ACTA UNIVERSITATIS SZEGEDIENSIS

# ACTA PHYSICA ET CHEMICA

NOVA SERIES

TOMUS XVII FASCICULI 3—4

SZEGED, HUNGARIA
1971

Adiuvantibus

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redigit

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Edit

Facultas Scientiarum Naturalium Universitatis Szegediensis de Attila József nominatae

Editionem curant

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Nota

Acta Phys. et Chem. Szeged

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Szerkeszti

KOVÁCS KÁLMÁN

A szerkesztőbizottság tagjai:

CSÁNYI L., FEJES P., GILDE F., HUHN P., KETSKEMÉTY I., MÁRTA F.,
SIPOS GY., SZALAY L. és SZÁNTÓ F.

Kiadja

a József Attila Tudományegyetem Természettudományi Kara
(Szeged, Aradi Vértanúk tere 1.)

Szerkesztőbizottsági titkárok:

BERNÁTH G., GALIBA I., HALMOS M. és SÜLI Á.

Kiadványunk rövidítése:

Acta Phys. et Chem. Szeged

# DETERMINATION OF THE DIFFUSION COEFFICIENT IN A LACQUER LAYER BY MEANS OF A RADIOACTIVE SUBSTANCE

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*(Received May 1, 1971)*

A method of calculating the diffusion coefficient, adjusted to a method of measurement important for the application, is given. The method is based upon an exact solution of the differential equation describing the diffusion in the homogeneous substance filling up the half-space and the diffusion coefficient is obtained graphically.

Several methods to characterize lacquer layers used for protecting metals are known. One of these [1, 2] uses the diffusion coefficient of the damaging substance diffusing into the lacquer layer to characterize the protecting effect. In the process of measurement, for a certain time, the lacquer layer is brought into contact with a corroding substance containing a radioactive isotope. Thereafter layers of definite thickness are ground off the lacquer layer and activity is measured at the new surfaces obtained. However, a method of calculation which could yield a theoretically correct diffusion constant has not been available so far. In the following such a way of calculation is described.

Let us start with considering a well known diffusion problem [3]. Let the half-space $x>0$ be filled by a homogeneous substance. At the moment $t=0$ let it be brought into contact with a solution of concentration $c_0$, filling the half-space $x<0$. The molecules of the dissolved substance diffuse into the substance in the half-space $x>0$. The phenomenon can be treated by the following differential equation:

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2} \tag{1}$$

where $D$ is the diffusion coefficient. The well known solution of the equation for $t>0$ and $x>0$, with given initial conditions $c=c_0$ for $x<0$ and $c=0$ for $x>0$ is:

$$c(x, t) = \frac{c_0}{2}\left\{1 - \Phi\left(\frac{x}{2\sqrt{Dt}}\right)\right\} \tag{2}$$

where $\Phi$ is the error integral defined by the equation

$$\Phi(y) = \frac{2}{\sqrt{\pi}}\int_0^y e^{-t^2}\,dt. \tag{3}$$

The process of diffusion is interrupted at a time moment $t>0$, by removing the solution in half-space $x<0$. Then the concentration distribution for $x>0$ is given by (2). Let the concentration of the radioactive substance be designed by $c$. If $\mu$ is the absorption coefficient of the homogeneous substance, its activity measured on the surface $x=0$ will be

$$N_0 = \alpha \int_0^\infty c(\xi, t) e^{-\mu\xi}\, d\xi. \tag{4}$$

Here the factor $\alpha$ depends on the finite dimensione of the surface $x=0$ and on the relatively small time of measuring compared to $t$. After removing a layer $(0, x)$, the activity measured at the new surface $x>0$ is given by

$$N(x) = \alpha \int_x^\infty c(\xi, t) e^{-\mu(\xi - x)}\, d\xi = \alpha \frac{c_0}{2} e^{\mu x} \int_x^\infty \left\{1 - \Phi\left(\frac{\xi}{2d}\right)\right\} e^{-\mu\xi}\, d\xi; \tag{5}$$

wherein the notation

$$d = \sqrt{Dt} \tag{6}$$

is introduced. The result of the integration of (5) is:

$$N(x) = \frac{A}{\mu}\left\{1 - \Phi\left(\frac{x}{2d}\right) - e^{\mu^2 d^2 + \mu x}\left[1 - \Phi\left(\frac{x}{2d} + \mu d\right)\right]\right\} \tag{7}$$

where $A = \alpha c_o/2$. $N(x)$ can be measured by grinding off layers of different thickness $(0, x)$. The characteristic $d$ or $D$ cannot be expressed from (7) in explicite form. Besides, due to causes inherent in the method of measurement, $N(0) = N_o$ is uncertain, therefore (4) also yields uncertain values for $\alpha$. The required result can be obtained from (7) and the measured $N(x)$ in the following way. In the case of a given $\mu$ we can write the following function

$$\frac{N(x_1)}{N(x_2)} = f(x_1, x_2, d) \tag{8}$$

which, at fixed $x_1$ and $x_2$ depends only on $d$, thus it can be plotted. (8) is a monotonous function of $d$. We read $N(x_1)$ and $N(x_2)$ from $N(x)$ determined by measurements. Their quotient gives $f(x_1, x_2, d)$ thus $d$ can be read from the curve and $D$ is given by (6).

In case of substances interesting for practice $\mu = 2.124$. In carrying out the measurements $x_1 = 0{,}001$, $x_2 = 0.002$ and $x_3 = 0.003$ cm, respectively. The values of $f(x_1, x_2, d)$ and $f(x_2, x_3, d)$ in the range from $d = 0.01$ to 0.00063 are listed in Table I.

*Table I*

| $d$ | $f(x_1, x_2, d)$ | $f(x_2, x_3, d)$ |
|---|---|---|
| 0.01 | 1.096 | 1.101 |
| 0.008 | 1.124 | 1.129 |
| 0.0063 | 1.162 | 1.172 |
| 0.005 | 1.213 | 1.231 |
| 0.004 | 1.280 | 1.307 |
| 0.0032 | 1.376 | 1.422 |
| 0.0025 | 1.525 | 1.623 |
| 0.002 | 1.735 | 1.913 |
| 0.0016 | 2.071 | 2.404 |
| 0.00125 | 2.748 | 3.443 |
| 0.001 | 4.021 | 5.771 |
| 0.0008 | 6.407 | 12.491 |
| 0.00063 | 14.936 | 43.670 |

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## ОПРЕДЕЛЕНИЕ ДИФФУЗИОННОГО КОЭФФИЦИЕНТА В СЛОЕ ЛАКА РАДИОАКТИВНЫМ ВЕЩЕСТВОМ

*Ф. Й. Гилде*

Автором дается метод вычисления диффузионного коэффициента применяя к методу измерения важному для употребления в практике. Метод основан на точном решении дифференциального уравнения диффузии относительно вещества заполняющего полупространство. Диффузионный коэффициент получается графическим методом.

# DETERMINATION OF THE WAVE FUNCTION CORRESPONDING TO A REMOVED ELECTRON

By

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*(Received May 1, 1971)*

Using the methods of second quantization a formula for determining the wave function of an electron removed from an $n$-electron system can be derived by variation method.

Let us consider a k-electron system with the Hamiltonian

$$H^{(k)} = \sum_{i=1}^{k} h(x_i) + \frac{1}{2} \sum_{i,j}{}' v(x_i, x_j) \tag{1}$$

where $x$ is an abbreviated notation for the space and spin variables. Let $\Phi^{(n)}(x_1, \ldots, x_n)$ be the wave function of the n-electron system in ground state:

$$H^{(n)} \Phi^{(n)} = E_0^{(n)} \Phi^{(n)}. \tag{2}$$

Operator $a_{n-1,n}[\chi]$ defined by

$$a_{n-1,n}[\chi] \Phi^{(n)} = \sqrt{n} \int dx_n \chi^*(x_n) \Phi^{(n)}_{(x_1, \ldots, x_{n-1}, x_n)} \equiv \Phi^{(n-1)}_{(x_1, \ldots, x_{n-1})} \tag{3}$$

is usually interpreted [1] as an operator removing an electron with the square integrable wave function $\chi(x)$ from the n-electron system described by the wave function $\Phi^{(n)}(x_1, \ldots, x_n)$.

The problem is to find the function $\chi_0(x)$ such that the function $\Phi^{(n-1)}$ defined by Eq. (3) be the best possible approximation of the ground state of the $n-1$-electron system.

Let us introduce the functional

$$E[\chi] = \frac{(\Phi^{(n-1)}, H^{(n-1)} \Phi^{(n-1)})}{(\Phi^{(n-1)}, \Phi^{(n-1)})}. \tag{4}$$

According to the variation principle, the best approximation of ground state energy $E_o^{(n-1)}$ of the $n-1$ electron system which can be found by varying the function $\chi(x)$ is just the minimum value of the functional $E[\chi]$. In this way Eq. (4) can serve to determine the function $\chi_0(x)$ by variation method.

We can write Eq. (4) in a simpler form. Let $\boldsymbol{\Phi}$ denote an element of the Fock-space [1], and let us assume that except its $n^{\text{th}}$ component $\Phi^{(n)}(x_1, \ldots, x_n)$ all the other components vanish. Introducing the operators in the Fock space [1] $\mathbf{a}[\chi]$,

$\psi(x)$ and $\psi^*(x)$, supposing that the operator $v(x, y)=v(y, x)$ is independent of the momentum operator, one can find:

$$E[\chi]-E_0^{(n)} = -\frac{\int dx\, dy\, \chi^*(y)\left[h(y)\mu(y; x)+\int dz\, v(y, z)\sigma(z, y; z, x)\right]\chi(x)}{\int dx\, dy\, \chi^*(y)\mu(y; x)\chi(x)} \tag{5}$$

where $\mu$ and $\sigma$ are tehe first-and second-order density matrices, respectively, [2, 3]:

$$\mu(y; y') = (\Phi, \Psi^+(y')\Psi(y)\Phi) = n\int dx_1 \ldots dx_{n-1}\Phi^{(n)*}_{(x_1, \ldots, x_{n-1}, y')}\Phi^{(n)}_{(x_1, \ldots, x_{n-1}, y)},$$

$$\sigma(z, y; z', y') = \left(\Phi, \Psi^+(y')\Psi^+(z')\Psi(z)\Psi(y)\Phi\right) =$$

$$= n(n-1)\int dx_1 \ldots dx_{n-2}\,\Phi^{(n)*}_{(x_1, \ldots, x_{n-2}, z', y')}\,\Phi^{(n)}_{(x_1, \ldots, x_{n-2}, z, y)}.$$

In the particular case of function $\Phi^{(n)}$

$$\Phi^{(n)}_{(x_1, \ldots, x_n)} = \sqrt{n!}\, A_n\{\varphi_1(x_1) \ldots \varphi_n(x_n)\} \tag{6}$$

where $A_n$ denotes the antisymmetrizer

$$\mu(y; y') = \sum_{i=1}^{n}\varphi_i(y)\varphi_i^*(y'),$$

$$\sigma(z, y; z', y') = \mu(z; z')\mu(y; y') - \mu(z; y')\mu(y; z').$$

are obtained [3]. Function (6) can be used as approximate ground state wave function of the n-electron system if the functions $\varphi_i(x)$ $(i=1, 2, \ldots, n)$ are the Hartree-Fock orbitals:

$$\left\{h(y)+\sum_{j=1}^{n}\int dz\, \varphi_j^*(z)v(z, y)\,[1-P_{ij}]\varphi_j(z)\right\}\varphi_i(y) = \varepsilon_i\varphi_i(y)$$

where $P_{ij}\varphi_j(z)\varphi_i(y)=\varphi_i(z)\varphi_j(y)$. In this approximation

$$E[\chi] = E_0^{(n)} - \frac{\sum_{i=1}^{n}|\lambda_i|^2\varepsilon_i}{\sum_{i=1}^{n}|\lambda_i|^2}, \quad \lambda_i \equiv \int dx\, \varphi_i^*(x)\chi(x),$$

i. e. the minimum of $E[\chi]$ obtained by varying the function $\chi(x)$ is given by $E_0^{(n)}-\varepsilon_n$, where it is supposed that $\varepsilon_n = \max \varepsilon_i$. The corresponding function is: $\chi_0(x)=\varphi_n(x)$ According to (3), the ground state wave function of the $n-1$ electron system in this approximation is:

$$\Phi^{(n-1)}_{(x_1, \ldots, x_{n-1})} = \sqrt{(n-1)!}\, A_{n-1}\{\varphi_1(x_1) \ldots \varphi_{n-1}(x_{n-1})\}$$

In this case value $E[\chi_0]-E_0^{(n)}$ is connected with the ionization energy [4] and the same can be expected in the general case, too.

It is known, that the natural spin orbitals of a function of the type (6) are just the functions $\varphi_i(x)$, thus in such cases the function $\chi_0(x)$ determined from (5) is one of the natural spin orbitals; in this way $\chi_0(x)$ can be expected in general to be an approximation of a natural spin orbital. Numerical calculations for Li and $Be^+$, with the aim of supporting these conclusions, are in course.

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## ОПРЕДЕЛЕНИЕ ВОЛНОВОЙ ФУНКЦИИ УНИЧТОЖЕННОГО ЭЛЕКТРОНА

*И. К. Дьемант*

Применением метода второй квантизации описывается формула, с помощью которой вычисляется волновая функсия электрона, уничтоженного из системы электронов.

# DEPENDENCE ON VISCOSITY OF THE DECAY TIME OF LUMINESCENCE IN VISCOUS DYE SOLUTIONS

By

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*(Received July 15, 1971)*

The fluorescence decay time $\tau$ is brought into connection with the volume ($v$) of the Frenkel holes characteristic for the solvent. According to our measurements $1/\tau$ is a linear function of $v$ both for fluorescein of $10^{-4}$ M concentration in water-glycerol mixture and for rhodamine 6G of $10^{-4}$ M concentration in alcohol-glycerol mixture.

According to our earlier investigations [1—2], the decay time of luminescence resulted to be dependent on the viscosity of the solution both in the case of fluorescein of $10^{-4}$ M concentration in water-glycerol mixture containing 1 per cent NaOH and rhodamine 6G of $10^{-4}$ M concentration in ethanol-glycerol mixture with $10^{-2}$ M $CH_3COOH$. The true decay time of luminescence [3] was determined at 303 °K [1] with the phase fluorometer and the method desscribed in [2] eliminating the tedious calculations for correction.

To obtain further information on the dependence of the decay time on viscosity, Frenkel's parameters [4] $U$ (activation energy for the formation of the holes) and $r$ (radius of the holes) were determined for sets of different glycerol content of both solvents mentioned above. We measured the viscosity of the mixtures as a function of temperature and their surface tension at 303 °K. From the temperature dependence of the viscosity the activation energy $U$, then, knowing $U$ and the surface tension, the radius $r$ can be determined [5]. The measurements were made at normal atmospheric pressure. Our results are listed in Table I.

*Table I*

| $10^{-4}$ M fluorescein in water-glycerol | | | $10^{-4}$ M rhodamine 6G in ethanol-glycerol | | |
|---|---|---|---|---|---|
| $\mu$ | $1/\tau$ (1/nsec) | $r^3 \cdot 10^{24}$ (cm$^3$) | $\mu$ | $1/\tau$ (1/nsec) | $r^3 \cdot 10^{24}$ (cm$^3$) |
| 0.00 | 0.286 | 5.8 | 0.0 | 0.172 | 36 |
| 0.04 | 0.287 | 7.0 | 0.1 | 0.183 | 39 |
| 0.12 | 0.282 | 11 | 0.2 | 0.185 | 42 |
| 0.21 | 0.316 | 14 | 0.3 | 0.188 | 44 |
| 0.22 | 0.316 | 15 | 0.4 | 0.176 | 46 |
| 0.34 | 0.307 | 21 | 0.5 | 0.177 | 46 |
| 0.49 | 0.320 | 27 | 0.6 | 0.187 | 47 |
| 0.66 | 0.330 | 36 | 0.7 | 0.179 | 48 |
| 0.96 | 0.342 | 48 | 0.8 | 0.182 | 48 |
| | | | 0.9 | 0.184 | 49 |
| | | | 1.0 | 0.187 | 49 |

$\mu$ = molar ratio of glycerol in the solvent

The common characteristic of the theories dealing with probability of spontaneous transition in luminescence

[6—10] is that all of them contain the so-called absorption integral and some function of the refractive index of the solution. Both the absorption integral and the refractive index being mostly dependent on viscosity, these theories give the possibility to clear up the dependence of the lifetime of lunescence on viscosity. This would lead to a phenomenologic description of the phenomenon. We tried, however, to approach the problem from another side, namely from the point of view of one of the models concerning the structure of liquids, the so called Frenkel's model.

Our conception concerning the explanation of this experimental dependence is exposed in the following. Let us examine which of Frenkel's parameters could be used to characterise the fluctuations of pressure ($\Delta p$) taking place in the envi-

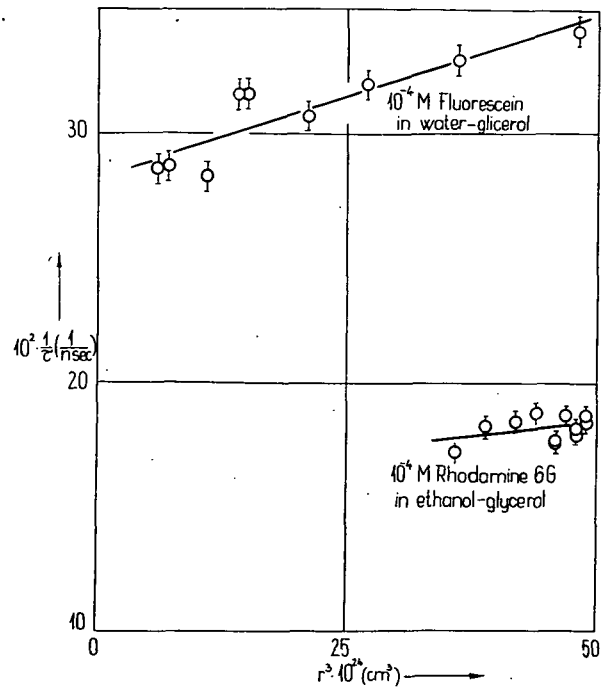


*Fig. 1*

ronment of the molecule capable of luminescence. The lifetime ($\tau^*$) of the holes does not seem to be suitable, being the life-time of a settled and static state. Surely there exist identical fluctuations of pressure having different „lifetime". The activation energy $U$ is the measure of the fluctuation of energy. At constant temperature and external pressure the macroscopic volume of the liquid does not change, and so the hole of volume $v$ formed in the liquid can only be produced on account of local increases in pressure. We suppose that the absolute value of the fluctuation of pressure is linearly proportional to the volume of the hole, i. e. $|\Delta p| \sim v$.

The probability of spontaneous transitions in luminescence is determined by fluctuation phenomena which partly occur inside of the molecule capable of luminescence and thus exist also in absence of external fields, and partly are brought about by the action of possibly present external fields. Let us suppose that the fluctuation inside the molecule originating from changes in the external field is linearly proportional to the fluctuation of pressure mentioned above. Then, approximately,

$$\frac{1}{\tau_e} = \frac{1}{\tau_0} + \text{const} \cdot r^3$$

where $1/\tau_0$ is the probability of spontaneous emission taking place also in absence of external field, $r$ the radius of the hole considered as of spherical form, $\tau_e$ the so called natural decay time of luminescence, which in the case of our measurements differs only in a constant factor from the true decay time $\tau$ obtained by measurements.

Plotting $1/\tau$ as a function of $r^3$ in both solutions according to data of Table I, Fig. 1 is obtained.

It can be seen that the relation between $1/\tau$ and $r^3$ can be approximated by a straight line within the errors of measurements for both sets of solutions. This means that there exists a linear relation between the probability of spontaneous transition $1/\tau$ and the fluctuation of pressure in the solution.

* * *

The authors are indebted to sincere thanks to Prof. I. KETSKEMÉTY, Director of the Institute of Experimental Physics, for valuable discussion and suggestions during the measurements.

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## ЗАВИСИМОСТЬ ВРЕМЕНИ ЗАТУХАНИЯ ЛЮМИНЕСЦЕНЦИИ ВЯЗКИХ РАСТВОРОВ КРАСИТЕЛЕЙ ОТ ВЯЗКОСТИ

*Л. Визе и Л. Гати*

Устанавливается связь между временем затухания $\tau$ и обьемом $v$ дырки Френкеля, характерного для растворителя. По нашим экспериментальным данным значения $1/\tau$ в зависимости от $v$ оказывается линеарным для смеси флуоресцеина ($10^{-4}$ моль/л) воды и глицерина, и родамина 6Ж ($10^{-4}$ моль/л) спирта и глицерина.

# INFLUENCE OF THE TEMPERATURE ON THE LOCAL TEMPERATURE OF EXCITED MOLECULES IN DYE-DETERGENT SYSTEMS

By

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*(Received June 20, 1971)*

The dependence of the local temperature of excited molecules on detergent concentration (from $2 \cdot 10^{-3}$ to $8 \cdot 10^{-3}$ M/l) and on the experimental temperature (from 298 to 343 °K) was investigated. The observed appearence of a minimum in the local temperature near the c. m. c. is explained by the dependence of the absorption and fluorescence on the concentration of detergent. A relation between local temperature and fluorescence yield of the luminescent substances was also determined.

## *Introduction*

A relation between the absorption and the fluorescence spectra of luminescent solutions found by MERRIT [1] could not be experimentally verified due to early apparata. Recently STEPANOV [2] derived an universal relation between these spectra:

$$\frac{f_e(\nu)}{k(\nu)} = D(T)\nu^3 \exp(-h\nu/kT), \tag{1}$$

where $f_e(\nu)$ and $k(\nu)$ denote the fluorescence and the absorption spectra, respectively, $D(T)$ — a constant independent of $\nu$, $T$ — the absolute temperature, $h$ and $k$ — Planck's and Boltzmann's constants.

In order to establish the validity of Eq. (1) ALENTSEV [3] suggested to re-write it in the form:

$$F(\nu) \equiv \lg f_e(\nu) - \lg k(\nu) - 3 \lg \nu = -h\nu/kT + \text{const.} \tag{2}$$

$F(\nu)$ is a linear function of the frequency $\nu$, (or the wave number $\bar{\nu}$) and from the slope of the straight $T$ can be calculated. Usually a local temperature ($T^*$) higher than the experimental temperature ($T$) can be obtained from the slope. This local temperature is due to the non-dissipation of excess energy of excitation during the vibrational relaxation. This statement is verified theoretically by JABLONSKI [13] and is supported by several experimental results ([3], [5], [9] and [14]).

The validity of the relation was investigated by several authors [4]—[6] and it was established for gases, solutions and solid luminescent systems. For chlorophylls the problem was first studied by KRAVTSOV [7]. Systematical investigations on the influence of solvents on the local temperature were carried out by SINGHAL and HEVESI [8]. In [9] the applicability of the relation to solutions of different chloro-

phyll derivatives; pheophytin-a and chlorin-$e_6$ was studied. RABINOWITCH *et al.* [10] and DAS *et al.* [11] applied the Stepanov's relation and its modified form given by KETSKEMÉTY *et al.* [12] to suspensions of photosynthetizing algae.

In this paper the applicability of Stepanov's relation to dye-detergent solutions is studied and the dependence of the local temperature on the detergent concentration modifying the structure of the system and on the ambient temperature is investigated.

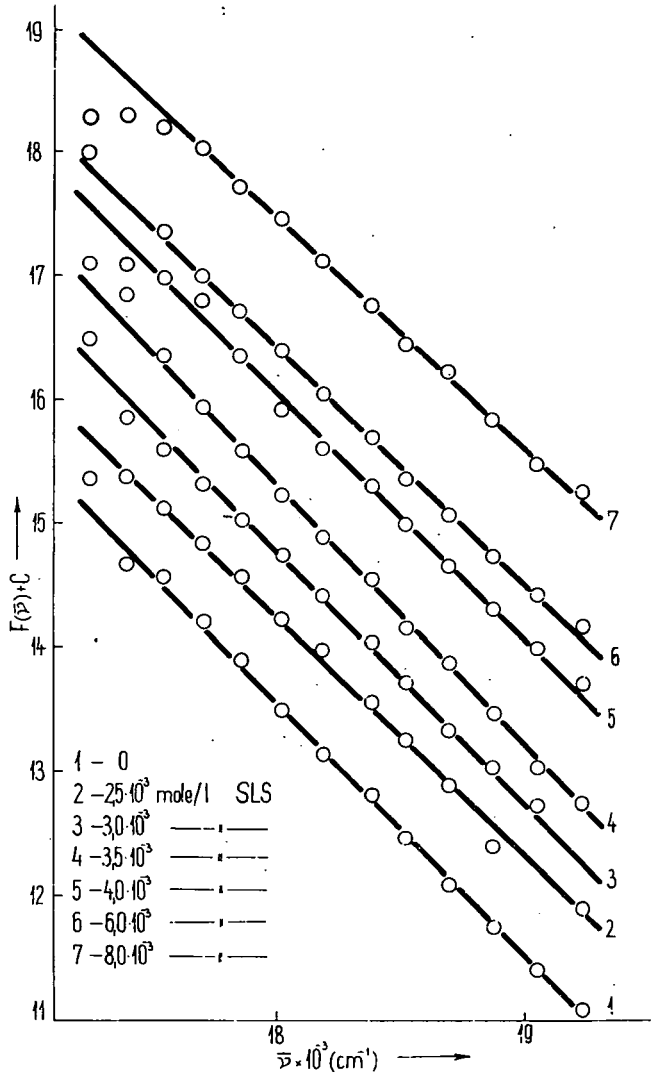


*Fig. 1.* The Stepanov's straights for aqueous solutions of $5\times10^{-6}$ M Rhod 6G at different concentrations of SLS.

*Results and Discussion*

The substances studied, also the experimental methods, the composition of the systems were discussed earlier in [15—18]. In this paper only those data are given which were not discussed in the earlier papers.

In Fig. 1 the straights from Eq. (2) for aqueous solutions of $5\times10^{-6}$ M/l rhodamine 6G (Rhod. 6G) with different concentrations of sodium lauryl-sulphate (SLS) are shown. The linearity of the function $F(\nu)$ from Eq. (2) is well fulfilled in a wide range of the spectra. A similar picture was found for all the other dye-detergent systems unambiguously proving that Stepanov's relation is valid for dye-detergent systems, too. The deviation from the linearity at lower frequencies are explained in [12].

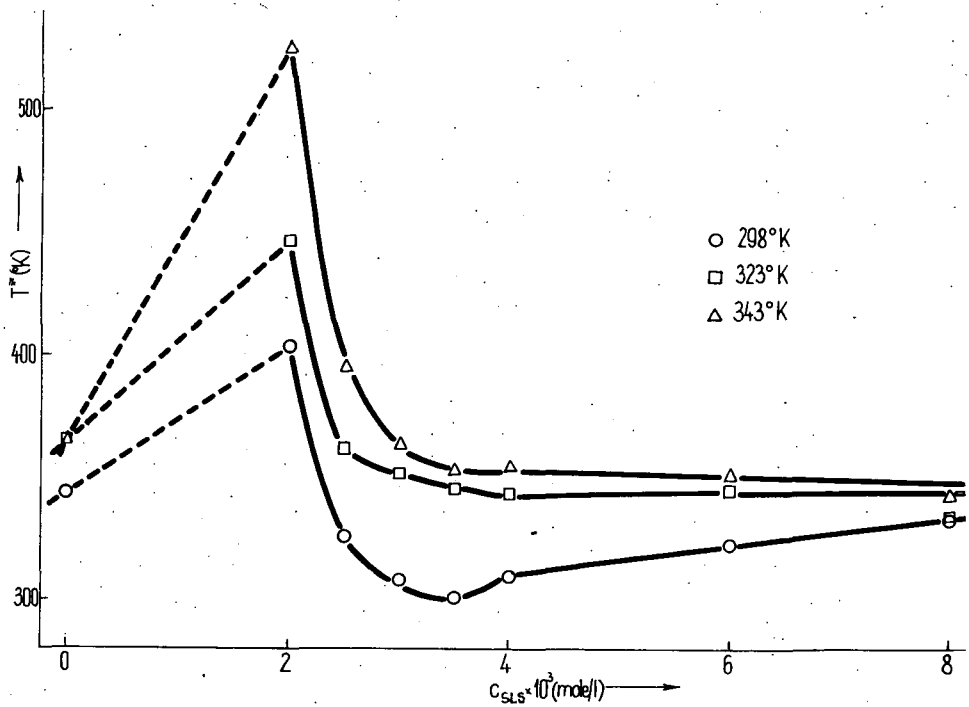


*Fig. 2.* The local temperatures, $T^*$ in Rhod 6G solutions as a function of the detergent concentration and the temperature

The local temperatures $T^*$ in solutions of Rhod 6G as a function of the concentration of detergent and the temperature are given in Fig. 2. $T^*$ shows a maximum at $2\times10^{-3}$ M/l detergent content and a minimum near the critical micelle concentration (c. m. c.), while it is constant or slightly increasing at higher detergent concentrations. Figure shows that $T^*$ depends also on the experimental temperature. The local temperatures for $2\times10^{-3}$ M/l detergent concentration are essentially higher than the experimental temperature. This can be explained by consulting

Table I, where the maximum absorption coefficients, $k(\lambda)_{max}$, from [18] and the relative fluorescence intensities, $I_{rel}$, from [17], as well as the calculated values of local temperatures, $T^*$, are tabulated for different detergent concentrations and experimental temperatures. While $k(\lambda)_{max}$ of detergent solutions shows a decrease of 16% compared to that of the pure aqueous solution at 298°K and 343°K, $I_{rel}$ is as low as 4% and 7%, respectively. This formally explains the high values of $T^*$. In addition, $I_{rel}$ practically does not change at concentrations above the c. m. c., which explains the constancy of $T^*$ in this concentration range.

