate ligand concentration $[\Lambda]$
$[Zn^{2+}] = 2 \cdot 10^{-5}$ M, [DEHPA] = 0.1 F, ionic strength: 0.75 M as perchlorate

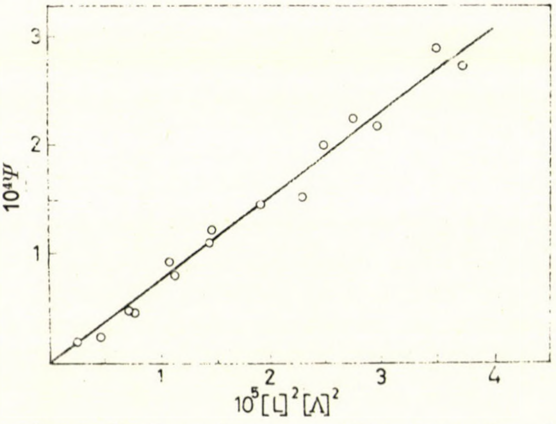

Fig. 4. The term ψ (determined according to Eq. (12) as a function of $[L]^2$ $[\Lambda]^2$ in the system zinc—glycolic acid—α-hydroxyisobutyric acid
$[Zn^{2+}] = 2 \cdot 10^{-5}$ M, [DEHPA] = 0.1 F, ionic strength: 0.75 M as perchlorate

Table III summarizes the results of equilibrium measurements performed with the aim of mixed complex formation. Based on these data the plot of Ψ *vs.* $[L]^2 [\Lambda]^2$ shown in Fig. 4 was constructed using Eq. (12).

Table III

Results of equilibrium measurements in the mixed complex system zinc—glycolate—α-hydroxyisobutyrate

pH	$1/D^\circ$	$1/D_L$	$1/D_\Lambda$	$1/D_m$	$[L]$	$[\Lambda]$	$10^6 \cdot [L]^2[\Lambda]^2$	$10^6 \cdot \psi$
2.63	0.0445	0.206	0.260	0.640	0.0326	0.0480	2.45	19.9
2.65	0.0410	0.256	0.251	0.684	0.0421	0.0500	4.45	23.3
2.67	0.0382	0.319	0.242	0.809	0.0521	0.0515	7.21	46.0
2.71	0.0309	0.620	0.102	0.920	0.0960	0.0285	7.47	45.0
2.71	0.0309	0.620	0.122	1.038	0.0960	0.0341	10.70	92.0
2.68	0.0357	0.390	0.234	0.939	0.0630	0.0530	11.20	79.2
2.68	0.0357	0.468	0.234	1.076	0.0720	0.0530	14.60	108.5
2.71	0.0309	0.620	0.145	1.108	0.0960	0.0400	14.75	120.0
2.71	0.0309	0.620	0.168	1.160	0.0960	0.0457	19.18	140.0
2.68	0.0357	0.650	0.234	1.330	0.0900	0.0530	22.90	151.0
2.69	0.0340	0.641	0.231	1.362	0.0920	0.0544	25.10	196.0
2.68	0.0357	0.650	0.265	1.463	0.0900	0.0583	27.60	220.0
2.67	0.0375	0.660	0.302	1.525	0.0879	0.0621	29.80	212.0
2.67	0.0375	0.660	0.338	1.655	0.0879	0.0673	35.00	282.0

From the figure it is striking that, in accordance with previous expectations, a straight line with slope $K_m = 7.5$ is obtained. The reliability of the graphic presentation is indirectly also proved by the fact that the straight line starts from the origin.

The formation constant of the mixed $[ML\Lambda]$ complex as defined in Eq. (2) and those of the systems zinc—glycolate and zinc—α-hydroxyisobutyrate are compiled in Table IV. The error of the determination of the K_1 and K_2 val-

Table IV

Formation constants of complex species in the system zinc—glycolic acid—α-hydroxyisobutyric acid

System	$\log K_1$	$\log K_2$	β_2	$\log K_m$
Zn-glycolate	1.86	1.25	1280	—
Zn-α-hydroxyisobutyrate	1.74	1.23	950	—
Zn-glycolate-α-hydroxyisobutyrate	—	—	—	0.88

ues did not exceed 0.02 units on logarithmic scale which corresponds to a maximum error of ± 0.05 for the value of $\log K_m$.

These data imply that the complex species of the two ligands investigated reveal similar stabilities and that the formation of the mixed complex is not distinctly favoured under the conditions chosen. However, the value obtained for K_m is about twice of that to be expected from theoretical considerations, as according to Eqs (1) and (2) the statistic partition would yield

$$K_m = \frac{(0.5)^2}{(0.25)\ (0.25)} = 4 \tag{13}$$

Symbols

D°	distribution ratio in the absence of complexing agent
D_L	distribution ratio in the presence of glycolate ligand
D_Λ	distribution ratio in the presence of α-hydroxyisobutyrate ligand
D_m	distribution ratio in the presence of glycolate and α-hydroxyisobutyrate ligands
K_i	successive formation constant of the species $[ML_i]$ and $[M\Lambda_i]$, respectively
K_m	formation constant of the mixed complex as defined in Eq. (2)
L	glycolate ligand
M	metal (zinc)
Λ	α-hydroxyisobutyrate ligand
Ψ	term defined in Eq. (12)

Indices

w	aqueous phase
o	organic phase

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STEREOCHEMICAL STUDIES, V*

QUATERNIZATION OF 1,2-DISUBSTITUTED 1,2,3,4-TETRAHYDROISOQUINOLINES III.* STEREOCHEMISTRY OF DIASTEREOMERIC QUATERNARY SALTS AS STUDIED BY PROTON RESONANCE SPECTROSCOPY

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The proton magnetic resonance spectra of diastereomeric 1-phenyl-, 1-isopropyl-, and 1-(3',4'-dimethoxybenzyl)-2,2-dialkyl-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinolinium salts have been studied. It has been established that the substituent in position 1 is *trans* to bulkier substituent at the nitrogen and the quaternary salts have highly preferred conformations that are characteristic of all stereoisomeric derivatives with a given substituent in position 1. The 1-phenyl group is probably *pseudo-equatorial* in the preferred conformation, while the 1-isopropyl and 1-(3,4-dimethoxybenzyl) groups are probably *pseudo-axial.* It is concluded from stereochemical properties and stereoselectivity data that the steric course of quaternization is strongly influenced by the interaction of the entering alkyl group with the substituents in positions 1 and 2. The preferred direction of attack for the quaternizing group is *trans* relative to the substituent in position 1.

Introduction

Recently we investigated the stereochemistry of diastereomeric quaternary salts obtained by alkylation of 1-methyl-2-alkyl-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline bases and the steric course of the quaternization reaction [1]. In order to check the correctness of some of our assumptions made in [1] and at the same time to estimate the possible effect of the substituent at C—1 on the stereoselectivity of quaternization we extended our studies on further tetrahydroisoquinoline bases containing, respectively, phenyl-, isopropyl- and 3,4-dimethoxybenzyl groups at C—1. The synthesis of parent bases and the fractional yields of diastereomeric quaternary salts in the crude reaction mixtures of "direct" (N-methyl base + alkyl iodide) and "reverse" (N-alkyl base + methyl iodide) reactions were described in the previous part of this series [2]. In this paper we present the proton resonance study of the isolated diastereomeric quaternary salts and discuss the results in terms of their stereochemistry. Furthermore, additional deductions are made about the steric course of quaternization of 1,2-disubstituted tetrahydroisoquinoline bases.

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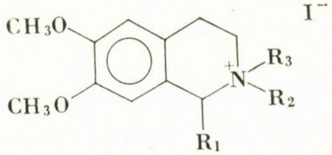
* For parts III (I) and IV (II) of this series, see Bernáth, G., Koczka, K., Kóbor, J., Radics, L. and Kajtár, M. This Journal **55**, 331 (1968), and Kóbor, J., Bernáth, G., Radics, L. and Kajtár, M. This Journal **60**, 255 (1969)

The quaternary salts studied are given by Formula I.



$R_1 = (CH_3)_2CH,\ C_6H_5,\ 3{,}4\text{-}(CH_3O)_2C_6H_3CH_2;$
$R_2 = CH_3;$
$R_3 = H,\ CH_3,\ CH_3CH_2,\ C_6H_5CH_2.$

Formula I

For quaternary salts with unsymmetrically substituted nitrogen I refers to diastereomeric pairs the members of which are usually formed simultaneously in the "direct" and "reverse" quaternization reactions.

In the case of cyclic N-bases with highly preferred (or rigid) and known conformations the problem of stereochemical characterization of the quaternization can be reduced to the determination of the stereochemistry of diastereomeric salts. Once these are known it is usually possible to distinguish between an *equatorial* or *axial* attack of incoming group resulting in a given diastereomer. The fractional yields of the two diastereomers, along with the conformational equilibrium constant of the parent base then allow one to decide in which direction is the attack sterically preferred. More quantitative information about the steric course is obtainable from kinetic measurements [3] yielding specific rates of quaternization in both steric directions (*e.g.* k_{ax}, and k_{equ}). The stereochemistry of the diastereomers is usually determined by combined use of various chemical and physical methods [4—10]. A most powerful technique is provided by proton resonance spectroscopy, a simple way of its application in the study of diasteromeric quaternary salts being due to CLOSS [11].

Little, and mainly qualitative, information is available about the conformational properties of tetrahydroisoquinoline bases. In the first place the recent series of work by KNABE *et al.* on mercury (II) acetate dehydrogenation of 1,2-dialkyl-1,2,3,4-tetrahydroisoquinoline derivatives should be mentioned [12—16]. From the chemical structure and relative yields of dehydrogenation products the above authors concluded that the parent bases exist mostly in preferred conformations, the extent of preference and the actual conformation being determined by the steric requirements of the substituents at positions 1 and 2. In laudanosine [1-(3',4'-dimethoxybenzyl)-2-methyl-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline], for example, the benzyl group at C—1 possesses a preferred *pseudo-axial* and the N-methyl group an *equatorial* position, whereas for other 1,2-disubstituted derivatives conformations with *pseudo-equatorially* oriented C—1 substituents are favoured. It should be noted, however, that the authors do not give satisfactory evidence that the product ratio is governed solely by the conformer ratio of the parent base (*i.e.* the CURTIN—HAMMETT rule [17] does not hold for this reaction) and therefore, their deductions on the conformational properties of tetrahydroisoquinoline derivatives do not seem perfectly justified. If, in spite of this, their conclusions are accepted, it should follow that the stabilizing effect of a *pseudo-equatorial* substituent in position 1 relative to that of a *pseudo-axial* one is considerably less than the well-known stabilizing effect of an *equatorially* oriented group in cyclohexane-like molecules. This seems to be in agreement with recent data reported on some *cis-trans* 1,2,4-trisubstituted tetrahydroisoquinoline derivatives [18] and observations made on other systems with 1,2-disubstituted cyclohexene ring [19, 20, 21].

There are no data in the literature concerning the conformational properties of the tertiary and quaternary salts of tetrahydroisoquinoline bases.

It follows from the above considerations that an exact treatment of the steric course of quaternization would require quantitative conformational analysis of the parent bases and quaternary salts, as well as detailed kinetic measurements of the quaternization reaction. However, certain deductions about the stereochemistry of diastereomeric salts can be made by means of their proton resonance spectra. These in turn, combined with our previously reported results (stereoselectivity data, relative stability and chromatographic properties of N-benzyl-methyl salts [2]), allow us to give the quaternization of 1,2-disubstituted tetrahydroisoquinoline bases a first order characterization.

Results and discussion

The components isolated from the crude reaction mixtures by fractional crystallization can be divided, according to their proton resonance spectra (and R_f values in the case of the N-benzyl-N-alkyl salts [2]), into two groups, isomers *A* and *B*, where the label *A* refers to the stereoisomers predominating in the direct reactions. The symmetrically substituted N,N-dimethyl derivatives are in all cases, regardless of the substituent at C—1, stereochemically homogeneous. This is in accordance with the expectation that the asymmetrically substituted isomers *A* and *B* are related between themselves as diastereomers rather than conformational isomers. The proton resonance characteristics of the tertiary and quaternary salts investigated, such as the chemical shifts of the assignable protons and proton groups, some of the more important multiplicities and coupling constants, are collected in Table I, complete for convenience with the fractional yields of diastereomeric salts published earlier [2]. Some of the spectra are reproduced to illustrate the experimental data.

In order to determine the stereochemistry of the diastereomers decision should be made as to whether or not the quaternary salts can be characterized by a preferred conformation, *i.e.* whether the conformational equilibria given by

Table I

Proton resonance characteristics of tertiary and quaternary salts and fractional yields of diastereo-

Solvent: $CDCl_3$; chemical shifts, δ (ppm);

Isomer	Substituent					
	R_1	R_2	R_3	C8—H	C5—H	C1—H
	$(CH_3)_2CH$	CH_3	H	6.77	6.66	4.02 (~2.0)
	$(CH_3)_2CH$	CH_3	CH_3	6.67	6.78	4.87
A	$(CH_3)_2CH$	CH_3	CH_3CH_2	6.69	6.78	4.73
B	$(CH_3)_2CH$	CH_3CH_2	CH_3	6.82	6.78	4.68
A	$(CH_3)_2CH$	CH_3	$C_6H_5CH_2$	6.91	6.62	4.57
B	$(CH_3)_2CH$	$C_6H_5CH_2$	CH_3	6.78	6.61	4.92
More stable	C_6H_5	CH_3	H	6.05	6.70	5.79 (6.0)
Less stable	C_6H_5	H	CH_3	6.33	6.73	5.73 (~2.5)
	C_6H_5	CH_3	CH_3	6.35	6.83	6.50
A	C_6H_5	CH_3	CH_3CH_2	6.48	6.85	6.43
B	C_6H_5	CH_3CH_2	CH_3	6.48	6.83	6.60
A	C_6H_5	CH_3	$C_6H_5CH_2$	6.43	7.00	6.50
B	C_6H_5	$C_6H_5CH_2$	CH_3	6.43	6.93	6.82
	$3,4\text{-}(CH_3O)_2C_6H_3CH_2$	CH_3	H	5.65	6.53	4.40 (~2.0)
	$3,4\text{-}(CH_3O)_2C_6H_3CH_2$	CH_3	CH_3	5.75	6.67	5.17

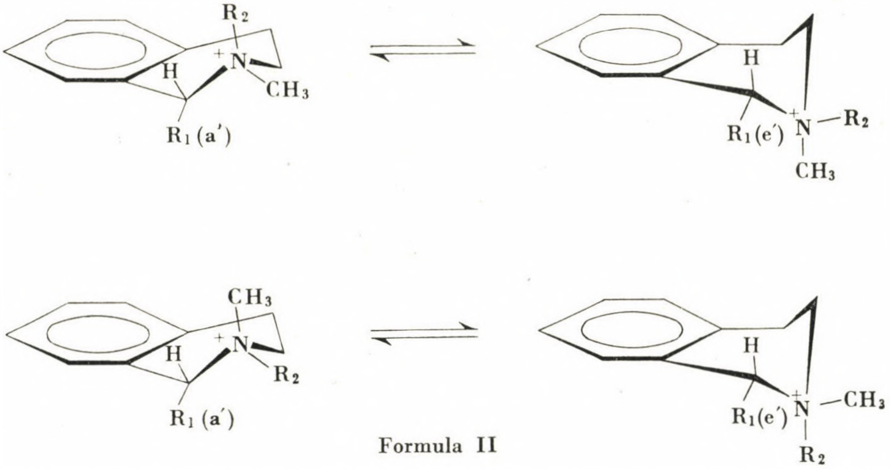
mers in "direct" and "reverse" quaternization reactions
coupling constants (in parentheses) (Hz)

Protons							Fractional yields of isomers, %	
$C6—OCH_3$	$C7—OCH_3$	NCH_3	NH	NCH_2CH_3	$NCH_2C_6H_5$	$CH(CH_3)_2$	"Direct" quaternization	"Reverse" quaternization
3.89		3.00 (3.5)	10.9	—	—	0.97 1.33	—	—
3.91		3.43 3.73	—	—	—	0.65 1.36	—	—
3.91		3.55	—	1.60	—	0.65 1.38	60	17
3.91		3.24	—	1.61	—	0.63 1.30	40	83
3.93		3.48	—	—	4.78 4.94	0.68 1.23	95	40
3.88 3.90		3.10	—	—	5.22 5.47	0.72 1.37	5	60
3.88	3.55	2.92 (5.0)	9.6	—	—	—	—	—
3.88	3.65	2.59 (5.0)	10.3	—	—	—	—	—
3.91	3.66	3.24 3.68	—	—	—	—	—	—
3.92	3.67	3.08	—	1.58	—	—	76	14
3.91	3.67	3.50	—	1.49	—	—	24	86
3.94	3.70	2.95	—	—	5.08 5.18	—	100	35
3.90	3.70	3.45	—	—	5.62 6.00	—	0	65
3.50 3.83 3.87		2.96 (5.0)	10.5	—	—	—	—	—
3.40 3.85		3.51 3.82	—	—	—	—	—	—

Table I

Isomer	Substituent					
	R_1	R_2	R_3	C8–H	C5–H	C1–H
A	3,4-$(CH_3O)_2C_6H_3CH_2$	CH_3	CH_3CH_2	5.74	6.68	4.98
B	3,4-$(CH_3O)_2C_6H_3CH_2$	CH_3CH_2	CH_3	5.88	6.68	4.98
A	3,4-$(CH_3O)_2C_6H_3CH_2$	CH_3	$C_6H_5CH_2$	5.77	6.68	4.93
B	3,4-$(CH_3O)_2C_6H_3CH_2$	$C_6H_5CH_2$	CH_3	5.65	6.65	4.90

Formula II are shifted in one direction or the other. (In Formula II, and throughout in the following discussion, only the generally accepted half-chair conformations are taken into account.)