*Table I*

*The maximum absorption coefficients, $k(\lambda)_{max}$, relative fluorescence intensities, $I_{rel}$, and the local temperatures, $T^*$, of Rhod 6G with $5 \cdot 10^{-6}$ M concentration at different temperatures and different detergent concentrations*

| $C_{SLS} \cdot 10^3$ (M/l) | 298°K | | | 323°K | | | 343°K | | |
|---|---|---|---|---|---|---|---|---|---|
| | $k(\lambda)_{max}$ | $I_{rel}$ (%) | $T^*$ (°K) | $k(\lambda)_{max}$ | $I_{rel}$ (%) | $T^*$ (°K) | $k(\lambda)_{max}$ | $I_{rel}$ (%) | $T^*$ (°K) |
| 0 | 0.89 | 100 | 343.5 | 0.84 | 100 | 365.5 | 0.79 | 100 | 365.5 |
| 2.0 | 0.75 | 4.08 | 403.3 | 0.80 | 11.1 | 446.5 | 0.67 | 7.19 | 525.3 |
| 2.5 | 0.79 | 15.6 | 325.6 | 0.79 | 21.9 | 361.4 | 0.76 | 17.9 | 395.6 |
| 3.0 | 0.84 | 33.3 | 307.9 | 0.81 | 40.0 | 351.2 | 0.75 | 25.7 | 363.4 |
| 3.5 | 0.88 | 86.7 | 300.6 | 0.85 | 54.5 | 345.4 | 0.79 | 48.7 | 353.2 |
| 4.0 | 0.92 | 91.9 | 309.5 | 0.84 | 70.9 | 343.5 | 0.78 | 55.8 | 355.2 |
| 6.0 | 0.94 | 90.4 | 322.3 | 0.88 | 77.5 | 345.4 | 0.83 | 72.0 | 351.2 |
| 8.0 | 0.94 | 80.5 | 332.5 | 0.89 | 79.7 | 334.3 | 0.83 | 80.5 | 343.5 |

In Fig. 3 the dependence of $k(\lambda)_{max}$, $I_{rel}$ and $T^*$ is shown for thionin (Th) solutions of $5 \times 10^{-6}$ M/l on the concentration of detergent at experimental temperatures of 298°K, 323°K and 343°K. The change of $T^*$, at least up to the c. m. c., is similar as that for Rhod 6G, though the absolute values are somewhat less. The

*Table II*

*The maximum absorption coefficients, $k(\lambda)_{max}$, relative fluorescence intensities, $I_{rel}$, and the local temperatures, $T^*$, of Th with $5 \cdot 10^{-6}$ M concentration at different temperatures and different detergent concentrations*

| $C_{SLS} \cdot 10^3$ (M/l) | 298°K | | | 323°K | | | 343°K | | |
|---|---|---|---|---|---|---|---|---|---|
| | $k(\lambda)_{max}$ | $I_{rel}$ (%) | $T^*$ (°K) | $k(\lambda)_{max}$ | $I_{rel}$ (%) | $T^*$ (°K) | $k(\lambda)_{max}$ | $I_{rel}$ (%) | $T^*$ (°K) |
| 0 | 0.22 | 100 | 345.4 | 0.23 | 100 | 351.2 | 0.24 | 100 | 374.3 |
| 2.0 | 0.09 | 7.0 | 378.9 | 0.17 | 13.2 | 397.0 | 0.21 | 33.5 | 416.8 |
| 2.5 | 0.19 | 13.5 | 359.3 | 0.22 | 17.8 | 378.9 | 0.23 | 38.6 | 393.2 |
| 3.0 | 0.25 | 23.1 | 355.2 | 0.24 | 31.1 | 374.3 | 0.24 | 39.1 | 378.9 |
| 3.5 | 0.27 | 39.0 | 344.5 | 0.25 | 45.9 | 365.6 | 0.25 | 51.3 | 374.3 |
| 4.0 | 0.28 | 99.4 | 357.3 | 0.26 | 81.9 | 365.6 | 0.25 | 64.0 | 378.9 |
| 6.0 | 0.29 | 159.6 | 367.7 | 0.27 | 141.6 | 378.9 | 0.25 | 129.0 | 395.2 |
| 8.0 | 0.28 | 177.8 | 374.3 | 0.27 | 152.3 | 388.3 | 0.25 | 141.0 | 395.7 |

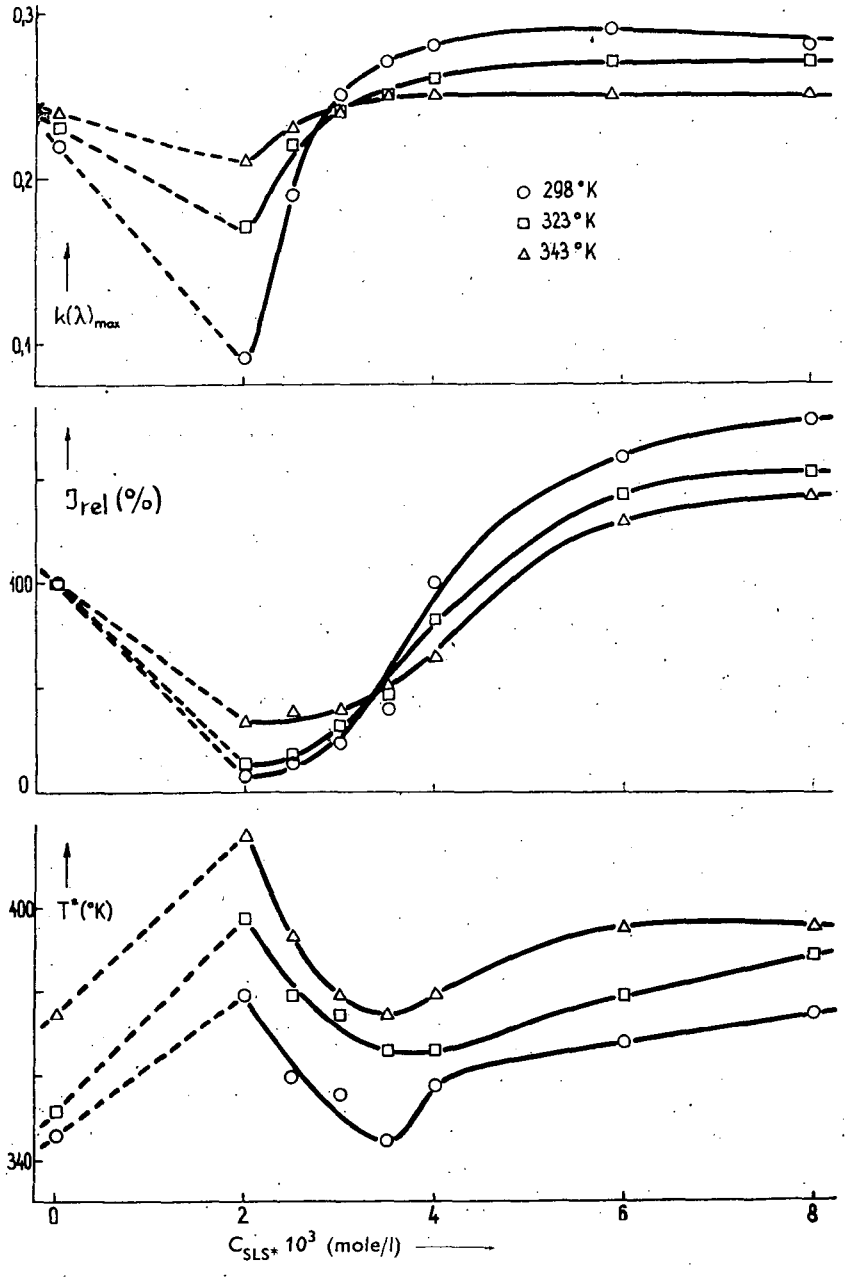


*Fig. 3.* The values of $k(\lambda)_{max}$, $I_{rel}$ and $T^*$ of Th solutions with $5\times10^{-6}$ M concentration at different temperatures and at different detergent concentrations.

numerical values of the quantities mentioned above, taken from [17, 18], are listed in Table II. While for $2\times10^{-3}$ M/l detergent solution, at $T=298$ °K, the value of $k(\lambda)_{max}$ is about 40% of that in pure aqueous Th solutions, $I_{rel}$ is only 7%. Consequently, the excess of the exciting energy results in a relative high local temperature, $T^*=378.9$ °K, exceeding the experimental temperature by 81 degrees. In the same system at 323 and 343 °K the value of $k(\lambda)_{max}$ is lowered by about 10% compared to $k(\lambda)_{max}$ of the pure aqueous solution, while the values of $I_{rel}$ for these are only 13% and 33%, respectively. This again should result in higher local temperatures. In fact, the values of $T^*$ are higher by 74 degrees than the experimental temperatures.

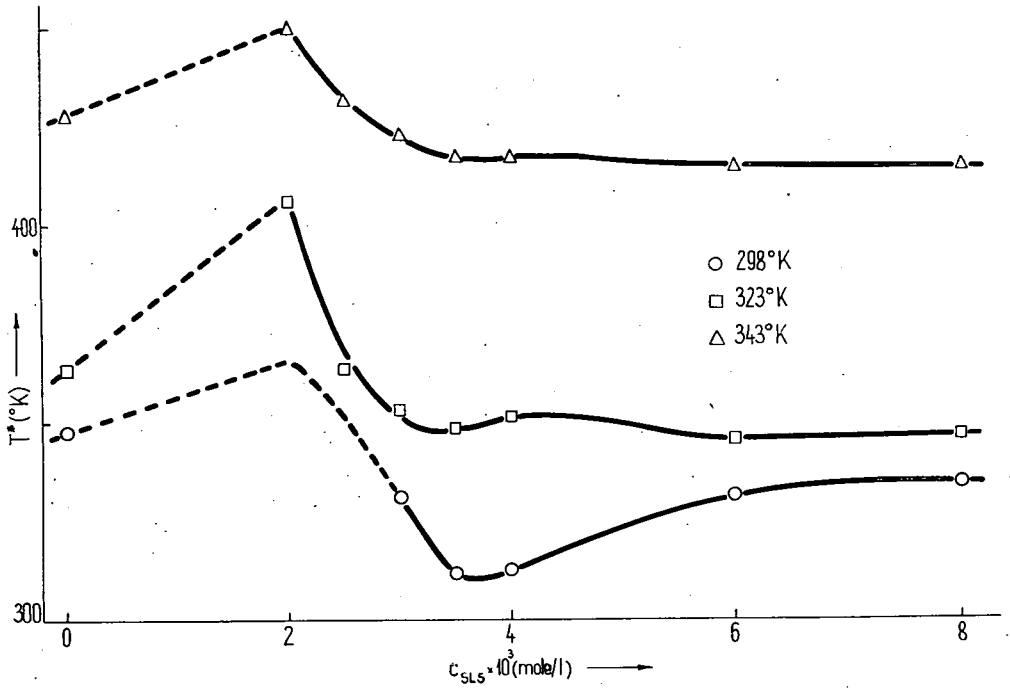


*Fig. 4.* The local temperatures, $T^*$ in MB solutions *versus* detergent concentration at different temperatures

Fig. 4 shows the values of $T^*$ *versus* detergent concentration for methylene blue (MB) solutions of $5\times10^{-6}$ M/l at three experimental temperatures. It is to be mentioned that the fluorescence yield of MB solutions at 298°K is very low and the fluorescence is practically totally quenched at low detergent concentrations ([16], [19]), therefore experimental results for calculation of $T^*$ at this temperature and concentrations were not available. As it can be seen from Fig. 4 the dependence of $T^*$ on the concentration of detergent is not so expressed as in the case of the other dyes investigated. This can be understood by considering the absorption of the system showing similar changes. In Table III $k(\lambda)_{max}$ and $I_{rel}$ are taken from [16] and the calculated values of $T^*$ are given. While for $2\times10^{-3}$ M/l detergent solution at

*Table III*

*The maximum absorption coefficients, $k(\lambda)_{max}$, relative fluorescence intensities, $I_{rel}$, and the local temperatures, $T^*$, of MB with $5 \cdot 10^{-6}$ M concentration at different temperatures and different detergent concentrations*

| $C_{SLS} \cdot 10^3$ (M/l) | 298 °K | | | 323 °K | | | 343 °K | | |
|---|---|---|---|---|---|---|---|---|---|
| | $k(\lambda)_{max}$ | $I_{rel}$ (%) | $T^*$ (°K) | $k(\lambda)_{max}$ | $I_{rel}$ (%) | $T^*$ (°K) | $k(\lambda)_{max}$ | $I_{rel}$ (%) | $T^*$ (°K) |
| 0 | 0.76 | 100 | 347.3 | 0.75 | 100 | 363.5 | 0.74 | 100 | 428.2 |
| 2.0 | 0.48 | 7.1 | — | 0.63 | 36.1 | 406.0 | 0.68 | 27.3 | 449.8 |
| 2.5 | 0.56 | 29.3 | — | 0.72 | 56.0 | 363.3 | 0.70 | 49.5 | 431.1 |
| 3.0 | 0.73 | 80.6 | 330.7 | 0.77 | 94.2 | 353.2 | 0.76 | 73.2 | 422.4 |
| 3.5 | 0.86 | 167.7 | 311.8 | 0.83 | 149.3 | 348.3 | 0.79 | 115.6 | 416.8 |
| 4.0 | 0.94 | 257.6 | 312.6 | 0.87 | 192.8 | 351.1 | 0.83 | 157.0 | 416.8 |
| 6.0 | 0.95 | 348.6 | 330.8 | 0.92 | 271.2 | 345.4 | 0.89 | 281.3 | 414.0 |
| 8.0 | 0.96 | 371.4 | 334.3 | 0.94 | 277.6 | 346.4 | 0.92 | 331.0 | 414.0 |

343 °K the value of $k(\lambda)_{max}$ is 92% of that of pure aqueous solution the value of $I_{rel}$ is only 27%. This accounts for the high local temperature exceeding the experimental temperature by 107 degrees.

The appearance of minimum of $T^*$ at detergent concentration near to the c. m. c. can be explained by the appearance of an optimum of the ratio of the emitted and the absorbed energies at this detergent concentration. Thus, only a small amount of the exciting energy remains in the system, consequently, the local temperature is low. At detergent concentrations above the c. m. c. the increase in $I_{rel}$ is slightly greater than that in $k(\lambda)_{max}$, therefore the local temperature is fairly constant, or shows a slow increase.

According to earlier publications [20—22] the decrease of fluorescence yield results in an increase in the local temperature. Similar results were found earlier for dye-detergent systems, too [9]. The differences between the local and the experimental temperatures, $\Delta T (\equiv T^* - T)$, for Rhod 6G, Th and MB solutions are given in Table IV. for different detergent concentrations at 343 °K. It can be seen that $\Delta T$ is the lowest for Rhod 6G and the highest for MB. This is in correlation with the fluorescence yield being 1; 0,3 and 0,15 for aqueous solutions of Rhod 6G, Th and MB, respectively [17, 19]. These values differ somewhat for higher temperatures but the difference can be neglected. The changes in the fluorescence yield due to changes in detergent concentration were nearly identical for the three dyes considered, thus the connection between the local temperature and the fluorescence yield is about the same for higher temperatures, as illustrated by the data of Table IV.

*Table IV*

*The differences between the local and the experimental temperatures, $\Delta T (\equiv T^* - T)$, for Rhod 6G, Th and MB solutions at different detergent concentrations and at $T = 343$ °K.*

| $C_{SLS} \cdot 10^3$ (M/l) | $\Delta T$ (°K) | | |
|---|---|---|---|
| | Rhod 6G | Th | MB |
| 0 | 22,5 | 31.3 | 85.2 |
| 2.0 | 182.3 | 73.8 | 106.8 |
| 2.5 | 52.6 | 50.2 | 88.1 |
| 3.0 | 20.4 | 35.9 | 79.4 |
| 3.5 | 10.2 | 31.3 | 73.8 |
| 4.0 | 12.2 | 35.9 | 73.8 |
| 6.0 | 8.2 | 52.2 | 71.0 |
| 8.0 | 0.05 | 52.7 | 71.0 |

The results presented prove that the Stepanov-relation is fulfilled for dye-detergent solutions; the local temperature $T^*$ is higher than the experimental temperature for all systems examined. The dependence of $T^*$ on the concentration of detergent and on the experimental temperature is in close correlation with the changes in absorption and fluorescence. A similar close connection between the fluorescence yield and the local temperature of the excited molecules exists in detergent solutions, too.

The authors are indebted to Professor Dr. L. SZALAY, Director of Institute of Biophysics, for helpful discussions in the course of this work.

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## ВЛИЯНИЕ ТЕМПЕРАТУРЫ НА ЭФФЕКТИВНУЮ ТЕМПЕРАТУРЫ ВОЗБУЖДЕННЫХ МОЛЕКУЛ КРАСИТЕЛЕЙ В РАСТВОРАХ ДЕТЕРГЕНТА

*Э. Балинт, Я. Хевеши, и Э. Лехоцки*

В настоящей работе исследовалось влияние температуры и концентрации детергента на эффективную температуры возбужденных флуоресцирующих молекул. Установили, что эффективная температура во всех исследованных случаях имеет минимальное значение при критической концентрации мицелобразования детергента. Это явление хорошо объясняется абсорбционными и люминесцентными свойствами краситель-детергент систем. Удалось установить связь между эффективной температурой возбужденных молекул и выходом люминесценции красителей.

# THE DEPENDENCE OF ABSORPTION AND FLUORESCENCE OF DYE-DETERGENT MICELLE SYSTEMS ON THE DYE CONCENTRATION

By

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*(Received June 1, 1971)*

The shape of the absorption spectra is found to be changed by the increase of concentration of donor dye. At higher concentrations a band at 640 nm belonging to the form of higher dye-aggregates can be observed. In presence of detergent a new band at 465 nm appears, which can be attributed to the formation of water-insoluble complex salts. The local temperature of the excited molecules was found to decrease with increasing dye concentration.

## *Introduction*

The migration of electron excitation energy from thionine (Th) to methylene blue (MB) in micelles was studied in [1]. It was shown, that the position of the main absorption bands of these dyes permits energy transfer from Th to MB, but not *vice versa*. The investigations reported in [2] showed that the yield of transfer is optimal at equivalent concentrations of Th and MB for the critical micelle concentration (c. m. c.) of the detergent. It was also shown that a very small amount of the detergent strongly bleaches the solution, i. e. decreases the value of $k(\lambda)_{max}$, the maximum of the absorption coefficient.

From a study of the influence of temperature on the structure of dye-detergent systems [3] it was obtained that the efficiency of transfer from Th to MB is the highest at c. m. c. and at a temperature of 25°C. It was also found [4] that the increase of temperature shifts the c. m. c. towards higher detergent concentrations and promotes the dissociation of the water-insoluble complex salts and dimers. From these results we concluded that the solubilization of complex salts and dimers contributes to the increase of the effectivity of the energy migration in mixed dye solutions.

The influence of the temperature on the energy migration was studied also in [5]. It was shown that the effectivity of the energy migration is in a very close connection with the number of the micelles present in the system and with the structure of the dye-detergent system.

On the base of the examinations mentioned above, it seemed to be very interesting to study the influnce of the change in dye concentration on the absorption and also on the luminescence properties of the dye-detergent systems. The aim of our present investigations was to establish the influence of the change in the donor dye (Th) concentration on the optical properties of the systems mentioned above.

*Experimental results and discussion*

The absorption and the luminescence properties of the Th solutions were studied at different detergent concentrations and at different dye concentrations. The experimental methods used are described in [2—5]. The detergent (sodiumlauryl--sulphate; SLS) concentrations were between 2 and $8 \cdot 10^{-3}$ M/l, while the Th concentration were changed from $2 \cdot 10^{-6}$ M/l to $1 \cdot 10^{-4}$ M/l. The absorption and the luminescence of the examined systems seemed to be influenced both by the detergent and the dye concentration.

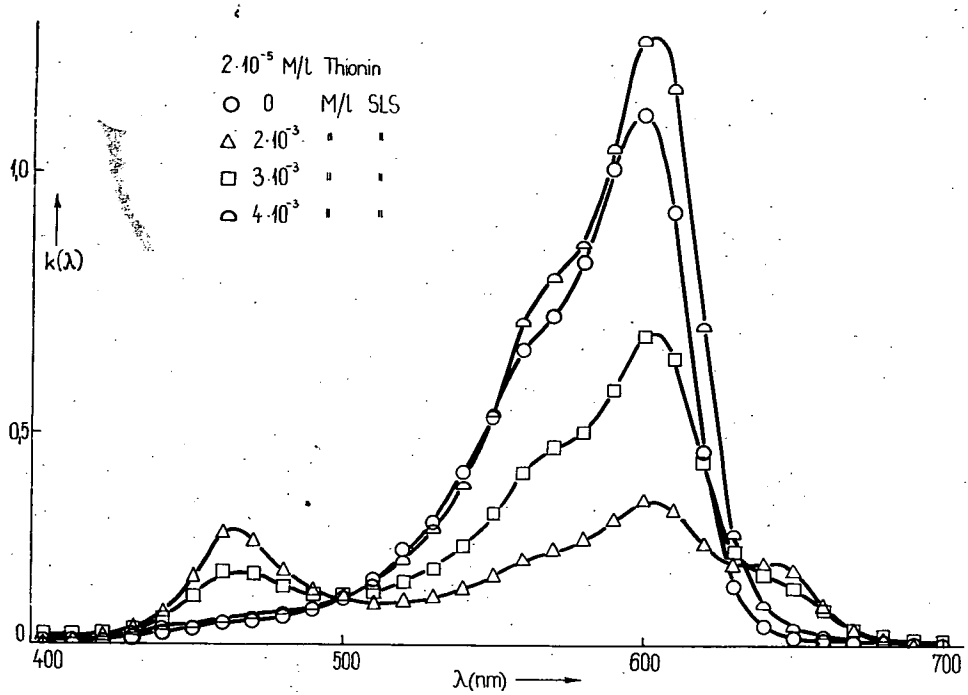


*Fig. 1.* Absorption spectra of $2 \cdot 10^{-5}$ M/l solutions of thionin different detergent concentrations

Fig. 1 shows *the absorption spectra* of the solutions of $2 \cdot 10^{-5}$ M/l of Th at different detergent concentrations. The maximum of the main absorption band ($\alpha$-maximum) of aqueous solution is at 600 nm, that of the solutions containing different amounts of detergent is at about 605 nm. The addition of detergent to the system shifts the location of maximum towards the longer waves by 3—5 nm, in a good accordance with the results of [1].

Fig. 1 also shows that in solutions containing detergent — in addition to the $\alpha$-maximum — three satellite maxima can be observed: the first is the so-called $\gamma$-band at 465 nm, the second is the $\beta$-band at 565 nm (due to dimer forms of the dye) and the third is the $\delta$-band at 640 nm.

The curves belonging to different concentration of SLS have an isosbestical point at 500 nm, near to the $\gamma$-band, probably due to an equilibrium of monomer and

dimer forms of the dye present in the solutions at low dye concentrations. With increasing dye concentration higher associates can be formed [6], therefore this point disappears at higher concentrations. This explanation seems to be corroborated by the appearence of the $\delta$-band at 640 nm possibly due to the absorption of higher aggregates.

*Table I*

*The maxima of absorption coeffients, $k(\lambda)_{max}$, for the $\alpha$-bands at different dye concentrations and at different amounts of detergent*

| $C_{SLS} \cdot 10^3$ (M/l) | $C_{Th}$ (M/l) | | | | | |
|---|---|---|---|---|---|---|
| | $2 \cdot 10^{-6}$ | $5 \cdot 10^{-6}$ | $1 \cdot 10^{-5}$ | $2 \cdot 10^{-5}$ | $5 \cdot 10^{-5}$ | $1 \cdot 10^{-4}$ |
| 0 | 0.25 | 0.41 | 0.86 | 1.90 | 4.95 | 11.42 |
| 2 | 0.05 | 0.06 | 0.12 | 0.26 | 0.58 | 2.09 |
| 2.5 | 0.08 | 0.11 | 0.17 | 0.31 | 0.65 | 2.20 |
| 3 | 0.14 | 0.18 | 0.25 | 0.38 | 0.78 | 2.33 |
| 3.5 | 0.22 | 0.26 | 0.34 | 0.56 | 1.02 | 2.49 |
| 4 | 0.26 | 0.44 | 0.75 | 1.18 | 2.15 | 3.64 |
| 6 | 0.28 | 0.73 | 1.45 | 2.69 | 6.04 | 13.15 |
| 8 | 0.29 | 0.73 | 1.47 | 2.90 | 6.40 | 15.00 |

The maximum absorption coefficients for the $\alpha$-bands determined at different dye concentrations are listed in Table I. It can be seen that $k(\lambda)_{max}$ for a solution containing $5 \cdot 10^{-6}$ M/l Th, decreases from 0.409 to 0.068 on addition of $2 \cdot 10^{-3}$ M/l detergent to the solution. These results are in a good accordance with the data of MUKARJEE and MYSELS [7] and can be interpreted by the formation of highly water-insoluble complex salts of the detergent anion and the dye cation.

The formation of this kind of complex salts was studied in [7] and in [4], too. It was shown that the $\gamma$-band originating from the absorption of complex salts has a maximum at $2 \cdot 10^{-3}$ M/l detergent content, above this concentration it decreases up to the c. m. c. and remains constant or disappears at higher detergent concentrations. The disappearence of the $\gamma$-band is due to the solubilization of dye-detergent complex salts.

In Fig. 2 $k(\lambda)_{max}$ is plotted for different concentrations of Th *versus* detergent concentration. This figure shows that around and above the c. m. c. $k(\lambda)_{max}$ increases with increasing concentration of SLS and reaches an almost constant value at a concentration of $6 \cdot 10^{-3}$ M/l of detergent. Also this phenomenon is due to the solubilization of the dye-detergent complex salts, i. e. incorporation of dye into the micelles. The spectroscopical evidence suggests that the micelles carry mainly monomeric dye cations, with a certain proportion of dimers [1].

It is to be noted, however, that at higher detergent concentrations $k(\lambda)_{max}$, in most cases, exceeds the value measured in aqueous solution. This results, probably, can be interpreted by the presence of non-absorbing dye-aggregates in aqueous solution containing higher dye concentrations [3]. The solubilization of these non-absorbing dye-aggregates results the „recolarization" of the system observed with increasing detergent concentration.

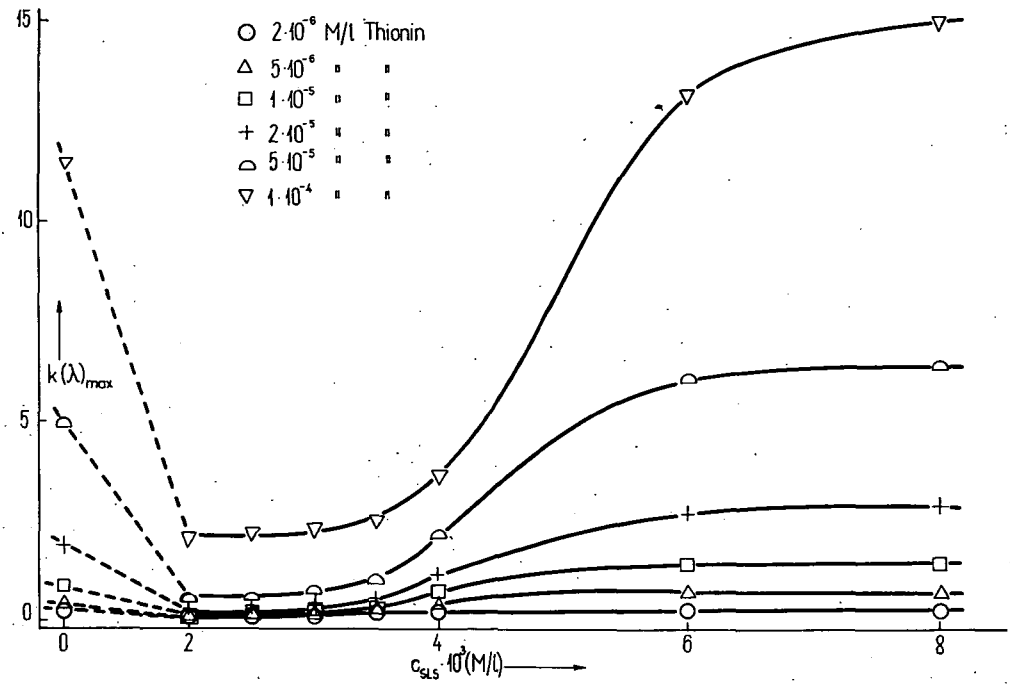


*Fig. 2.* Absorption coefficients of thionin solutions with different dye concentrations *versus* detergent concentration

The *fluorescence spectra* of the systems show a similar change with the concentrations of dye and detergent. In Table II the maxima of the fluorescence intensity, $f_q(\lambda)_{max}$, measured in solutions of different Th concentrations containing different amounts of detergent, are entered. The fluorescence is almost completely quenched at very low concentrations of the detergent. As it was shown in [1], this is due to the formation of neutral molecules. After the solubilization of these molecules by the detergent anions, the fluorescence is restored. Our data clearly show that the solubilization depends both on the concentration of dye and of detergent.

It can also be observed that $f_q(\lambda)_{max}$ — similarly to $k(\lambda)_{max}$ mentioned above — from $4 \cdot 10^{-3}$ M/l detergent concentrations exceeds the values measured in aqueous solutions. The higher values of $f_q(\lambda)_{max}$ can be attributed to the solubilization of the dye-aggregates present in aqueous solutions. This leads to the interesting observation that in solutions with high detergent concentrations no quenching of fluorescence appears [8—9], but — instead of quenching — an increase of fluorescence occurs with increasing dye concentration. This is in good accordance with results given in [1] for Th at detergent concentrations near to the c. m. c.

Between the absorption and the fluorescence spectra an universal relation was given by STEPANOV [10]:

$$\frac{f_q(\bar{\nu})}{k(\bar{\nu})} = D(T)\bar{\nu}^3 \exp(-h\bar{\nu}/kT), \tag{1}$$

*Table II*

*The maxima of fluorescence intensity, $f_q(\lambda)_{max}$, solutions of different thionin concentrations and at different amounts of detergent*

| $C_{SLS}\cdot 10^3$ (M/l) | $C_{Th}$ (M/l) | | | | | |
|---|---|---|---|---|---|---|
| | $2\cdot10^{-6}$ | $5\cdot10^{-6}$ | $1\cdot10^{-5}$ | $2\cdot10^{-5}$ | $5\cdot10^{-5}$ | $1\cdot10^{-4}$ |
| 0 | 19.68 | 28.92 | 40.19 | 98.22 | 271.70 | 525.30 |
| 2 | 2.05 | 1.88 | 1.13 | 1.77 | 3.69 | 4.59 |
| 2.5 | 4.32 | 3.04 | 1.80 | 3.12 | 3.24 | 4.73 |
| 3 | 8.06 | 4.49 | 3.01 | 5.17 | 3.73 | 4.82 |
| 3.5 | 15.16 | 8.76 | 4.85 | 7.34 | 5.54 | 5.88 |
| 4 | 19.49 | 23.44 | 19.65 | 24.14 | 46.81 | 17.09 |
| 6 | 26.12 | 43.54 | 54.32 | 140.40 | 215.30 | 289.10 |
| 8 | 30.40 | 43.31 | 57.32 | 163.70 | 321.50 | 642.10 |

where $f_q(\bar{\nu})$ and $k(\bar{\nu})$ denote the fluorescence and the absorption spectra, respectively, $D(T)$ is a constant independent of $\bar{\nu}$, $T$ is the absolute temperature, $h$ and $k$ are Planck's and Boltzmann's constants.

In order to check the validity of this equation it should be re-written in the form [11]:

$$F(\bar{\nu}) \equiv \frac{h}{kT}\bar{\nu} = \\ = 3\log\bar{\nu} - \log[f_q(\bar{\nu})/k(\bar{\nu})]. \tag{2}$$

According to this function $F(\bar{\nu})$ has to be linear and from the slope of the straight line the temperature, $T$, can be obtained. Experimentally $F(\bar{\nu})$ was found to be linear, but the temperature calculated from the slope, $T^*$, was in most cases higher than the macroscopical (experimental) temperature ($T^* \geqq T$). It was interpreted by many authors (see e. g. in [12]) that the local temperature of the excited molecules in the instant of fluorescence is higher than the macroscopical temperature of the system.

The validity of Eq. (1) and Eq. (2) for dye-detergent systems was checked by BÁLINT *et al.* [13]. They found a minimum local temperature near to the c. m. c.

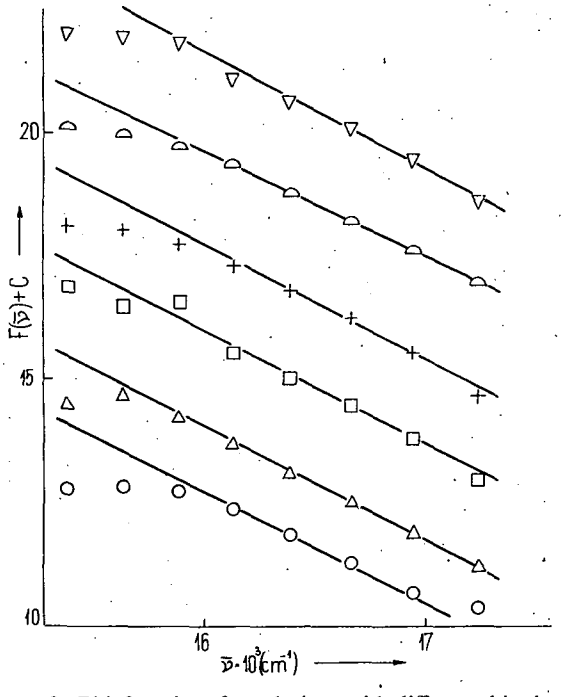


*Fig. 3.* $F(\bar{\nu})$ functions for solutions with different thionin concentrations; $0-2\cdot10^{-6}$M/l, $\triangle-5\cdot10^{-6}$M/l, $\square-1\cdot10^{-5}$ M/l, $+-2\cdot10^{-5}$ M/l, $\frown-5\cdot10^{-5}$ M/l and $\triangledown-1\cdot10^{-4}$ M/l.

in all cases investigated. A correlation between the local temperature and the fluorescence yield was also obtained in [13].

For our aqueous systems $F(\bar{\nu})$ is plotted in Fig. 3. The linearity of $F(\bar{\nu})$ is well fulfilled in all cases, the slopes of the straight lines are different for solutions of different dye concentration. The local temperature, $T^*$, calculated for aqueous solutions and for solutions containing $6 \cdot 10^{-3}$ M/l detergent are given in Table III. $T^*$ decreases in both cases with the increase of dye concentration. For the first sight this seems to be in a contradiction to the results of [14], where an increase of $T^*$ was found on increasing the dye concentration. This contradiction can be solved by taking into consideration the fact mentioned above that in detergent solutions the concentration quenching of fluorescence can not be observed. In this case the lifetime of excited state is longer, a larger fraction of the excess energy is dissipated by the instant of emission and this results in a lower $T^*$, i. e. the local temperature of the excited molecules decreases.

*Table III*

*The local temperatures, $T^*(°K)$, calculated for aqueous solutions of thionin and for thionin solutions containing detergent with concentration of $6 \cdot 10^{-3}$ M/l*

| $C_{Th}$ (M/l) | $T^*$ (°K) | |
|---|---|---|
| | $C_{SLS}=0$ | $C_{SLS}=6 \cdot 10^{-3}$ (M/l) |
| $2 \cdot 10^{-6}$ | 329.1 | 373.7 |
| $5 \cdot 10^{-6}$ | 312.6 | 357.9 |
| $1 \cdot 10^{-5}$ | 303.5 | 346.6 |
| $2 \cdot 10^{-5}$ | 296.3 | 336.1 |
| $5 \cdot 10^{-5}$ | 288.8 | 324.9 |
| $1 \cdot 10^{-4}$ | 285.4 | 320.3 |

There is no clear explanation, however, for the higher values of $T^*$ in solutions containing detergent with concentration of $6 \cdot 10^{-3}$ M/l. A trivial source of this phenomenon is revealed by comparison of $k(\lambda)_{max}$ and $f_q(\lambda)_{max}$ for the solutions containing equal amounts of dye and different amounts of detergent. In the case of solutions with $1 \cdot 10^{-4}$ M/l concentration of Th, at detergent concentration of $6 \cdot 10^{-3}$ M/l, the increase in $k(\lambda)_{max}$ is 15,1% and for the $f_q(\lambda)_{max}$ a decrease can be obtained. Why the spectra behave in this manner it is still not understood.

It has to be noted that the local temperatures of the excited molecules obtained for solutions of Th with concentrations of $5 \cdot 10^{-6}$ M/l are in a good accordance with the values given in [13], where $T^* = 345.4$ °K was found for aqueous solution of Th, and $T^* = 367.7$ °K for solution containing SLS with concentration of $6 \cdot 10^{-3}$ M/l. The latter is very near to our result ($T^* = 357.3$ °K), but the difference between the values of $T^*$ obtained for aqueous solutions is found to be significant. Let be mentioned, however, that looking at Fig. 2 given in [13], $T^* = 355.4$ °K seems to be too high.

The authors are indebted to Professor Dr. L. SZALAY, Director of Institute, for helpful discussions and valuable advices during the preparation of the text.

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## ЗАВИСИМОСТЬ АБСОРБЦИОННЫХ И ФЛУОРЕСЦЕНТНЫХ СВОЙСТВ КРАСИТЕЛЬ-ДЕТЕРГЕНТ СИСТЕМЫ ОТ КОНЦЕНТРАЦИИ КРАСИТЕЛЯ

*Я. Хевеши и Ж. Рожа*

Экспериментальные результаты показывают, что ход спектра поглощения изменяется при повышении концентрации детергента. При более высокой концентрации красителя при 640 нм появляется полоса поглощения, которая относится к агрегатам красителя высшего порядка. При наличии детергента в растворе наблюдается и полоса поглощения при 465 нм возникающая из-за нерастворимых в воде солей. Между локальной температурой возбужденных молекул и изменением концентрации красителя наблюдается обратное отношение.

# EXCITATION SPECTRA AND CONCENTRATION-DEPENDENT LUMINESCENCE OF $Mn^{2+}$ IN METAPHOSPHATE GLASSES

By

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*(Received June 20, 1971.)*

Emission and excitation spectra of $Mn^{2+}$-activated magnesium metaphosphate glasses were investigated using two base glasses at different $Mn^{2+}$ concentrations. The spectral position of the peaks of the normalized excitations spectra is independent of concentration, while the relative height of the different excitation bands is concentration-dependent. In the case of low $Mn^{2+}$ concentrations a green band appears in the emission spectra consisting generally of a single broad red band. The peaks of emission are shifted from 595 nm to 677 nm with increasing manganese concentration. Our results show that the explanation given by TURNER and TURNER for the concentration dependence of $Mn^{2+}$ luminescence in silicate glasses seems to be applicable also for phosphate glasses.

In the last years several authors [1, 2, 3, 4, 5, 6] dealt with the luminescence of $Mn^{2+}$-activated glasses studying also the question of the validity of the classical LINWOOD-WEYL model. LINWOOD *and* WEYL [7, 8] stated that in silicate glasses the $Mn^{2+}$ is of tetrahedral coordination and emits green fluorescence, whereas in phosphate glasses it is of octahedral coordination, the fluorescence being dominatly red. According to their investigations on concentration quenching, this effect occurred at significantly lower manganese concentrations in silicate glasses than in phosphate glasses. They consider these results as supporting the tetrahedral or octahedral symmetry of the $Mn^{2+}$ coordination in the respective glasses. KREIDL [9] obtained analogous results. The first quantitative investigations on absorption and fluorescence of manganese activated glasses were made by BINGHAM and PARKE [1]. Their results, supported by calculations based on the ligand-field theory, confirmed the suggestion of LINWOOD and WEYL concerning the position of $Mn^{2+}$ in the glass. They already noticed the shifting of the emission peak with increasing manganese concentration irrespective of the composition of the base glass without giving however, quantitative data. According to WILKE's observations on metaphosphate glasses [10], the colour of luminescence becomes more and more red with increasing manganese concentration. LUNTER and KARAPETJAN [2] found a shift of the emission maxima from 16155 $cm^{-1}$ to 13650 $cm^{-1}$ by increasing the $MnO_2$ concentrations from 0.05 wt% to 50 wt% in $ZnO.P_2O_5$ glasses. TURNER and TURNER [5] investigated in detail the concentration dependence of the luminescence in manganese activated silicate glasses. They found significant spectral changes and suggested exchange coupled groupings as explanation, which may also explain the changes in colour found by other authors in borate and phosphate glasses.

Therefore it seemed justified to investigate the concentration dependence of the luminescence of manganese activated magnesium metaphosphate glasses. In the present paper the dependence of luminescence emission on exciting wavelength glass composition, and activator concentration is dealt with. Instead of the poorly resolved absorption spectra excitation spectra were measured.

## *Experimental*

To prepare our samples, according to the method described by WILKE, MgO and $(NH_4)H_2PO_4$ was thoroughly mixed and thermolysed until ammonia was totally expelled. The charges were melted in alumina crucibles in an electric furnace at temperatures from 1200 to 1300°C for 12 and 16 hours, respectively, depending on the $MgO:PO_3$ ratio. The melted glass was poured in steel moulds preheated to 500°C and subjected to annealing for 16 hours. The measurements were performed on samples polished on both sides. The manganese concentration of the samples was determined colorimetrically.

A home-built spectrophotometer consisting of light sources XBO 500 W or HBO 200 W, quartz prism and glass prism monochromators SPM 2, a multiplier EMI 9558 AQ and a Zeiss recorder G1B1, and a digital Voltmeter EMG 1361 and a printer was used.

In measuring the excitation spectra, the exciting light was divided into two parts by a quartz plate placed behind the exit slit of the quartz prism monochromator. One of these beams was focused on the sample, the luminescence light of which was observed through suitable filters and a light pipe using a multiplier RCA 1P21. The other beam was focused on a 2 mm quartz cuvette filled with alcoholic fluorescein solution. After passing a crossed filter, the fluorescence light fell on a multiplier Zeiss M10FS25. The photocurrents were detected with the aid of recorders G1B1.

The quantum yield of fluorescein being independent from the exciting wavelength up to the long wave absorption maximum, the excitation spectrum was calculated with the formula

$$Exc(\lambda) = \frac{I_s(\lambda)}{I_{fl}(\lambda)}\left(T_c(\lambda) - T_{fl}(\lambda)\right),$$

where $I_s$ and $I_{fl}$ are photocurrents proportional to the quantum emission of the sample and of the fluorescein, $T_{fl}$ and $T_c$ the transmission of the cuvettes filled with fluorescein solution and with the solvent, respectively, compared with that of air.

## *Results and discussion*

Before measuring the excitation spectra, it has been examined whether the emission spectrum for a given glass composition and $Mn^{2+}$ concentration depends on the exciting wavelength. According to our measurements, in case of excitation with the 366, 406 and 436 nm line-groups of a mercury lamp the relative quantum distribution of the red band of the emission spectra is independent from the exciting wavelength. Therefore in measuring the excitation spectra, only one pair of filters was used for eliminating the exciting light.

In Fig. 1 excitation spectra of glasses of composition $MgO:PO_3 = 1:3$ are shown. The reference numbers 1, 2, 3, 4 of the curves normalized at 409 nm denote manganese concentration of 0.1, 1.6, 3.8 and 7.7 wt% respectively. The band width of excitability increases with increasing concentration, the spectral position of the bands remaining the same, while the intensity of the band with maximum at 346 nm increases significantly as compared with that of the 409 nm maximum, the secondary maxima becoming more and more pronounced at the same time.

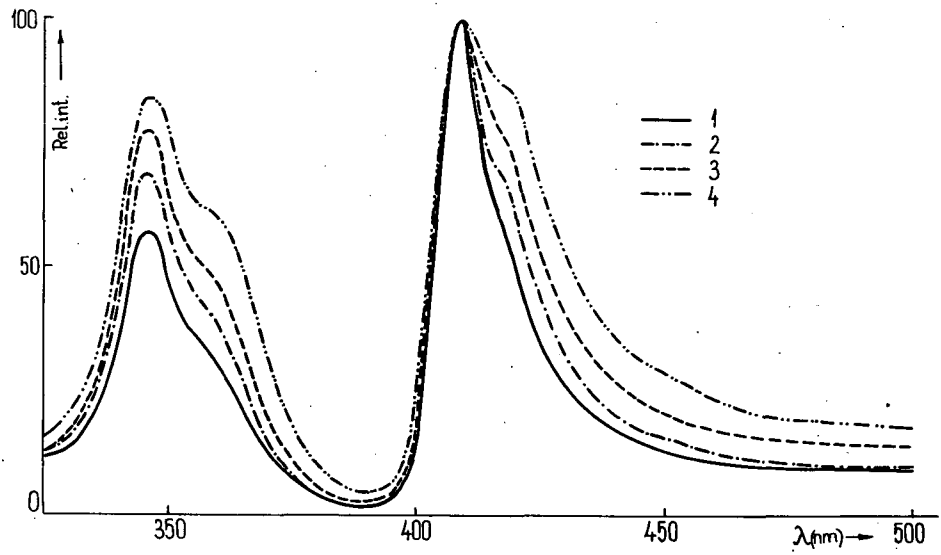


*Fig. 1.* Concentration-dependence of the excitation spectra

In the literature, the emission of the $Mn^{2+}$ activated phosphate glasses has been characterized chiefly by the visual emission colour which was found to change from yellow to red, depending on concentration and composition. According to LUNTER and KARAPETJAN [2, 3] the changes in colour of the emission of phosphate glasses are due to the shift of the single red band towards longer waves. The visual emission colour of our samples was found to change from light yellow to deep red. At low concentrations a green band appears in the spectrum near 518 nm (see curves 1, 2, 3 in Fig 2 and 3), with improved resolution at the temperatures of liquid air. Our apparatus was calibrated to obtain correct luminescence quantum spectra. The green band becomes weaker with increasing concentration (it is not observable at concentrations higher than 3 wt%), the long wave band being shifted towards red at the same time. For the green band, such a shift of the spectral position could not be observed for the concentration range investigated. Our results seem rather surprising, because for phosphate glasses the green band is not predicted by the Linwood—Weyl model.

A change in the composition of our base glass from 1:3 to 1:2 did not cause any essential changes in the concentration dependence of the $Mn^{2+}$ luminescence (see Figures 2 and 3, respectively). Emission spectra of glasses with $Mn^{2+}$ concentration

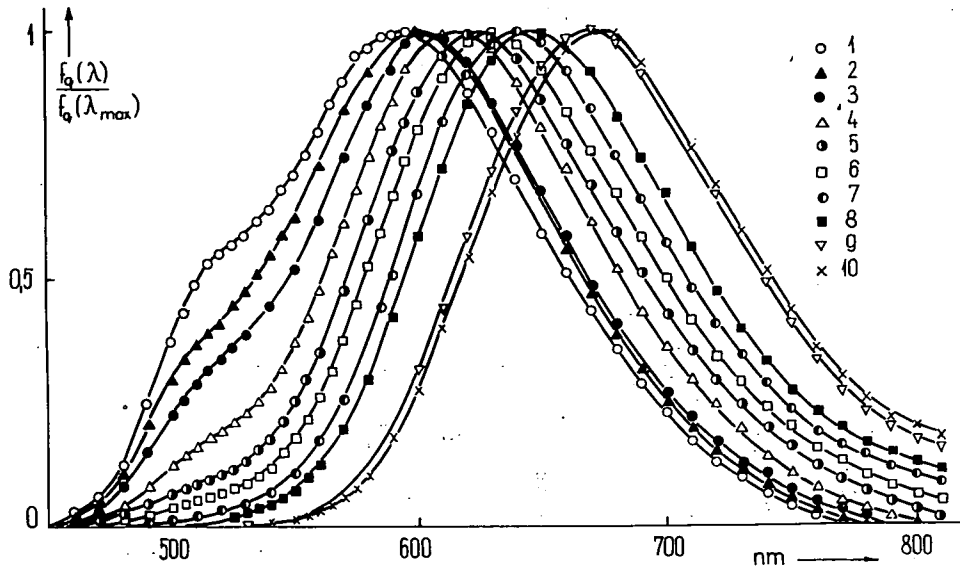


*Fig. 2.* Room temperature fluorescence spectra of $MgO.3PO_3$:0.07 wt% Mn (1); 0.47 wt% Mn (2); 0.79 wt% Mn (3); 1.60 wt% Mn (4); 2.31 wt% Mn (5); 3.09 wt% Mn (6); 3.80 wt% Mn (7); 4.22 wt% Mn (8); 6.29 wt% Mn (9); 7.70 wt% Mn (10). $\lambda_{exc}$ 410 nm.

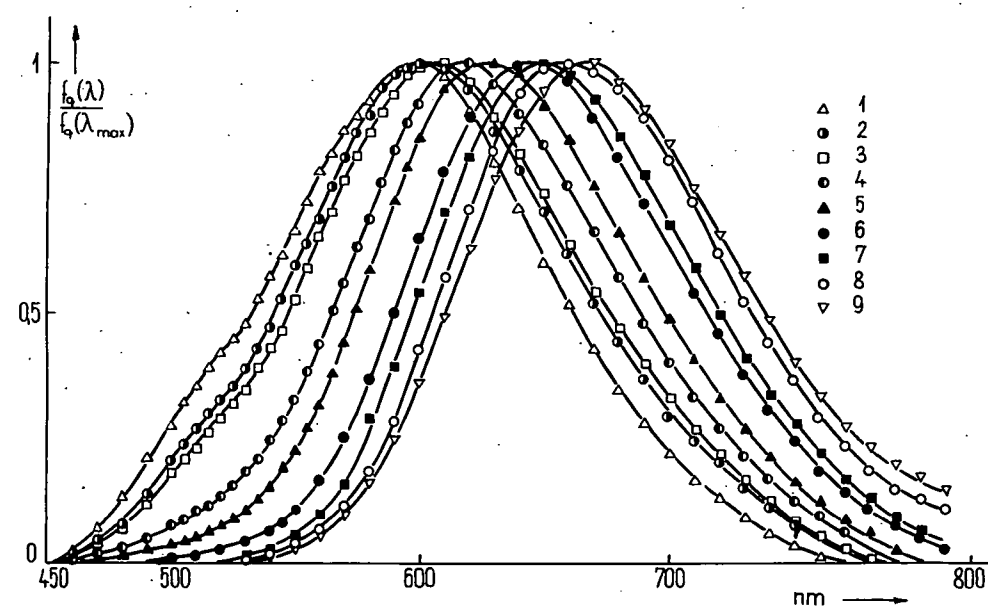


*Fig. 3.* Room temperature fluorescence spectra of $MgO.2PO_3$:0.10 wt% Mn (1); 0.56 wt% Mn (2) 0.67 wt% Mn (3); 1.94 wt% Mn (4); 3.13 wt% Mn (5); 4.12 wt% Mn (6); 5.03 wt% Mn (7); 6.20 wt% Mn (8); 8.16 wt% Mn (9). $\lambda_{exc}$ 410 nm.

lower than 0.1 wt% could not be determined because of the very low luminescence intensity. It is remarkable that, with increasing temperatures, the spectra are shifted towards the green spectral region. Detailed observations concerning the temperature dependence of luminescence are to be published later.

A plausible interpretation of the observed shift of the emission spectra can be found in the supposition, suggested by TURNER and TURNER [5], that by changing the distance between the $Mn^{2+}$ ions in specific position able to emit, new emitting centres responsible for the red luminescence are produced.

The formation of such centres should implie changes in the absorption spectrum. However, because of the very low absorptivity of the samples, such changes could not be found in the case of $Mn^{2+}$ either by [1] or by [5]. The existence of such new centres seems to be supported by our observations on excitation spectra.

Measurements and calculations concerning interactions between $Mn^{2+}$ ions are in course in order to find a model describing the luminescence of $Mn^{2+}$ activated glasses.

The authors express their thanks to Prof. GY. GRASSELLY for his advices and the help of the Institute of Minerology and Petrography in polishing the samples, and to Prof. I. KETSKEMÉTY, Director of the Institute of Experimental Physics for his interest in the research work.

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## ЗАВИСИМОСТЬ СПЕКТРЫ ЛЮМИНЕСЦЕНЦИИ И ВОЗБУЖДЕНИЯ СТЕКОЛ ИЗ МЕТАФОСФАТА МАГНИИ ОТ КОНЦЕНТРАЦИИ $Mn^{2+}$

*Л. Селлеши и Т. Сереньи*

Исследовались спектры излучения и возбуждения стекол из метафосфата магнии активированных с различными концентрациями $Mn^{2+}$. Место максимумов нормированных спектров возбуждения не зависит от концентрации марганца, а относительная интенсивность полос возбуждения показывает концентрационную зависимость. При маленьких концентрациях $Mn^{2+}$ кроме красной полосы излучения появляется и полоса в зеленой области спектра. Максимумы спектров излучения при увеличении концентрации марганца смешается от 595 нм до 677 нм. Наши результаты позволяют применять объяснение Турнера концентрационной зависимости данного для объяснения люминесценции стекол из силикатов.

# THERMAL DECOMPOSITION OF *n*-PENTANE. II* EFFECT OF UNSATURATED PRODUCTS AND MECHANISM OF THE REACTION

By

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The pyrolysis of *n*-pentane has been investigated at 520°C at initial pressures of 200 torr in the presence of ethylene, propylene and butene-1, respectively. The composition of the products was strongly altered in the presence of olefines. The effect has been explained by addition reactions between alkyl radicals and olefines.

## *Introduction*

In the investigations of thermal decomposition of simple saturated hydrocarbons, significant self-inhibition was observed in some cases. The self-inhibition was generally explained by the reactions between chain carrier radicals and some unsaturated products. Inhibition by propylene and *i*-butene was observed in the pyrolysis of *n*-pentane [1, 2]. LEATHARD and PURNELL pointed out that only the addition of hydrogen atoms to olefines can bring about self-inhibition [3].

In order to study the inhibiting effects of unsaturated products in the pyrolysis of *n*-pentane, experiments were carried out in the presence of added unsaturated products, *i. e.* ethylene, propylene and butene-1.

## *Experimental*

The applied system and method have been described previously [4]. 200 torr of *n*-pentane and different quantities of ethylene, propylene of butene-1 were mixed and admitted into the reaction vessel at 520°C. Samples were taken at different stages of the reaction and analysed by a Carlo Erba Fr. Mod. C. gas chromatograph, equipped with a thermal conductivity detector. The products of the reaction were identified on a Finnigan 1015 mass spectrometer combined with a gas chromatograph. Propylene and ethylene were taken from cylinders, and distilled three times at low temperature. Butene-1 was prepared from butanol by catalytic dehydration. Butene-1 contained 5 per cent *cis*- and *trans*-butene-2 as impurities.

*Part I: Acta Phys. et Chem. Szeged **17**, 33 (1971).

## *Results and Discussion*

*Effect of Ethylene.* The following effects of added ethylene have been observed. 1. Added ethylene increased the initial rate measured manometrically and by gas chromatography (Fig. 1).

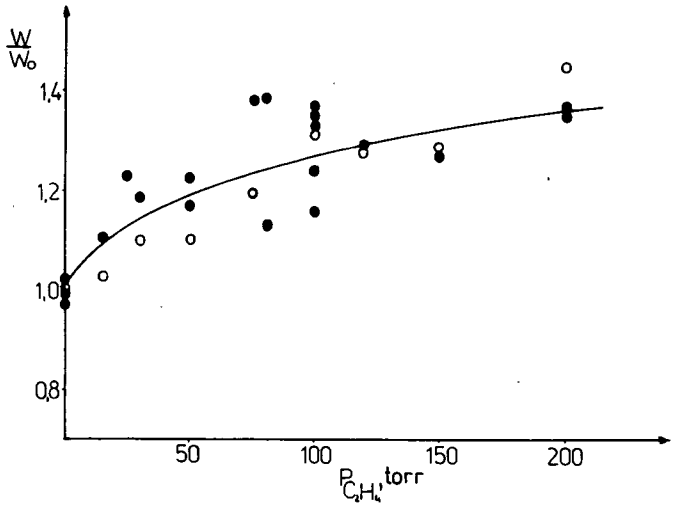


*Fig. 1.* Effect of ethylene on the initial rate measured manometrically (●) and by gas chromatography (o). Initial pressure of pentane 200 torr, T=520°C.

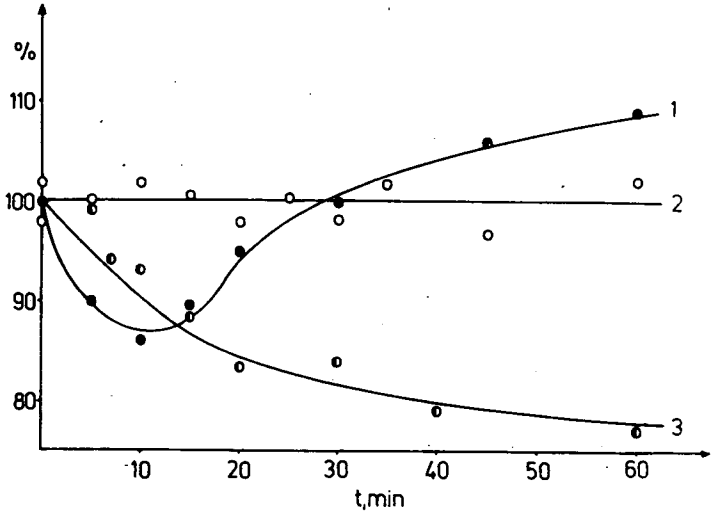


*Fig. 2.* The measured quantities of ethylene (1), propylene (2), and butene-1 (3), as a function of time in the influenced reactions, expressed as the percentage of the initially added quantities of olefines. Initial pressures: ethylene 50 torr, propylene 200 torr, butene-1 75 torr. Initial pressure of pentane was 200 torr, in each case. T=520°C.

2. A part of the added ethylene was consumed in the first thirty minutes of the reaction, as it can be seen from curve 1 in Fig. 2.
3. The rate of product formation strongly changed; the rate of formation of butene-1, propylene and methane increased, while that of ethane and hydrogen decreased (Fig. 3).