Formula II

On the basis of the literature mentioned in the introduction, a certain degree of conformational preference can already be expected in 1,2-disubstituted tetrahydroisoquinoline bases. Further, it seems reasonable to assume that the presence of an additional substituent on the nitrogen atom will make an energetically favourable conformation even more stable in the quaternary salts. This concept is supported by our proton resonance results, as demonstrated by the following considerations. The spectra of the N,N-dimethyl deriva-

continued

Protons							Fractional yields of isomers, %	
C6 – OCH_3	C7 – OCH_3	NCH_3	NH	NCH_2CH_3	$NCH_2C_6H_5$	$CH(CH_3)_2$	"Direct" quaternization	"Reverse" quaternization
3.40 3.84		3.71	—	1.45	—	—	65	30
3.43 3.83		3.27	—	1.68	—	—	35	70
3.74 3.78 3.88		3.43	—	—	4.80	—	95	40
3.30 3.78 3.84		3.09	—	—	5.30 5.85	—	5	60

tives show considerable chemical shift differences (0.30 – 0.45 ppm) between the two N-methyl groups. A similar phenomenon is observed when the spectra of diastereomeric salt pairs are compared. The following factors are obviously responsible for these relative shifts: the steric arrangement of the N-methyl groups relative the to molecule as a whole (*axial* or *equatorial*), and relative to the substituent in position 1 (*cis* or *trans*). If the molecule has no preferred conformation the contribution of the first factor will obviously be reduced by the averaging effect of the rapid conformational changes. According to the literature, the observed relative shifts of N-methyl protons (*cf.* Table II) are too high to be attributed only to the second factor, and as it will be shown in the following, they are actually related to the *axial* and *equatorial* orientations of the N-methyl groups. A satisfactory explanation of the relative shifts is provided by the anisotropy effect of the aromatic ring giving rise to different shieldings of the differently oriented N-methyl protons. Obviously this can be the case only if the N-methyl groups possess well defined orientations relative to the molecule as a whole, *i.e.* if one of the conformations is predominating.

One more conclusion is possible concerning the conformation of the diastereomers. According to the relative shifts of the N-methyl protons, the N-methyl groups in isomers *A* and *B* have different orientations. Since *A* and *B* are diastereomers, this means that the orientation of the substituent in position 1, and together with this, the preferred ring conformations, are identical in both diastereomers.

Although PMR studies suitable for conformational analysis have not been performed, the importance of these problems prompted us to investigate

Table II

Chemical shifts and relative chemical shifts of the N-methyl protons in quaternary salts
Solvent: $CDCl_3$

Substituent			δ (ppm) in isomers		Δ δ (ppm)
R_1	R_2	R_3	*A*	*B*	
$(CH_3)_2CH$	CH_3	CH_3	3.43 3.73		0.30
$(CH_3)_2CH$	CH_3	CH_3CH_2	3.55	3.24	0.31
$(CH_3)_2CH$	CH_3	$C_6H_5CH_2$	3.48	3.10	0.38
C_6H_5	CH_3	CH_3	3.24 3.68		0.44
C_6H_5	CH_3	CH_3CH_2	3.08	3.50	0.42
C_6H_5	CH_3	$C_6H_5CH_2$	2.95	3.45	0.50
$3,4\text{-}(CH_3O)_2C_6H_3CH_2$	CH_3	CH_3	3.51 3.82		0.31
$3,4\text{-}(CH_3O)_2C_6H_3CH_2$	CH_3	CH_3CH_2	3.71	3.27	0.44
$3,4\text{-}(CH_3O)_2C_6H_3CH_2$	CH_3	$C_6H_5CH_2$	3.43	3.09	0.34

the temperature dependence of the spectra of some tertiary and quaternary salts. These measurements, however, did not give conclusive results since the relative shifts of the N-meihyl protons were independent of the temperature within the range investigated (20—150°C).

The next step was the determination of the actual relative orientation of the substituents in the diastereomeric salts. Equilibration of the N-methyl-N-benzyl salt pairs in chloroform [2] has indicated that isomers *A* are more stable in all cases. General stability considerations permit to conclude that in these diastereomers the substituent at C—1 and the bulkier (benzyl) group attached to the nitrogen atom are *trans* oriented. Similar conclusions can be made on the bases of the proton resonance spectra of the relevant salt pairs. It is known [22, 23] that the methylene protons of the benzyl group attached to a centre of assymmetry are magnetically non-equivalent. The extent of the non-equivalence becomes larger if the rotation of the benzyl group is restricted. The data in Table III show a smaller chemical shift difference for methylene protons in isomers *A* (0—0.15 ppm) than in the corresponding isomers *B* (0.25—0.55 ppm). Thus, higher barrier to free rotation of N-benzyl group is present in isomers *B* which, in accordance with similar observations [22], suggests that isomers *B* represent the less stable form in that R_1 and the N-benzyl group are *cis* oriented, whereas isomers *A* the more stable form with *trans* orientation of relevant groups. Since the magnitude and direction of the changes

Table III

Chemical shifts and relative chemical shifts of the N-benzyl methylenic protons
Solvent: $CDCl_3$

Substituent			Isomer *A*		Isomer *B*	
R_1	R_2	R_3	δ (ppm)	Δ δ (ppm)	δ (ppm)	Δ δ (ppm)
$(CH_3)_2CH$	CH_3	$C_6H_5CH_2$	4.78 4.94	0.16	5.22 5.47	0.25
C_6H_5	CH_3	$C_6H_5CH_2$	5.08 5.18	0.10	5.62 6.00	0.38
$3,4\text{-}(CH_3O)_2C_6H_3CH_2$	CH_3	$C_6H_5CH_2$	4.80	0	5.30 5.85	0.55

in the chemical shift of the N-methyl protons between isomers *A* and *B* are identical within a series (with identical substituents in position 1) and independent of the N-alkyl group, the above statement concerning the N-methyl-N-benzyl quaternary salt pair is probably valid for N-methyl-N-ethyl diastereomers, too. In other words, the bulkier substituent on the nitrogen is *trans* to the substituent in position 1 in all isomers *A*, and *cis* in all isomers *B*. Since the N-substituents introduced in the present quaternization studies do not differ strongly from a conformational point of view, the stereochemistry of the main products obtained in a given (*e.g.*, the "direct") type of reaction is expected to be identical, and therefore, the above generalization seems to be justified.

The following two conclusions can be drawn about the stereochemistry of the diastereomers: the quaternary salts have a highly preferred conformation and, therefore, defined orientations of the substituents. Within a given salt pair the orientation of N-methyl groups is different for isomers *A* and *B* which, in view of the existing diastereoisomerism, means that the orientation of R_1 is the same. Since, moreover, all isomers *A* are *trans* and all *B cis*, it follows that presumably the same conformation may be ascribed to each diastereomer with identical substituent at C—1.

The actual conformation of the diastereomers can be determined most easily for the 1-phenyl derivatives, since in this case the proton resonance spectra of the corresponding tertiary salts provide direct information about the orientation of substituents in positions 1 and 2.

The spectrum of the tertiary salt formed from 1-phenyl-2-methyl-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline and trifluoroacetic acid is shown in Fig. 1. (In order to avoid overlapping of important lines, this spectrum has been recorded in a 1 : 1 mixture of $CDCl_3$ and C_6D_6. Values given in Table I were obtained with a solution of the corresponding iodide in $CDCl_3$.) The spectrum exhibits two N-methyl doublets of different intensities (the doublet character of absorption is due to spin—spin coupling between the N-methyl and N—H protons), and resonance doubling of the other lines with the same intensity ratio. This means that the tertiary salt under consideration is a mixture of two isomers, the one present in excess being obviously more stable. The magnitude of the spin—spin coupling constant between the C—1H and the N^+—H protons (which is equal to the splitting of the C—1H line) gives information about the orientation of the substituents in positions 1 and 2. From the doublets at 5.08 and 5.58 ppm in Fig. 1, this value for the more and the less stable isomer is 6.0 and 2.5 Hz, respectively. According to recent data [24], the value of the vicinal H—C—N—H coupling constant is not influenced by the positive charge on the nitrogen atom, the measured values always being smaller than those for the corresponding H—C—C—H coupling constants [25]. The dependence on the dihedral angle can be described [26] by a function similar to the Karplus equation [27]. The data pertaining to the last statement are incomplete, rendering a more precise estimation of the dihedral angle impossible. However, the fact that the coupling constant for the more stable isomer is higher than 5 Hz, corresponding to free rotation about the C—N bond (*cf.* the splitting of the N-methyl doublets in Fig. 1), and much larger than 2.5 Hz found for the less stable isomer, indicates that in the more stable isomer the dihedral angle between the protons under consideration assumes its maximum value for the given skeleton, *i.e.* the protons have a *trans pseudo-axial—axial* arrangement. Consequently, the substituents in positions 1 and 2 are *pseudo-equatorial* and *equatorial.* Obviously, the less stable isomer is the diastereoiso-

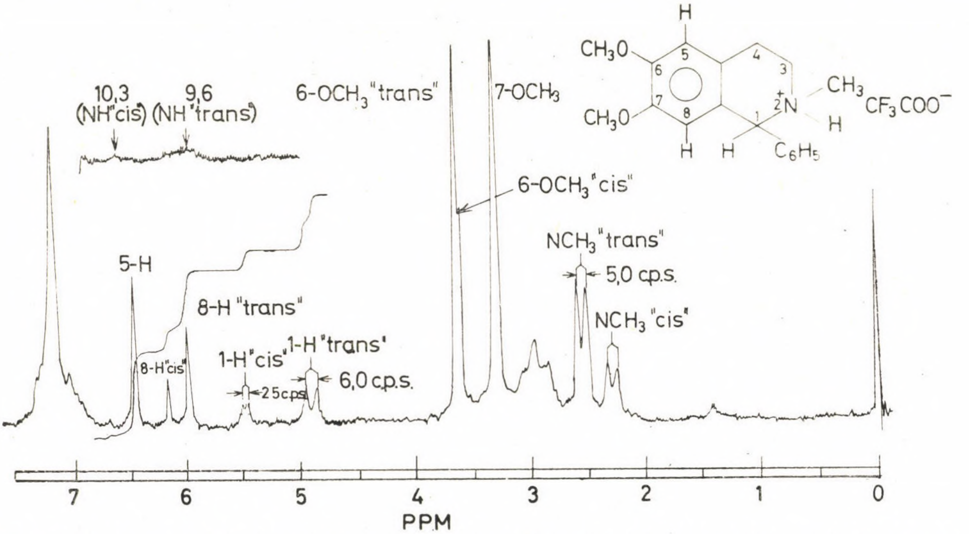


Fig. 1. Spectrum of 1-phenyl-2-methyl-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinolinium trifluoroacetate. Solvent: $CDCl_3—C_6D_6$

meric pair of the former because of the new centre of asymmetry formed as a result of protonation. The relative shift found for the N-methyl protons (0.33 ppm), therefore, indicates different orientation for the N-methyl group in the two isomers, *i.e.* *axial* in the less stable *cis* isomer.

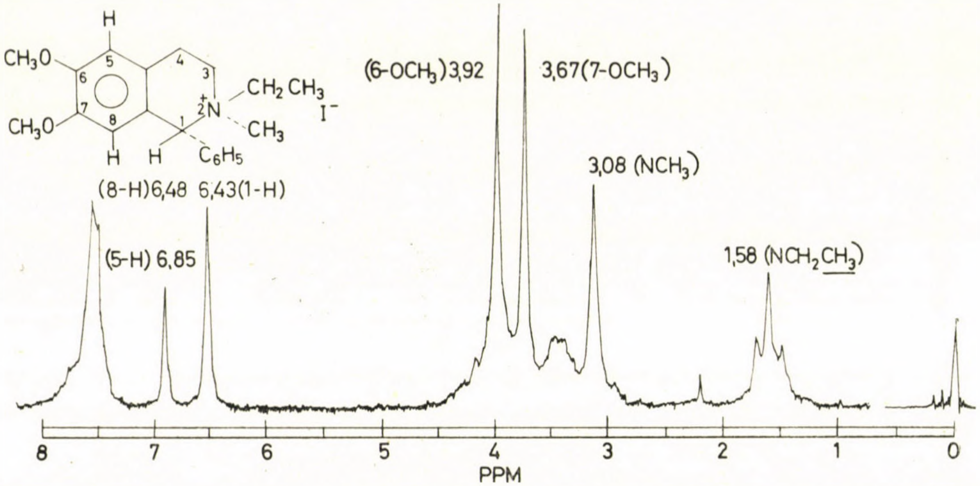


Fig. 2. Spectrum of 1-phenyl-2-methyl-2-ethyl-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinolinium iodide (isomer *A*). Solvent: $CDCl_3$

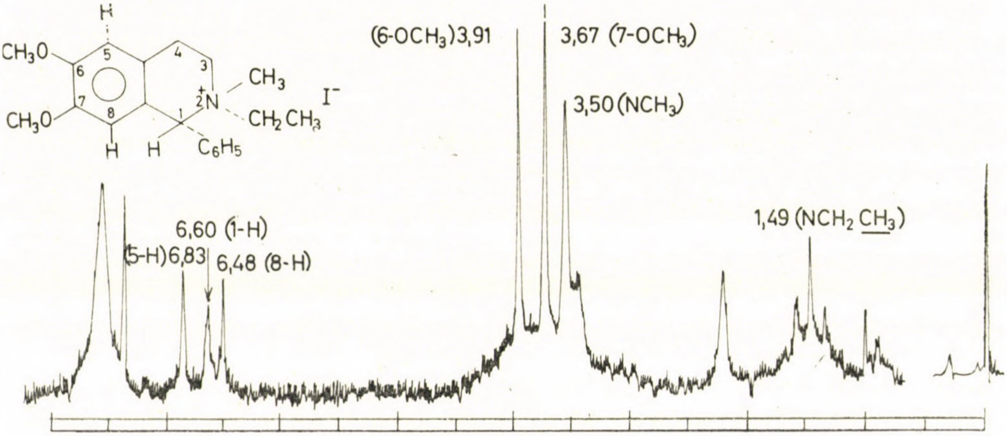


Fig. 3. Spectrum of 1-phenyl-2-methyl-2-ethyl-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinolinium iodide (isomer *B*). Solvent: $CDCl_3$

Comparison of the chemical shifts of $N-CH_3$ protons of the two differently oriented N-methyl groups shows that in the case of 1-phenyl-N-methyl tertiary salts larger value corresponds to the *equatorial* and lower one to the *axial* orientation of the relevant groups.