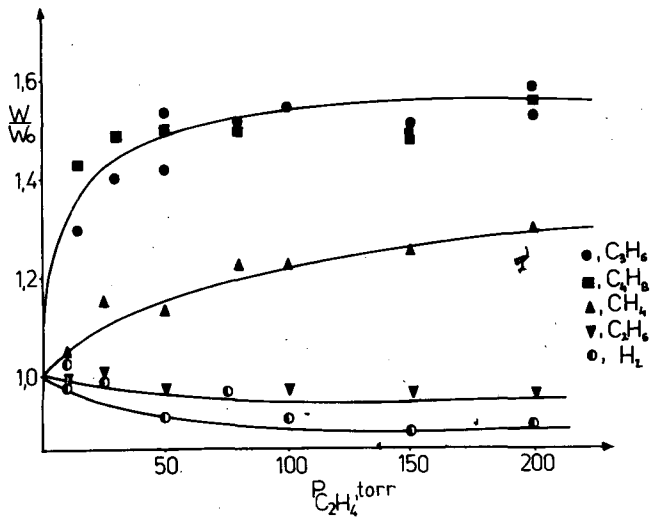


*Fig. 3.* Initial rate of formation of the products in the ethylene influenced reaction. Initial pressure of pentane 200 torr, T=520°C.

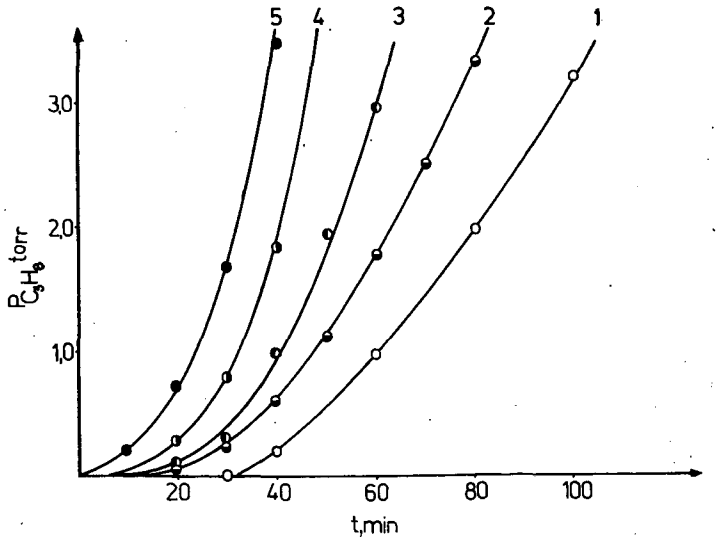


*Fig. 4.* Partial pressure of propane in the course of the reaction in the presence of 0 torr (1), 25 torr (2), 50 torr (3), 100 torr (4), and 200 torr (5) of ethylene.

4. In the presence of added ethylene, formation of propane was observed in the earliest part of the reaction, while without added ethylene there was an induction period in the formation of propane (Fig. 4).

*Effect of Propylene.* In the presence of added propylene the following effects have been observed:

1. Added propylene increased slightly the rate of decomposition of *n*-pentane. The effect of added propylene on the initial rate, measured manometrically, was similar to the earlier results [1, 2] (Fig. 5).

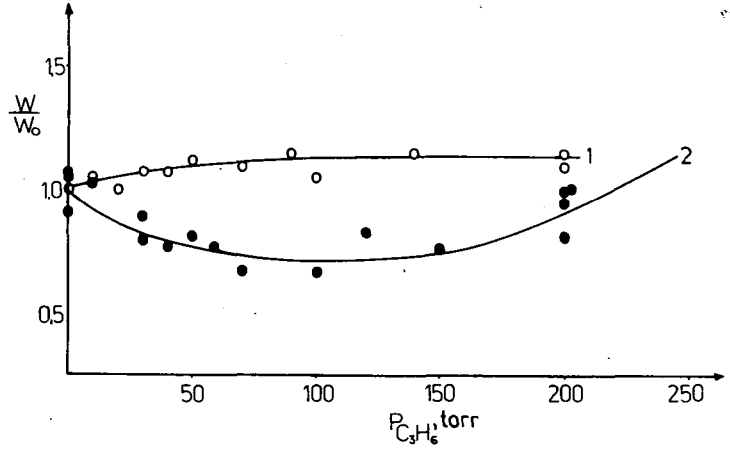


*Fig. 5.* Effect of added propylene on the initial rate measured by gas chromatography (1) and manometrically (2). Initial pressure of pentane 200 torr, T=520°C.

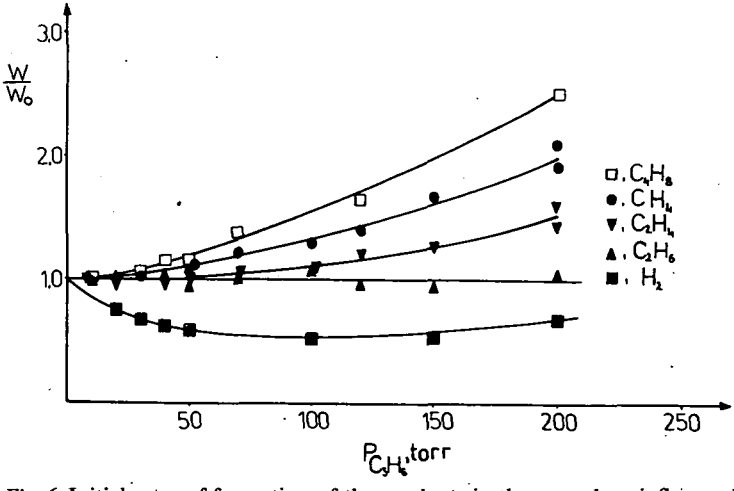


*Fig. 6.* Initial rates of formation of the products in the propylene influenced decomposition of pentane. Initial pressure of pentane 200 torr, T=520°C.

2. The partial pressure of added propylene was constant in time (Curve 2 in Fig. 2).
3. The rate of formation of the products was stronly altered; the rate of formation of butene-1, methane, ethylene increased, while the rate of formation of ethane remained constant and that of hydrogen decreased (Fig. 6).
4. In the presence of added propylene, propane was formed without an induction period. Similar observation was made in the case of added ethylene.

*Effect of Butene*-1. The effect of butene-1 can be summarised as follows:
1. Added butene-1 influenced the initial rate, measured manometrically, according to a minimum curve and increased slightly the rate of decomposition of *n*-pentane measured by gas chromatography (Fig. 7).

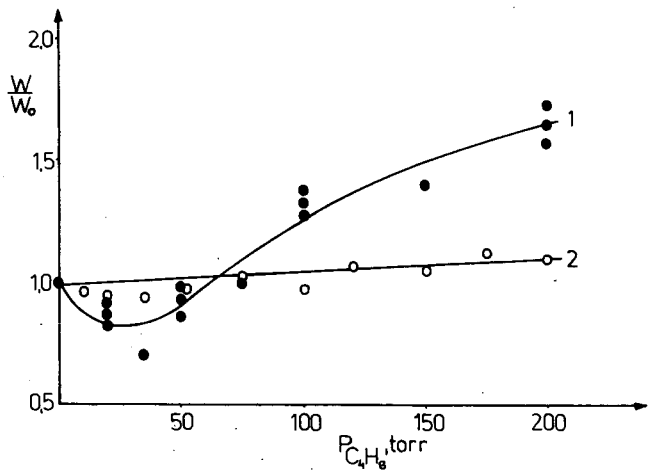


*Fig. 7.* Effect of butene-1 on the initial rates measured manometrically (●) and by gas chromatography (o). Initial pressure of pentane 200 torr, T=520°C.

2. Added butene-1 was consumed in the whole course of the reaction (Curve 3. in Fig. 2).
3. Added butene-1 altered the rate of formation of the products. The rate of formation of methane increased with increasing amount of butene-1. The rate of formation of propylene, ethane, ethylene and hydrogen increased according to a minimum curve (Fig. 8).
4. In the presence of added butene-1, propane was formed even in the earliest part of the reaction. Similar observations were made in the presence of ethylene and propylene.

## *Mechanism of the Reaction*

The results can be interpreted by the following steps.
Initiation:

$$C_5H_{12} \rightarrow CH_3 + C_4H_9 \quad (1)$$

$$C_5H_{12} \rightarrow C_2H_5 + C_3H_7 \quad (2)$$

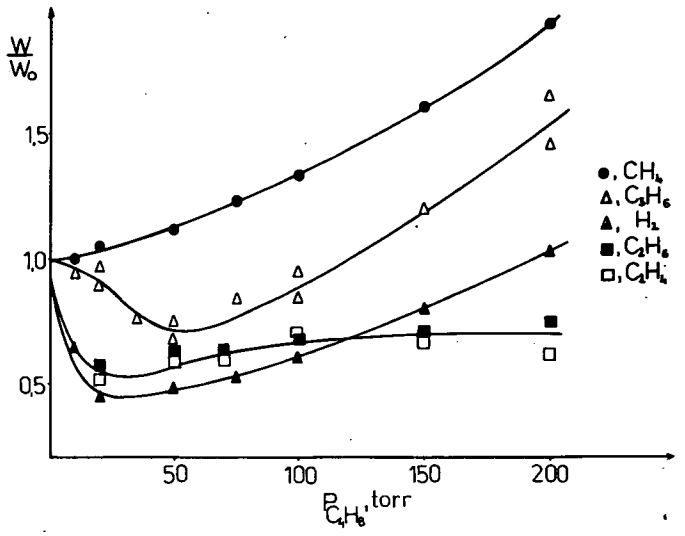


*Fig. 8.* Initial rates of formation of the products in the butene-1 influenced reaction.

The possibility of splitting off a hydrogen atom in the initial step can be neglected because of a greater activation energy [5]. As propane has been observed only in small quantities and butane has not been detected, methyl and ethyl radicals were accepted as the main chain carriers. This is supported by the fact that methane and ethane are major products. With methyl and ethyl radicals the following propagation steps were selected:

$$C_5H_{12} + CH_3 \rightarrow CH_4 + C_5H_{11} \quad (3)$$

$$C_5H_{12} + C_2H_5 \rightarrow C_2H_6 + C_5H_{11} \quad (4)$$

Pentyl radicals can reproduce the chain carriers as follows:

$$1\text{—}C_5H_{11} \rightarrow C_2H_4 + C_3H_7 \quad (5)$$

$$2\text{—}C_5H_{11} \rightarrow C_2H_5 + C_3H_6 \quad (6)$$

$$3\text{—}C_5H_{11} \rightarrow CH_3 + C_4H_8 \quad (7)$$

Among the reactions of the propyl radicals, the decomposition has the most important role [6]:

$$C_3H_7 \rightarrow CH_3 + C_2H_4 \quad (8)$$

The production of hydrogene can be explained by the decomposition of alkyl radicals into an olefin molecule and a hydrogen atom:

$$R \rightarrow \text{olefin} + H \quad (9)$$

H radical with *n*-pentane can give hydrogen:

$$H + C_5H_{12} \rightarrow H_2 + C_5H_{11} \quad (10)$$

To estimate the relative importance of the termination steps, the ratios of the concentrations of the radicals have been calculated.

In the earliest stages of the pyrolysis of *n*-pentane the following rate equations can be taken:

$$W_{H_2} = \frac{d[H_2]}{dt} = k_{H_2}[H]\,[\text{Pentane}]$$

$$W_{CH_4} = \frac{d[CH_4]}{dt} = k_{CH_4}[CH_3]\,[\text{Pentane}]$$

$$W_{C_2H_6} = \frac{d[C_2H_6]}{dt} = k_{C_2H_6}[C_2H_5]\,[\text{Pentane}]$$

$$W_{C_3H_8} = \frac{d[C_3H_8]}{dt} = k_{C_3H_8}[C_3H_7]\,[\text{Pentane}]$$

The ratios of the radicals can be expressed as follows:

$$\frac{[C_2H_5]}{[CH_3]} = \frac{W_{C_2H_6}}{W_{H_2}} \cdot \frac{k_{H_2}}{k_{C_2H_6}}$$

$$\frac{[C_2H_5]}{[C_3H_7]} = \frac{W_{C_2H_6}}{W_{C_3H_8}} \cdot \frac{k_{C_3H_8}}{k_{C_2H_6}}$$

$$\frac{[C_2H_5]}{[H]} = \frac{W_{C_2H_6}}{W_{H_2}} \cdot \frac{k_{H_2}}{k_{C_2H_6}}$$

*Table I*

*Kinetical parameters at 520°C*

| Reaction | Formation rate in $torr^{-1}\cdot min^{-1}$ [4] | Rate constant in $cm^3\cdot mol^{-1}\cdot sec^{-1}$ [9] |
|---|---|---|
| $H + C_5H_{12} \rightarrow H_2 + C_5H_{11}$ | $W_{H_2} = 0.1$ | $5.1\cdot10^{11}$ |
| $CH_3 + C_5H_{12} \rightarrow CH_4 + C_5H_{11}$ | $W_{CH_4} = 0.7$ | $1.0\cdot10^{9}$ |
| $C_2H_5 + C_5H_{12} \rightarrow C_2H_6 + C_5H_{11}$ | $W_{C_2H_6} = 0.6$ | $1.04\cdot10^{8}$ |
| $C_3H_7 + C_5H_{12} \rightarrow C_3H_8 + C_5H_{11}$ | $W_{C_3H_8} = 0.05$ (uncertain) | $1.04\cdot10^{8}$ (estimated) |

Using the values listed in Table I the following relationship has been found:

$$[C_2H_5]:[CH_3]:[C_3H_7]:[H] = 2802:340:233:1$$

On the basis of this relationship the most important termination steps are:

$$C_2H_5 + C_2H_5 \rightarrow n\text{-}C_4H_{10} \qquad (11)$$

$$C_2H_5 + C_2H_5 \rightarrow C_2H_4 + C_2H_6 \qquad (12)$$

Less important steps are the following:

$$C_2H_5 + CH_3 \rightarrow C_3H_8 \quad (13)$$

$$C_2H_5 + C_3H_7 \rightarrow n\text{-}C_5H_{12} \quad (14)$$

$$C_2H_5 + C_3H_7 \rightarrow C_2H_6 + C_3H_6 \quad (15)$$

$$C_2H_5 + C_3H_7 \rightarrow C_2H_4 + C_3H_8 \quad (16)$$

In order to interpret the increasing rate of formation of propylene, methane and butene-1 and the decresaing rate of formation of ethane and hydrogen in the presence of added ethylene, the following possible steps can be considered in accordance with literature [7, 8]:

$$C_2H_5 + C_2H_4 \rightleftharpoons C_4H_9 \quad (17)$$

$$C_4H_9 + C_2H_4 \rightleftharpoons CH_3—(CH_2)_4—CH_2 \quad (18)$$

$$CH_3—(CH_2)_4—CH_2 \rightleftharpoons CH_3—CH—(CH_2)_3—CH_3 \quad (19)$$

$$CH_3—CH—(CH_2)_3—CH_3 \rightarrow C_3H_6 + C_3H_7 \quad (20)$$

The propyl radical produced in reaction 20 decomposes according to step 8 giving methane.

The formation of surplus butene-1, due to the addition of ethyl radical to ethylene, can be explained by the following steps:

$$CH_3—(CH_2)_4—CH_2 + C_2H_4 \rightleftharpoons CH_3—(CH_2)_6—CH_2 \quad (21)$$

$$CH_3—(CH_2)_6—CH_2 \rightleftharpoons CH_3—(CH_2)_4—CH—CH_2—CH_3 \quad (22)$$

$$CH_3—(CH_2)_4—CH—CH_2—CH_3 \rightleftharpoons C_4H_8 + C_4H_9 \quad (23)$$

The consumption of ethyl radical in step 17 would require a decrease in ethane production. This is compensated in part by the reaction between ethylene and hydrogen atom; the decrease in the formation of hydrogen can be explained in this way:

$$C_2H_4 + H \rightarrow C_2H_5 \quad (24)$$

Propyl radicals are responsible for propane formation. In the reactions influenced by ethylene there is greater opportunity to form propyl radicals in the following step as in the uninfluenced reaction.

$$CH_3 + C_2H_4 \rightarrow C_3H_7 \quad (25)$$

In the reaction influenced by propylene the larger amount of butene-1 can be explained by the reaction between ethyl radical and propylene. There are two ways for this reaction:

$$C_2H_5 + C_3H_6 \rightarrow CH_3—(CH_2)_2—CH—CH_3 \quad (26)$$

$$C_2H_5 + C_3H_6 \rightarrow CH_3—CH_2—\underset{\displaystyle CH_2}{\underset{|}{CH}}—CH_3 \quad (27)$$

*i*-Pentyl radical can decompose in this case as follows:

$$\begin{array}{l} CH_3—CH_2—CH—CH_3 \rightarrow CH_3 + C_4H_8 \\ \quad\quad\quad\quad\quad\quad | \\ \quad\quad\quad\quad\quad\quad CH_2 \end{array} \tag{28}$$

The excess amount of ethylene can be formed as follows:

$$CH_3 + C_3H_6 \rightarrow C_4H_9 \tag{29}$$

$$C_4H_9 \rightarrow C_2H_5 + C_2H_4 \tag{30}$$

The consumption of hydrogen can be understood as before.

The formation of propane in the early part of the reaction can be explained by the growing importance of propyl radical which can be formed from the relatively greater quantity of ethylene and methyl radical.

The larger amount of methane and propylene in the butene-1 influenced reaction can be interpreted as follows:

$$C_4H_8 + C_2H_5 \rightarrow CH_3(CH_2)_4\,CH_2 \tag{31}$$

In the early stage of the reaction the formation of propane can be explained with reaction 31 (steps 19—20). In the initial rate of formation *versus* concentration of butene-1 curves the minimum can not be interpreted in a satisfactory way.

From the experimental data it can be seen that in the decomposition of *n*-pentane the olefines produced in the process have no inhibiting effect.

It seems desirable to study the effect of nitric oxide which is known as a strong inhibitor of the reaction.

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## ТЕРМИЧЕСКОЕ РАЗЛОЖЕНИЕ н-ПЕНТАНА. II. ВЛИЯНИЕ НЕНАСЫЩЕННЫХ ПРОДУКТОВ И МЕХАНИЗМ РЕАКЦИИ

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Изучалось пиролиз н-пентана при температуре 520°C и начальных давлениях 200 мм рт. ст. при наличии этилена, пропилена и 1-бутена. В присутвии олефинов наблюдалось резкое изменение состава продуктов реакции. Эти эффекты истолкованы предположением аддиции алкильных радикалов к олефинам.

# INVESTIGATION OF THE EXCHANGE REACTIONS OF c-ALKYL IODIDES OF DIFFERENT RING SIZE WITH $I^{131}$ LABELLED KI. II*

## Solvent Effect in Ethanol. Anomalous Exchange Reaction of c-Butyl Iodide in Different Solvents

By

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*(Received July 15, 1971)*

The exchange reactions of c-pentyl, c-hexyl, c-heptyl, c-octyl and 2-methyl-c-hexyl iodides with $I^{131}$ labelled KI were studied in absolute ethanol at different temperatures. The exchange reactions of c-butyl iodide were studied at different temperatures in absolute ethanol, dimethylformamide and dimethyl sulfoxide as solvents. The kinetic data and activation constants obtained were brought into correlation with the solvent effect and with the change in the ring size of the cycloalkyl iodides. It was found that changes in the dielectric constant do not affect the rates of the exchange reactions in a clear-cut way. In ethanol H-bonding probably plays an important role. The investigations show that there is an anomaly in the exchange reactions of c-butyl iodide.

In investigations of the relation between molecular structure and reactivity, the study of exchange reactions provides characteristic data. Several authors have studied the external factors: the effect of the solvent or of the solvent mixture [1—3], and the effects of proton-containing solvents [4, 5] for different homologous series.

For the comparison of the c-alkane homologous series, in the main physical measurements describing the ground states of the molecules, calculations concerning their symmetries have been applied. The aim of our investigations was to study the effect of the molecular structure on the reaction under substitution reaction conditions, and to find a connection between these and the various experimental and calculable constants and parameters.

In an earlier communication [6] we reported data on the exchange reactions of c-pentyl, c-hexyl, c-heptyl, c-octyl and 2-methyl-c-hexyl iodides with labelled KI, and with dimethylformamide and dimethyl sulfoxide as solvents. The present paper summarizes the data referring to ethanol, a strongly solvating proton-containing solvent, and supplies the studies concerning the homologous series with data on the exchange reactions of c-butyl iodide. For the correlation with the molecular structure, the activation energies, activation free enthalpies and activation entropies referring to the activation state of the reaction were determined under different reaction conditions. The experimental results obtained and partly reported are brought into relation with the molecular structures of the hydrocarbons of different ring size.

* Part I: Acta Phys. et Chem. Szeged **17**, 49 (1971).

## *Experimental methods*

The method of measuring the kinetic data of the exchange reactions in the present investigation was described in our previous paper [6]. The c-alkyl iodides necessary for the study were prepared with methods described in the literature, purified on the basis of their physical constants and checked chromatographically.

The activities of the solutions were measured with a scintillation detector using of a hollow gamma-crystal.

## *Experimental results and discussion*

### 1. *Exchange reaction in absolute ethanol*

For the individual c-alkyl iodides the specific activity values measured in a benzene phase for the exchange reaction, and those arising from the incorporation of the labelled iodide, refer to initial reaction mixtures of identical activities. The kinetic curves for c-pentyl and c-octyl iodides were linear; they were of saturation type for c-heptyl and 2-methyl-c-hexyl iodides. It was not possible to observe an exchange in the case of c-hexyl iodide in ethanol. The reactions were carried out in the temperature range 65—80°C; the extent of the exchange increased with increasing temperature.

*Table I*

| | °C | $W_0$ mole·l$^{-1}$·sec$^{-1}$ | $k$ mole$^{-1}$·l·sec$^{-1}$ | $E$ kcal·mole$^{-1}$ | $\Delta S^{+}_{+}$ cal·mole$^{-1}$·degree$^{-1}$ | $\Delta G^{+}_{+}$ kcal·degree$^{-1}$ |
|---|---|---|---|---|---|---|
| c-pentyl iodide | 65 | $6.5\cdot10^{-8}$ | $2.62\cdot10^{-4}$ | 18.1 | −21.2 | 25.3 |
| | 70 | $9.7\cdot10^{-8}$ | $3.90\cdot10^{-4}$ | | −21.4 | 25.5 |
| | 75 | $15.0\cdot10^{-8}$ | $6.00\cdot10^{-4}$ | | −21.5 | 25.6 |
| c-heptyl iodide | 65 | $0.9\cdot10^{-7}$ | $3.50\cdot10^{-4}$ | 17.2 | −23,2 | 25.2 |
| | 70 | $1.2\cdot10^{-7}$ | $4.90\cdot10^{-4}$ | | −23,7 | 25.4 |
| | 75 | $1.8\cdot10^{-7}$ | $7.30\cdot10^{-4}$ | | −23,8 | 25.9 |
| c-octyl iodide | 70 | $2.4\cdot10^{-8}$ | $0.96\cdot10^{-4}$ | 19.4 | −20.5 | 26.3 |
| | 75 | $3.8\cdot10^{-8}$ | $1.50\cdot10^{-4}$ | | −20.6 | 26.6 |
| | 80 | $5.3\cdot10^{-8}$ | $2.17\cdot10^{-4}$ | | −20.6 | 26,7 |
| 2-methyl-c-hexyl iodide | 70 | $1.7\cdot10^{-8}$ | $0.68\cdot10^{-4}$ | 20.7 | −17.1 | 26.5 |
| | 75 | $2.7\cdot10^{-8}$ | $1.08\cdot10^{-4}$ | | −17.1 | 26.6 |
| | 80 | $4.2\cdot10^{-8}$ | $1.60\cdot10^{-4}$ | | −17.2 | 26.7 |

From a comparison of the experimental results with the dielectric constants of the solvents used (25.8 for ethanol, 39.0 for dimethylformamide, and 46 for dimethyl sulfoxide) and with the solvent effects observed for $S_N2$ reactions [7], it was to be expected that, since the reaction rate is decreased by the use of a more polar solvent, the exchange reaction would be the greatest in ethanol, less in dimethylform-

amide, and even less in dimethyl sulfoxide. The experiments showed that the exchange was the greatest in dimethylformamide, less in dimethyl sulfoxide, and the least in ethanol. If only the dielectric constants were taken into account, this would mean an anomaly with regard to ethanol as solvent. Ethanol is a proton-containing solvent and belongs to the most strongly solvating solvents, while the other two are of aprotic nature. The lower rate obtained in ethanol clearly indicates that in this solvent the primary factor is the specific interaction between the anions and the ethanol molecules, the hydrogen-bond. Therefore the ordering of the system is more extensive, and the internal energy is lower than that to be expected on the basis of the dielectric constant. The initial rate values, the rate coefficients and the activation data for the reactions carried out in absolute ethanol at different temperatures are given in Table I.

2. *Exhange reactions of c-butyl iodide*

The exchange reactions of c-butyl iodide were studied in all three solvents, at different temperatures, under the conditions described in the previous paper. The kinetic curves in dimethylformamide and in dimethyl sulfoxide pass through maxima. The positions of the maxima shifted towards shorter reaction times with the increase of temperature. The elimination accompanying the substitution in dimethyl-

*Table II*

| | °C | dimethyl-formamide | dimethyl sulfoxide | ethanol |
|---|---|---|---|---|
| $W_0$ (mole·l$^{-1}$·sec$^{-1}$) | 55 | $13.6 \cdot 10^{-6}$ | $6.5 \cdot 10^{-6}$ | — |
| | 65 | $25.7 \cdot 10^{-6}$ | $13.3 \cdot 10^{-6}$ | $0.8 \cdot 10^{-6}$ |
| | 75 | $46.6 \cdot 10^{-6}$ | $28.2 \cdot 10^{-6}$ | $1.7 \cdot 10^{-6}$ |
| $k$ (mole$^{-1}$·l·sec$^{-1}$) | 55 | $5.46 \cdot 10^{-2}$ | $2.60 \cdot 10^{-2}$ | — |
| | 65 | $9.33 \cdot 10^{-2}$ | $5.33 \cdot 10^{-2}$ | $3.38 \cdot 10^{-3}$ |
| | 75 | $18.60 \cdot 10^{-2}$ | $11.30 \cdot 10^{-2}$ | $6.83 \cdot 10^{-3}$ |
| $E$ (kcal·mole$^{-1}$) | | 15.5 | | 16.7 |
| $\Delta S^{+}$ (cal·mole$^{-1}$·degree$^{-1}$) | 55 | −17,3 | −18.3 | — |
| | 65 | −17.4 | −18.4 | −20.8 |
| | 75 | −17.4 | −18.4 | −20.9 |
| $\Delta G^{+}$ (kcal·degree $^{-1}$) | 55 | 21.7 | 22.0 | — |
| | 65 | 21.9 | 22.2 | 23.7 |
| | 75 | 22.1 | 22.4 | 24.0 |

formamide became dominant already from the fifth minute. In ethanol saturation curves were obtained. The data calculated from the experimental results obtained are given in Table II.

The kinetic and activation data obtained in the three solvents at different temperatures were brought into correlation with the ring size and with the internal struc-

tures of the molecules. $S_N2$ reactions involve a reversible $sp^3 \rightarrow sp^2$ electron shell hybridization in the transition state. The strain theory of BROWN [8], which takes into account the extent of steric strain in the arrangement of the $sp^2$ and $sp^3$ shells and explains the inhibited or favoured natures of the $sp^3 \rightarrow sp^2$ and $sp^2 \rightarrow sp^3$ reactions on this basis, is applicable to cyclic systems.

In cyclic systems the hybridization of the bond is accompanied by angular strain, torsional strain and ring deformation. These changes may be either favourable or unfavourable with respect to the reaction.

In the case of small, three and four-membered rings, the angular strain being high any change results in a significant deformation. In the cyclobutane system the normal bond angle is 90°, which shows a smaller decrease from the tetrahedral bond angle (109° 28′) than from the trigonal bond angle (120°), i. e. the $sp^3$ electron distribution is more favoured than the $sp^2$. This phenomenon can be affected by other factors. The kinetic data obtained by us also show differences from those expected on the basis of the theory. In the case of c-butyl iodide the activation entropy values are significantly decreased, and are less negative compared with those of the other compounds, although on the basis of the $w_0$ values the largest negative activation entropy values were to be expected here. A comparison of our results with the experimental results obtained by other authors for similar systems [9, 10] permits the conclusion that in the case of the c-butyl iodide, as a result of the stabilizing effects of the polar solvents, a carbonium ion complex is formed in advance, at least in part, and this takes part in the substitution reaction.

In the five and seven-membered rings the torsional strain predominates: in the case of cyclopentane, if a planar system is assumed there are oppositions of ten C—H bonds, which result in a torsional strain of about 10 kcal.mole$^{-1}$. Since the molecule is puckered, the total strain is less. On any carbon atom the electron transfer $sp^3 \rightarrow sp^2$ results in a decrease of the strain energy to a value of 4 kcal · mole$^{-1}$. This means that the substitution reactions of the c-pentane systems are relatively fast. Similar conclusions can be drawn for the c-heptane ring, which is likewise a mobile and closed system, although the opposition of the corresponding C—H bonds is of somewhat less importance than for the five-membered rings.

In the six-membered rings the chair-form is free of the bond opposition. The change of the hybridization from $sp^3$ to $sp^2$ brings about the bond opposition, this increases the internal energy, and as a result the substitution reactions are slow in the c-hexyl systems.

The c-octane skeleton is a closed system with angular deformation, bond opposition and ring deformation: since the number of C—H bonds taking part in the opposition will be smaller, the $sp^2$ configuration is more favoured than the $sp^3$ arrangement, and this increases the rate of the substitution reaction.

On the basis of the experimental results, in the case of the homologous series investigated, the rate of the bimolecular nucleophilic substitution decreases in the following order: c-butyl iodide > c-pentyl iodide > c-heptyl iodide > c-octyl iodide > > c-hexyl iodide > 2-methyl-c-hexyl iodide.