Since the alkyl group introduced by quaternization is not expected to change the sign of the relative shift of N-methyl protons (it cannot lead to an "interchange" of the N-methyl resonances), the above statement can presumably be extended to the quaternary salts. Thus the N-methyl group is *axial* in the *trans A* isomers (exhibiting higher field N-methyl resonances), and *equatorial* in the *cis B* isomers. (This obviously implies that the tertiary and quaternary salts are supposed to have the same preferred conformation.)

The same conclusion can be made concerning the orientations of N-methyl groups if, as previously mentioned, it is assumed that the relative chemical shift of N-methyl protons are determined mainly by the anisotropy effect of the aromatic ring (ring *A* of the tetrahydroisoquinoline molecule). Molecular models and calculations made on the basis of JOHNSON—BOVEY tables [28] indicate that protons of the *axial* N-methyl group which are closer to, and above the plane of the aromatic ring are shielded (lower shift values), while protons of the *equatorial* N-methyl group, situated more remote from the ring but closer to its plane are deshielded (higher shift values).

Comparing the N-methyl shift in Table II, it is found that for quaternary salts with isopropyl or 3,4-dimethoxybenzyl group at C—1 the shift values are larger for the *trans* isomers, *i.e.* the situation is opposite to that observed with the 1-phenyl derivatives. Following the above assignation scheme this means that in these quaternary salts the N-methyl group is oriented *equatorially* in the more stable *trans* diastereomers (isomers *A*) and *axially* in the less stable *cis* (*B*) isomers. A possible objection to this may be that such an interchange of N-methyl shifts is due to the anisotropy effects associated with the presence of the aromatic ring at C—1 in the case of 1-phenyl derivatives rather than to a change in the orientation of N-methyl groups. Measurements on Dreiding model and calculations based on the JOHNSON—BOVEY tables, however, unambiguously preclude this possibility. The maximum anisotropy effect calculated for the 1-phenyl group in both of its possible orientations (*i.e. pseudo-axial* and *pseudo-equatorial*) on the chemical shifts of the *axial* and *equatorial* N-methyl protons is 0.2—0.3 ppm, and has a sign that would cause the two N-methyl resonances to shift closer to each other. In order to obtain interchange of the N-methyl lines and a relative shift of 0.45—0.5 ppm between them, the anisotropy effect of the phenyl group should be at least 0.8 ppm. The interatomic distances in these molecules, however, do not make such a high value possible.

Owing to the *cis-trans* relationship between the diastereomers this conclusion also involves that the orientation of the substituent R_1 in the preferred conformation of the 1-isopropyl and 1-(3',4'-dimethoxybenzyl) quaternary derivatives is also different from that of the 1-phenyl group, *i.e. pseudo-axial.* This statement receives support from the proton resonance data for the tertiary salts, specifically from values of the $H—C(1)—N^+—H$ coupling con-

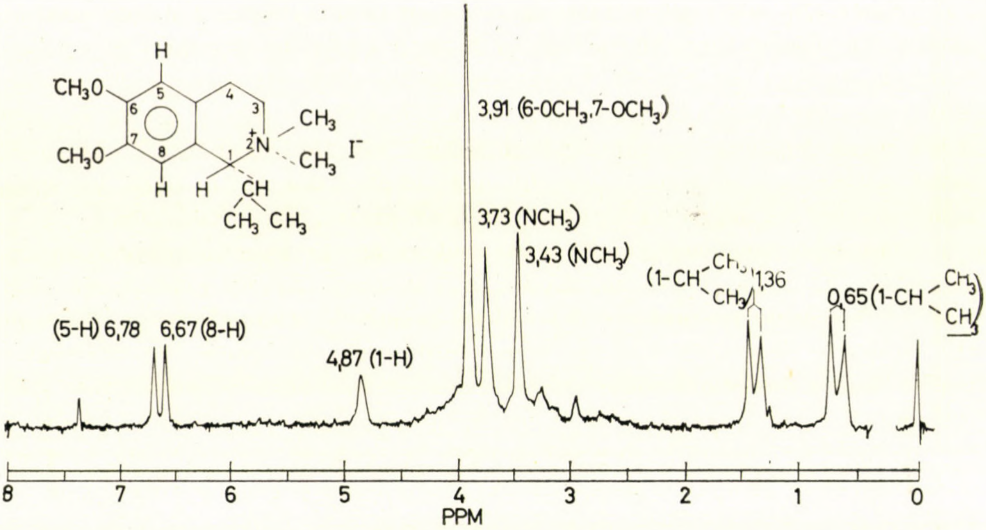


Fig. 4. Spectrum of 1-isopropyl-2,2-dimethyl-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinolinium iodide. Solvent: $CDCl_3$

stants. In the proton resonance spectra of both 1-isopropyl- and 1-(3',4'-dimethoxybenzyl)-2-methyl-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinolinium iodide only the lines due to the more stable *trans* isomer can be identified. (Only one isomer of the first compound is formed, and in the second case the less stable isomer is present only in minor amounts, therefore, the most important spectral lines cannot be identified.) The values of the $H-C-N^+-H$ coupling constant could only be estimated indirectly, from the line-narrowing caused by deuterium exchange of the N^+-H protons (with D_2O) (*cf.* Fig. 7). For both tertiary *trans* salts this value was about 2—2.5 Hz, thus precluding a *trans diaxial* position of the interacting protons, *i.e.* the orientation of the groups in positions 1 and 2 is actually *pseudo-axial* and *axial.*

The statements concerning the stereochemistry of the quaternary salts, particularly the actual orientation of the substituents in position 1, obviously need further confirmation. The different orientations found for the isopropyl and phenyl groups in the preferred conformation are of particular interest. These results are not surprising in the light of the special conformational properties of position 1, as described in the literature.

After having elucidated the stereochemistry of the diastereomers, it is possible to make some deductions about the steric course of the quaternization reactions.

On the basis of the fractional yields found for the components of diastereoisomeric pairs (*cf.* the last column of Table I), the following statements can be made. The stereoselectivity of quaternization is, in general, moderate,

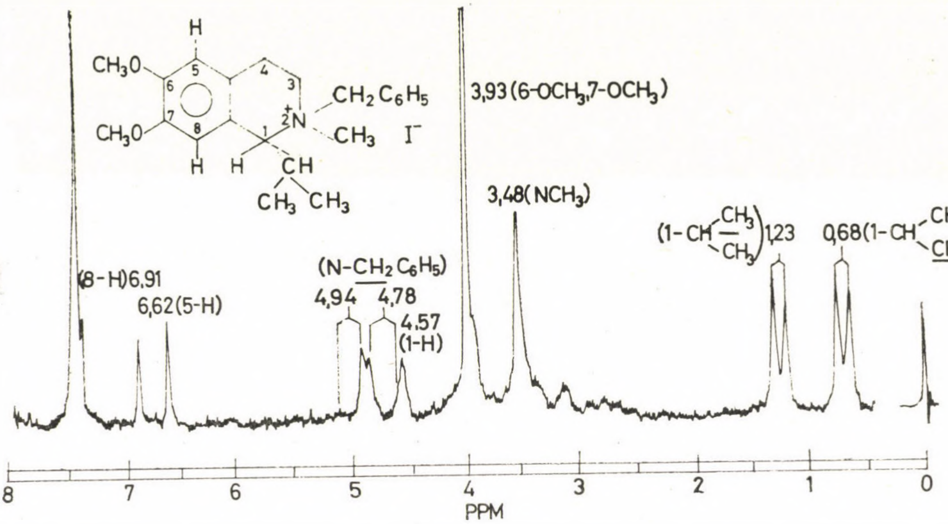


Fig. 5. Spectrum of 1-isopropyl-2-methyl-2-benzyl-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinolinium iodide (isomer *A*). Solvent: $CDCl_3$

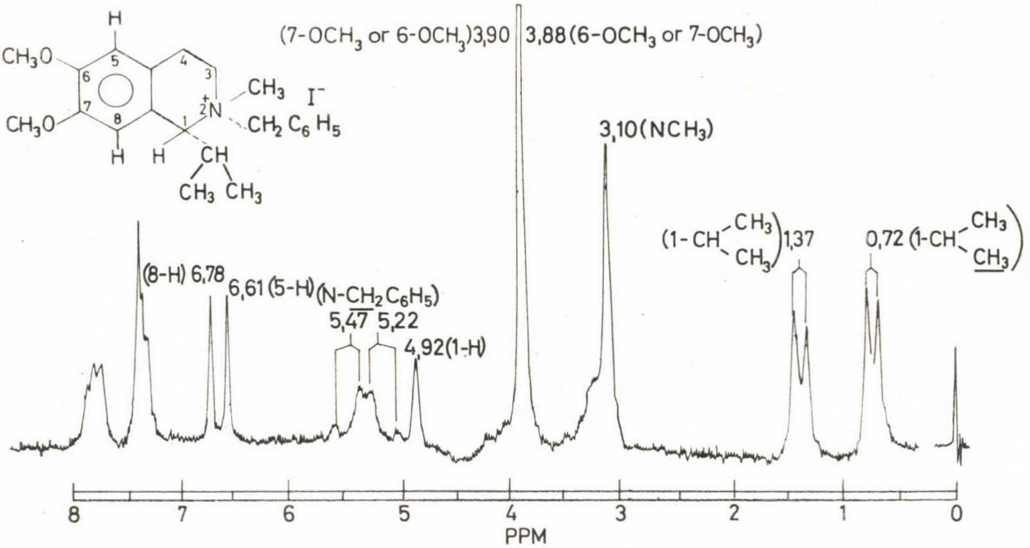


Fig. 6. Spectrum of 1-isopropyl-2-methyl-2-benzyl-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinolinium iodide (isomer *B*). Solvent: $CDCl_3$

similarly to the case of the 1-methyl derivatives [1]. However, with the latter compounds, the direct reaction clearly had higher selectivity. In the present case, when the size of R_1 is larger than that of the methyl group, higher stereoselectivity is observed either in the direct or in the reverse reaction, depending on the relative steric requirements of the R_2 and R_3 groups. For example, if $R_1=(CH_3)_2CH$ or C_6H_5, and both R_2 and R_3 are small (CH_3 or CH_3CH_2), the reverse reaction is more stereoselective. On the other hand, if R_2 and R_3 are of different size (*e.g.*, CH_3 and $C_6H_5CH_2$), higher product ratios are observed again with the direct reaction. Since we are dealing with derivatives of the same molecule, these changes in selectivity should probably be ascribed to the interaction of the substituents in positions 1 and 2.

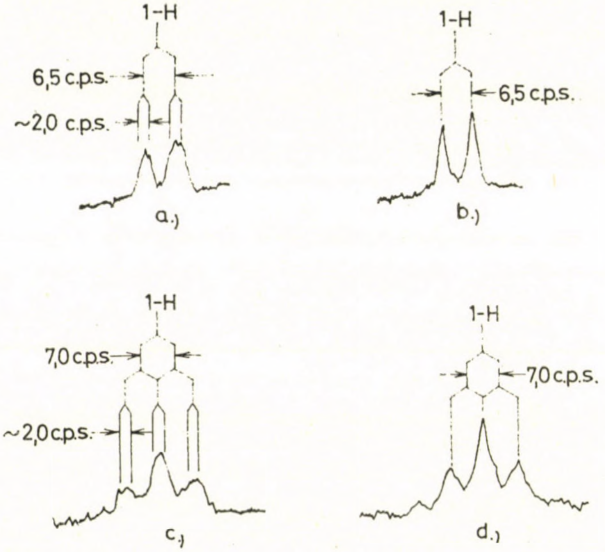


Fig. 7. Resonance patterns of C-1H proton in 1-isopropyl-2-methyl-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinolinium trifluoroacetate (*a* and *b*), and in 1-(3',4'-dimethoxybenzyl)-2-methyl-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinolinium trifluoroacetate (*c* and *d*); *a* and *c* before, and *b* and *d* after, deuterium exchange. Solvent: acetone-d_6

On the basis of the known relative steric positions of groups R_1 and R_3 in stereoisomers *A* and *B*, and taking into account that in the majority of direct quaternizations isomers *A* are formed predominantly (in benzylation almost exclusively), we may interpret the stereoselectivity data by assuming a *preferred trans N-alkylation with respect to the actual orientation of substituent at C—1.* The degree of preference then should be influenced by the effective steric demands of the interacting groups in the transition state. Thus the unexpected higher product ratios in the methylation reaction of 1-phenyl-N-ethyl and 1-isopropyl-N-ethyl bases may also be understood in this approximation if we suppose that in these cases the *trans* orientation of methyl, rather than the ethyl group is favoured, *i.e.* the factors determining the effective steric requirement of the incoming group [7] are such that methyl will act as a "larger" quaternizing group.

Conclusions concerning the steric course in terms of preferred *axial* or *equatorial* attack can be derived from the above stereochemical considerations, however, it must be assumed that the formation of quaternary salts is not accompanied by conformational changes of the hetero ring. With this admission, our results indicate that the *trans* N-alkylation corresponds to a preferred *equatorial* approach of incoming group with the 1-phenyl bases, and an *axial* one with the other (1-isopropyl and 1-dimethoxybenzyl) derivatives.

Within a given molecular framework changes in the direction of preferred steric approach of incoming quaternizing group, if concluded from the product ratios in the crude reaction mixtures, may quite generally be attributed either to changes in the ratio of the rate constants of N-alkylation in the respective directions (k_{ax} *vs.* k_{equ}), or to a considerable shift in the conformational equilibrium of the parent base. This is so because the rate of formation of a given diastereomeric salt (and consequently its percentage in the crude reaction mixture) is determined by the product of the rate constant and the concentration of the reacting base conformer. It has been observed in previous quaternization studies (*e.g.* [3]) that the rate constants corresponding to the two directions differ by orders of magnitude, and, therefore, it is their ratio what primarily determines the composition of the diastereomeric mixtures. Thus, a drastic shift in the conformational equilibrium of the reacting bases is required that, due to the lack of the corresponding conformer, the rate of quaternization in the preferred direction should be less than the rate in the unfavoured direction. In the present case the relative conformational energies of substituents R_1 and R_2 are not expected to differ to such an extent as to overcompensate the large difference between the rate constants corresponding to the *axial* and *equatorial* directions. It is also conceivable that the CURTIN—HAMMETT principle [17] is not valid, *i.e.* the activation energy for the interconversion of the base conformers is larger than that of the reaction, therefore, the product composition is primarily determined by the conformational equilibrium of the bases. In such a case the *cis* to *trans* isomer ratio in the products is expected to be independent of the character of the R_3 group. However, this is not observed in the present case.