This order of the reaction rates is in agreement with both the regularities of the external effects exerted on the reaction and the physical data expected on the basis of the steric structure of the molecule.

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## ИЗУЧЕНИЕ РЕАКЦИЙ ЗАМЕЩЕНИЯ РАЗЛИЧНЫХ ЦИКЛИЧЕСКИХ АЛКИЛЙОДИДОВ МЕЧЕННЫХ ЙОДИСТЫМ КАЛИЕМ. II.

*Влияние этанола как растворителя. Аномальные реакции замещения циклобутилйодида в различных растворителях*

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Иследовались реакции замещения циклопентил-, циклогексил-, циклогептил-, циклооктил-2-метил-циклогексилйодида меченных йодистым калием ($I^{131}$) в среде абсолютного этанола при разных температурах. Реакции замещения циклобутилйодида изучены также в среде диметилформамида и диметилсульфоксида. Обнаружена корреляция между числом членов цикла и природой растворителей с одной стороны и полученными кинетическими характеристиками и константами активации — с другой. Показано отсутствие прямой связи между величиной диэлектрической постоянной среды и скоростью реакций замещения. Большое значение имеют, по-видимому, водородные связи на кинетику реакций в среде этанола. Для реакций замещения циклобутилйодида при любых условиях обнаружены аномалии.

# INFRARED SPECTRA OF METAL-REINECKE COMPOUNDS

By

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*(Received: December 1, 1970)*

The infrared spectra of the Reineckates of metal ions, ammines and complex ions have been studied. It was found that in the infrared spectra of Reineckates of metal ions the C—N band splits into multiplets depending on the electropositivity of the metal ion in the outer sphere.

It is known that Reinecke salt forms stable compounds with metal ions, alkaloids, antibiotics and complex ions [1—7]. CSÁSZÁR [8] has reported on a study of the physico-chemical properties of the Reineckates of transition metal ions. He studied the UV spectra of Reineckates of saturated and unsaturated metal ions in solution, their reflexion spectra, and also their magnetic properties. The results were interpreted on the basis of the ligand field theory. TAKEUCHI and SAITO [9] determined the bond distances in several Reineckates. In a study of the infrared spectra of thiocyanate complexes, NAKAHARA and co-workers [10] stated that in cobalt(III)-hexammine complexes the N—H stretching frequency depends on the outer sphere. Relying upon this experimental fact we found it interesting to study the infrared spectra of some Reineckates.

## *Experimental*

The Reinecke salt $NH_4[Cr(NCS)_4(NH_3)_2H_2O$ was a Reanal product of A. R. grade. Preparation of the respective Reineckates was carried out according to literature data [8, 11]. Acidic (HCl) or neutral solutions of the corresponding components were allowed to react, the precipitate was filtered, washed with water and ethanol, and dried over anhydrous $CaCl_2$ and $P_2O_5$.

The IR spectra were taken as follows: samples were prepared in Merck Uvasol KBr. Spectra were registered by a Zeiss UR—10 spectrophotometer.

## *Discussion*

IR spectral data of Reineckates of ammines are summarized in Table I.

It can be seen that in the case of Reineckates of ammines all the vibrations appear at the same frequency and the $\gamma C \equiv N$ vibrations is a singlet.

In the case of Reineckates of different metal ions marked differences are found in several bands. The most striking feature is that the $\gamma C \equiv N$ band appears as a multiplet for all compounds. The $\delta NCS$ band similarly appears as a doublet.

*Table I*

*IR spectral characteristics of Reineckates of ammines (400—3500 $cm^{-1}$)*

| | $\nu C\equiv N$ | $\delta_a(NH_3)$ | $\delta_s(NH_3)$ | $\varrho r$ | $\delta NCS$ |
|---|---|---|---|---|---|
| *n*-butylamine-R | 2090 | 1590 | 1270 | 694 | 480 |
| triethylamine-R | 2085 | 1600 | 1270 | 700 | 490 |
| 8-hydroxyquinoline-R | 2085 | 1603 | 1275 | 705 | 480 |
| pyridine-R | 2090 | 1595 | 1260 | 698 | 490 |
| piperidine | 2085 | 1612 | 1263 | 700 | 490 |

$R=[Cr(SCN)_4(NH_3)_2]^+$

*Table II*

*IR spectral characteristics of Reineckates of metal ions (400—3500 $cm^{-1}$)*

| | $\nu(NH_3)$ | $\nu C\equiv N$ | $\delta_a(NH_3)$ | $\delta_s(NH_3)$ | $\varrho_r(NH_3)$ | $\delta$ NCS |
|---|---|---|---|---|---|---|
| AqR | 3450—2750 | 2120, 2105, 2090 | 1620 | 1390 | 720 | 455, 425 |
| $CdR_2$ | 3430—3000 | 2135, 2080 | 1605 | 1275 | 720 | 503, 460 |
| $PbR_2$ | 3450—3000 | 2125, 2030 | 1605 | 1270 | 715 | 505, 462 |
| TlR | 3450—3050 | 2120, 2050 | 1610 | 1268 | 718 | 505, 465 |
| $HgR_2$ | 3400—3050 | 2160, 2055, 2075 | 1607 | 1276 | 700 | 500, 472 |
| $CuR_2$ | 3430—3000 | 2112, 2088 | 1610 | 1260, 1270 | 700 | 492, 470 |
| $NH_4R\cdot H_2O$ | 3500—2750 | 2110, 2050 | 1660 | 1265 | 700 | 485 |

$R = [Cr(SCN)_4[NH_3)_2]^+$

The frequencies of $\gamma C\equiv N$ and $\delta N—C—S$ bands of Reineckates of different cobalt(III)-ammine complexes do not differ markedly from those of ammines, and similarly to them do not show multiplets. IR spectral data are shown in Table III.

The effect of the outer ion on the $\gamma C\equiv N$ stretching frequency can be well interpreted by TAKEUCHI and SAITO's results on bond distances [9]. With decreasing C—S bond distances in Reineckates of pyridine and choline, the N—C bond distance simultaneously increases. Thus, the N—C and C—S distances vary depending on the cation in the outer sphere of the Reineckate.

*Table III*

*IR spectral characteristics of Reineckates of some Co(III)-ammine complexes (400—5000 $cm^{-1}$)*

| | $\nu(NH_3)$ | $\nu C\equiv N$ | $\delta_a(NH_3)$ | $\delta_s(NH_3)$ | $\varrho_r(NH_3)$ | $\delta NCS$ |
|---|---|---|---|---|---|---|
| $[Co(NH_3)_6]R_3$ | 3400—2900 | 2095 | 1610 | A 1270, 1255R | 705 | 492 |
| $[Co(NH_3)_5NO_2]R_2$ | 3400—2900 | 2090 | 1610 | A 1320, 1265R | 700 | 492 |
| $[Co(NH_3)_4(NO_2)_2]R$ | 3400—2900 | 2070 | 1630 | A 1320, 1295R | 705 | 495 |

$R=[Cr(SCN)_4(NH_3)_2]^+$ A = ammine of the complex R = ammine of the Reineckate

In the case of the metal ions studied by us with outer ions silver(I), cadmium(II), lead(II), thallium(II), mercury(II) and copper(II), the $\gamma C \equiv N$ band was split into doublets or multiplets. This splitting into multiplets can be interpreted by the mutual effect $Cr—N^{(+)}$ $C—S^{(-)}...Me^{(n+)}$ This interaction is different in the case of cadmium(II), lead(II), and copper(II) ions when $\gamma C \equiv N$ is a doublet, and in the case of silver(II) and mercury(II) compounds which show a triplet.

In Reineckates of complexes and ammines there is no splitting, since the electropositivity of the outer ions is rather small. From the spectral data obtained, it can be stated that the splitting of the $\gamma C \equiv N$ band in Reineckates depends on the electropositivity of the outer ion.

## ИНФРАКРАСНЫЕ СПЕКТРЫ РЕЙНЕКАТОВ СОЕДИНЕНИЙ МЕТАЛЛОВ

*Велимир Николашев, Йожеф А. Сабо и Габор Сепеши*

Авторы изучали инфракрасные спектры различных рейнекатов. Было установлено, что в инфракрасных спектрах рейнекатов полоса $\gamma C \equiv N$ распадает в зависимости от электроположительности иона металла в внешней сфере.

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# STEREOCHEMICAL STUDIES ON 1,3-DIFUNCTIONAL CYCLOPENTANE, CYCLOHEXANE AND CYCLOHEPTANE DERIVATIVES*

By

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*(Received: July 10, 1971)*

The authors give a review of their synthetic and stereochemical studies on cyclic 1,3-aminoalcohols.

The stereospecific synthesis of *cis*- and *trans*-2-aminomethylcyclopentanol and *cis*- and *trans*-2-hydroxymethylcyclopentylamine as well as their cyclohexane and cycloheptane analogues are described. Kinetic and preparative studies of the N → O acyl migration reaction of the cyclopentane and cyclohexane derivatives are discussed. The solvolysis and NMR spectroscopical analysis of tetrahydrooxazines prepared from *cis*- and *trans*-2-aminomethylcyclohexanol and *cis*- and *trans*-2-hydroxymethylcyclohexylamine is interpreted. Preparation and investigation of some other derivatives, mainly acid amides, of the above aminoalcohols of pharmacological interest is also discussed.

## *Introduction*

In our investigations in the field of cyclic 1,3-difunctional derivatives [1—13] we aimed at a comparative kinetic study of cyclopentane, cyclohexane and cycloheptane derivatives synthesized in a stereospecific way, by clearing up the dependence of the reaction rate on ring size, configuration and conformation. The first model compounds studied were the *cis*- and *trans*-1,3-aminoalcohols (I—XII) shown in Fig. 1. One functional group and the methylene group bearing the other are attached to the ring in 1,2 position.

By evaluation of the reactions of these 1,3-aminoalcohols and the intermediates of their stereospecific synthesis, — *i.e.* the *cis*- and *trans*-β-aminocarboxylic acids and *cis*- and *trans*-β-hydroxycarboxylic acids and their derivatives — we wished to clear up the reaction mechanism in detail and to obtain data concerning the conformational relations of the bicyclic intermediates. We hoped that the reaction mechanism of these 1,3-difunctional compounds, based on the kinetic and thermodynamic parameters would permit, in some cases, also a deeper insight into the reaction mechanism of the related 1,2-difunctional compounds investigated earlier. Moreover, our stereohomogeneous model compounds and their numerous homologous derivatives seemed promising for a systematic study of the relation between chemical structure, configuration, conformation, and pharmacological effect.

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* This Paper is based on a lecture of the authors presented at the „Symposium on Reaction Mechanism and Synthesis" organised by the Committee of Organic Chemistry of the Hungarian Academy of Sciences, Mátrafüred, 22nd May, 1971.

Normal, medium and large ring compounds have often been used as models for studying the influence of configuration and conformation on reaction rate and reaction mechanism of organic compounds. Monosubstituted as well as 1,1- and 1,2-disubstituted cyclic compounds, among them 1,2-aminoalcohols, have been most widely investigated, whereas a considerably lower number of publications dealing with the reaction mechanism of 1,3-difunctional compounds are available.

An important impulse to stereochemical studies on cyclic aminoalcohols was due to streptamine, one of the decomposition products of streptomycine, which proved to be 1,3-diamino-2,4,5,6-tetrahydroxycyclohexane [15]. To clarify the steric structure of this compound, MCCASLAND *et al.* investigated the configuration of simpler analogues, *cis*- and *trans*-2-aminocyclohexanol. While in 1949 even the configuration of these compounds was dubious, twenty years later more than 40 of the theoretically possible 80 aminocyclitol isomers were known [19].

Numerous reactions of cyclic 1,2-aminoalcohols, mainly of 2-aminocyclopentanol and 2-aminocyclohexanol, even of their medium and large ring homologues were thoroughly investigated [16—18, 47]. Fused ring analogues, such as 2-amino-3-hydroxytetralin [20] and 1-amino-2-hydroxytetralin, 1-amino-2-hydroxytetralin, 1-amino-2-hydroxyindane [21] were prepared and their stereospecific reactions intensively studied. The synthesis of *cis*- and *trans*-6-amino-6,7,8,9-tetrahydro-5H--benzocycloheptanol-5 and their N→O acyl migration reaction were published quite recently [22]. The same can be said about other cyclic 1,2-amino-alcohols [23] with highly condensed skeleton. The investigation of the mentioned 1,2-aminoalcohol derivatives, as ephedrine analogues, is important also from a pharmacological point of view.

Considering the numerous studies on monosubstituted 1,1- and 1,2-disubstituted normal, medium and large ring compounds, it is difficult to understand why investigations on 1,3-difunctional derivatives have received considerably less attention. This can be scarcely explained by the difficulties in synthesizing the 1,3-difunctional compounds, though the stereospecific synthesis of 1,3-aminoalcohols,

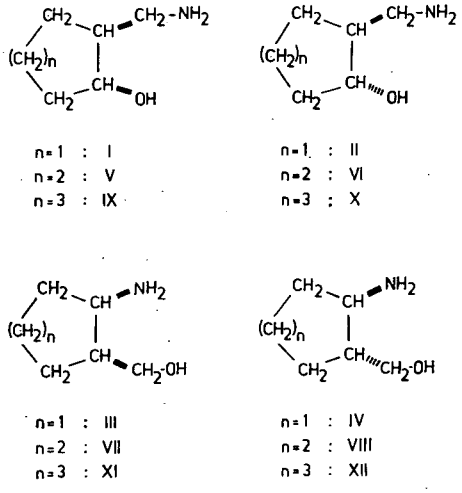



*Fig. 1*

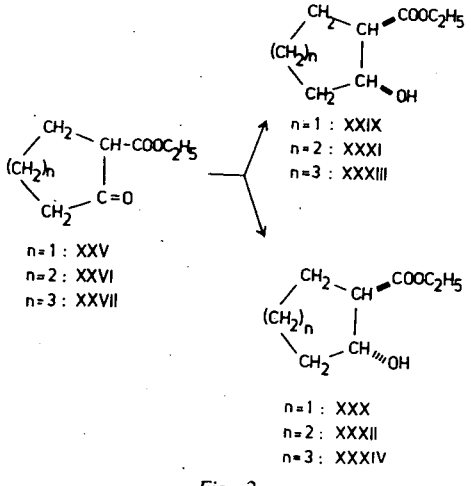



*Fig. 2*

*e.g.* of our model compounds is evidently much more difficult and time-consuming than that of the cyclic 1,2-aminoalcohols. It can be stated (see *e.g.* [6]) that, except a few earlier individual papers, no systematic investigations on 1,3-aminoalcohols, especially on the cyclic ones, were published. Our model compounds (I—XII) were not described or, as we pointed out [5], the earlier syntheses were not stereospecific, *i.e.* the compounds regarded as homogeneous proved to be mixtures of the *cis* and *trans* isomers.

## *Synthesis of model compounds*

The stereospecific synthesis of *cis*- and *trans*-2-aminomethylcyclopentanol (I, II) and *cis*- and *trans*-2-hydroxymethylcyclopentylamine (II, IV), as well as of their analogues with cyclohexane and cycloheptane skeleton (V—VIII, IX—XII) was performed by lithium aluminium hydride reduction of the corresponding *cis*- and *trans*-$\beta$-hydroxycarboxamides and $\beta$-aminocarboxylic acids, respectively (Fig. 3).

Methods for preparing *cis*- and *trans*-2-hydroxycyclopentanecarboxylic acid, *cis*- and *trans*-2-hydroxycyclohexanecarboxylic acid (XLVII, XLVIII), *cis*- and *trans*-2-hydroxycycloheptanecarboxylic acid (XLIX, L) were elaborated by PASCUAL *et al.*, who also determined the configuration of these compounds.

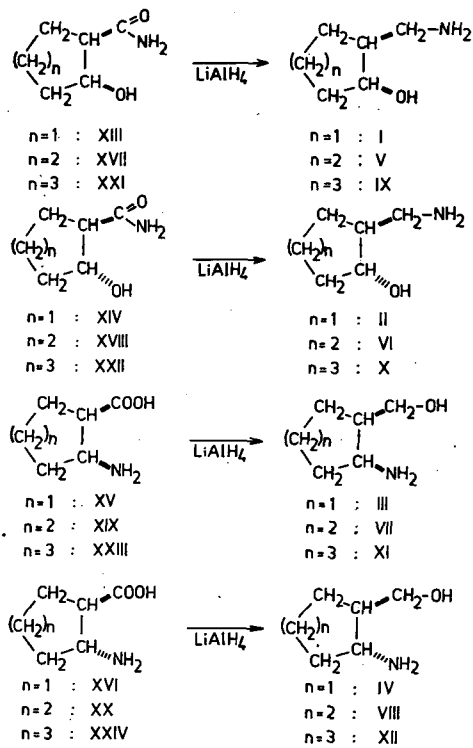



*Fig. 3*

Reduction of 2-carbethoxycyclopentanon (XXV) [24] in the presence of Adams' $PtO_2$ catalyst gave *cis*- and *trans*-2-carbethoxycyclopentanol (XXIX, XXX) [25]. The *cis* and *trans* isomers were separated by a tedious fractional crystallization of their 3,5-dinitrobenzoates, then, by hydrolysis, *cis*- and *trans*-2-hydroxycyclopentanecarboxylic acid was obtained. Though recent application of this method is mentioned in literature [26], it does not seem to be convenient for preparing larger quantities, especially of the *trans* isomer obtainable from the mother liquor.

Recently a continuous countercurrent distribution method for the separation of *cis*- and *trans*-2-carbethoxycyclopentanol (XXIX, XXX) was elaborated by MÖHRLE and BAUMANN [27]. Also this method is suitable only for the separation of smaller quantities, like the separation by preparative gas chromatography [92].

PASCUAL *et al.* studied the reduction of 2-carbethoxycyclopentanon (XXV) with different methods. Reduction with sodium borohydride gave mainly *trans*-2-hydroxycyclopentanecarboxylic acid instead of *cis*- and *trans*-2-carbethoxycyclopentanol (XXIX, XXX) [28].

We found that the most convenient method for the preparation of *cis*- and *trans*-2-carbethoxycyclopentanol (XXIX, XXX) was the separation of the isomeric mixture obtained with sodium borohydride or Raney nickel reduction of 2-carbethoxycyclopentanone (XXV) by fractional distillation on a column of high efficiency. Reduction with Raney nickel catalyst in ethanolic solution at 60°C, starting from 120 atm. pressure, yielded 87.3% *cis*- and 12.7% *trans*-2-carbethoxycyclopentanol, according to gas-chromatographic analysis. The sodium borohydride reduction, especially at lower temperatures, gave the *trans* isomer as the main product [11]. This is in good accordance with our earlier results obtained with sodium borohydride reduction of 2-carbethoxy-4-*t*-butylcyclopentanon [14], where the ratio of the isomers containing the hydroxyl and carbethoxyl groups in *trans* position increased with decreasing temperature.

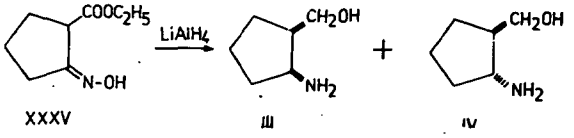



*Fig. 4*

The reduction of the acid amides (XIII, XIV) obtained from the stereohomogeneous 2-carbethoxycyclopentanols was performed in tetrahydrofurane solution with lithium aluminium hydride at 60°C in 20 hrs and gave *cis*- and *trans*-2-aminomethylcyclopentanol (I, II) with good yield [12].

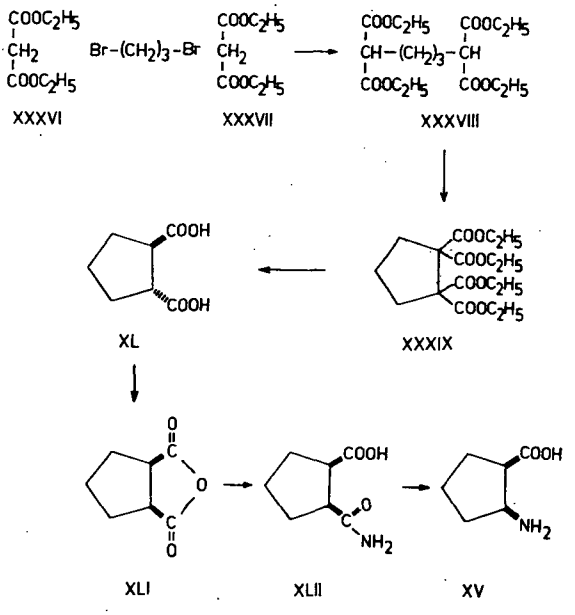



*Fig. 5*

The preparation of *cis*- and *trans*-2-hydroxymethylcyclopentylamine (III, IV) was achieved with lithium aluminium hydride reduction of *cis*- and *trans*-2-aminocyclopentanecarboxylic acid (XV, XVI) [12]. The synthesis of 2-hydroxymethylcyclopentylamine described by GASSMAN and HECKERT [30] cannot be regarded as stereospecific, because the lithium aluminium hydride reduction of the 2-carbethoxycyclopentanon oxime (XXXV) evidently gives a mixture of the *cis* and *trans* isomers (III, IV) (Fig. 4).

We synthesized *cis*-2-aminocyclopentanecarboxylic acid (XV) applying PERKIN's synthesis [31] modified by BAILEY and SORENSON [32] with some further modifications, as shown in Fig. 5.

*Trans*-2-aminocyclopentanecarboxylic acid (XVI) can be prepared from 1-cyclopentene-1-carboxylic acid (XLIII) by ammonia addition [33, 34] (Fig. 6). For the preparation of 1-cyclopentene-1-carboxylic acid, we found the dehydration

of *cis*- and *trans*-2-hydroxycyclopentanecarboxylic acid, occurring during the distillation at atmospheric pressure, as the most convenient method.

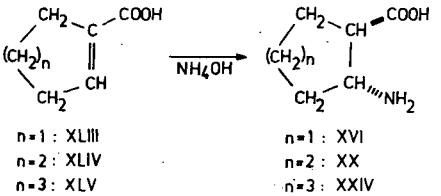



*Fig. 6*

*Cis*- and *trans*-2-hydroxycyclohexanecarboxamide (XVII, XVIII) was obtained similarly to the cyclopentane analogues [5]. For preparing *trans*-2-hydroxycyclohexanecarboxylic acid, besides separation by fractional distillation of *cis*- and *trans*-2-carbethoxycyclohexanol (XXXI, XXXII) furnished by sodium borohydride or Raney nickel reduction of 2-carbethoxycyclohexanon (XXV) [36], isomerization of *cis*-2-hydroxycyclohexanecarboxylic acid with 30—40% sodium hydroxide can also be applied [4, 37] (Fig. 7). This alkaline isomerization is also suitable for the preparation of *trans*-2-hydroxycycloheptanecarboxylic acid (L) [38, 39], while it cannot be used to prepare the *trans*-2-hydroxycylcopentanecarboxylic acid because, on heating in alkaline solution, dehydration yielding 1-cyclopentene-1-carboxylic acid (XLIII) takes place [35].

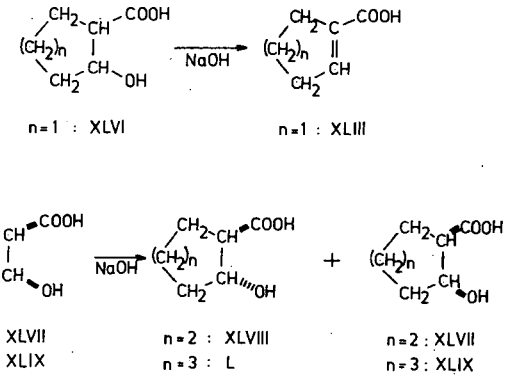



*Fig. 7*

*Cis*- and *trans*-2-aminomethylcyclohexanol (V, VI) were earlier described by MOUSSERON *et al.* [40, 41]. They prepared *trans*-2-aminomethylcyclohexanol (VI) *via* *trans*-2-chlorocyclohexanol → 2-cyanocyclohexanol with subsequent reduction by sodium in ethanol. MORICONI and MAZZOCCHI [42] considered *trans* configuration of this compound as questionable. They found the argument used by MOUSSERON *et al.*, namely that the alkaline hydrolysis of the 2-cyanocyclohexanol gives *trans*-2-hydroxycyclohexanecarboxylic acid, was not convincing because in alkaline medium isomerization can take place [37]. MORICONI and MAZZOCCHI synthesized *cis*-2-azabicyclo-(4,2,0)-octane from N,O-ditosyl-*cis*-2-aminocyclohexanemethanol prepared in a stereospecific way. Since the product was identical with that obtained from the ditosylate of the aminoalcohol prepared from 2-cyanocyclohexanol, they considered the configuration of the latter to be proved.

On the base of preparative, IR and NMR spectroscopic evidences, we could unambiguously prove [5] that the *trans*-2-aminomethylcyclohexanol described by MOUSSERON *et al.* was a mixture of the *cis* and *trans* isomers (V, VI). The deficiency of the indirect proof used by MORICONI and MAZZOCCHI can be explained by the circumstance that they obtained the N-tosyl-*cis*-7-azabicyclo-(4,2,0)-octane with a poor yield, which can also be the case starting from a mixture of isomers. It is evident, that the Cl → CN replacement reaction occurs with neighbouring hydroxyl participation, however, even the cleveage of an epoxide ring cannot be considered as a proof

of the configuration [44]. Furthermore, as it is known from experiments of SZÁNTAY and TŐKE [45], the hydroxyl-nitrils can isomerize in alkaline medium.

The *cis*-2-aminomethylcyclohexanol described by MOUSSERON *et al.* did not prove to be stereohomogeneous either. They obtained the *cis* isomer from the N-benzoyl derivative of the above *trans*-2-aminomethylcyclohexanol *via* the oxazoline derivative. MOUSSERON *et al.* gave 172—174°C as m.p. of *cis*-2-aminomethylcyclohexanol hydrochloride, whereas the authentic hydrochloride prepared by us *via* lithium aluminium hydride reduction of *cis*-2-hydroxycyclohexanecarboxamide (XVII) melts at a considerably higher temperature: 182.5—183°C. The stereohomogeneity of our product is proved by IR and NMR spectra.

*Cis*- and *trans*-2-hydroxymethylcyclohexanol (VII, VIII) were prepared by MORICONI and MAZZOCCHI [42]. We reported [1] on the sysnthesis of these compounds at the same time as the American authors. Though the synthetic pathway was essentially the same, the *trans*-2-hydroxymethylcyclohexylamine hydrochloride described by MORICONI and MAZZOCCHI melted at 140—142°C, whereas the m.p. of our compound was 151.5—152°C. The validity of our data is supported by an earlier publication of MOUSSERON *et al.* [43], who reported the m.p. of the 2-hydroxymethylcyclohexanol hydrochloride (without indicating the configuration), obtained by treatment of 2-hydroxymethylcyclohexylbromide with ammonium hydroxyde, to be 148—150°C. As the m.p. of the *cis*-2-hydroxymethylcyclohexylamine hydrochloride prepared by us is 133—134°C, in accordance with the data given by MORICONI and MAZZOCCHI, it follows that the compound described by MOUSSERON *et al.* [43] (not cited by MORICONI and MAZZOCCHI) must be *trans*-2-hydroxymethylcyclohexylamine hydrochloride contaminated with some *cis* isomer. The essentially lower m.p. found by MORICONI and MAZZOCCHI can be explained by the fact that, instead of purifying the *trans*-2-aminocyclohexanecarboxylic acid (XX) obtained from 1-cyclohexene-1-carboxylic acid (XLIV), they subjected the reaction product immediately to esterification and lithium aluminium hydride reduction.

*Cis*- and *trans*-2-carbethoxycycloheptanol (XXXIII, XXXIV) used for the preparation of *cis*- and *trans*-2-aminomethylcycloheptanol (IX, X) was obtained by reduction of 2-carbethoxycycloheptanon (XXVII), which can be prepared by condensing cycloheptanone (LI) and diethyl oxalate with sodium ethylate, or by condensation of cycloheptanon and diethyl carbonate with sodium hydride or sodium amide [38, 39]. We performed these reactions under various conditions [11].

Reduction of 2-carbethoxycycloheptanon (XXVII) was performed by PALAU, PASCUAL and RÁFOLS in ethanolic solution in the presence of $PtO_2$ catalyst or in methanolic solution with sodium borohydride [38]. They did not separate the *cis*- and *trans*-2-carbethoxycycloheptanol, nor did they determine the isomer ratio. As the main product of the catalytic reduction is the *cis* isomer, they obtained the *cis*-2-hydroxycycloheptanecarboxylic acid (XLIX) by fractional crystallization of the acids (XLIX, L) resulting from the hydrolysis of the reduction product. They prepared the *trans* isomer (L) by alkaline isomerization and controlled the stereohomogeneity of both acids by IR spectra.

BHARGAVA, MATHUR and SAHARIA, in a quite recent publication [39], also dealt with the preparation of *cis*- and *trans*-2-hydroxycycloheptanecarboxylic acid, without mentioning the above paper [38] of the Spanish authors. They described the reduction product of 2-carbethoxycycloheptanone (XXVII) with sodium borohydride as stereohomogeneous *cis*-2-carbethoxycycloheptanol, without giving any

proof of the stereohomogeneity. They similarly considered the reaction product of XXVII in ethanolic solution at atmospheric pressure in the presence of W-7 Raney nickel catalyst as a stereohomogeneous *cis* compound.