As a consequence of what has been said, the ratio of diastereomers is probably determined by the ratio of the corresponding rate constants. The change of the preferred direction of attack can be interpreted by assuming that the actual value of rate constants depends on the direction relative to the substituent in position 1, rather than on the absolute direction with respect to the nitrogen atom. Therefore, altogether 4 rate constants should be taken into account, namely

$$k_{\mathrm{ax}}^{\mathrm{cis}},\ k_{\mathrm{equ}}^{\mathrm{cis}},\ k_{\mathrm{ax}}^{\mathrm{trans}},\ \text{and}\ k_{\mathrm{equ}}^{\mathrm{trans}}$$

which obey the following inequality:

$$k_{\mathrm{ax}}^{\mathrm{trans}},\ k_{\mathrm{equ}}^{\mathrm{trans}} \gg k_{\mathrm{ax}}^{\mathrm{cis}},\ k_{\mathrm{equ}}^{\mathrm{cis}}.$$

In other words, the steric course of quaternization of 1,2-disubstituted tetrahydroisoquinolines is determined by the interaction of the groups in positions 1 and 2.

On the basis of the above conclusions, the results obtained with 1-methyl derivatives [1] can be interpreted more precisely from the point of view of both the stereochemistry of the diastereomers, and the steric course of quaternization. In diastereomeric salts containing methyl group in position 1 the relative shifts of the N-methyl protons are considerably smaller than those for the derivatives described in the present paper. In addition to this, in the spectrum of carnegine hydroiodide, indicating the presence of two tertiary salts (*cf.* Fig. 8), the relative shift of the two $N^+—H$ protons is significantly smaller (0.15 ppm) than the value obtained for the 1-phenyl-2-methyl tertiary salt pair (0.7 ppm). This is explained by assuming that from among the factors determining the relative shifts of these protons, the steric contribution is more or less averaged out. Therefore, the 1-methyl derivatives are presumably conformationally labile, *i.e.* the diastereomers — first of all those of the *cis* form — are equilibrium mixtures containing both conformers in about equal proportion. Such conformational properties do not justify that the preferred direction of attack of the alkyl group entering in quaternization be defined as either *axial* or *equatorial* with respect to the nitrogen atom.

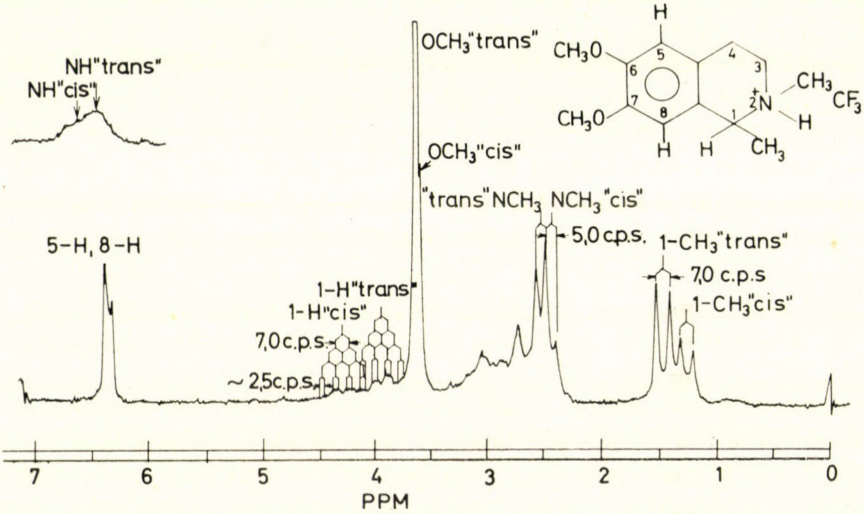


Fig. 8. Spectrum of 1-methyl-2-methyl-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinolinium trifluoroacetate. Solvent: $CDCl_3$-C_6D_6

Experimental

The proton resonance spectra were recorded at 60 MHz with an AEI RS-2 high-resolution spectrometer, at room temperature. Deuterochloroform was used as the solvent, with tetramethylsilan internal reference. In general, 5—10% (W/V) solutions were used. The spectra were calibrated by side-band technique. The chemical shifts are accurate to ±0.01 ppm.

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LABELLED AMINO ACIDS AND THEIR DERIVATIVES, II

PREPARATION OF DL-GLUTAMIC-1-^{14}C ACID, DL-ORNITHINE-1-^{14}C, AND DL-ARGININE-1-^{14}C

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The Strecker synthesis has been used for the preparation of DL-glutamic-1-^{14}C acid from β-cyanopropionaldehyde diethylacetal. From γ-benzoylaminobutyraldehyde, prepared from β-cyanopropionaldehyde diethylacetal, DL-ornithine-1-^{14}C, and from this, DL-arginine-1-^{14}C have been synthesized.

Modern biochemical research requires many amino acids specifically labelled with isotopes. The preparation of DL-glutamic acid, DL-ornithine, and DL-arginine is closely connected, since the known methods, including the various radio-syntheses, proceed through a common intermediate, and ornithine is the intermediary product in all known syntheses of arginine [1].

For the preparation of amino acids labelled with carbon-14 in the carboxyl group, the Strecker synthesis is used almost exclusively [2, 3]. The method is equally known for the preparation of inactive DL-glutamic acid [4, 5, 6, 7] and DL-ornithine [8]. DL-glutamic acid is readily prepared from the hemi-aldehyde of succinic acid [4, 6], from the ethyl ester of the hemi-aldehyde of succinic acid [5, 6] and from β-cyanopropionaldehyde [6, 7]; DL-ornithine has been prepared from γ-benzoylaminobutyraldehyde, which can be easily synthesized from β-cyanopropionaldehyde [8]. In spite of the synthetic methods worked out in principle, no reference could be found in the literature concerning the preparation of derivatives labelled with carbon-14 in the carboxyl group.

On the other hand, a number of methods have been proposed for the synthesis of the various radioisomers of DL-glutamic acid and DL-ornithine from labelled acylaminomalonic esters or from acylaminocyanoacetic esters, using the corresponding acrylic acid or propionic acid derivatives. Thus, DL-glutamic-5-^{14}C acid has been prepared by Speer *et al.* [9] by the condensation of β-bromopropionic-1-^{14}C acid ethyl ester with phthalimidomalonic ester, and by Tiedmann [10] by the reaction of acrylonitrile (nitrile-^{14}C) and formamidomalonic ester. An interesting variant of this reaction, also due to Tiedmann [10], consists in the reaction of acetoacetic-1-^{14}C ester with acrylonitrile (nitrile-^{14}C) followed by treatment with hydrogen azide and hydrolysis, to give

DL-glutamic-1,5-^{14}C acid. The labelled acrylonitrile for these syntheses was prepared by **Tiedmann** by the reaction of ethylene oxide with labelled potassium cyanide and subsequent elimination of water. Starting with labelled acetylene **Pichat** *et al.* [11] synthesized the methyl ester of acrylic-2,3-^{14}C acid, which was then allowed to react with acetamidomalonic ester, and hydrolyzed to obtain DL-glutamic-3,4-^{14}C acid.

In a reaction of acetamidocyanoacetic acid-2-^{14}C ethylester and N-(γ-iodopropyl)phthalimide, **Fields** *et al.* [12] obtained a product which, on hydrolysis, gave DL-ornithine-2-^{14}C. Essentially, this method is a further development of the original ornithine synthesis worked out by **Fischer** [13] and **Sörensen** [14].

Lately, **Pichat** *et al.* [15] have worked out a radiosynthesis for the preparation of DL-glutamic-5-^{14}C acid and DL-ornithine-5-^{14}C. Cleavage of α-benzoylaminobutyrolactone with labelled potassium cyanide gives α-benzoylamino-γ-cyano-^{14}C-butyric acid; the hydrolysis of this product yields DL-glutamic-5-^{14}C acid, while reduction and subsequent hydrolysis afford DL-ornithine-5-^{14}C. Also the synthesis of DL-arginine-5-^{14}C from labelled ornithine has been described by these authors. In spite of the relatively difficult accessibility of the starting materials and rather poor chemical and radiochemical yields, this seems to be the best method among the syntheses known for glutamic acid and ornithine labelled with radiocarbon in their carbon chains.

In order to prepare DL-glutamic acid, DL-ornithine, and DL-arginine labelled with ^{14}C in the carboxyl group, we selected the Strecker method, using β-cyanopropionaldehyde diethylacetal as a starting substance. The use of this compound gives possibility at the same time for the preparation of some further amino acids specifically labelled with carbon-14, or with tritium. Our studies in this direction will be reported in a later communication.

The diethylacetal of β-cyanopropionaldehyde was prepared according to **Wohl** [16]. The reactions used for the preparation of DL-glutamic-1-^{14}C acid, DL-ornithine-1-^{14}C, and DL-arginine-1-^{14}C are summarized in Fig. 1.

Instead of the general procedure of hydrolysis with dilute acid, hydrolysis with Dowex-50 (H^+) ion exchanger was employed for the preparation of the free aldehyde from β-cyanopropionaldehyde diethylacetal, since in this way neutralization and extraction, operations that involve substantial losses, were unnecessary. After the ion exchange resin has been filtered off, a de-ionized solution suitable for immediate use in the further steps of the synthesis was available.

Utilizing the reversibility of cyanohydrin formation, **Kourim** and **Zikmund** [17] developed a radiochemical modification of the Strecker synthesis. According to this modification, labelled cyanohydrins are prepared by exchange reaction between the inactive cyanohydrin and labelled potassium cyanide; the labelled amino acids are then produced by treatment with ammo-

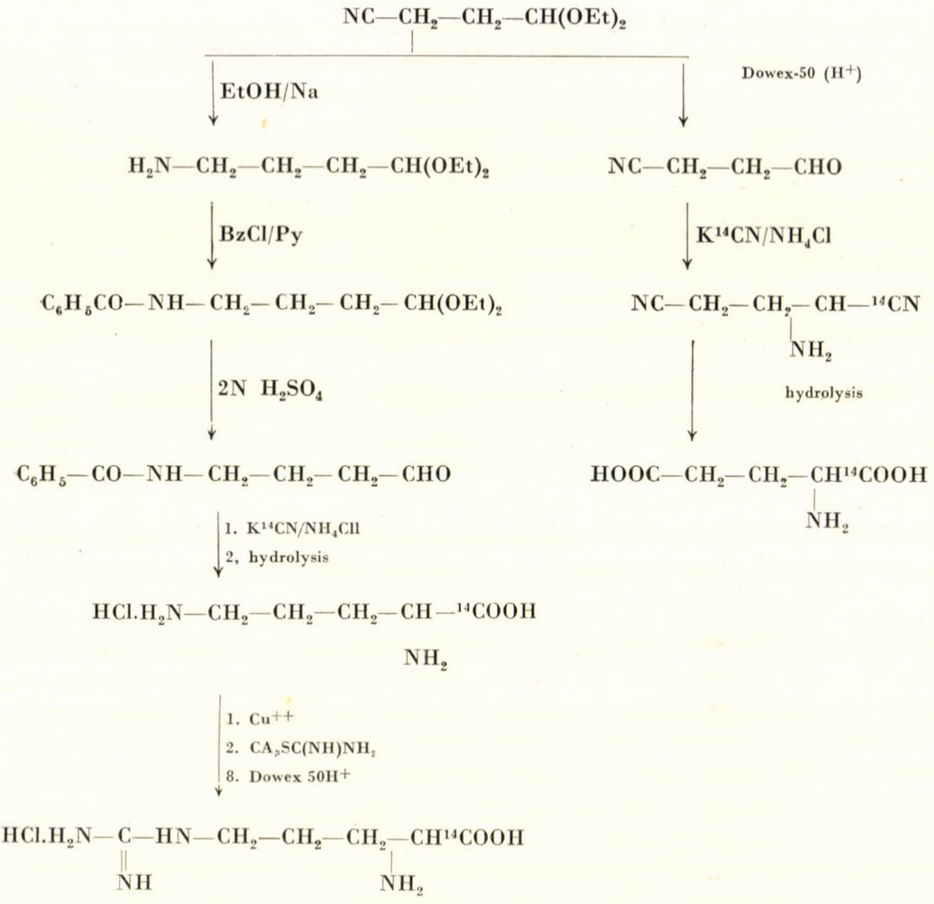

Fig. 1. Reactions applied for the preparation of DL-glutamic-1-^{14}C acid, DL-ornithine-1-^{14}C, and DL-arginine-1-^{14}C

nia and hydrolysis. From the radiochemical point of view, we found it more suitable to allow the labelled potassium cyanide of high specific activity to react first without dilution for 15—20 minutes, then to add inactive potassium cyanide according to the specific activity required, and to complete the reaction by continued heating. Under these experimental conditions no, or very little, labelled aminonitrile will participate in the reversible exchange reaction with the inactive cyanide ions subsequently added, also the tar-like by-products will mainly be formed from the inactive cyanide, consequently the specific activity and radiochemical yield of the product will increase. This is especially conspicuous in the synthesis of ornithine where, by this change of technique, at a chemical yield of 28%, a radiochemical yield of 49%, and an increase by about 39% of the specific activity was achieved.

According to the method of PICHAT *et al.* [15], the intermediate in the synthesis of ornithine is α-benzoylaminoornithine. Thus, during the synthesis of arginine labelled with radiocarbon in the carbon chain, the α-amino group of the labelled ornithine was protected by benzoylation. In our synthesis of arginine, however, DL-ornithine-1-^{14}C was available as an intermediate, therefore it seemed better to protect the α-amino group by the formation of a copper complex [18] instead of selective benzoylation, and then to convert the δ-amino group into guanidine group by means of S-methyl isothiourea sulfate in the usual way [15]. However, this reaction is never quantitative, thus the arginine produced must be separated from the unchanged ornithine. PICHAT *et al.* [15] achieved this by elution of the unreacted labelled ornithine with 2 *N* hydrochloric acid from the mixture bound to Dowex 50X-12 (H^+), and then arginine was eluted with 4 *N* hydrochloric acid. We have found that, owing to a more selective elution, better separation can be achieved with 1.5 *N* hydrochloric acid, since thus the unchanged labelled ornithine can be recovered in a chemically and radiochemically pure state. After elution with 4 *N* hydrochloric acid, arginine-1-^{14}C must be purified by repeated chromatography. Even after repeated purification there are instances when a 2 to 4% contamination with labelled ornithine persists, which can be removed by repeated chromatographic purification.

Experimental

β-Cyanopropionaldehyde diethylacetal was prepared from β-chloropropionaldehyde diethylacetal in aqueous alcoholic medium with potassium cyanide in the presence of potassium iodide, according to WOHL [19, 20].

[DL-glutamic acid-1-^{14}C

β-Cyanopropionaldehyde diethylacetal (3 ml) in water (20 ml) was stirred with Dowex-50 (H^+) resin ($\sim$ 5 ml, moist) at 40°C, for 1.5 hr. The resin was filtered off, and the aldehyde content of the aqueous solution was determined with hydroxylamine in the presence of Bromophenol Blue indicator. A portion (19 ml) of the aqueous solution containing 6.6 mM of β-cyanopropionaldehyde was stirred with a cc. solution of NH_4OH (10 ml). NH_4Cl (0.4 g; 7.45 mM) and active $K^{14}CN$ (65.8 mg; 12.56 μCi per mM) were added; in 20 min. this was followed by the addition of inactive KCN (328 mg; or 6.05 mM, in total). This mixture was allowed to stand for 1 hr. at room temperature, then warmed at 70—80°C for 2 hrs. The cooled solution was acidified to pH = 1 with cc. HCl, then evaporated to dryness in vacuum, the residue was dissolved in 35 ml of cc. HCl and refluxed for 10 hrs. The hydrolysate was evaporated in vacuum, from the residue water was distilled off, finally it was dissolved in water and poured on a Dowex-50 (H^+) column. There it was washed until neutral, and the labelled amino acid was eluted with a solution of ammonium hydroxide. The eluate was evaporated in vacuum. The residue was dissolved in water (4 ml) and its acidity adjusted to pH 3.1 with a few drops of cc. HCl, and the labelled amino acid was precipitated with ethanol (20 ml). After standing for 2 hrs in a refrigerator, the precipitate was filtered off, and washed with ethanol, to obtain 0.6325 g of the crude product. This was dissolved in water (4.5 ml), clarified, and filtered. The aqueous solution (about 6 ml) was mixed with ethanol (18 ml). Crystalline DL-glutamic-1-^{14}C acid separated; this was filtered off and washed with ethanol; weight 374 mg.

Specific activity 15.97 μCi per mg.
Molar activity 2.34 mCi per mM.
Radiochemical purity 97.85%.

The mother liquor was evaporated and, after the addition of inactive DL-glutamic acid, treated in the way just described. The weight of the DL-glutamic-1-^{14}C acid was 212 mg. Specific activity 10.16 μCi per mg.

Molar activity 1.459 mCi per mM
Activity introduced 12.7 mCi
Activity recovered 8.126 mCi
Yield in activity 64%.

DL-ornithine-1-^{14}C hydrochloride

β-Cyanopropionaldehyde diethylacetal was converted into γ-aminobutyracetal, according to the method of SCHÖPF [21]. After distillation, the amino acetal was benzoylated with benzoyl chloride in pyridine. The ethereal solution of benzaminobutyracetal was extracted with a solution of sodium hydrogen carbonate. The crude γ-benzaminobutyracetal left behind after the removal of ether was used in the synthesis.

Crude γ-benzaminobutyracetal (20 g) was stirred for 2 hrs at 30—40°C with 2 *N* H_2SO_4 (100 ml). The aqueous emulsion was neutralized with $NaHCO_3$ and extracted with ether. The ether extract was washed with a solution of $NaHCO_3$, and dried over dehydrated K_2CO_3. The solvent was then distilled off to leave a yellow oil (12.8 g). Determined in an aqueous alcohol according to the hydroxylamino method, the aldehyde content of this crude aldehyde was 65.8%.

The crude γ-benzaminobutyraldehyde (11.3 g; $0.685 \times 11.3 = 7.44$ g; 39 mM) was dissolved in ethanol (30 ml) and the stirred solution was mixed with ammonium hydroxide (15 ml), which was added in several portions. After 20 min, $K^{14}CN$ (127 mg; 1.95 mM. 50 mCi; of 25.65 mCi per mM activity) and ammonium chloride (0.2 g) were added in a mixture of cc. ammonium hydroxide (2 ml) and water (1 ml). The reaction mixture was stirred for 20 min, then a solution of inactive KCN (2.193 g; 33.7 mM) and ammonium chloride (2.1 g) was prepared in a mixture of cc. ammonium hydroxide (15 ml) and water (6 ml), and added to the reaction mixture. Stirring was continued at room temperature for 2 hrs, then at 70—80°C. Evaporation under reduced pressure left a viscous liquid which was diluted with cc. HCl and again evaporated. After the addition of cc. HCl (75 ml), the mixture was refluxed for 7 hrs, then the solution was clarified with activated carbon, and evaporated in vacuum. The residue was stirred with a 90% ethanol (25 ml) and the inorganic salt that separated was filtered off. The filtrate was adjusted to pH 5, whereupon the labelled amino acid slowly crystallized. After standing in a refrigerator for 3 hrs, DL-ornithine-1-^{14}C hydrochloride was collected by filtration (2.117 g; chemical yield 28.1%).

Specific activity 11.55 μCi per mg
Molar activity 1.946 mCi per mM
Activity introduced 50 mCi
Activity recovered 24.45 mCi
Yield in activity 49%
Radiochemical purity 96%.

DL-arginine-1-^{14}C hydrochloride

A solution of $CuSO_4 \cdot 5\,H_2O$ (3.59 g; 15.8 mM) in water (10 ml) was mixed with a solution of Na_2CO_3 (1.75 g; 16.5 mM) in water (10 ml). To this suspension of copper carbonate, a solution of S-methyl isothiourea sulfate (4.42 g; 31.8 mM) in water (10 ml) was allowed to flow. Then a solution of DL-ornithine-1-^{14}C hydrochloride (2.663 g; 15.8 mM; activity 1.8 mCi per mM) in water (10 ml), and finally cc. ammonium hydroxide (6.5 ml) were added to the reaction mixture. The dark blue solution was warmed at 70°C for 6 hrs. After cooling, it was acidified with cc. HCl, and the copper ions were removed with gaseous hydrogen sulphide. Filtration and evaporation in vacuum left a residue which was dissolved in a small volume of water. This solution was passed through a Dowex-50 (H^+) column. The resin bed was washed until neutral, and unreacted DL-ornithine-1-^{14}C was eluted with about 1.5 l of 1.5 *N* HCl, until the Sakaguchi reaction became positive in the eluate. Then the elution was continued with a 4 *N* solution of HCl. This eluate gave a strong Sakaguchi reaction. This solution was evaporated, the residue dissolved in a small amount of water, mixed with ethanol and the aqueous etha-

nolic solution was adjusted to pH 6 with aniline. An oily substance separated which solidified but did not crystallize. This crude substance was dissolved in water and passed again through the Dowex column, and then eluted as before. The eluate in 4 *N* HCl was evaporated in vacuum, the residue dissolved in water (1 ml) and, after the addition of ethanol (15 ml), clarified. The solution was adjusted to pH 6 with a 1 : 1 mixture of aniline and ethanol. The substance separated first as an oily liquid, but it rapidly became crystalline. The mixture was allowed to stand in a refrigerator, the product washed with ethanol and dried to obtain 1.3225 g of DL-arginine-1-^{14}C hydrochloride.

Specific activity 6.645 μCi per mg
Molar activity 1.40 mCi per mM
Activity recovered 8.788 mCi
Radiochemical purity 94.0% DL-arginine-1-^{14}C
4.5% DL-ornithine-l-^{14}C

The 1.5 *N* HCl eluate was evaporated, and the residue dissolved in a mixture of water (1 ml) and ethanol (15 ml). The solution was adjusted to pH 5. The product rapidly crystallized. The weight of DL-ornithine-1-^{14}C hydrochloride recovered was 401 mg.

Specific activity 8.90 μCi per mg
Molar activity 1.5 mCi per mM
Recovered activity 3.56 mCi
Radiochromatogramm 97.43% ornithine-1-^{14}C
2.2% arginine-1-^{14}C

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PREPARATION AND DETERMINATION OF FLUORESCENT STEROIDS

(PRELIMINARY COMMUNICATION)

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A method has been developed for the preparation of ketosteroid naphthylglycine esters. The absorption and fluorescence spectra of these compounds have been recorded. The above steroids can be quantitatively determined by a modified liquid scintillation method where the naphthylglycine esters of the steroids function as scintillators.

It has been known since the studies of GRAY and HARTLEY [1] that the preparation of fluorescent derivatives helps to solve numerous analytical problems in biology and chemistry. The simplicity of the detection and determination of fluorescent substances on filter paper [2] or on a thin-layer [3] has prompted us to attempt the preparation and quantitative analysis of new fluorescent derivatives.

In this work, we prepared fluorescent derivatives of three characteristic representatives of ketosteroids carrying no side chain.

N-α- and N-β-Naphthylglycine ester of androst-5-ene-3β-ol-17-one (dehydroepiandrosterone) (**I**); m.p. 169—170°C and 174—75°; *Anal.* Calcd. for $C_{31}H_{37}O_3N$: C 78.94; H 7.91. Found: C 79.01; H 7.90; and C 78.69; H 7.80%.

N-α-Naphthylglycine ester of oestra-1,3,5(10)-triene-3-ol-17-one (oestrone) (**II**); m.p. 170—172°C. *Anal.* Calcd. for $C_{30}H_{31}O_3N$: C 79.43; H 6.89. Found: C 79.18; H 7.06%.

N-α-Naphthylglycine ester of 5-α-androstane-17 β-ol-3-one (**III**); m.p. 175—177°C. *Anal.* Calcd. for $C_{31}H_{39}O_3N$: C 78.60; H 8.30. Found: C 78 38; H 8.17%.

The steroids were first converted to chloroacetates with chloroacetic anhydride at room temperature in pyridine solution [4]. Since chloroacetates are not sufficiently reactive, they were converted into the corresponding iodoacetates with NaI. The reaction of the latter compounds with naphthylamines resulted in the formation of the corresponding naphthylglycine esters. The general procedure is shown in Fig. 1 for dehydroepiandrosterone (**I**).

The chloroacetates were not purified. The product was extracted from the reaction mixture after acidification, the solvent evaporated and the residue reacted with NaI in propanol solution. The alkylation of naphthylamine was carried out in this same solution. By this procedure nearly quantitative yields were achieved with respect to the steroids, which is an important factor when working with biological samples.

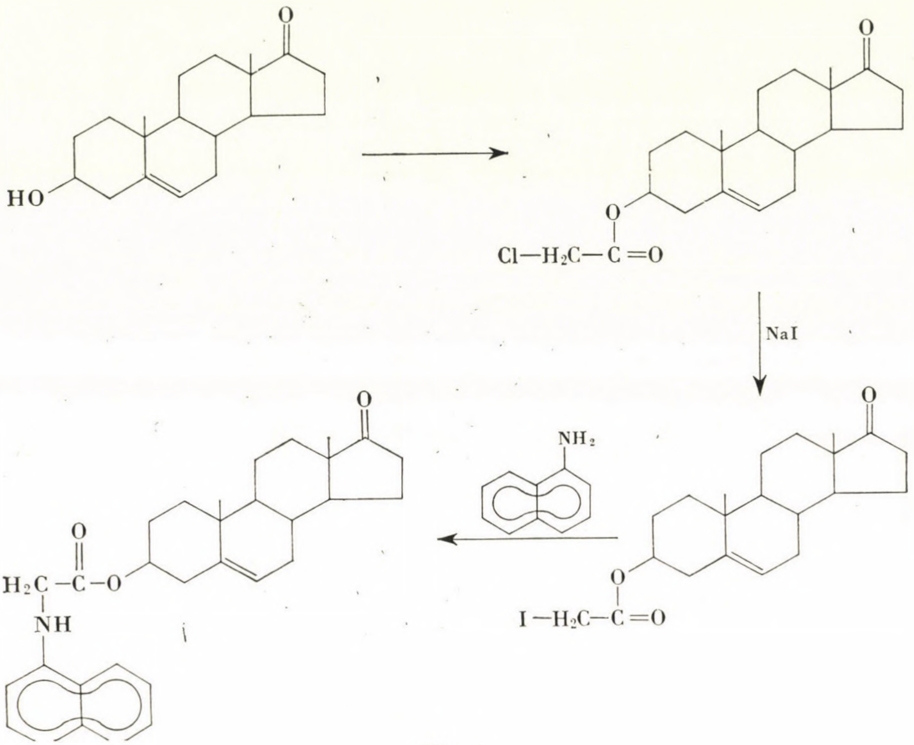

Fig. 1

The absorption and fluorescence spectra of the naphthylglycine esters have been recorded in dichloromethane, the concentration being 2μ g/ml (Fig. 2). The spectra show that the wavelength of the emission is solely determined by the fluorophore and is not influenced by the steroid skeleton even in the presence of an aromatic ring. A comparison of the N-α- and N-β-naphthylglycine esters of dehydroepiandrosterone shows that the preparation of the α-naphthylamine derivatives should be preferred for practical purposes.

The spectrofluorimetric determination of the naphthylglycine esters of steroids can also be carried out on the submicro scale if suitable microcells are used.

In order to make the direct determination of fluorescent steroids possible on filter paper, we utilized the principle generally employed in the analysis of radioactive substances using liquid scintillators. In the latter case, various amounts of radioactive substances are determined at a constant concentration of the scintillator. We measure various concentrations of the scintillator, *i.e.* of the naphthylglycine ester, by counting the number of light impulses produced by a radiation source of constant activity.

A glass plate was attached to the end window of an EMI 9514 S photo-

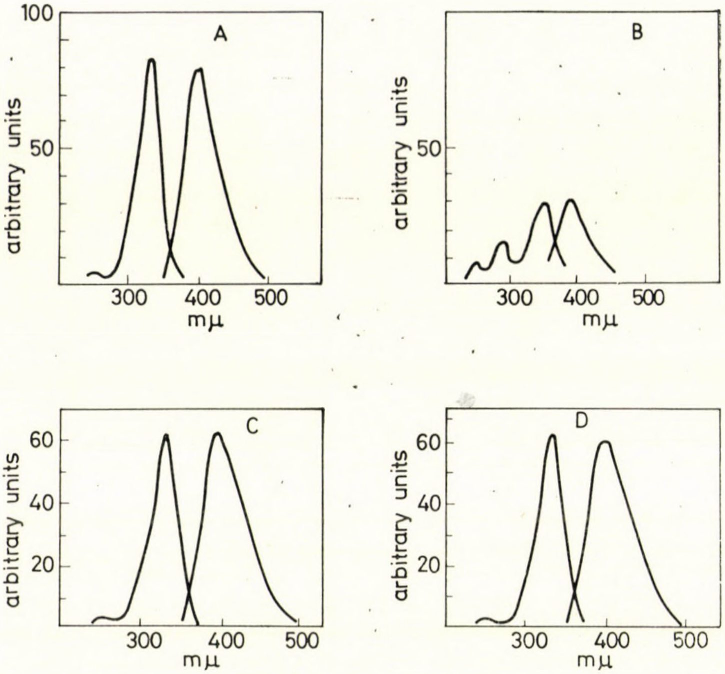

Fig. 2. A: N-α-naphthylglycine ester of I; B: N-β-naphthylglycine ester of I; C: N-α-naphthylglycine ester of II; D: N-α-naphthylglycine ester of III

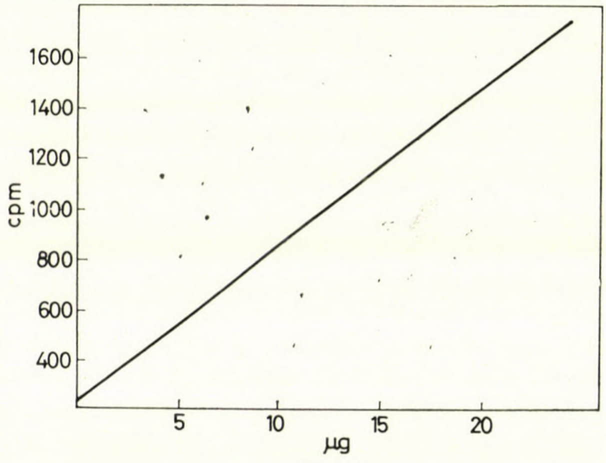

Fig. 3

multiplier, using silicon oil. The naphthylglycine ester sample was applied to a piece of filter paper (diameter 20 mm), which was then saturated with anisole and placed on the glass plate. On top of the filter paper a radiation source with the same diameter (C^{14}, 1.05×10^4 cpm) was placed. The impulses were led to a counter through a discriminator and amplifier.

In Fig. 3 the number of impulses is shown as a function of the concentration of the oestrone-α-naphthylglycine ester. The curve was obtained by taking the average number of counts obtained with 10 samples at each concentration. The deviation from the mean value is ±17%, and ±20% for 5 and 10 μg samples, respectively. The large scatter around the mean value is probably due to non-uniform window sensitivity of the photomultiplier, because the diameter of the filter paper was smaller than that of the window.

Work on improving the technique of determination of fluorescent derivatives of steroids and other natural substances is in progress. At lower temperatures toluene can be used as a solvent, which is characterized by a better efficiency. Other sources of radiation with more suitable geometry are expected to permit analyses on submicro scale.

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THE ISOMERIZATION OF *N*-PHENYL-*N*-TRITYLCYANAMIDE TO *N*-PHENYL-*N*'-TRITYLCARBODIIMIDE

(PRELIMINARY COMMUNICATION)

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A recent communication [1] by American authors describing the photochemically and, in one instance, also thermally induced isomerization of disubstituted carbodiimides into the corresponding disubstituted cyanamides, has prompted us to report our preliminary results concerning a case of the reversed isomerization.