We found [11] the product obtained by the reduction of the 2-carbethoxycycloheptanone (XXVII) in ethanolic solution, using Raney nickel catalyst at 70°C with 100 atm. starting pressure, to contain *cis*- and *trans*-2-carbethoxycycloheptanol in the ratio 85:15, determined by gas-chromatographic analysis. Reduction with sodium borohydride gave approximately the same ratio, though, according to our experience, the formation of the *trans* isomer in the cyclopentane and cyclohexane analogues by sodium borohydride reduction is more pronounced.

*Cis*- and *trans*-2-carbethoxycycloheptanol (XXXIII, XXXIV) could also be separated on a column of high efficiency, and hydrolysis of the resulting gas-chromatographically homogeneous esters yielded authentic *cis*- and *trans*-2-hydroxycycloheptanecarboxylic acids (XLIX, L).

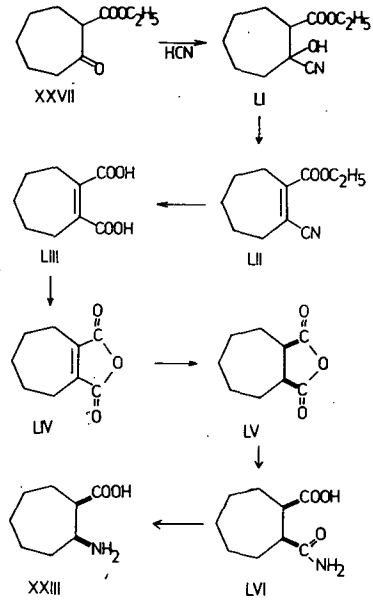



*Fig. 8*

The preparation of the *trans* amino acid (XXIV) used for the synthesis of the *trans*-2-hydroxymethylcycloheptylamine (XII) was achieved from the corresponding olefinic carboxylic acid (XLV) by ammonia addition (Fig. 6), whereas the *cis*-2-aminocycloheptanecarboxylic acid (XXIII) was obtained starting from 2-carbethoxycycloheptanone (XXVII) (Fig. 8) [46].

### N→O *acyl migration reaction of* N-*benzoyl- and p-substituted* N-*benzoyl-derivatives of cis- and trans-2-aminomethylcyclohexanol and cis- and trans-2-hydroxymethylcyclohexylamine*

N→O acyl migration of amino alcohols was reviewed in numerous communications [47—51]. Mechanism, kinetics, stereochemistry, preparative and other application of the process were thoroughly studied. The importance of N→O, O→O, N→N and N→S acyl migration and acyl exchange in biology has also been reviewed [51]. A very comprehensive survey of the acyl migration processes is to be found in the paper of PAVLOVA and RACHINSKII [47], who give a detailed review of the investigations on acyl migration up to 1968, with 228 references.

In contrast to the numerous investigations on the N→O acyl migration reaction of acyclic and alicyclic 1,2-aminoalcohols, only a few papers dealing with acyclic and alicyclic 1,3-aminoalcohol derivatives were published. N→O acyl migration of cyclic 1,3-aminoalcohols has been investigated mainly on models containing the nitrogen in a piperidine ring. Representants of this type are the N-benzoyl-2-(2'-piperidyl)-2-phenylethanol diastereomers studied by WEISZ and DUDÁS [62]. The authors found no difference in reactivity between the *erythro* and *threo* isomers in the N→O acyl migration reaction.

A review of further publications can be found in our earlier paper [6]. The simplified mechanism of the N→O acyl migration reaction occuring with retention (R) mechanism is shown in Fig. 9, that of the reaction with inversion (I) mechanism in Fig. 10. The participation of water in this latter process has been recently proved by WELSH [52] using isotope technique.

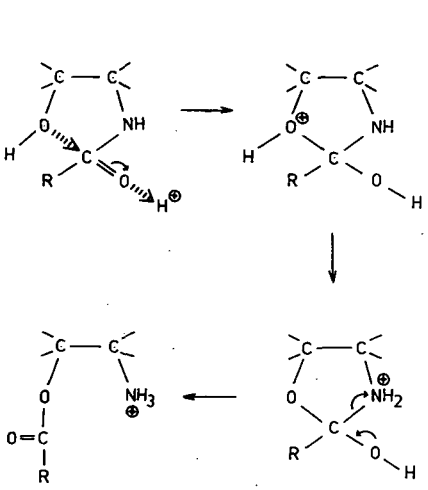


*Fig. 9*

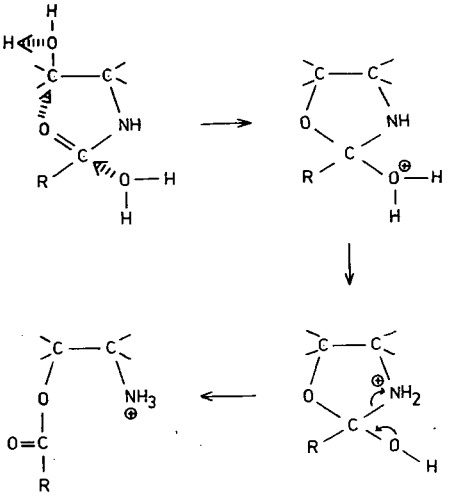


*Fig. 10*

We studied [1, 2, 6] the N→O acyl migration reaction of N-benzoyl and *p*-substituted N-benzoyl derivatives of *cis*- and *trans*-2-aminomethylcyclohexanol and of *cis*- and *trans*-2-hydroxymethylcyclohexylamine (LVII—LXVIII) (Fig. 11) in abs. dioxane solution in presence of a 0.5 mole excess of hydrochloric acid under nitrogen protecting blanket at 2—4 different temperatures in the temperature range 70—112.3°C for each compound. The rate constants determined at $100 \pm 0.3$°C, as well as the activation energies and activation entropies are listed in Table I. In these 1,3-aminoalcohols the N→O acyl migration proceeds faster in the *trans* isomers, whereas in the case of 1,2-aminoalcohols with cyclohexane skeleton, in the *cis*- and *trans*-2-benzamidocyclohexanol [53—55], the rate of the N→O acyl migration reaction of the *cis* isomer is significantly higher.

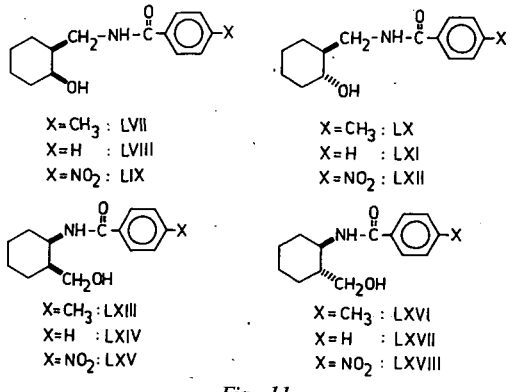



*Fig. 11*

The bicyclic transition state of the N→O acyl migration reaction of 2-benzamidocyclohexanols is of monoazamonooxahydrindane structure, while that of the 1,3-amino-

*Table I*

*Rate constants and thermodynamic parameters for* N→O *acyl migration of* N-*benzoyl and p-substituted* N-*benzoyl derivatives of cis- and trans-2-aminomethylcyclohexanol and cis- and trans-2-hydroxymethylcyclohexylamine*

| Compound | Configuration | No. | °C | $k_2 \cdot 10^3 \cdot \cdot sec^{-1}$ | $\Delta E^{+}_{+}$ (kcal/mole) | $\Delta S^{+}_{+}$ e. u. | $\frac{k_{trans}}{k_{cis}}$ |
|---|---|---|---|---|---|---|---|
| N-*p*-methylbenzoyl-2-aminomethylcyclohexanol | *cis* | LVII | 100.3 | 2.93 | 18.3 | −23.6 | 1.64 |
| | *trans* | LX | 100.3 | 4.83 | 15.4 | −30.3 | |
| N-benzoyl-2-aminomethylcyclohexanol | *cis* | LVIII | 100.0 | 2.02 | 15.8 | −30.7 | 2.18 |
| | *trans* | LXI | 100.0 | 4.78 | 14.7 | −32.2 | |
| N-*p*-nitrobenzoyl-2-aminomethylcyclohexanol | *cis* | LIX | 100.1 | 1.17 | 18.2 | −25.7 | 2.04 |
| | *trans* | LXII | 100.3 | 2.14 | 14.8 | −33.6 | |
| N-*p*-methylbenzoyl-2-hydroxymethylcyclohexylamine | *cis* | LXIII | 99.7 | 7.50 | 14.7 | −31.2 | 3.20 |
| | *trans* | LXVI | 99.7 | 24.04 | 12.6 | −32.4 | |
| N-benzoyl-2-hydroxymethylcyclohexylamine | *cis* | LXIV | 100.3 | 5.15 | 11.7 | −40.0 | 3.93 |
| | *trans* | LXVII | 100.3 | 20.28 | 11.1 | −38.7 | |
| N-*p*-nitrobenzoyl-2-hydroxymethylcyclohexylamine | *cis* | LXV | 100.3 | 5.13 | 14.7 | −32.7 | 4.67 |
| | *trans* | LXVIII | 99.7 | 13.17 | 11.8 | −25.9 | |

alcohols has a monoazamonoxadecalin arrangement. The interpretation of the relative reaction rates of the N→O acyl migration reaction merely on the basis of the energetics of the transition state involves, however, some problems. As known, the tendency of ring closure does not go parallel with the stability of the product [56] even if the product is isolable and stable, because other factors (*e.g.* probability factor, ring strain, etc.) influence the process.

The bicyclic transition states (LXIX—LXXII) of the N→O acyl migration reaction of N-benzoyl and *p*-substituted N-benzoyl derivatives of *cis*- and *trans*-2-aminomethylcyclohexanol and of *cis*- and *trans*-2-hydroxymethylcyclohexylamine are shown in Fig. 12. The *trans*-monoazamonooxadecalin-like transition states (LXXI, LXXII) of the N→O acyl migration reaction of the *trans* isomers (LX—LXII, LXVI—LXVIII) are evidently more easily formed than the *cis*-monoazamonooxadecalin-like transition states (LXIX, LXX) of the *cis* isomers (LVII—LIX, LXIII—LXV), because there are three *gauche*-butane interactions more in *cis*-decalin than in *trans*-decalin. This leads to an enthalpy difference of 2.4—3.1 kcal/mole [57].

In first approximation, the mechanism of these N→O acyl migration reactions may be regarded as analogous to that of the 1,2-aminoalcohols, proceeding with

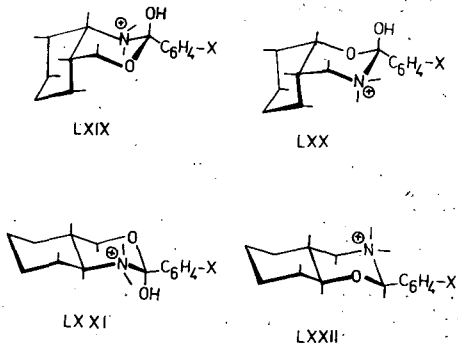



*Fig. 12*

retention (Fig. 9). The elementary steps and thermodynamic characteristics of this reaction are similar to those of the reactions of the acid catalysed A-2 type bimolecular hydrolysis of esters and acid amides [58]. BENDER [59] described the latter processes as involving six steps. However, most of the steps are very fast, as is general in the case of acid catalysed reactions [60], therefore the first two steps are rate determining [61].

In acid catalysed reactions the reaction proceeds through an activated complex formed by proton addition. If solvation of the activated complex takes place in the rate determining step, the rate equation will include the activity coefficient of the solvent. The degree of solvation is of importance from the point of view of proton transfer and for determining the compression of the transition state.

As indicated by NMR results [63, 64], the protonation of acid amides, which is important in the N→O acyl migration reaction, takes place on the carbonyl oxygen. The next step is an intramolecular nucleophilic attack of the alcoholic hydroxyl group on the carbon atom of the protonated carboxyl group, leading to the formation of the cyclic transition state. This proceeds, instead of a „back side" attack on the protonated carbonyl carbon atom of the acid amide, perpendicularly to the plane of the three substituents attached to it. This steric course is widely accepted in the reactions of the carboxylic acid derivatives. In the hydrolysis of esters, BENDER [59] pointed out, that the perpendicular attack is energetically favoured because it allows the maximum overlap of the nucleophil and of the carbonyl $\pi$-orbitals. The rearrangement of the transition complex into O-acyl product proceeds in several steps, by protonation, deprotonation and cleavage of the carbon-nitrogen bond.

The reaction rate of the cyclohexylamine derivatives (LXIII—LXVIII) is higher than that of the aminomethylcyclohexanol derivatives (LVII—LXII), the formation of the cyclic transition state beeing obviously easier with the less shielded hydroxymethyl group. The energy of activation is the lowest for the N→O acyl migration reaction of N-acyl-*trans*-2-hydroxymethylcyclohexylamine (LXVI—LXVIII) derivatives. The two substituents attached to the cyclohexane ring are in *equatorial* position and the formation of the *trans*-monoazamonooxadecalin-like transition state (LXIX) requires a relatively low activation energy (11.1—12.6 kcal/mole). This is less than the activation energy of the N→O acyl migration reaction of the *cis*-2-benzamidocyclopentanol (12.9 kcal/mole) and significantly lower then the activation energies for *cis*- and *trans*-2-benzamidocyclohexanol (15.2 and 17.2 kcal/mole, respectively [53]). The energy of activation for the acyl migration reaction in the corresponding N-benzoyl-*cis*-2-hydroxymethylcyclohexylamine (LXIV) is 11.7 kcal/mole, while that of the *trans* hydroxymethyl derivative (LXVII) is 11.1 kcal/mole.

Comparing the N→O acyl migration reaction of *cis*- and *trans*-2-benzamidocyclohexanol and of the analogous 1,3-aminoalcohols, lower energies of activation in the latter are to be found associated with larger negative entropies of activation. We found the entropies of activation for the N→O acyl migration of *cis*- and *trans*--N-benzoyl-2-aminomethylcyclohexanol (LVIII, LXI) and *cis*- and *trans*-N-benzoyl-2-hydroxymethylcyclohexylamine (LXIV, LXVII) to be —30.7, —32.2 and —40.0, 38.7 e.u., respectively. These are significantly more negative than the values —25.3 and —20.1 e.u., reported for *cis*- and *trans*-2-benzamidocyclohexanol [53]. The energies of activation of all 1,3-aminoalcohol derivatives investigated (LVII—LXVIII) are higher for the *cis* isomers (LVII—LIX, LXIII—LXV) than for the

*trans* isomers (LX—LXII, LXVI—LXVIII), whereas the entropies of activation are more negative in *trans*-2-aminomethylcyclohexanol (LX—LXII) and *cis*-2-hydroxymethylcyclohexylamine derivatives (LXIII, LXV).

LXIX was indicated as the most probable transition state of the N→O acyl migration of N-benzoyl-*cis*-2-hydroxymethylcyclohexylamine. Among the transition states of isomeric 1,3-aminoalcohols this is apparently the most crowded (Fig. 12). This explains the high negative entropies of activation of *cis*-2-hydroxymethylcyclohexylamine derivatives.

The four theoretically possible transition states in which the hydroxyl group corresponds to that of the *cis-trans*-2-decalol (LXXIII, LXXIV) and *cis-cis*-2-decalol (LXXV, LXXVI) are shown in Fig. 13. As can be seen, the internal strain due to *axial* 1,3-interactionsis the lowest for structure LXXIII. The phenyl group is *equatorial* also in LXXV, however in this conformation the *gauche*-butane interaction of the hydroxyl group and of the $C_8$—$C_9$ carbon-carbon bond is much stronger than the interaction of the hydrogen and the C—C bond in LXXIII. In the other two conformations the phenyl group is *axial*, therefore these conformations of the transition states are energetically not favoured. As a conclusion, it can be stated, that the large negative entropy of activation of the *cis*-2-hydroxymethylcyclohexylamine derivatives (LXIII—LXV) is to be explained by the crowded steric arrangement of the transition state of the N→O acyl migration reaction, the inability of the transition state to undergo conformational changes, and by the low probability factor of its formation.

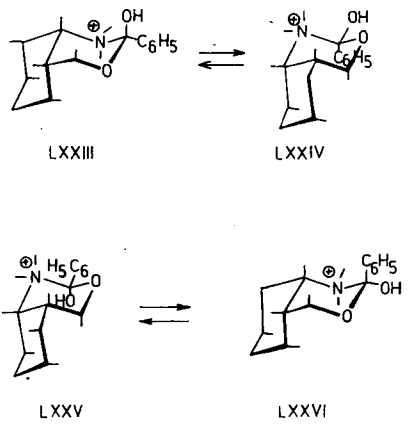



*Fig. 13*

The logarithms of the rate constants at 100°C are shown in Fig. 14, in the or-

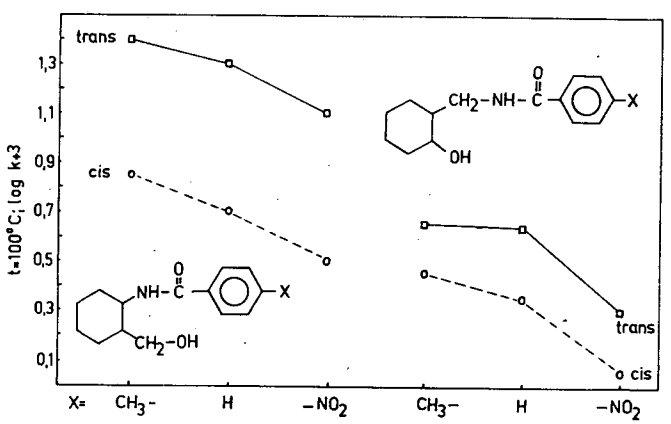



*Fig. 14*

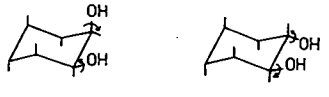
der of the *p*-substituent of the benzoyl group. Investigations on the effect of further *p*-substituents are in course. The N→O acyl migration reaction being a multistep process and the electrostatic effect of the *p*-substituents attached to the benzoyl group being different in the part-processes, a nonlinear Hammett relation [65] is to be expected. By determining the reaction rates for other *p*-substituents and evaluating the nonlinear Hammett relation, deeper insight into the part-processes of the reaction may be expected.

The above mechanism of the N→O acyl migration process leads to a deeper understanding of the N→O acyl migration reaction of the *cis*- and *trans*-2-benzamidocyclohexanol. Namely, the earlier explanation of the significant difference in the reactions rates of the N→O acyl migration reaction of *cis*- and *trans*-2-benzamidocyclohexanol and related cyclic 1,2-aminoalcohols included some difficulties. The lower reactivity of the *trans* isomers was explained by the *trans diaxial* conformation of substituents both in the 2-benzamidocyclohexanol [53] and in 2-amino--3-hydroxytetralin derivatives [20]. However, on the basis of the principles of conformational analysis, the *diequatorial* arrangement of the substituents in the *trans* isomers is most favoured.

ANGYAL and MCDONALD [66] pointed out that, though the dihedral angle between the *equatorial-axial* hydroxyl groups in *cis*-cyclohexane-1,2-diol (LXXVII) and *diequatorial trans*-2-cyclohexane-1,2-diol (LXXVIII) is equal to 60° and their distance is 2.86 Å in both cases, the *cis* diol readily gives acetonid, while the *trans* does not. The motion of hydroxyl groups of the *trans* isomer in the direction shown by the arrows (Fig. 15) results in increasing the 1,3 *axial-axial* hydrogen-hydrogen interactions, while in the *cis* isomers it corresponds to a chair-chair interconversion.

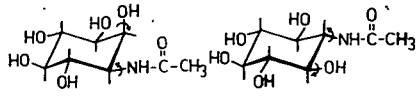
In addition to the 1,3-*axial* interactions, the conformational requirements involved in the formation of the bicyclic transition state by perpendicular attack of the alcoholic hydroxyl should also be taken into account. In the N→O acyl migration reaction of *cis*-2-benzamidocyclohexanol the substituents attached to the amide-carbon atom can occupy in-plane positions relative to the plane of the cyclohexane skeleton, the *axial* hydroxyl attacking from above, as part of a chair-chair conformational change. On the other hand, the above substituents of the *diequatorial trans* isomer should lie in a plane perpendicular to the cyclohexane ring, which is apparently less favourable. In the case of the *trans* isomer the bicyclic transition state forms by the attack of the *equatorial* hydroxyl from the side, this process being also less favourable.

Considering the great difference in the rate constants of the N→O acyl migration reaction of *cis*- and *trans*-inosamine derivatives (LXXIX, LXXX), (Fig. 16), it follows that besides the 1,3 *axial-axial* interactions also the approach of the *equatorial* substituents plays a role. The *equatorial* substituents being hydroxyls in this case the difference in the reaction rates is more pronounced, than in the case of the *cis*- and *trans*-2-benzamidocyclohexanol, where hydrogen-hydrogen interactions occur.




LXXVII LXXVIII

*Fig. 15*




LXXIX LXXX

*Fig. 16*

### N→O *acyl migration reaction of* N-*benzoyl-cis- and trans*-2-*aminomethylcyclopentanol and* N-*benzoyl-cis- and trans*-2-*hydroxymethylcyclopentylamine*

N→O acyl migration reactions of the cyclopentane derivatives (LXXXI—XXXIV) (Fig. 17) were investigated [3, 12] under the same conditions as those of the analogous cyclohexane derivatives [2, 12]. The N→O acyl migration reaction of N-benzoyl-*cis*-2-aminomethylcyclopentanol (LXXXI) was studied in the temperature range 100.8 to 125°C, that of the N-benzoyl-*cis*-2-hydroxymethylcyclopentylamine (LXXXIII) between 84.0 and 110.0 °C. The reactivity of the corresponding *trans* isomers being essentially lower, the N→O acyl migration reaction of N-benzoyl-*trans*-2-aminomethylcyclopentanol (LXXXII) and N-benzoyl-*trans*-2-hydroxymethylcyclopentylamine (LXXXIV) could only be studied at 130.2°C. Because of the extremely low reactivity of the *trans* isomers (LXXXII, LXXXIV) at lower temperatures and side reactions occuring at higher temperatures, it was not possible to obtain well reproducible rate constants and to determine the activation energies and activation entropies of these reactions.

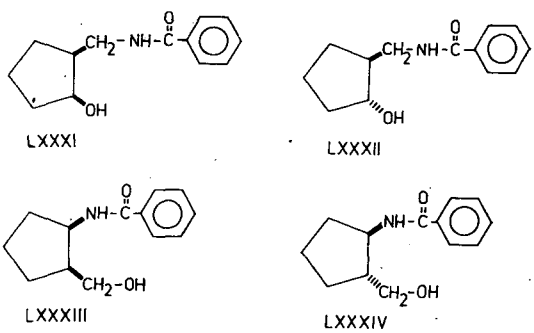



*Fig. 17*

Rate constants calculated from the second order equation, activation energies and activation entropies are listed in Table II. In contrast with the analogous cyclohexane derivatives, the reaction rate, as well as the activation energy and activation entropy of N-benzoyl-*cis*-2-aminomethylcyclopentanol (LXXXI) and N-benzoyl-*cis*-2-hydroxymethylcyclopentylamine (LXXXIII) are essentially higher than those of the corresponding *trans* isomers (LXXXII, LXXXIV).

A similar relation has been found in the N→O acyl migration reaction of *cis*- and *trans*-2-benzamidocyclopentanol and *cis*- and *trans*-2-*p*-nitrobenzamidocyclopentanol [67], where the reaction rate of the *cis* isomer also exceeds that of the *trans* isomers by orders of magnitude. The striking rate difference is due to the fact that the N→O acyl migration reaction of the *trans*-2-aminocyclopentanol derivatives occurs with inversion.

However, as we pointed out [6], the relative rates of the N→O acyl migration reaction of 1,2- and 1,3-aminoalcohols do not necessarily show parallelism. Namely, while the reaction rate of the N→O acyl migration reaction of *cis*-2-benzamidocyclohexanol significantly exceeds that of the *trans* isomer (303:76), in the case of *cis*- and *trans*-2-aminomethylcyclohexanol and *cis*- and *trans*-2-hydroxymethylcyclohexylamine derivatives (LVII—LXII and LXIII—LXVIII) it is the *trans* isomer which has the higher reaction rate (see Table I).

In the acyl migration reactions of N-benzoyl-*cis*-2-aminomethylcyclopentanol (LXXXI) and N-benzoyl-*cis*-2-hydroxymethylcyclopentylamine (LXXXIII) the reaction rate of the latter is higher — as found also with the analogous cyclohexane deriv-

*Table II*

*Reaction rate constants, activation energies and activation entropies of the* N→O *acyl migration reactions of cis- and trans-*N*-benzoyl-2-aminomethylcyclopentanol and cis- and trans-*N*-benzoyl--2-hydroxymethylcyclopentylamine*

| N-benzoyl-*cis*-2-aminomethylcyclopentanol (LXXXI) | | N-benzoyl-*cis*-2-hydroxymethylcyclopentylamine (LXXXIII) | |
|---|---|---|---|
| t = °C | $k_2 \cdot 10^3 \cdot sec^{-1}$ | t = °C | $k_2 \cdot 10^3 \cdot sec^{-1}$ |
| | | 84 | 3.87 |
| 100.8 | 2.89 | 100.4 | 7.80 |
| 110.0 | 3.37 | 110.4 | 10.31 |
| 125.0 | 5.33 | | |
| $\Delta E^{\ddagger} = 11.7$ kcal/mole | | $\Delta E^{\ddagger} = -11.2$ kcal/mole | |
| $\Delta S^{\ddagger} = -41.8$ e.u. | | $\Delta S^{\ddagger} = -36.9$ e.u. | |
| N-benzoyl-*trans*-2-aminomethylcyclopentanol (LXXXII) | | N-benzoyl-*trans*-2-hydroxymethylcyclopentylamine (LXXXIV) | |
| t = °C | $k_2 \cdot 10^3 \cdot sec^{-1}$ | t = °C | $k_2 \cdot 10^3 \cdot sec^{-1}$ |
| 130.2 | 0.74 | 130.2 | 0.87 |

atives (LVIII, LXIV) — the hydroxymethyl group being less shielded than the secondary hydroxyl group.

There are no marked differences between the activation energies of the N→O acyl migration reactions of N-benzoyl-*cis*-2-aminomethylcyclopentanol (LXXXI) and N-benzoyl-*cis*-2-hydroxymethylcyclopentylamine (LXXXIII) ($\Delta E^{\ddagger} = 11.70$ and 11.22 kcal/mole, respectively). The difference in the reaction rate of the above compounds can be explained by the fact that the activation entropy of the N-benzoyl--*cis*-2-hydroxymethylcyclopentylamine (LXXXIII) is less negative ($\Delta S^{\ddagger} = -36.9$ e.u.) than that of the N-benzoyl-*cis*-2-aminomethylcyclopentanol (LXXXI) ($\Delta S^{\ddagger} = -41.8$ e.u.). It is to be mentioned, that in the N→O acyl migration reaction of the cyclopentane derivatives (LXXXI, LXXXIII) the activation entropy of the compound LXXXI containing a secondary hydroxyl group is higher, whereas in the analogous cyclohexane derivatives (LVIII, LXIV) the compound LXIV containing a primary hydroxyl group has higher activation entropy.

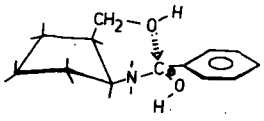



*Fig. 18*

The formation of the bicyclic transition state of the N-benzoyl-*cis*-2-hydroxymethylcyclopentylamine (LXXXIII) is shown in Fig. 18. According to the mechanism described for the cyclohexane derivatives, the three substituents involved in the formation of the transition state of the protonated acid amide in the half-chair conformation of the cyclopentane skeleton [4, 26, 68,

69] are in a plane perpendicular to that of the figure, the hydroxyl group attacking in the plane of the figure at right angle to the plane determined by the three substituents.

The formation of the bicyclic transition state from the N-benzoyl-*cis*-2-aminomethylcyclopentanol is, of course, less favoured; this explains the very high negative entropy of activation of the reaction, though in the present case, in contrast to the *trans* isomer, the hydrogen-hydrogen interactions in the formation of the transition state do not increase.

It is surprising that the rate constants of the N→O acyl migration reaction of the N-benzoyl-*trans*-2-aminomethylcyclopentanol (LXXXII) and of the N-benzoyl-*trans*-2-hydroxymethylcyclopentylamine (LXXXIV) are lower by about an order of magnitude even at 130.2°C than those of the *cis* isomers (LXXXI, LXXXIII) determined at 100.8 and 100.4°C, respectively (see Table II). Namely, the formation of the six-membered transition state from these 1,3-aminoalcohols could be expected to occur without difficulties even in the *trans* isomers, the energy difference between the analogous *cis*- and *trans* carbocyclic compounds (*cis*- and *trans*-hydrindane) being negligible.

However, examination of Dreiding models shows convincingly the great difference in the distances of the substituents in the *cis* and *trans* isomers. While the distance of the atoms taking part in the reaction is small in the *cis* isomers (LXXXI, LXXXIII) and so the attack of the alcoholic hydroxyl on the protonated carbonyl group of the acid amide can easily occur (Figs 19 and 20), in the *trans* isomers the

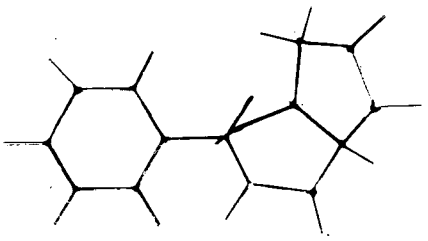


*Fig. 19*

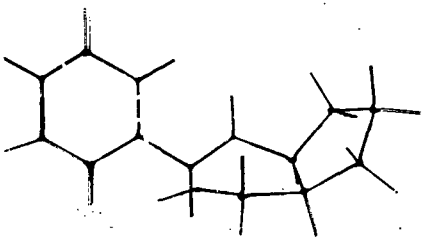


*Fig. 20*

functions are so far from each other owing to the rigidity of the cyclopentane skeleton that the attack of the hydroxyl group is markedly more difficult even in the hydroxymethyl derivative (LXXXIV) (Fig. 21).