Recently [2] we have described the preparation of phenyl-tritylcarbodiimide (m.p. 85—87 °C; IR in KBr pellet, $\nu_{as}N{=}C{=}N$: 2125 cm^{-1}) in 79% yield by refluxing anhydrous sodium phenylcyanamide with trityl chloride for 4 hrs. in dry acetone; under these conditions not even traces of the isomeric phenyl-tritylcyanamide [3] were obtained.

By slight modification of the conditions (using the potassium instead of the sodium salt of phenylcyanamide; trityl bromide instead of trityl chloride; the less polar benzene rather than acetone as the solvent; and working at about 0 °C), the course of the reaction was dramatically changed, and phenyl-tritylcyanamide** (m.p. 117—120 °C, by precipitation from a *cold* benzene solution with *cold* petroleum ether;*** IR in KBr pellet, $\nu C{\equiv}N$: 2215 cm^{-1}) was obtained in 42% yield under these conditions.

When the *original* KBr pellet was allowed to stand for a few weeks, and the IR spectrum of phenyl-tritylcyanamide was obtained again, a new and strong $\nu_{as}N{=}C{=}N$ band was observed besides the original $\nu C{\equiv}N$ band whose intensity had considerably diminished. This observation suggested that the cyanamide gradually rearranged to the isomeric carbodiimide on standing. The correctness of this assumption has been demonstrated by the results of experiments No. 2 and 4 in Table I, as well as by the observation that, on refluxing an about 2% solution of phenyl-tritylcyanamide in carbon tetrachloride, phenyl-tritylcarbodiimide is obtained in 69% yield (after recrystallization).

** The analysis agreed with the C, H and N values expected for this compound.

*** Lit. [3] m.p. 124°C. In view of our observations to be described below, this sharp m.p. seems doubtful to us.

In order to gain deeper insight into the nature of this isomerization, kinetic studies were started; the preliminary, semiquantitative results are collected in Table I. We have found that rearrangement occurs both in the crystalline state and in solution, its rate being enhanced in both cases by raising the temperature. Increase of the reaction rate was also observed when the apolar solvent carbon tetrachloride was replaced by the dipolar-aprotic dimethyl sulfoxide. The latter observation seems to indicate that the rearrangement occurs by an ionic mechanism.

Table I

Influence of the reaction conditions on the rate of isomerization of phenyl-tritylcyanamide into phenyl-tritylcarbodiimide

Medium	Temperature, °C	Reaction time	Result
—[1]	r.t.	4 hrs.	A weak ν_{as} N=C=N band has appeared
—[1]	100 °C	1 hr.	The original νC≡N band has completely disappeared; the IR spectrum is identical with that of an authentic sample of phenyl-tritylcarbodiimide
KBr[2]	r.t.	380 hrs.	A strong ν_{as}N=C=N band is observed, the intensity of the νC≡N band being, however, still the greater
KBr[2]	100 °C	2 hrs.	The νC≡N band has practically completely disappeared; the IR spectrum is almost[3] identical with that of an authentic sample of phenyl-tritylcarbodiimide
CCl_4	r.t.	200 hrs.	The νC≡N band has practically disappeared[4]
CCl_4	50 °C +60 °C +70 °C	2 hrs. 1 hrs. 45 min	The νC≡N band has practically disappeared[4]
DMSO	r.t.	46 hrs.	The νC≡N band has practically disappeared[4]
DMSO	60 °C	1 hr.	The νC=N band has practically disappeared[4]

[1] Pure starting material (phenyl-tritylcyanamide), from which a KBr pellet was made immediately before obtaining the IR spectrum.

[2] KBr pellet prepared from the pure starting substance.

[3] Slight differences (in the contoures and the splitting of certain bands) between the two spectra were observed, pointing perhaps to polymorphism.

[4] A very weak absorption at 2215 cm^{-1} was found even in the IR spectrum of a sample of phenyl-tritylcarbodiimide prepared by structure proving synthesis [2, 4]. Should this absorption prove to be attributable to the presence of traces of phenyl-tritylcyanamide, then it would demonstrate the reversibility of the isomerization described in the present paper, *i.e.* the existence of a non-prototropic tautomeric equilibrium between phenyl-tritylcyanamide and phenyl-tritylcarbodiimide, extremely shifted towards the latter.

Further studies with the purpose to obtain the rate constants and the activation parameters of the reaction, to investigate substituent and solvent effects, and to elucidate the reaction mechanism as well as to demonstrate the tautomeric equilibrium mentioned in footnote No. 4 of Table I, are in progress.

*

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REARRANGEMENTS OF STEROIDS, II

SCHMIDT REACTION AND BECKMANN REARRANGEMENT OF 3β-,17β-DIACETOXY 5α-ANDROSTAN-6-ONE AND -6-ONE OXIME

(PRELIMINARY COMMUNICATION)

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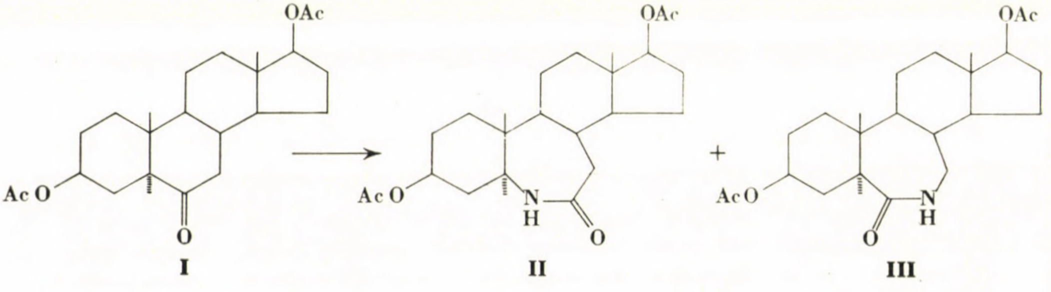
The behaviour of oximes with androstane skeleton has been described only for compounds bearing the =NOH group at positions 3 and 17 [1—3].

As an extension of our earlier work on the steric configuration of steroid oximes [4, 5], we undertook a study of 3β-,17β-dihydroxy- and -diacetoxy-5α-androstan-6-one and its oximes (**IX, IV, V**).

By reducing dihydroepiandrosterone with $NaBH_4$ and subsequent acetylation, we prepared 3β-,17β-diacetoxyandrost-5-ene. This compound was converted by nitration to 3β-,17β-diacetoxy-6-nitroandrost-5-ene which was reduced to 3β-,17β-diacetoxy-5α-androstan-6-one (**I**), the starting material for further reactions (m.p. 164 °C).

The Schmidt reaction of **I** was carried out with HN_3 and conc. H_2SO_4, or with NaN_3 in polyphosphoric acid. The reactions gave the isomeric homolactams, 3β-,17β-diacetoxy-6-aza-B-homo-5α-androstan-6a-one (**II**) (m.p. 133—135 °C), and 3β-, 17β-diacetoxy-6a-aza-B-homo-5α-androstan-6-one (**III**) (m.p. 217—218 °C). Lactams **II** and **III** formed in approximately 1 : 1 ratio. The mixture was separated by chromatography (*cf.* Table I).

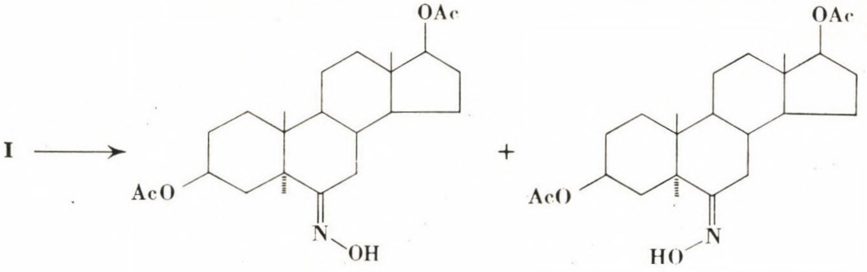


Condensation of **I** with $NH_2OH \cdot HCl$ yield a mixture of *anti-* (**IV**) (m.p. 253—256°) and *syn*-3β-,17β-diacetoxy-5α-androstan-6-one oxime (**V**) (m.p. 110—115 °C), the ratio of the isomers depending on the reaction conditions. Only **IV** could be isolated if the reaction was carried out in ethanol in the

Table I

Schmidt reaction					
Solvent	Reagent	Temperature, °C	Reaction time	Yield	
				II	III
1. Benzene-aconc. H_2SO_4	HN_3	20°	2 hr.	25.8%	22%
2. Polyphosphoric acid	NaN_3	50–60°	9 hr.	23.4%	28%

presence of pyridine or sodium acetate at 100 °C, and **V** was only detected by thin-layer chromatography. However, if the condensation was effected at room temperature using sodium acetate and ethanol, both **IV** and **V** formed in isolable amounts. The isomers were separated by fractional crystallization.



IV **V**

Beckmann rearrangement was used to determine the steric configuration of oximes **IV** and **V**. The rearrangement was performed only with **IV** as this was available in larger quantities. In the presence of thionyl chloride or *p*-acetylaminobenzenesulfonyl chloride (PAABSCl), lactams **II** and **III** were obtained, like in the Schmidt reaction of **I**, in ratios depending on the conditions (*cf.* Table II).

The products from oxime **IV** indicate that the rearrangement must have been preceded by partial isomerization. This isomerization is most significant

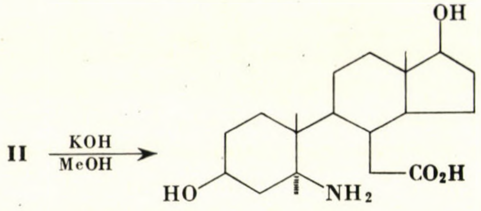
$$\mathbf{IV} \rightarrow \mathbf{II} + \mathbf{III}$$

Table II

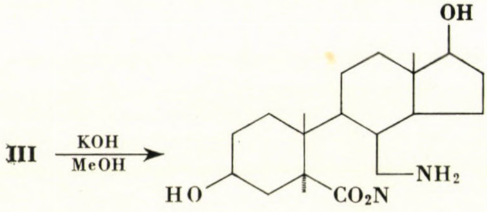
Beckmann rearrangement					
Solvent	Reagent	Temp. °C	Reaction time	Yield	
				II	III
1. $SOCl_2$	$SOCl_2$	−15 °C	40 min.	73%	Detected by TLC, not isolated
2. Dioxan	$SOCl_2$	20 °C	25 min.	60%	Detected by TLC, not isolated
3. Absolute pyridine	PAABSCl	20 °C	24 hr.	16,2%	40%

in absolute pyridine in the presence of PAABSCl, as indicated by the formation of a larger amount of lactam **III** derived from oxime **V**.

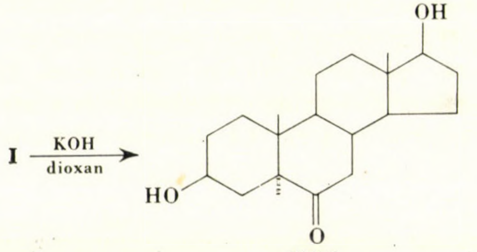
In order to determine the structures of lactams **II** and **III** and oximes **IV** and **V**, the former were hydrolyzed with KOH in methanol. Hydrolysis



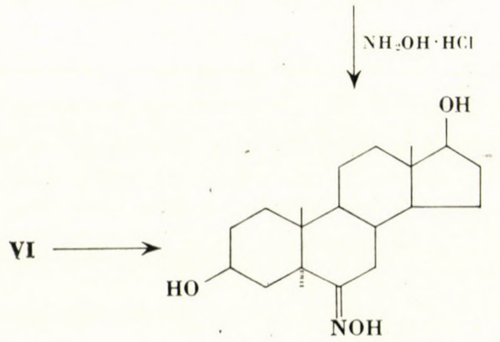
VI



VII



VIII

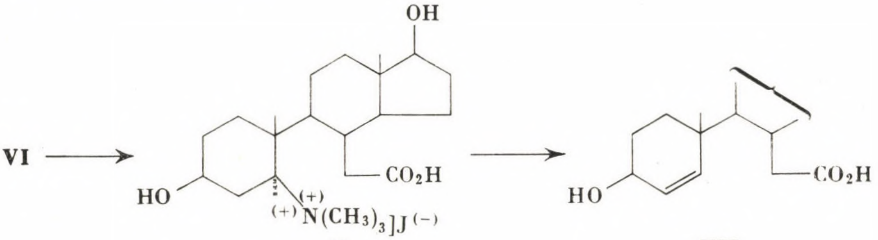


IX

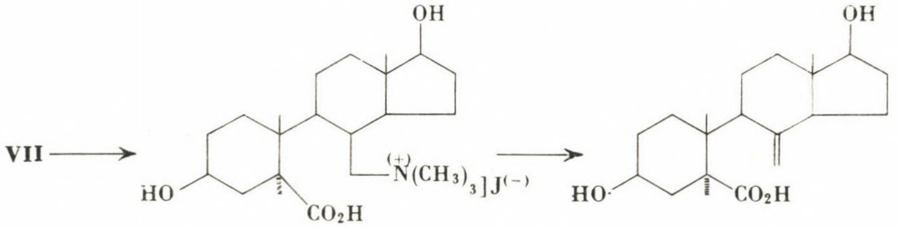
gave the corresponding deacetylated *seco*-amino acids **VI** (m.p. 312—314 °C) and **VII** (m.p. 306—309 °C).

For comparison, 3β-, 17β-dihydroxy-5α-androstan-6-one oxime (**IX**) (m.p. 280—285 °C) was prepared from ketone **VIII** (m.p. 210—215 °C) obtained by hydrolysis of **I**. The Beckmann rearrangement of oxime **IX** in dioxan with $SOCl_2$, opposite to previous experience, yielded the *seco*-carboxylic acid **VI**, which was also obtained by the hydrolysis of lactam **II**.

In order to prove the structures of compounds **VI** and **VII**, they were converted to quaternary ammonium salts (**X**, m.p. 315—318 °C; **XI**, m.p. 294—304 °C) which were subjected to Hofmann elimination. The IR spectra of the products (**XII**, m.p. 109—110 °C; **XIII**, m.p. 125—128 °C) showed characteristic shifts permitting conclusion about the structures of the lactams used as starting materials.



X **XII**



XI **XIII**

Results and discussion

The experiments led to the isolation of two isomeric ketoximes (**IV** and **V**) in the case of ketone **I**. These isomers can be regarded as 5α-*syn*- (**V**) and -*anti*-ketoximes (**IV**), depending on whether or not the hydroxyl group of the oxime is close to the 5α-hydrogen. The B-homo-lactams (**II**, **III**) derived from the known steric course of the Beckmann rearrangement and Schmidt reaction, performed under various conditions, have also been isolated. The structures of these products were also proved by converting them into *seco*-amino acids. Work is in progress to obtain more exact information on the stereochemical changes involved.

The hydrolysis of **I** in aqueous dioxan yielded **VIII**. Preparation of the corresponding oxime (**IX**) followed by Beckmann rearrangement gave a hydrolyzed *seco*-amino acid (**VI**), a derivative of B-homo-lactame **II**.

The described reactions represent an example of geometrical isomerism in steroid ketoximes with 5α-androstane skeleton. The structures of the isomers are unambiguously proved by rearrangement reactions.

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BOOK REVIEWS — BUCHBESPRECHUNGEN — РЕЦЕНЗИИ КНИГ

E. Bodor: *Szervetlen Kémia* (Inorganic Chemistry; in Hungarian) Tankönyvkiadó, Budapest, 1968. 735 pages, 231 illustrations

All over the world, teaching of modern inorganic chemistry is a great problem to lecturers and text-book writers. Certainly, introduction of results of quantum chemistry presents the greatest difficulties. It is well known, that the average student of chemical engineering or chemistry — especially when learning inorganic chemistry in the first year of his studies — does not possess sufficient knowledge of mathematical fundamentals to understand the basic principles and application of quantum chemistry. However, this is not the only difficulty. Methods providing the best results in quantum chemistry require very much calculation, and do not have such descriptiveness which is a natural demand of a student just getting acquainted with science. Beginners need distinct regularities to guide them in arranging and mastering a large subject. The most confortable solution would be to disregard the results of quantum chemistry, but this cannot be done, as to teach things which are known to be false goes against our basic principle of teaching. Thus, inorganic chemical university text-books must acquaint the student with the basic principles of quantum chemistry, and must give an aspect reflecting the results of quantum chemistry and modern structural research.

"Inorganic Chemistry" by E. Bodor is the first text-book written by a Hungarian author which gives by basic principles of quantum chemistry and a consistent discussion of structural problems of inorganic chemistry based on these principles.

The author deduces the Schrödinger equation from the equation of wave motion. The solution of this equation is shown in the case of an electron in a potential box, then the eigenfunctions of the hydrogen atom are discussed in detail, and the electronic, structures of polyelectronic atoms are briefly described. Bond relations in molecules are illustrated by means of the most simple theory of molecular orbitals. This is followed by a detailed description of hybridization which is justified since this relatively readily understandable approximation provides good qualitative results, and it is suitable for a consistent treatment of stereochemical problems in inorganic chemistry.

In connection with the structures of complex compounds, some important results of the crystal-field and ligand-field theories are also summarized.

Part I dealing with the structure of matter is followed by Part II discussing the elements, and Part III which treats inorganic compounds. Such an arrangement and treatment of inorganic chemistry — based in detail on the Szabó—Lakatos periodic system — is undoubtedly very advantageous, since it allows, and even invites, both the author and reader to present and recognize general relationships. This advantage is particularly revealed by the general summaries, *e.g.*, of hydrides, halides and oxides, which precede and greatly facilitate the detailed discussion of these compounds.

This arrangement also makes possible consistent application of the fundamental principles of stereochemistry discussed in Part I. In the course of discussing the individual elements, the reader obtains a clear picture of the possible hybridization states allowed by the electronic structures of the given atoms, resulting in the structural characteristics of their compounds. The illustrations of the book, with lucid pictures of steric arrangements, will certainly be of great use to the students. Carefully collected data of bond lengths, bond orders and electron densities further increase the value of the book.

The author, while making full advantage of the treatment of inorganic chemistry in the above arrangement, in Part II also compares the physical and chemical characteristics of elements in identical columns of the periodic system, where great help is rendered to the reader by very carefully constructed tables.

The importance of oxidation-reduction processes in inorganic chemistry need not be emphasized. Therefore, neglecting mention of the concept of redox potential is surprising and may be criticized, since any treatment of oxidation-reduction processes can hardly be carried out at the required level without this concept.

Commenting the parts of the book dealing with quantum chemical questions, we expect that vivid dispute may evolve in connection with this book of E. Bodor. It is almost natural, that in a book, giving new aspects in the treatment of branch of science, some concepts of the author will provoke the criticism of specialists and particularly of teachers. Before turning to the parts of the book disputable in our opinion, the reviewers would like to point two insufficiences certainly present. The first is that things which are known to lack validity should never be stated, not even for the sake of descriptiveness; so it must not be written, *e.g.*:

$$\Psi_{(21-1)} = f(r)y = p_y \quad \Psi_{(21+1)} = f(r)x = p_x$$

etc.

Though these functions are solution of the Schrödinger equation, they are not eigenfunctions of the operator corresponding to component z of the angular momentum. Therefore, the statement that these functions represent states with the magnetic quantum numbers $+1$ and -1 is incorrect. The other point to be corrected is the repeated statement in the book that l-splitting in the case of polyelectronic atoms is caused by a deviation of the potential field from spheric symmetry. According to group theory, spherical functions having different l values belong to different species of the three-dimensional rotational group, therefore they represent states of different energies. It is known that, from this point of view, the hydrogen atom is to be considered a special case.

We understand the author in his endeavour to avoid giving a too complicated picture to the student; however, too serious discussion of elementary quantum chemical approximations gives a feeling of insufficiency, and it may adversely affect scientific discernment. More emphasis ought to have been laid upon the quantitative character of the picture obtained, mentioning that reality and methods providing better approximations are far more complicated. Another defect is again the result of neglecting closer approximations: several times the author makes comparison between the valence bond and molecular orbital methods, mostly to the effect that the latter one gives better results. However, if closer approximations are also considered, the two methods are found to give the same final results. In our opinion, refusal of the author to discuss mesomeric limiting structures will give rise to problems for many students, since this concept is often mentioned in the literature and, in correct interpretation, it is an approximative method, just like molecular orbital theory.

Today, writing of a modern inorganic chemical text-book requires far-reaching knowledge in so very diverse fields that this can only be provided by a co-ordinated collaboration of specialists of several branches of science; such a co-operation is unfortunately, rarely realized. With this fact in mind, true appreciation is due to the great work of the author who under took the task alone.

Students eager for new knowledge and new aspects of treatment, as well as chemist who obtained their diplomas several years ago but like to follow up-to-date results, will certainly welcome the book of Professor Bodor. This work is considered a brave and pioneering initiative to modernite teaching of inorganic chemistry in Hungary.

B. Csákvári and F. Török

D. T. Elmore: *Peptides and Proteins.* Cambridge University Press, London, New York, 1968. XI + 154 pages (Paperback.).

This book has written for senior undergraduates in chemistry and biochemistry. Its purpose is to give a comprehensive, consistent and modern picture of the fundamental results in the rapidly developing field of the chemistry and biochemistry of peptides and proteins. The author has masterfully accomplished this difficult and complex task, and his book affords very good reading. The order of the chapters and their relative lengths well reflect the main trends of modern peptide research.

After a description of the isolation and separation of peptides and proteins, the book deals with the elucidation of the primary structure of proteins, the determination of the amino acid sequence. Further on the macromolecular nature and steric structure of proteins are considered, followed by a brief review of the principles of peptide synthesis. The volume is concluded by treating the problem of the biosynthesis of proteins and by a discussion of the relationship between structure and biological effect of peptides and proteins. It is characteristic of each chapter that after a clear presentation of the minimum amount of fundamental concepts, the logical treatment rapidly leads to the presentation and evaluation of the most modern results. The general subject is often illustrated by properly selected actual examples, making easy the understanding even to a reader unfamiliar with the subject matter.

Concerning the experimental details which are beyond the scope of the volume, reference is made to seventy, mainly of secondary, sources. The modern, up-to-date nature of the book published in 1968 is well shown by the fact that the overwhelming majority of the references cover publications which appeared after 1960, and about one third of them fall within the years 1965 to 1967. Just this inclusion of the most modern literature makes the book an interesting reading even to researchers well acquainted with the field of peptide and protein chemistry.

Both the selection of the subject matter and its consistent and concise treatment have elicited the highest appreciation of the reviewer. If this review is to offer criticism at all, perhaps objection could be made to the necessity of devoting one page to the treatment of E. FISCHER's peptide synthesis using α-chloroacyl derivatives, though, doubtless, this method is of decisive significance from a science historical point of view. This part seems to be in contrast with the modern approach consistently maintained throughout the book.

All in all, it can be stated that this book, owing to the uniform presentation of the chemical and biochemical results of investigations on peptides and proteins, will provide a useful and enjoyable reading to senior undergraduates of chemistry and biochemistry, as well as to chemists who wish to study peptides and proteins, or even those who are familiar with the field.

A. KÓTAI

F. GERSON: *Hochauflösende ESR-Spektroskopie (dargestellt anhand aromatischer Radical-Ionen)*

Chemische Taschenbücher 1.

(High-Resolution ESR Spectroscopy as Presented on the Example of Aromatic Radical-Ions) Chemical Pocket Books No. 1. (In German)

Edited by Wilhelm Foerst and Helmut Grünewald. Verlag-Chemie, Weinheim, 1967. 210 + X pages

In recent years, the high resolution version of electron resonance spectroscopy, dealing with dilute solutions of organic free radicals and radical-ions, has made important contributions to our knowledge in organic and particularly theoretical organic chemistry. The hyperfine coupling constants obtainable from electron resonance experiments are directly related to the spin-density distribution and, consequently, to the geometry and electron configuration of the molecule. In order to establish a quantitative relationship between the coupling constants and the molecular parameters mentioned, it became necessary to refine the simple Hückel-model which had been formerly in general use. For the checking of the new theoretical models, which were constructed mainly on the basis of electron interactions, excellent experimental material was furnished by the high-resolution electron resonance spectra of stable radical-ions prepared from aromatic compounds. The monograph by F. GERSON, published as the first volume of the series Chemical Pocket-Books, makes use of this experimental material. The aim of the author has been to give, on hand of these data, a readily understandable introduction to organic chemists for the interpretation of high-resolution electron resonance spectra.

The book is divided into two nearly equal parts: In the first, general part, the author discusses briefly the fundamentals of electron resonance spectroscopy, the various methods of preparation of aromatic radical-ions, and the experimental requirements and techniques of obtaining high-resolution spectra. This is followed by a theoretical explanation of high-resolution spectra. In view of the fact that the emphasis in the monograph is on the relationship between electron resonance spectra and the electron configuration of the molecules investigated, chapters in the theoretical part deal primarily with the determination and interpretation of the hyperfine coupling constants. Factors influencing the line shape as well as the *g*-factor, are discussed only to an extent required for the understanding of some anomalies of high-resolution spectra. The theoretical chapters lead the reader to up-to-date methods for the calculation of spin density. The problems of sigma-pi and pi-pi spin polarization, forming the basis of these calculations, and theoretical methods of their determination are discussed in the appendix to Part 1.

In the second, special part, the author summarizes electron resonance data on aromatic radical-ions, grouped according to the following types of compounds: aromatic hydrocarbons, heterocyclic compounds, quinones, aldehydes and ketones, and substituted derivatives. A separate chapter is devoted to the electron resonance spectra of non aromatic systems. In the appendix to this special part, the author gives a short account of the characteristics of hyperfine structures connected with ^{13}C, of the association of radical-anions with alkali metal cations, and finally, of the effects of time-dependent intramolecular processes (primarily of conformation equilibra) on electron resonance spectra.

The style of the book is simple, its reasoning lucid. Only a knowledge of the fundamental quantum-chemical concepts is required from the reader. The volume contains about fifty well-selected figures (spectra), 14 tables, and an extensive review on the literature of the subject, involving about 300 references. The book is recommended in general to organic chemists interested in the applications of electron resonance spectroscopy in organic chemistry, and particularly to those engaged in theoretical organic chemistry. Owing to the abundant and well arranged references, the book will be of value also for research workers active in this field.

L. RADICS

C. HAMILTON and J. A. IBERS: *Hydrogen Bonding in Solids* W. A. Benjamin Inc., New York—Amsterdam, 1968. 286 pages.

Hydrogen bonding is one of the most extensively studied specific intermolecular interactions. Owing to its important role in chemistry and biology, it has been in the centre of interest of research workers for a considerable time, and almost every method of structural investigation has been applied to elucidate the nature of hydrogen bonding. Notwithstanding the great and steadily increasing number of publications on this subject, only a few monographs are available for those who want to get acquainted with this field. Therefore, the publication of the book by HAMILTON and IBERS is certainly timely.

The value of the book does not rest solely on the factual information offered concerning the results of modern research; the principle applied by the authors in the treatment of the subject deserves special credit. The discussion of the various methods of structural chemistry used in the study of the hydrogen bond is not restricted to the presentation of a few examples of the applications, but a critical analysis of the techniques is given yielding valuable information to the reader about the possibilities and limitations of each method. Instead of an encyclopedic discussion of the results in this field or a detailed analysis of any one particular topic, the authors emphasize the pertinent facts concerning the chemical and chemical-physical characteristics of the hydrogen bond. Therefore, this book is not only a useful guide to the reader to modern literature, but also enables him to make a critical evaluation of the publications.

The book is divided into eight chapters. Chapter 1 gives an introduction to the discussion of specific molecular interactions, and summarizes the physical and chemical requirements for the hydrogen bonds in solids. Chapter 2 deals with the diffraction methods of structural analysis (electron-, X-ray- and neutron diffraction); the theoretical and experimental bases of these methods are discussed and systematic errors in diffraction experiments, wich may affect the validity of the derived geometric structure, are dealt with in detail. Chapter 3 is concerned with spectroscopic methods suitable for the investigation of hydrogen bonding, thus primarily with infrared and NMR spectroscopy. Within this scope, the particular features of the information provided by spectroscopic methods are discussed and compared with the information given by diffraction techniques; thus the complementary character of the two methods is pointed out. Chapter 4 is devoted to rotational motions in solids, and how these are reflected in NMR and neutron spectra. The discussion of the fundamentals of neutron inelastic scattering is of particular value, since this modern experimental technique, less known to chemists, is gaining in importance as a structural tool of solid systems. Chapter 5 presents some examples of hydrogen bonding in organic crystals, with particular emphasis on the geometrical characteristics of proteins and nucleic acids. Chapter 6 deals with hydrogen bonding in inorganic systems, discussing primarily the structure of ice, crystalline hydrates and ammonium salts. Chapter 7 is concerned with ferroelectric materials containing hydrogen bonds, and finally, in Chapter 8, the authors give a brief summary of future developments in the field discussed.

The book has simple and extremely lucid style. The arrangement of the subject matter bears witness to the excellent pedagogical sense of the authors. It assumes only fundamental knowledge in chemistry and physical-chemistry, and therefore, can be recommended primarily to advanced university students. Further merits of the book are the careful selection of the experimental material and the excellent stereoscopic drawings (which may be viewed with the enclosed stereo viewer). These are of great help in understanding the spatial arrangement of the molecules. The book will be of immediate interest to all research workers concerned with the structural analysis of solid systems.

L. RADICS

J. HEYROVSKY and P. ZUMAN: *Practical Polarography. An Introduction for Chemistry Students.* Academic Press, London, New York, 1968. VIII + 237 pages

The book is the latest revised edition of the series which started with the Polarographisches Praktikum (Springer, Berlin, 1948). Since then it has been published in more or less revised form in Slovakian, Czech, Hungarian, Polish and German. Generations of students and chemists have used it as a guide in their first steps in the art of polarography. The present edition has some very welcome additions and the subject matter has been slightly rearranged. The main additions, as far as the author of this review can see, are the inclusion of some polarographic vessels which were not included earlier, an account of general polarographic instrumentation including pen-recording instruments, with special emphasis on the problems of damping, a few hints on the problem of polarographic reversibility, and a more detailed discussion of maxima. The tables also contain some additions.

The arrangement of the book is the following: The introductory chapter contains the main principles of polarography, a discussion of the dropping electrode and the simplest method of recording a polarographic curve. The fundamental properties of the polarographic curve are discussed. This is followed by a description of reference electrodes and polarographic cells, the necessity of using a supporting electrolyte including the possibilities given by the use of complexing agents, and various pH values for the separation of coalescing waves, methods of removal of oxygen and the cautionary measures against mercury poisoning.

The second chapter deals with the interpretation of polarographic waves, and the significance of the mercury head in differentiating various polarographic currents. The third chapter deals with polarographic instrumentation, the general procedure of recording curves and the checking and simple serviceing of the apparatus.

Chapters 4 and 5 give very detailed instructions for various simple determinations, while Chapter 6 discusses some examples of the practical application of polarography in various fields (metallurgy, organic chemistry, pharmacy and biochemistry, food industry, medicine) and also discusses methods of microanalysis and polarometric (amperometric) titrations.

A table of buffers, half-wave potentials and a bibliography complete the book.

As the book is meant for students and as a first practical introduction, the methods are described in great detail. It should be easy for the average student or reasonably experienced technician to work through the book and learn the technique of polarographic analysis without outside help. The book is also excellent as a basis for a practical course.