Inspection of the Dreiding model shows that, because of the great distance of the substituents involved the N→O acyl migration reaction of the N-benzoyl-*trans*-2-aminomethylcyclopentanol can proceed more favourably with inversion, though the inversion mechanism is, in general, energetically much less favoured than the retention mechanism. In this case of LXXXII, however, the oxygen atom of the acid amide group may approach the cyclopentane ring, permitting the inversion mechanism, as could be proved by preparative and spectroscopical evidences [12], so the low reaction rate is not surprising. The moderate reaction rate of the N→O acyl migration reaction of the N-benzoyl-*trans*-2-hydroxymethylcyclopentylamine (LXXXIV), seeming less evident because of the primary hydroxyl group, may also be well interpreted on the basis of the Dreiding model (Fig. 21).

Comparison of the changes with temperature in the reaction rates of the N→O acyl migration reaction of analogous cyclopentane and cyclohexane derivatives shows the rigidity of the cyclopentane ring. Namely, the rate constant of the N→O acyl migration of the N-benzoyl-*cis*-2-aminomethylcyclohexanol (LVIII)

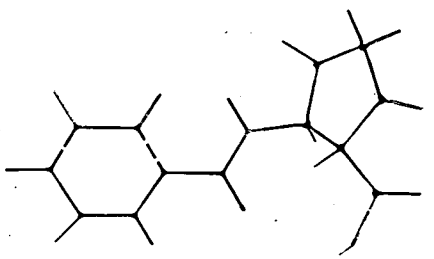


*Fig. 21*

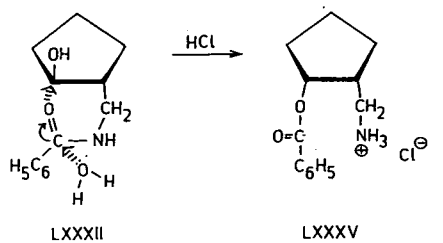



*Fig. 22*

increases to its threefold value by rising the temperature from 80 to 100°C and is approximately the same at 100°C as that of the analogous cyclopentane compound (LXXXI), while in case of N-benzoyl-*cis*-2-aminomethylcyclopentanol a rise of the temperature by 25°C increases the rate constant only by a factor of 1.5.

Investigations on the N→O acyl migration reaction of derivatives of analogous 1,3-aminoalcohols with cycloheptane skeleton (IX—XII) are in course.

*Solvolysis and NMR spectroscopical data of cis- and trans-3-p-nitrophenyl-1-aza-3-oxadecalin and cis- and trans-3-p-nitrophenyl-2-aza-4-oxadecalin*

*Cis*- and *trans*-3-*p*-nitrophenyl-2-aza-4-oxadecalin (LXXXVI, LXXXVII) and *cis*- and *trans*-2-*p*-nitrophenyl-1-aza-3-oxadecalin (LXXXVIII, LXXXIX) were prepared by reaction of the aminoalcohols V—VIII with *p*-nitrobenzaldehyde [10]. These monoazamonooxadecalin derivatives (Fig. 23) are closely related with the bicyclic transition states (Fig. 13) of the N→O acyl migration reaction of N-benzoyl derivatives of *cis*- and *trans*-2-aminomethylcyclohexanol (V, VI) and *cis*- and *trans*-2-hydroxymethylcyclohexylamine (VII, VIII) [2, 6].

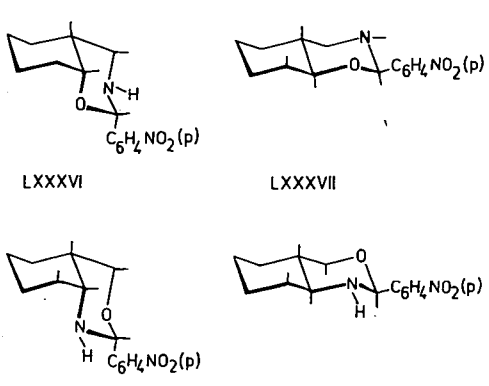



*Fig. 23*

LUKEŠ, BLÁHA and KOVÁŘ [70] determined the configuration of sedamine and *allo*-sedamine by showing that the tetrahydrooxazine derivative prepared from nor-*allo*-sedamine with *p*-nitrobenzaldehyde hydrolyzed much more easily than the tetrahydrooxazine formed from nor-sedamine. The importance of this method [18] is evident because, in comparison with 1,2-aminoalcohols, the stereospecific reactions of the 1,3-aminoalcohols received less

attention so far. Mechanical application of the rules found valid for 1,2-aminoalcohols in earlier studies [72] later proved to be incorrect [73]. LUKEŠ, BLÁHA and KOVÁŘ also investigated mainly reactions and condensation products of diastereomeric cyclic 1,2-aminoalcohols with *p*-nitrobenzaldehyde [18, 70, 71, 74] and found that the oxazolidine derivatives obtained from *trans* isomers were less stable both in the cyclohexane and tetralin series than *cis*-oxazolidine derivatives. The ratio $k_{trans}/k_{cis}$ was found to be ranging from 63 to 1:420. The factors determining the reaction rate and mechanism of the reaction were discussed in detail by the Czechoslovakian authors [18, 74].

The above method has been applied recently for the determination of the configuration of 1,2-, 1,3- and 1,4-diols [75] and of some carbohydrates [76], by comparing the rate of hydrolysis of their cyclic acetals formed with benzaldehyde. SCHÖPF *et al.* in their paper published in 1970 [77] used the relative rate of hydrolysis of oxazine derivatives formed from stereoisomeric *meso*-1,3-di(2-piperidyl)-propan-2-ols with formaldehyde for determining the configuration of the parent compounds.

Recently also the NMR spectroscopy of tetrahydrooxazine derivatives has been studied [78, 79, 81]. Similar models were investigated by CRABB *et al.* [80]. The relationship between the above oxazidines and our model compounds is evident, though the starting aminoalcohols being piperidine derivatives in the former studies, the products obtained by ring closure of piperidines, differently from our model compounds (LXXXVI—LXXXIX), contain bridgehead nitrogen atoms. These tetrahydrooxazines, similarly to the analogous quinolizidine derivatives undergoing *cis*-*trans* inversion [82—84] are not configuratively stable. In contrary, our tetrahydrooxazine derivatives, like *cis*- and *trans*-decalin, are configuratively stable, their nitrogen atom being not in bridgehead position.

Table III contains the rate constants of the solvolysis reaction of the tetrahydrooxazines, determined in the presence of an excess of 2,4-dinitrophenylhydrazine at 50°C [70]. The stability of the tetrahydrooxazine derivatives studied desrease in the order LXXXIX > LXXXVII > LXXXVIII > LXXXVI. The stability of the *trans* isomers (LXXXIX, LXXXVII) exceeds that of the *cis* isomers (LXXXVI, LXXXVIII), in accordance with the general principles of conformational analysis. The relative

*Table III*

*Rate of solvolysis and NMR data of tetrahydrooxazine derivatives*

| Compound | $k_1 \cdot 10^5 \cdot sec^{-1}$ | C—2H | C—4H$^a$ | C—4H$^b$ | C—9H | $J_{4a,4b}$ | $J_{1a,10}$ | $J_{4b,10}$ |
|---|---|---|---|---|---|---|---|---|
| LXXXVI | 8.95 | 5.21 | 2.93 | 3.26 | 4.00≠ | −13.5 | 1.8 | 3.2 |
| LXXXVII | 3.54 | 5.25 | 2.71 | 3.11 | 3.20*x* | −13.2 | 10.7 | 4.0 |
| LXXXVIII | 8.63 | 5.23 | 3.98 | 3.98 | 3.36≠ | + | + | + |
| LXXXIX | 1.42 | 5.26 | 3.52 | 4.10 | 2.63*x* | −11.2 | 10.2 | 4.1 |

Remarks:
*Chemical shifts in δ ppm. Coupling constants in Hz units; solvent:* $CDCl_3$
≠ Line width ~ 12 Hz; *x* Line width ~ 25 Hz;
+ Not meassured because of accidental coincidence of C—4H$^a$ and C—4H$^b$ chemical shifts.

rates found can be well interpreted with the reaction mechanism and energetical conditions of the transition state.

The conformations of the investigated compounds are shown in Fig. 23. In the favourable conformations the *p*-nitrophenyl group is evidently *equatorial*. According to recent investigations [85] the proton on the nitrogen can also be considered to be *equatorial*. In piperidines the „conformational rivalry between the non-bonding electron pair and the proton on nitrogen" (see: [86, 87]) has been extensively discussed [88] up to the present time. According to a quite recent paper [85] based on dipole moment measurements, the preferred *equatorial* position of the proton on the nitrogen and, consequently, the *axial* orientation of the lone pair seems to be unequivocally proved.

The enthalpy difference of *cis*- and *trans*-decalin in liquid phase is $2.69 \pm 0.31$ kcal/mole [89]. However, in interpreting the relative rate of decomposition it is not sufficient to consider the relative stability of decalins alone. *E.g.*, in the acid catalysed acetal hydrolysis of methyl-4,6-benzylidenehexosides the *trans* derivatives hydrolyse much faster [90]. The same was found [91] for the rate of solvolysis of 4,6-benzylidenehexosides, the *trans* derivative (XCI) solvolysing faster than the *cis* derivative (XC). In benzylidenehexosides the methylene groups are replaced by oxygen atoms, therefore the *axial* substituents on C-1, C-5 and C-6, destabilizing the *cis*-decalin, are absent. In the protonated *cis* isomer (XC) the hydrogen bonds formed with the aid of the oxygen atoms of the ring system also play a stabilizing role, which is absent in the *trans* isomer (XCI).

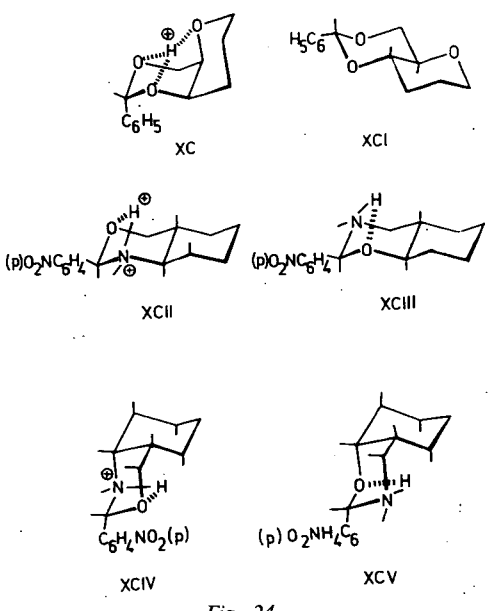



*Fig. 24*

Our model compounds are more nearly related to the decalin system than the above benzylidene derivatives. Under the conditions of reaction the nitrogen atom is protonated, and this plays an important stabilizing role. This stabilizing factor will appear in the *trans* isomers (XCII, XCIII). A hydrogen bond in *cis* isomers would result in a crowded system, which would compensate the stabilizing effect of the hydrogen bond by increased internal strain. In protonated *cis* isomers (XCIV, XCV) the internal strain is more pronounced in XCV, in accordance with the higher rate of solvolysis of *cis*-3-*p*-nitrophenyl-2-aza-4-oxadecalin. In the transition state XCVI produced by the attack of the 2,4-dinitrophenylhydrazine after protonation of LXXXIX, the increase of four 1,3 *axial-axial* interactions is to be taken into consideration, while in the other tetrahydrooxazine derivative LXXXVII only three 1,3 *axial-axial* interactions are increased (Fig. 25).

We compared the relative stability of the tetrahydrooxazine derivatives studied

earlier with that of our model compounds. The relative stability of our oxazine derivatives (LXXXVI—LXXXIX) compared with the rate of the N→O acyl migration reaction of the N-*p*-nitrobenzoyl derivatives (LIX, LXII, LXV, LXVII) of the parent 1,3-aminoalcohols (V—VIII) was also evaluated. The protonated forms of these oxazines show a very close similarity to the bicyclic transition state of the N→O acyl migration reaction (compare Fig. 13 and Fig. 23).

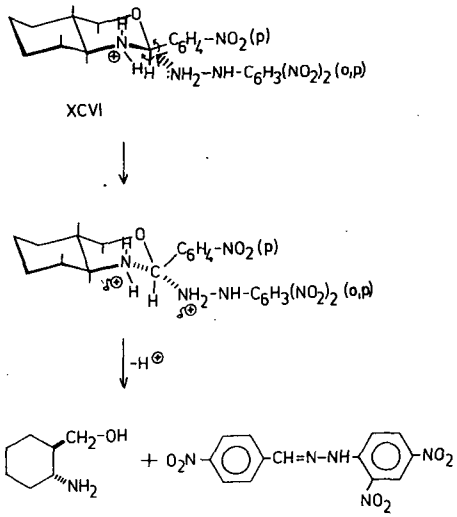



*Fig. 25*

The generation of the bicyclic transition state is the rate determining step in the N→O acyl migration reaction. The relative stability of the oxazine derivatives shows a reverse order compared with the rate of N→O acyl migration of the parent aminoalcohols. The rate of solvolysis of the tetrahydrooxazine derivatives (LXXXVI, LXXXVIII) prepared from aminoalcohols containing secundary hydroxyl (V, VII) exceeds that of the tetrahydrooxazine derivatives (LXXXVII, LXXXIX) prepared from hydroxymethylcyclohexylamines (VI, VIII). In accordance with the results obtained in the N→O acyl migration reaction, the oxazine derivatives prepared from the *trans* aminoalcohols (VI, VIII) show more marked differences in the reaction rates.

### *NMR spectroscopical studies on tetrahydrooxazine derivatives*

Table III contains the NMR spectroscopical data important from stereochemical point of view of the oxazine derivatives (compare also: [79—81]). The ring numbering used in the spectroscopical part of our paper is shown in Fig. 26. The carbon atoms of the methylene group used for the evaluation of the spectra obtained the number 4 in both pair of diastereoisomers, the bridgehead atom adjacent to the hetero atom is designed by number 9.

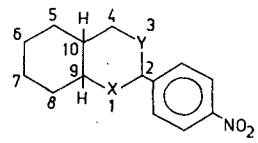


*Fig. 26*

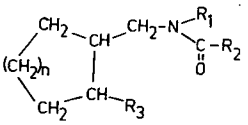
In the *trans* tetrahydrooxazine derivatives (LXXXVII, LXXXIX) the coupling contants of the C-4 methylene hydrogens with the adjacent angular proton have values of ~10 and ~4 Hz, respectively, showing that one of the hydrogens of the methylene group (C-4 $H^a$) and the C-10 are in the same *diaxial* position, therefore the angular proton on C-10 must be *axial*. The width of the resonance signal of C-9 H (~25 Hz) also shows that in the *trans* compounds this proton is in *trans* position to C-10 H, *i.e.* it is also *axial*; therefore the above are in accordance with the data resulting from the *trans* configuration.

The width of the resonance signal, of only about 12 Hz in the *cis* tetrahydrooxazine derivatives (LXXXVI, LXXXVIII), points to the fact, that in these compounds the proton is *equatorial* and in *cis* position to the angular C-10 H. In *cis* iso-

mers, the coupling constants of the methylene protons C-4 with the C-10 H could be determined only for the compound LXXXVI. The values found show that in the favourable conformation the proton C-10 is *equatorial* with respect to the hetero ring, in accordance with the *cis* ring system.

*Further investigations*

Without giving details, we shortly mention that we prepared a great number of N-acylaminomethylcyclopentane and cyclohexane derivatives (see Fig. 27) for pharmacological purposes. The N-cycloalkyl acid amides exert a very intensive



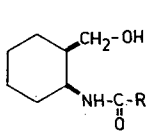
n = 1, 2

$R_1$ = H, $C_6H_5$-$CH_2$-, -$CH_2$-$C_6H_4$-$OCH_3$ (p)

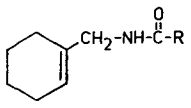
$R_2$ = $C_6H_5$-, -$C_6H_4$-Cl (o), -$C_6H_5$-Cl (p), -$C_6H_4$-Br (o), -$C_6H_4$-$OCH_3$ (m), -$C_6H_4$-$OCH_3$ (p), -$C_6H_4$-$CH_3$ (p), -$C_6H_2$-$(OCH_3)_3$ (m,m,p), -$C_6H_4$-$NO_2$ (p), -$C_6H_3$-$(NO_2)_2$ (m,m'), -$C_6H_5$-$NH_2$ (p)

$R_3$ = H, OH, Cl, Br

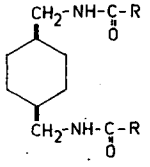
*Fig. 27*



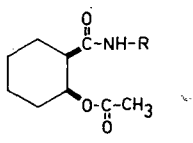
XCVII



XCVIII



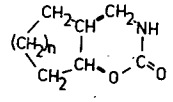
XCIX



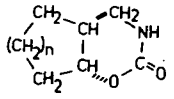
C

*Fig. 28*

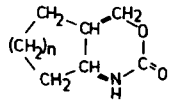
sedative effect on the central nervous system. In practice they can be used especially in the chemotherapy of epilepsy. It is advantageous that they are of low toxicity. The above compounds are subject of several patents [9, 13] (Fig. 27, 28).



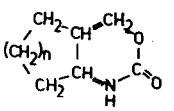
n=1 : CI
n=2 : CV
n=3 : CIX



n=1 : CII
n=2 : CVI
n=3 : CX



n=1 : CIII
n=2 : CVII
n=3 : CXI



n=1 : CIV
n=2 : CVIII
n=3 : CXII

*Fig. 29*

For similar purposes we also prepared some related N-acyl-*cis*-2-hydroxymethylcyclohexylamine derivatives (XCVII), N-acyl-1-aminomethylcyclohexene-1 derivatives (XCVIII), N,N'-diacyl-*cis*-1,4-diaminomethylcyclohexane derivatives (XCIX) and N-substituted-O-acetyl-*cis*-2-hydroxycyclohexane derivatives (XCIX) and N-substituted-O-acetyl-*cis*-2-hydroxycyclohexanecarboxamide derivatives (C) [8] (Fig. 28). In compounds XCVII—XCIX the acylating agents used were various substituted benzoic acids, whereas in the compounds of type C, R was *p*-methoxybenzyl, *i*-propyl, *i*-butyl and β-(3,4-dimethoxyphenyl)-ethyl.

Preparation of and investigations on

oxazinon derivatives with condensed skeleton, presented in Fig. 29, are in progress. As could be expected, in the cyclohexane series the *trans*-oxazinons (CVI—CVIII) prepared from aminoalcohols V—VIII were obtained with higher yield. NMR Spectroscopical investigation of these oxazinones, showing theoretically interesting features, is in progress.

* * *

This work was financially supported by Pharmaceutical Works G. RICHTER, Budapest, and by REANAL Factory of Laboratory Chemicals, Budapest. The authors express their thanks to Dr. P. SOHÁR (Pharmaceutical Research Institute, Budapest) for numerous NMR and IR spectra, to Mrs É. TOMORI (Pharmaceutical Research Institute, Budapest) for gas-chromatographical analyses, to Mrs. G. BARTÓK-BOZÓKI and Mrs. É. GÁCS-GERGELY for microanalyses. We are also indebted to Mr. L. GERA, Mrs. O. BITTÓ-CSAPÓ, Mrs. A. SÁNTHA-SZEGHY, Mrs. E. FELFÖLDI-CSÓKÁSI for taking part in some experiments, and to Miss A. VÍGH for valuable technical assistance.

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## СТЕРЕОХИМИЧЕСКИЕ ИССЛЕДОВАНИЕ 1,3-ДИФУНКЦИОНАЛЬНЫХ ПРОИЗВОДНЫХ ЦИКЛОПЕНТАНА, ЦИКЛОГЕКСАНА И ЦИКЛОГЕПТАНА

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Авторами даётая описание их синтетической и стереохимической работы с циклическими 1,3-аминоспиртами. Описывается стереоспецифический синтез *цис-* и *транс*-2-аминометилциклопентанола и *цис-* и *транс*-2-гидроксиметилциклопентиламина и их циклогексанных и циклогептанных аналогов. Тоже даётся кинетическое исследование и механизм N → O-миграции ацильных групп производных циклопентана и циклогексана.

Солволиз и ЯМР спектроскопический анализ тетрагидрооксазинов пригатовленных из *цис-* и *транс*-2-аминометилциклогексанола и *цис-* и *транс*-2-гидроксиметилциклогексиламина детально трактуруются. Авторам даётся описание пригатовления исследования нескольких других производных, в большинстве амидов вышеописанных аминоспиртов важных для фармакологии.

# STEROIDS. XV*

## Hydroxylation of dehydroepiandrosterone and dehydroepiandrosterone-3β-sulphonic acid sodium salt (Part 10)**

*(Preliminary Communication)*

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*(Received: March 1, 1971)*

Hydroxylation of dehydroepiandrosterone and dehydroepiandrosterone-3β-sulphonic acid sodium salt has been examined in different „in vitro" systems. In Fenton-Cier and Udenfriend systems considerable, while on the effect of adrenal slices milder 16α-hydroxydehydroepiandrosterone formation could be observed. 7α-, or 7β-hydroxylation could not be detected.

A number of hydroxylation processes are involved in steroid metabolism catalysed by specific hydroxylases. The hydroxylation takes place in several organs, as proved by various in vitro experiments [1].

During the metabolism of dehydroepiandrosterone mainly the C-7 and C-16 atoms are hydroxylated. For instance, in mammalian liver 7α-hydroxylation [2], in placenta and liver 16α-hydroxylation and 16β-hydroxylation [3] and in human skin 7α-hydroxylation and 16α-hydroxylation [4] were detected. SULCOVA [5], studying homogenates of different organs, observed 7α-hydroxylation of dehydroepiandrosterone in liver, kidney, spleen, lung, heart, blood and in muscle, while STARKA [6] pointed out 7α-hydroxylation in adrenal glands, and COLAS [7] observed the 16α-hydroxylating ability of rat liver slices.

Very scarce data are, however, available about the in vitro hydroxylation of steroids under well defined conditions [8].

In our experiments we examined the effect of some non-specific hydroxylating systems as well as of adrenal slices on dehydroepiandrosterone and dehydroepiandrosterone-3β-sulphonic acid sodium salt.

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## *Experimental*

Hydroxylation systems were used as follows:

a) *Fenton system* [9]: 3 mmole $FeSO_4 \cdot 7H_2O$, 6 mmole $H_2O_2$, 3 mmole substrate and 100 ml 4*N* $H_2SO_4$. Reaction time: 30—60 minutes at room temperature or at 37°C.

b) *Modified Fenton system* [9]: 1 mmole $FeSO_4 \cdot 7H_2O$, 1 mmole EDTA.2Na, 2 mmole $H_2O_2$, 2 mmole substrate and 100 ml 0.1 M phosphate buffer (pH 7.2) Reaction time and temperature as above.

c) *Fenton—Cier system* [10]: 1 mmole $FeSO_4 \cdot 7H_2O$, 1 mmole EDTA.2Na, 0.5 mmole L-ascorbic acid, 2 mmole $H_2O_2$, 2 mmole substrate and 100 ml 0.1 M phosphate buffer (pH 7.2). Reaction conditions as before.

d) *Udenfriend system* [11]: 0.5 mmole $FeSO_4 \cdot H_2O$, 2.6 mmole EDTA.2Na, 5.6 mmole L-ascorbic acid, 2 mmole substrate and 100 ml 0.1 M phosphate buffer (pH 6.7). Aeration by shaking. Reaction time: 2—24 hours at room temperature or at 37°C.

e) *UV irradiation:* 1 mmole $FeCl_3$, 1 mmole EDTA.2Na, 1 mmole substrate, 100 ml distilled water, pH 7.0, 24 hours.

f) *Incubation with adrenals:* 10 g finely cut ox adrenals, $10^{-4}$ M substrate, $10^{-3}$ M potassium-fumarate, $10^{-3}$ M L-ascorbic acid, 0.001 g ascorbic acid oxidase, $2 \cdot 10^{-5}$ M NADH at 37°C. The solutions were shaken for five hours in oxygen stream.

Dehydroepiandrosterone was dissolved in propylene glycol (1,2-propanediol). The products were extracted with peroxide-free ether.

The TLC separation was carried out on Silica gel G (Merck) adsorbent, using $20 \times 20$ cm plates with 0.25 mm adsorbent thickness. For preparative purposes the mentioned adsorbent was used in 1 mm thickness [12].

Solvent systems: benzene-ethyl acetate (3:2) [4], cyclohexane-chloroform-acetic acid (7:2:1).

After separation, the plates were dried at 110°C for about 20 minutes, the spots were developed by iodine vapour or UV light, the plates sprayed with 25% sulphuric acid and dried.

In some experiments dehydroepiandrosterone sulphate ester was used as substrate.

The methods described below proved to be fairly useful in preparing different steroid sulphate esters [13—16].

### *Dehydroepiandrosterone*

Gift of G. RICHTER Pharmaceutical Works (Budapest), repeatedly recrystallized from methanol, m. p.: 152—153°C.

The preparative methods for both salts, treated in detail in [16], are only briefly mentioned here.

Dehydroepiandrosterone-3$\beta$-sulphate was prepared with chlorosulphonic acid in pyridine and the salt was precipitated with petroleum ether. M. p.: 208 °C. The substance dissolves well in water.

The dehydroepiandrosterone-3$\beta$-sulphonic acid pyridinium salt, on the other hand, was converted to the sodium salt of the sulphate with sodium carbonate at a pH of about 7.5 in a saturated aqueous sodium sulphate solution. The salt was

finally precipitated similarly with petroleum ether. Mp.: 201°C. The salt is also well soluble in a phosphate buffer.

When the dehydroepiandrosterone sulphate salt was used for hydroxylation, the products were isolated in the following manner: The solution was saturated with sodium sulphate and then the sodium salt of the sulphates flocculated, which could be easily filtered. Then the solvolysis of sulphates [17] follows. For this purposes the sulphate salt was dissolved in 50 ml 2*N* sulphuric acid and extracted with ethyl acetate (about 60 ml) and about 100 ml ether previously saturated with water. The mixture was allowed to stand at room temperature for three days. Ethyl acetate-etheric solution was dried with anhydrous sodium sulphate, evaporated and chromatographed. The substances were identified by comparing their chromatographic properties with standards in different systems.

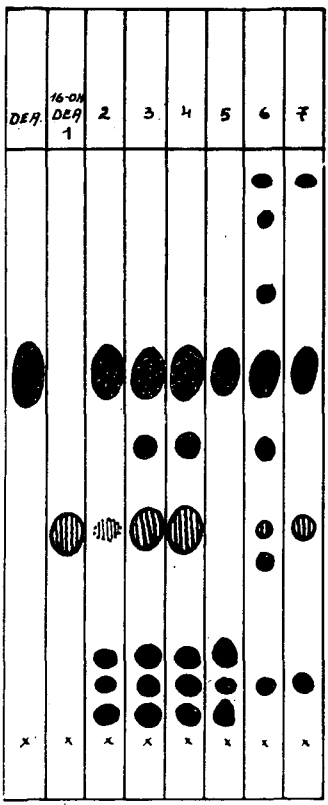


*Fig. 1*

## *Results*

Special attention was given to the formation of 16α-, 7α- or 17β-hydroxy derivatives. In this respect the following observations were made in different systems:

In the Fenton system no hydroxylation took place.

In the modified Fenton system 16α-hydroxydehydroepiandrosterone formed but only in a small amount (See Fig. 1 column 2).

In the Fenton-Cier and Udenfriend systems there was considerable 16α-hydroxylation (See Fig. 1 columns 3 and 4).

On the effect of UV light no 16α-hydroxylation took place (See Fig. 1 column 5).

With adrenal incubate there was a slight 16α-hydroxylation (See Fig. 1 column 7).

With adrenal incubate the dehydroepiandrosterone-3β-sulphonic acid sodium salt is also hydroxylated in the C-16 position (See Fig. 1 column 6). On the plate the chromatogram of the substances after solvolysis can be seen.

## *Discussion*

Up to this time merely the hydroxylation of a few corticosteroids has been studied in the mentioned chemical and in vitro systems [18, 19], however, the identification of the compounds was not quite convincing. Our experiments proved that the in vitro systems used by us are suitable for hydroxylation of certain steroids, which is unequivocally proved by 16α-hydroxylation of dehydroepiandrosterone.

Dehydroepiandrosterone-3$\beta$-sulphonic acid sodium salt was also hydroxylated the effect of adrenal slices.

Our experiments also proved that steroid sulphates, as water-soluble substrates can be easily prepared and are very useful substrates of different in vitro transformations. It is not surprising that more and more steroid sulphates have been detected in the last years and that they play a decisive role in the metabolism of steroids. Among others, a number of articles dealt with the biotransformation of dehydroepiandrosterone sulphate [20—22].

Data obtained so far are well supported by our experiments with adrenal slices, since we have proved the in vitro 16$\alpha$-hydroxylation of dehydroepiandrosterone. As supposed by several authors, L-ascorbic acid plays an important role in the steroid hydroxylations taking place in adrenals, but the role of the latter has not been completely clarified as yet. Our experiments were based on the concept that the electron transition between NADH and ascorbic acid is an important step of the formation of the hydroxylating agent. Really, the in vitro formation of NADH is accelerated by addition of ascorbic acid oxidase. We believe that our experiments described above furnish some additional data to the androgen biosynthesis depending on ascorbic acid in the adrenal gland.