Unfortunately, the book only deals with the classical form of polarography: DC polarography using the dropping mercury electrode and a slow potential scan. This automatically limits its usefulness for those who possess the more sophisticated polarographs (square wave, pulse, cathode ray) as the special pitfalls of these techniques are not mentioned. The treatment of the hanging mercury drop and its application for trace analysis is also omitted. Very little is said about polarography in organic solvents and the problems of I. R. compensation.

The outlook of the book in general is such that it only demonstrates the power of polarography as a quantitative analytical tool (doing this very well), and it tends to let the reader forget the other uses of the method. The possibilities of polarography in organic chemistry are definitely not limited to the quantitative analytical aspect, and it would have been a very welcome addition to the book if this technique had been included. The reader can, of course, follow up this subject from the bibliography, but even here some texts have been omitted. *E.g.*, ZUMAN—KOLTHOFF: Progress in Polarography (Interscience, 1962) is not mentioned, and the regular reviews in the journal "Analytical Chemistry" are also missing.

Nevertheless, the book in its present form will be very useful for students and practising chemists as a first course in polarography. The reviewer hopes that some of the omissions can be corrected in a further edition.

M. VAJDA

D. A. JOHNSON: *Some Thermodynamic Aspects of Inorganic Chemistry*, VI + 224 pages. Cambridge University Press, Cambridge, 1968.

This readable and useful book has been published in the Cambridge Chemistry Texts series. It consists of seven chapters. After a short introductory chapter — dealing mostly with the differences between kinetic and thermodynamic stability, and with the contribution of the entropy and enthalpy terms to free energy — the principles of the ionic model are thoroughly discussed. The ionic model is then applied to the compounds of alkali and alkaline earth metals. The following three chapters deal with problems of solution equilibria and electrode potentials, with the solubility of ionic crystals, and with transition-metal chemistry. The long concluding chapter is devoted to treatment of compounds in which covalent bonding predominates. A number of important books and papers are listed at the end of the chapters; in the references the reviewer did not find the excellent relevant papers and books by R. T. SANDERSON. In the five appendices some basic definitions and conventions are summarized, derivations of important relationships are given and a number of important thermodynamic data are listed.

Because of the purpose of the book the reviewer is forced to mention that the usefulness and didactic value of the book would be even greater if some confusing points would be corrected. Dealing with the oxidation of iron(II) with iodine — and the oxidation of iodide with iron(III) — the effect of pH is considered. It is stated that iodine is perfectly capable of oxidizing iron(II) hydroxide in alkaline solution. In this form this statement is misleading iodine not existing in alkaline solution. The oxidation state diagram for sulphur (p. 95) is also confusing partly because the oxidation states of the different sulphur atoms are averaged for compounds containing non-equivalent sulphur atoms; and partly because oxidation state *eight* is rendered to peroxydisulphate.

The printing is good, the text is practically free of misprints. As a whole this small volume presents a well-balanced treatment of thermodynamic aspects of modern inorganic chemistry and is warmly recommended both for teachers and for interested undergraduates.

M. T. BECK

The Practice of Gas Chromatography (Editors: L. S. ETTRE and A. ZLATKIS). Interscience Publishers, New York 1967. 591 pages

Gas chromatographic instrumentation now makes up part of the equipment of virtually all industrial and academic laboratories engaged in the analysis of organic compounds. This widespread use is remarkable when one consideres that in 1955 the gas chromatographic technique was known to but a few workers, and the few instruments in use were located in central analytical research facilities of large corporations or universities. The literature at that time consisted of about 40 papers, mainly devoted to descriptions of experimental apparatus, with described applications of the technique limited to fatty acid and light hydrocarbon analysis. By the close of 1966, over 50,000 gas chromatographs were in operation, and more than 10,000 papers has appeared reporting the application of the technique to virtually every conceivable area of science and technology in which the qualitative or quantitative analysis of volatile materials was of interest.

It is therefore remarkable that notwithstanding the great importance of the technique relatively so few surveys and monographies were published in this field in recent years. Thus readers wanting to get acquainted with this method or acquire deeper knowledge, were mostly restricted to the study of the original publications. However, this is not always the best approach for the beginners, particularly if they have to find their way in a deluge of publications. Therefore, the publishing of this book, edited by L. S. Ettre and A. Zlatkis, recognized experts of the subject, in co-operation with illustrous workers in the relevant field, is to be welcomed.

The objects of the book are clearly pointed out in the introduction by the editors: "There are three reasons why we think that this book is necessary. First, one should not forget that the basic English textbooks on gas chromatography were written without almost any exception before 1962, and during this five-year period significant contributions were made to the development of this technique. Secondly, while the existing books are strong in theory, the practical information contained in them is somewhat limited. We are aware that no practice can exist without a sufficient knowledge of theory; however, the practical gas chromatographers also need compilations which handle the practice of the technique in detail. Finally, many special methods and techniques exist, which are well documented in the scientific literature, but the large number of publications on the particular subject in many diverse publications makes a general understanding of the particular method by the practical gas chromatographer almost impossible . . . To summarize briefly, the intent of this book is to provide a basic guide to the practice of gas chromatography for the use of analytical chemists who are now employing or who are contemplating the actual employment of gas chromatographic instruments for the solution of particular problems in connection with separation, identification, and measurement of volatile compounds."

These aims of the book are to be attained in ten chapters, which survey all the important problems arising in the practice of gas chromatography, from fundamental principles to automated systems applied in the control of continuous industrial production.

This book consists of ten chapters each of which gives a detailed description of a different part of the gas chromatographic system or of a particular technique and its optimum use for the solution of analytical problems.

Chapter 1 includes descriptive information on the mechanism of the gas chromatographic process and the function and operation of a gas chromatographic instrument. An efficient step-by-step procedure is outlined for placing a chromatograph in operation and optimizing the analysis of an "unknown" sample. The sources of technical information useful to the analyst, such as literature, technical societies, and reference sources, are also compiled.

Chapter 2 considers the nature and effect of the carrier gas in the gas chromatographic process.

Chapter 3 discusses two questions. First it contains a detailed treatment on the various methods used to form certain volatile derivatives prior to actual sample introduction. This was felt necessary since the preparation of these derivatives is usually the task of the practical gas chromatographer. Secondly, this chapter describes the different sample introduction systems.

Chapter 4 discusses, in detail, the theoretical and practical performance aspects of the chromatographic columns.

Chapter 5 includes a systematic survey of the detector systems which have been employed in gas chromatography and the physical characteristics and practical advantages of each.

Chapter 6 discusses the application of digital electronic systems used in gas chromatography for data handling and evaluation.

Chapter 7 elaborates in detail the interpretation of the results of gas chromatographic analyses: the derivation of the qualitative and quantitative composition of the sample determined from the chromatogram.

Chapter 8 summarizes the auxiliary techniques used in connection with gas chromatography for the identification of the individual separated sample components.

Chapter 9 gives a summary of the so-called reaction gas chromatography, *i.e.* the techniques where the sample undergoes a chemical change in the GC system.

Finally, Chapter 10 discusses the application of gas chromatography as an automated analytical technique for process-control purposes.

This excellently edited book, appearing in a tasteful presentation, will be of great value to readers wishing to get acquainted with this technique, and to all those analytical and organic chemists concerned in the routine application of the method.

Gy. Deák

L. C. THOMAS: "*A New Chemical Structure Code for Data Storage and Retrieval in Molecular Spectroscopy*" Published by Heyden and Son Ltd. 1968. 60 pages

This monograph deals with the problems of spectroscopic documentation encountered in laboratories that have accumulated a large body of spectra. Throughout the discussion the main aspects are the speed and efficiency of data retrieval.

The author describes in detail the existing methods based on numerical, alphabetical and microfilm filing. Among the specific system examples he gives the critical evaluation of the "Spec-Finder" tabular band indices, punched card systems, like the well-known hand-sorted DMS cards and the machine-sorted Wyandotte-ASTM (IBM) cards. As a further possibility the superimposable card system for optical coincidence sorting is also described.

With regard to the use of computers for searching spectra the author holds the opinion that the larger data processing systems are not economic for this special purpose.

The main body of the monograph is concerned with the description of the Kodak Miracode system. The abbreviation stands for "Microfilm Information Retrieval Access Code" and the system was originally developed for the storage and rapid retrieval of information in document form. The inherent advantages are the speed of retrieval and the fact that when retrieved the spectra are displayed on a reader screen and are immediately available for either printing or comparison.

The modification of the original Miracode system by the author to spectroscopic data is given in details. Nine actual examples are given to illustrate the code and the operation of the system. This system can also be used for handling ultraviolet and magnetic resonance spectra.

In the Appendix the complete chemical structure code is given for the Miracode system from 000 to 999. The publication contains 19 Figures and is paperbound.

This work should prove useful to chemists and spectroscopists contemplating to develop or improve their own data storage and retrieval systems.

L. NEMES

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РЕЗЮМЕ

Электронная структура неорганических циклических соединений с ненасыщенными связями, II

Ультрафиолетовый спектр поглощения производных нитрита фосфора

Б. ЛАКАТОШ, А. ХЕС, Ж. ВЕТЭШИ и Г. ХОРВАТ

На основе изучения УФ-спектров поглощения нескольких циклических двухзамещенных нитридов фосфора и линейных производных, кажется вероятным, что в кольце нитридов фосфора не существует значительной, подобной ароматическому кольцу, $p(\pi) \rightarrow d(\pi)$ — электронной делокализации.

Электронная структура неорганических циклических соединений с ненасыщенными связями, III

Интенсивность инфракрасной полосы поглощения тримера псевдогалогенидов нитрида фосфора

П. ПУЛАИ, Б. ЛАКАТОШ, Г. ТОТ, А. ХЕС и Ж. ВЕТЭШИ

Величины интенсивности интегрированной полосы антисимметричного азида и изо-тиоцианата из ИК-спектров поглощения циклических тримеров диазида и ди-изотиоцианата нитрида фосфора, измеренные авторами, сравнивались со значениями для нескольких аналогичных алифатических и ароматических производных, а также с нециклическими кремниевыми, фосфорными и серными производными. На основе этого было установлено, что кольцо нитрида фосфора содержит не гетероморфную «ароматическую» π-электронную структуру, а менее делокализованное PNP трехцентровое π-электронное распределение.

Сорбция ионов металлов на карбоксицеллюлозе из смеси растворителей. Сорбция кобальта (II)

А. ЛАСТИТИ и М. ЕШИ

Изучалась сорбция кобальта (II) на карбоксицеллюлозе (кц) в Н-форме, из смесей вода-растворитель и формамид-растворитель. На основе экспериментальных данных было установлено, что если к менее основному растворителю с низкой диэлектрической постоянной добавить более основной растворитель с высокой диэлектрической постоянной, то в значительной степени возрастают количество сорбированного металла и скорость ионного обмена на карбоксицеллюлозе в Н-форме. Не наблюдается линейная зависимость между степенью сорбции и диэлектрической постоянной среды в смесях спирт-вода и спирт-формамид. Гораздо более важное влияние оказывает на обмен Co(II)-водород селективное набухание карбоксицеллюлозы, основность растворителя и комплексообразование, чем диэлектрическая проницаемость среды.

Молибденовый и вольфрамовый электроды для потенциометрической индикации при серийном определении молибдата, вольфрамата и свинца

Р. ГЕЙЕР и М. НЕЙМАНН

Зависимость потенциала молибденовых и вольфрамовых электродов от концентрации свинца приблизительно описывается уравнением Нернста. Появление потенциала в присутствии посторонних ионов объясняет давно известную возможность индикации при потенциометрическом титровании вольфрамата и молибдата двухвалентным свинцом в присутствии буфера. В отсутствии буфера появляется смешанный потенциал. Изменение pH, вследствие гидролиза, изменяет высоту скачка потенциала в точке эквивалентности.

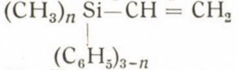
Виниловые производные элементов IV/I группы

Й. НАДЬ, Ш. ФЕРЕНЦИ-ГРЕС и С. Г. ДУРГАРЬЯН

I. Методами Онсагера и Уедестранда были определены дипольные моменты триметил-виниловых производных элементов IV/I группы,

$(CH_3)_3E-CH = CH_2$, где $E = C, Si, Ge, Sn$

а также некоторых фенил-виниловых производных кремния



$$\underset{(C_6H_5)_{3-n}}{(CH_3)_n\,Si}-CH = CH_2$$

где $n = 0$ и 2.

II. Для триметил-виниловых производных векторным путем рассчитывался дипольный момент виниловой группы, а также связи между атомом и углеродом. С помощью этих данных векторным путем рассчитывались результирующие дипольные моменты фенил-виниловых производных кремния.

III. Было установлено, что минимальным дипольным моментом среди триметил-виниловых производных обладают производные кремния. Это объясняется тем, что если в случае углерода имеется лишь индуктивный (+1) эффект, то в случае кремния, германия и олова нужно считаться и с мезомерным (—M) эффектом обратного направления.

IV. Для доказательства вышесказанного проводились упрощенные квантово-химические расчеты.

Изучение ионообменных равновесий радиоактивным методом, XV

Использование жидких ионообменников для исследования смешанного комплекса цинка с гликолевой и α-гидрокси-изомасляной кислотой

Т. ЛЕНДЬЕЛ

С помощью метода жидких ионообменников, используя ди-этилгексил-фосфорную кислоту, изучались возможности образования смешанных комплексов в системе цинк-гликолевая кислота-0-гидрокси-изомасляная кислота.

Основываясь на теоретических соображениях, константа образования смешанного комплекса (MLA) определялась графически. В результате было получено $\log K_m = 0{,}88$.

Образование четвертичных солей 1,2-двухзамещенных-1,2,3,4-тетрагидроизохинолинов, III

Изучение пространственной структуры диастереомерных солей методом протонного магнитного резонанса

Л. РАДИЧ, М. ҚАЙТАР, Й. ҚОБОР и Г. БЕРНАТ

Изучались спектры пмр 1-фенил-, 1-изопропил- и 1-(3',4'-диметоксибензил)-2,2-диалкил-6,7-диметокси-1,2,3,4-тетрагидро-изохинолиновых солей, диастереомернйх на азоте. Было установлено, что в диастереомерах, образующихся преимущественно при алкилировании соответствующих N-метильных оснований («прямая» реакция), заместитель на атоме углерода С—1 и группа на азоте, имеющая бо́льший эффективный радиус, находятся в *транс* положении. Далее, пространственная структура четвертичных солей может быть описана одной, наиболее выгодной конформацией, и эта конформация характерна для всех диастереомеров, имеющих тот же самый заместитель на атоме углерода С—1. Предпологается, что в этой наиболее выгодной конформации фенильная группа в положении *1 псевдоекваториальна*, в то время как изопропильная, или 3,4-диметоксибензильная группы — *псевдо-аксиальны*. На основе стереохимии диастереомерных солей, а также данных по стереоселективности их образования, выдвигается предположение о том, что на ход образования четвертичных солей существенное влияние оказывает взаимодействие присоединяющейся к азоту алкилной группы с заместителями, находящимися в положениях *1* и *2*. Наиболее выгодным направлением для присоединения является *транс* приближение алкильной группы по отношению к ориентации заместителя в положение *1*.

Меченые аминокислоты и их производные, II

Получение DL-глутаминовой-1-C^{14} кислоты, DL-орнитина-1-C^{14} и DL-аргинина-1-C^{14}

И. МЕЗЁ, И. ТЕПЛАН и Й. МАРТОН

Применялся синтез Стрекера для получения DL-глутаминовой-1-C^{14} кислоты из β-цианпропионацеталя. γ-Бензоил-аминобутиральдегид, полученный из α-цианпропионацеталя, использовался для получения DL-орнитина-1-C^{14}, а затем из последнего был получен DL-аргинин-1-C^{14}.

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