The chemical systems mentioned above may also lead to the formation of several other derivatives which are not yet identified. It can also be supposed that the 16$\alpha$-hydroxylation of dehydroepiandrosterone is a consequence of a non-specific hydroxylation and it plays an important role in the inactivations of androgens. Further experiments are necessary to clarify these problems.

The authors express their thanks to the SKF Lab. (Philadelphia) for NADH and to the English Steroid Collection (Prof. W. KLYNE, London) for 16$\alpha$-hydroxydehydroepiandrosterone.

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# СТЕРОИДЫ XV.
# ГИДРОКСИЛИРОВАНИЕ НАТРИЕВОЙ СОЛИ ДЕГИДРОЭПИАНДРОСТЕРОНА И ДЕГИДРОЭПИАНДРОСТЕРОН-3$\beta$-СУЛФАТА (ЧАСТЬ 10.).

(Предварительное сообщение)

*Б. Маткович, М. Мариан, Ш. Задор*

Исследовалось гидроксилирование натриевой соли дегидроэпиандростерона и дегидроэпиандростерон-3$\beta$-сулфата в разных „in vitro" системах. Показали образование 16$\alpha$-гидроксидегидроэпиандросте-рона в системах Фентона-Сиэ и Уденфренда в значительном количестве, и образование незначинетельного количества 16$\alpha$-гидроксидегидроэпиандростерона под воздействием срезов надпочечника. 7$\alpha$- и 7$\beta$-гидрокси-производные не образовывались.

# VERWENDUNG VON FURFUROL. XVI*

## Untersuchungen von Reaktoren für exotherme katalytische Prozesse. IV

## Ein wärmegradientenfreier heterogen-katalytischer Dampfphasen-Reaktor

Von

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*(Eingegangen am 24. Juni 1971)*

In früheren Arbeiten berichteten wir über Versuche und Berechnungen zur Ausmaßvergrößerung von heterogen-katalytischen Gasphasen-Reaktoren. Auf die früheren Untersuchungen gestützt wurde ein wärmegradientenfreier Reaktors entwickelt. Als Zentrifugalventilator dient eine rotierende Drahtbürste, die im Katalysatorraum die Reaktionsdämpfe mit einer so großen Geschwindigkeit zirkulieren läßt, daß weder längs der Achse, noch in der Längsrichtung ein Wärmegradient entstehen kann. Das gleiche Prinzip ist auch als kontinuierlicher Emulgator für Flüssigkeit/Flüssigkeit-Phasen oder als chemischer Reaktor verwendbar. Infolge der hohen Leistungsfähigkeit entspricht es den Forderungen der „Ausmaßvergrößerung".

Es wurde ein wärmegradientenfreier chemischer Reaktor entwickelt. Zur besseren Verständnis ist es zweckmäßig, drei Reaktoren kurz zu beschreiben, die der Entwicklung als Grundlage dienten.

1. Die Ausmaßvergrößerung linearer Reaktoren zu zwei- und dreidimensionalen Reaktoren konnte auf Grund linearer Berechnungen durchgeführt werden, die es gestatteten, die Ähnlichkeitsbedingungen soweit zu bewahren, daß die bestimmenden Faktoren der chemischen Reaktion nicht wesentlich verändert wurden [1].

2. Bei der Längenvergrößerung zylinderischer heterogen-katalytischer Dampfphasenreaktoren [2] muß — wenn die Reaktorlänge $l$ und der Radius $r$ um das $a$-fache vergrößert und die spezifische Einspeisegeschwindigkeit beibehalten werden soll — in das vergrößerten Volumen während der gleichen Zeit $t$ eine $n$-fache Menge der Reaktionskomponenten mit einer linearen Geschwindigkeit $nc$ eingeführt werden. Zu Beginn des theoretischen Versuchs war bei dem Wert $c$ die Strömung laminar. Der Wert von $n$ ist dabei so zu wählen, daß die ursprünglich laminare Strömung turbulent wird. In diesem Falle wird der Wärmegradient infolge der Turbulenz minimal. Dies ist dadurch zu erreichen, daß die Geschwindigkeit im Verhältnis zu den Apparaten mit granuliertem Festkörper-Katalysator groß gewählt wird.

3. Amerikanische Verfasser [3—5] haben sich mit heterogen-katalytischen organischen Reaktionen in der Dampfphase beschäftigt und dabei einen speziellen

* XV. Mitteil. s. Acta Phys. et Chem. Szeged **17**, 99 (1971).

Mikroreaktor von einigen ml Faßungsvermögen benützt, in dem 12 kugelförmige Katalysatorenkörner von etwa 5 mm∅ in einem Rahmen mit großer Geschwindigkeit rotierten, wodurch bei der Temperatur der Reaktion ein wärmegradientenfreier chemischer Reaktionsablauf erreicht wurde, da die gasförmige Reaktionskomponente den rotierenden Katalysatorraum mehrmals und mit großer Geschwindigkeit passierte. Der Vorteil ist auch hier in der relativ großen Geschwindigkeitsdifferenz zwischen dem festen granulierten Katalysator und der gasförmigen Reaktionskomponente zu finden.

4. Mit Benützung von rotierenden Drahtbürsten haben wir einen Superfilmreaktor, einen Superemulgator hergestellt [6, 7], der geeignet ist, das in einem geschlossenen Zylinder befindliche Gas das Katalysatorsystem unter kontinuierlicher Zirkulation mehrmals passieren zu lassen. Die Zahl der Rückführungen nimmt mit kleineren Einspeisegeschwindigkeit bzw. mit der Leistungsfähigkeit der Drehbürste — in allgemeinen mit der Umdrehungszahl — zu. Bei Reaktionssystemen in der Gasphase ist der Zylinder mit dem Katalysator zu füllen, durch den die Drahtbürste die gasförmigen Reaktionskomponenten zirkulieren läßt, wodurch die erwähnte Turbulenz gesichert und die Geschwindigkeitsdifferenz zwischen Katalysator und Reaktionsgaskomponente erreicht werden kann. In diesem Falle ist der gewünschte, zuvor mit *nc* bezeichnete, lineare Geschwindigkeitswert der turbulenten, wärmegradientfreien Strömung auch in einem wesentlich kürzeren zylinderischen Reaktorraum *nl* erreichbar: *l* kann sogar kürzer sein als ursprünglich. Auf diese Weise läßt sich sogar ein zu Oxydationszwecken dienender Reaktor von so großem Durchmesser herstellen, wie er bisher im Falle hoher Reaktionstemperaturen nicht angewandt wurde.

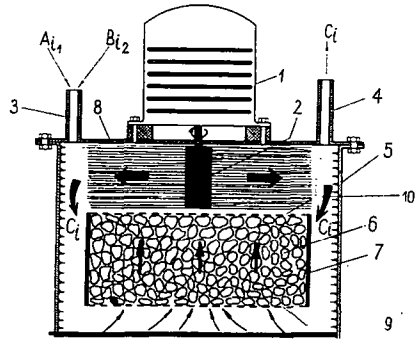


*Fig. 1*

Der Reaktor ist schematisch in Fig. 1 dargestellt. Die durch den Stutzen (3) mit der Einspeisegeschwindigkeit $Ai_1$ bzw. $Bi_2$ eingespeisten Ausgangstoffe verlassen den Reaktor — nach einer entsprechend langen Zirkulation — durch den Stutzen (4) mit der Abfuhrgeschwindigkeit *Ci*.

Der Reaktor besteht aus dem mit den Netzen (9) und (10) und dem Metallmantel (7) umgebenen Katalysatorraum (6), der im Reaktorraum (5) untergebracht ist. Auf dessen Deckel (8) befinden sich die Einspeise- und Abfuhrstutzen (3, 4), sowie die die Zirkulation im Katalysatorraum hervorrufende Drahtbürste (2) mit dem Antriebmotor (1).

Die Rotation der Drahtbürste erzeugt eine Zentrifugalkraft, die die Reaktionsgase aus dem Katalysatorraum durch die Drahtfäden der Bürste heraussaugt. Sie gelangen dann entlang der Wand des Reaktorraumes abwärts ziehend erneut in den Katalysatorraum. Infolge der intensiven Zirkulation in der Richtung der Pfeile passiert das Reaktionsgemisch den Katalysatorraum mehrere hundert Male, bevor es den Reaktor verläßt. Durch die regulierbare Anzahl der Rückführungen wird eine wärme- und konzentrationsgradientenfreie Zirkulation erreicht und die Kontaktzeit verlängert. Der Wärmeaustausch des ganzen Systems erfolgt am Boden und an der Seitenwand des Reaktors. Diese neue Möglichkeit erlaubt die Ausbildung

eines neuartigen Katalysatorraumes unter oxydativen Bedingungen auch im Falle eines Volumens von mehreren zehn Litern. Die Ausmaße sind auch dann zweckmäßig, wenn das Verhältnis zwischen Höhe und Durchmesser des Katalysatorraumes 1:1 beträgt. Die aus wärmebeständigem und gegen die Chemikalien bei der Reaktionstemperatur widerstandsfähigem Material bestehende Drehbürste wirkt als Zentrifugalventilator.

Die Leistung des Elektromotors ist bei hohen Drehzahlen am höchsten. Die feinen Metallfäden der Bürste intensivieren die Zirkulation. Die Geschwindigkeitsdifferenz zwischen Katalysator und Reaktionsgas kann den optimalen Wert der unter 2. und 3. geschilderten Reaktoren erreichen. Der beschriebene Reaktor 4 ist als eine Ausmaßvergrößerung von Reaktor 3 zu betrachten; beide Reaktoren sind durch die hohe Geschwindigkeitsdifferenz zwischen Katalysator und Reaktionsgas, das Fehlen von Wärme- und Konzentrationsgradienten und durch intensives Mischen charakterisiert. Gradienten der Wärmequellendichte im Reaktorraum sind bei beiden Reaktoren praktisch gleich Null. Der Reaktor besitzt auch die Vorteile des unter 2. beschriebenen Reaktors, indem es die lineare Geschwindigkeitsdifferenz zwischen den Gasen und dem Festkörperkatalysator auf kurzer Strecke, aber unter „ähnlichen" Bedingungen verwirklicht.

Prinzipiell zu erwähnen ist, daß — sofern kein Wärmegefälle zustandekommt — der ganze Raum mit Katalysator gefüllt werden könnte, der Zylinder (7) aber im Interesse der Zirkulation unverändert nötig ist. Die gleiche Einrichtung kann in der chemischen Technologie der kontinuierlichen heterogenen Flüssigkeit/Flüssigkeit-Reaktionen ebenfalls zur Intensivierung der Reaktion beuützt werden.

Ein die Erfahrungen mit unseren Apparaten zusammenfassendes Laboratoriumspraktikum ist erschienen. Auf diesen Prinzipien beruhende Laboratoriums- und Betriebseinrichtungen wurden erbaut [8, 9].

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## ГЕТЕРОГЕННЫЙ КАТАЛИТИЧЕСКИЙ РЕАКТОР В ГАЗОВОЙ ФАЗЕ БЕЗ ТЕПЛОВОГО ГРАДИЕНТА

*Л. Месарош и Дь. Керекеш*

Авторы проводили опыты и вычисления с гетерогенными каталитическими реакторами в газовой фазе для увеличения размера. В этой работе, упираясь на раннее полученных результатов описывается приготовление реактора без теплового градиента. Вращающаяся металлическая щетка применяется в роле центробежного вентилятора, который вводить нары реакций в циркуляцию в камеру реакций со скоростью, что ни аксиальный ни линейный тепловой градиент не получается. Такой же принцип применяется и как у химических реакторов или эмульгаторов в непрерывной фазе жидкость/жидкость. В вследствии высокого выхода, реактор удовлетворяется и критерий „увеличение размера".

# ÜBER DIE ABHÄNGIGKEIT DER ADHÄSION VON DER KONTAKTZEIT

Von

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*(Eingegangen am 15. Juli, 1971)*

Es wurde der Abreißwinkel von Quarzfraktionen verschiedenen Dispersitätsgrades in Wasser und in Methylalkohol in Abhängigkeit von der Kontaktzeit untersucht. Es wurde festgestellt, daß die Haftfähigkeit mit der Zunahme der Kontaktzeit der Teilchen mit der Bodenfläche zunimmt; die Adhäsion kleinerer Teilchen ändert sich nach an Adsorptionsisothermen erinnernden Kurven, diejenige größerer Teilchen linear.

## *Einleitung*

In unserer vorhergehenden Arbeit [1] wurde nachgewiesen, daß die Adhäsion in Flüssigkeiten suspendierter fester Teilchen von mikroskopischen Dimensionen an Festkörperflächen u. a. vom Dispersitätsgrad, und bei besonders kleinen Abmessungen in Wasser von der sog. Kontaktzeit abhängt. BUZÁGH [2, 3] beobachtete zuerst bei Haftzahlmessungen, daß die Kontaktzeit von Quarzteilchen von 1—2 μm Teilchendurchmesser in Wasser mit der Kontaktzeit zunimmt. Später stellten DERJAGIN und ZIMON [4, 5] mit der Zentrifugiermethode fest, daß die Haftfähigkeit von Glaspulverteilchen von 50 und 60—90 μm Teilchenradius, die eine mit einem Flüssigkeitsfilm überzogene Glasplatte berühren, mit der Kontaktzeit nahezu linear zunimmt. KRUPP und Mitarbeiter [6], die die Haftfähigkeit von Goldteilchen an verschiedenen Flächen ebenfalls mit der Zentrifugiermethode untersuchten, wiesen darauf hin, daß die Abhängigkeit der Adhäsionskraft von der Kontaktzeit wahrscheinlich mit dem zeitlich meßbaren Dünnerwerden des Flüssigkeitsfilms zwischen der Bodenfläche und den Teilchen in Zusammenhang steht. Aus diesen wenigen Mitteilungen geht hervor, daß die Adhäsion mit der Kontaktzeit zunimmt, doch stehen über den Ausmaß der Zunahme und ihre Abhängigkeit von den Teilchengröße Versuchsergebnisse kaum zur Verfügung. Deshalb führten wir diesbezügliche systematische Untersuchungen mit dem BUZÁGHschen Abreißwinkelmesser durch.

## *Versuchsmaterialien und Methoden*

Die bei den Versuchen benützten Materialien, deren Vorbereitung und die Durchführung der Messungen sind in unserer erwähnten Arbeit [1] beschrieben.

## *Versuchsergebnisse*

Es wurde der Abreißwinkel monodisperser Quarzpulver verschiedenen Dispersitätgrades in Wasser und Methylalkohol, in Abhängigkeit von der Kontaktzeit gemessen. Die Versuchsergebnisse in Wasser sind in Tabelle I und Fig. 1 dargestellt.

*Tabelle I*

*Abreißwinkel monodisperser Quarzpulver verschiedenen Dispersitätsgrades in Wasser in Abhängigkeit von der Kontaktzeit*

| Teilchenradius μm | sin α | | | | | | |
|---|---|---|---|---|---|---|---|
| | Kontaktzeit | | | | | | |
| | einige Minuten | 1 Stunde | 2 Stunden | 4 Stunden | 1 Tag | 2 Tage | 3 Tage |
| 3.7 | >0.96 | >0.96 | >0.96 | >0.96 | >0.96 | >0.96 | >0.96 |
| 7.5 | 0.40 | 0.48 | 0.60 | 0.64 | 0.66 | >0.96 | >0.96 |
| 15 | 0.25 | 0.26 | 0.32 | 0.50 | 0.54 | 0.78 | >0.96 |
| 25 | 0.65 | 0.67 | 0.71 | — | 0.74 | 0.90 | 0.96 |
| 35 | 0.61 | — | 0.62 | — | 0.76 | 0.86 | 0.94 |
| 50 | 0.55 | — | 0.56 | — | 0.66 | 0.76 | 0.93 |
| 80 | 0.51 | — | 0.52 | — | 0.61 | 0.70 | 0.90 |
| 120 | 0.48 | — | 0.48 | — | 0.54 | 0.69 | 0.82 |
| 140 | 0.45 | — | 0.46 | — | 0.57 | 0.70 | 0.82 |

Es ist ersichtlich, daß im Falle einer sehr kurzen Kontaktzeit (von einigen Minuten) der Sinus des Abreißwinkels des Quarzpulvers in destilliertem Wasser mit zunehmender Teilchengröße einer Maximum-Minimum-Kurve gemäß wächst. Das Minimum der Haftfähigkeit ist bei 15 μm, das Maximum bei 25 μm Teilchenradius zu finden; bei weiterer Zunahme der Teilchengröße nimmt die Haftfähigkeit wieder etwas ab. Es zeigt sich weiters, daß der Abreißwinkel auch von der Kontaktzeit mit der Glasplatte stark abhängig ist. Diese Abhängigkeit ist bei kleinen Teilchengrößen deutlicher: die Abreißwinkel bei 7.5 und 15 μm Teilchenradius sind nach zweistündiger Kontaktzeit viel größer als die nach einer kürzeren Kontaktzeit gemessenen. Nach eintägigem Stehen nimmt die Haftfähigkeit auch bei größeren Teilchen meßbar zu. Bei weiterer Verlängerung der Kontaktzeit verschiebt sich die immer stärker verflachende Minimum-Maximum-Kurve nach höheren

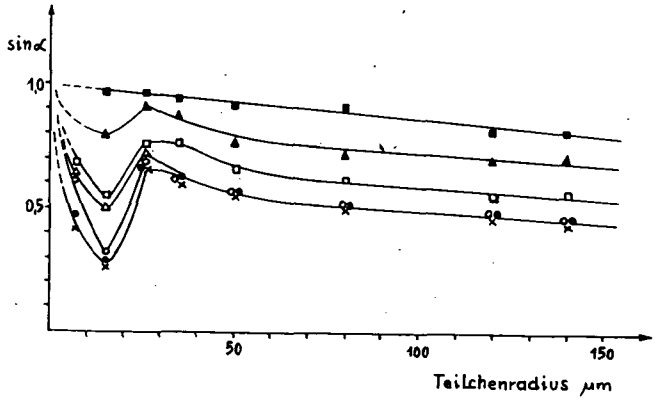


*Fig. 1.* Abreißwinkel in Wasser in Abhängigkeit von der Teilchengröße und der Kontaktzeit. Kontaktzeit: × einige Minuten, ● 1 Stunde, ○ 2 Stunden, △ 4 Stunden, □ 1 Tag, ▲ 2 Tage, ■ 3 Tage

Werten, und nach drei Tagen ändert sich die Haftfähigkeit einer mit der Zunahme der Teilchengröße stetig abnehmenden Kurve entsprechend, wie dies im Falle starker Adhäsion (z.B. Quarz in Benzol) auch in unserer früheren Mitteilung [1] nachgewiesen wurde.

In Methylalkohol (Tab. II, Fig. 2) nimmt der Abreißwinkel der Quarzteilchen verschiedenen Dispersitätsgrades mit der Zunahme der Kontaktzeit ebenfalls zu;

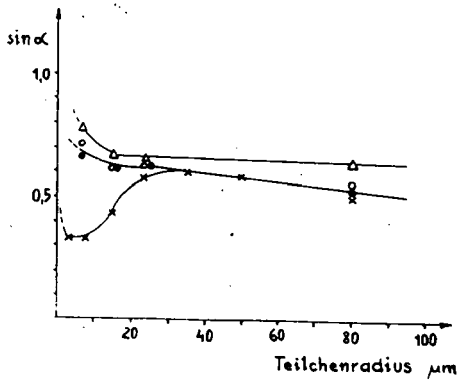


*Fig. 2.* Abreißwinkel in Methylalkohol in Abhängigkeit von der Teilchengröße und der Kontaktzeit Kontaktzeit: × einige Minuten, ● 1 Stunde, ○ 2 Stunden, △ 3 Stunden

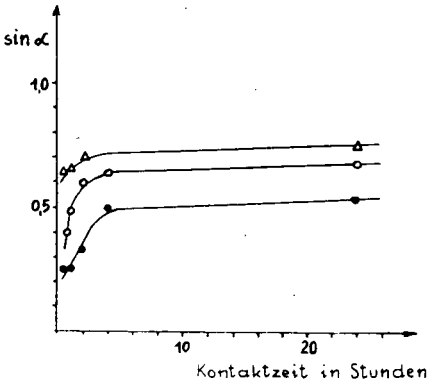


*Fig. 3.* Abreißwinkel in Wasser in Abhängigkeit von der Kontaktzeit. Teilchenradius: ○ 7.5 μm, ● 15 μm, △ 25 μm

nach einigen Minuten Kontaktzeit ergeben die Abreißwinkel in Abhängigkeit von der Teilchengröße eine Minimum-Maximum-Kurve, die einen dem im wässrigen System gefundenen ähnlichen Charakter aufweist. In Methylalkohol zeigt aber die Haftfähigkeit mit zunehmender Teilchengröße bereits nach einigen Stunden Kontaktzeit eine abnehmende Tendenz, was in Wasser erst nach einer Kontaktzeit von einigen Tagen zu beobachten ist.

Die Haftfähigkeit kleinerer Quarzteilchen ändert sich mit zunehmender Kontaktzeit nach an Adsorptionsisothermen erinnernden Kurven, wie aus Fig. 3 ersichtlich. Die Haftfähigkeit nimmt nach 1—2 stündiger Kontaktzeit steil zu, und erreicht nach mehrtägiger Wartezeit einen Grenzwert. (Eine derartige Zunahme der Adhäsion wurde von HOWE u. a. [7] bei der Messung des trockenen Haftens von Pyrexteilchen nachgewiesen). Eine solche Zunahme ist bei Quarzfraktionen mit Teilchenradius

*Tabelle II*

*Abreißwinkel monodisperser Quarzpulver verschiedenen Dispersitätsgrades in Methylalkohol in Abhängigkeit von der Kontaktzeit*

| Teilchenradius μm | sin α | | | |
|---|---|---|---|---|
| | Kontaktzeit | | | |
| | einige Minuten | 1 Stunde | 2 Stunden | 3 Stunden |
| 3.7 | 0.34 | — | — | — |
| 7.5 | 0.34 | 0.66 | 0.71 | 0.78 |
| 15 | 0.44 | 0.61 | 0.61 | 0.66 |
| 25 | 0.58 | 0.61 | 0.61 | 0.65 |
| 35 | 0.61 | — | — | — |
| 50 | 0.58 | — | — | — |
| 80 | 0.50 | 0.51 | 0.55 | 0.65 |

zwischen 7.5 und 25 μm zu finden. Bei Teilchen von größeren Dimensionen (Teilchenradius > 35 μm) nimmt die Haftfähigkeit mit der Kontaktzeit praktisch linear zu (Fig. 5).

Die Zunahme der Haftfähigkeit der Quarzteilchen mit der Kontaktzeit läßt sich dadurch erklären, daß die Deformation der Lyosphären auch bei Teilchen von geringem Gewicht möglich ist und dieser Prozeß in meßbarer Zeit abläuft [8].

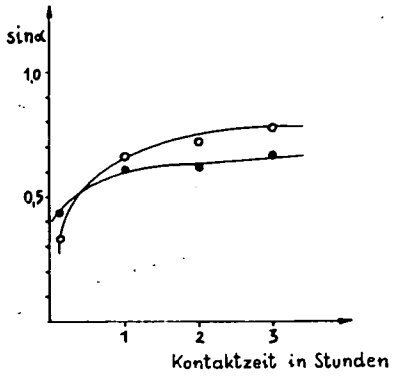


*Fig. 4.* Abreißwinkel in Methylalkohol in Abhängigkeit von der Kontaktzeit. Teilchenradius: ○ 7.5 μm, ● 15 μm

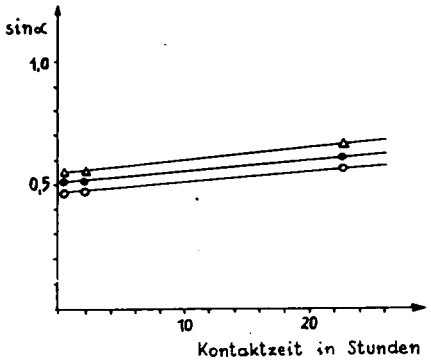


*Fig. 5.* Abreißwinkel in Wasser in Abhängigkeit von der Kontaktzeit. Teilchenradius: △ 50 μm, ● 80 μm, ○ 140 μm

Die stärkste Zeitabhängigkeit ergibt sich bei Teilchen von 15 μm Radius; die Zunahme der Haftfähigkeit mit der Kontaktzeit ist bei diesen am stärksten. Der nach einigen Minuten Kontaktzeit gemessene Abreißwinkel ist klein, da keine Zeit für die Deformation der Lyosphäre vorhanden ist; so kann das Teilchen am Flüssigkeitsfilm abgleiten. Mit zunehmender Kontaktzeit wird aber die Distanz zwischen Teilchen und Glasplatte infolge der stärkeren Deformation der Lyosphäre geringer, was eine Zunahme der Adhäsion mit sich bringt. Bei größeren Teilchen ist dieser Effekt weniger deutlich, wahrscheinlich deshalb, weil infolge der auch anfänglich starken Deformation der Lyosphären weniger Möglichkeit zu weiterer Deformation besteht und infolgedessen die Zunahme der Haftfähigkeit mit der Kontaktzeit geringer ist. Im Falle von genügend großen Teilchen bzw. bei einer Kontaktzeit von entsprechender Dauer können die aus Wasser oder Methylalkohol gebildeten, dikkeren, deformierbaren Lyosphären so dünn werden, daß die für schlecht benetzbare Systeme mit großer Adhäsion charakteristische Abhängigkeit von der Teilchengröße erhalten wird. Infolge der leichteren Deformierbarkeit der Lyosphäre verläuft dieser Prozeß in Methylalkohol schneller, als im Wasser.

Diese Erscheinung beweist überzeugend, daß die Deformierbarkeit der aus dem Dispersionsmittel gebildeten Lyosphäre — wie schon BUZÁGH [8] darauf hinwies — einer der wichtigsten Faktoren der Ausbildung der Haftfähigkeit bedeutet und auch weitere Möglichkeiten zur Erforschung der Eigenschaften von dünnen Flüssigkeitsfilmen ergibt.

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## О ЗАВИСИМОСТИ АДГЕЗИИ ОТ ВРЕМЕНИ КОНТАКТА

*А. Пацко, Ф. Санто и Б. Варкони*

Авторами изучалось угол отрыва кварцовых фракций различной степени дисперсии в воде и метиловом спирте в зависимости от времени контакта. Было установлено, что способность к прилипанию изменяется параллельно с временем контакта с основной плитой: адгезия частиц небольшого размера по кривым подобны адсорпционному изотерму, а большего размера линеарно.

## BOOK REVIEW

*H. S. Green and R. B. Leipnik, Sources of Plasma Physics, Volume 1, xiv + 630 pages, Wolters — Noordhoff Publishing, Groningen, 1970. $33.00*

The development of plasma physics has grown increasingly rapid during the past twenty years. The study of astrophysics and the exploration of space have provided the most important stimuli in the natural realm by realizing that most matter in the universe is in the highly ionized state.

This volume has been designed by the authors as a fundamental work containing the most essential source material from which an adequate theory of the ionized state can be developed. They have limited themselves to a discussion of the mathematical foundations of statistical mechanics, the principles of electromagnetism, electrodynamics and fluid mechanics and the kinetic theory of liquids. It is the first time that all those essential topics have been so comprisingly brought together in a single volume with the needs of magnetohydrodynamics and plasma physics in mind. The book is the fruit of the authors' experiences in attempting to formulate a theoretical exposition of plasma physics, which will be presented in a second volume, now in an advanced state of preparation.

We hope together with the authors that this book will be found useful by students and teachers of university courses preliminary to more specialized courses in magnetohydrodynamics and plasma physics. In the recent past such background material has been somewhat neglected in physics and engineering schools. We share the authors' opinion that this conjunction of classical theories provides a more fruitful study than the separate disciplines in isolation. The volume may therefore also prove suitable as a reference work to research workers in plasma and other related fields.

The volume is divided into five chapters. The first chapter — which contains the fundamentals — deals with origin and nature of magnetohydrodynamics and plasma physics, and describes the nature of the plasma state. The authors give the mathematical foundation of the theory (measures, distribution, probability, etc.), the conservation laws, the quantum theoretical formulation and the constants of the motion (additivity, equilibrium, etc.).

The second chapter deals with the introduction to electromagnetic field; it contains the electromagnetic theory, the physical basis of Maxwell's equations, special fields and potential theory, further the quasi-stationary theory, waves and Fourier analysis, the Hertz potentials and finally the interaction of charged particles.

Chapter 3 is devoted to fluid mechanics. After defining the fluid state, this chapter deals with the conservation laws (mass, momentum, energy), conditions for equilibrium, irreversible processes in fluids (diffusion, viscosity, etc.). The discussion of propagation and absorption of sound and the shock waves closes the chapter.

In chapter 4 the authors deal with advanced theories of electromagnetism. On the basis of a short exposition of special relativity, electromagnetism as a relativistic theory, electromagnetic waves (wave guides, etc.), and the radiation of moving charges are dealt with. The last section gives the principles of magnetohydrodynamics (fundamental equations and conservation laws of magnetohydrodynamics, etc.).

The fifth, closing chapter under the heading „Molecular theory of fluids" discusses the molecular structure, the transport of momentum and energy, surface phenomena and statistical mechanics of equilibrium. After a short review of computational methods (the Monte Carlo and integral equation methods), the statistical mechanics of irreversible processes.

Eight detailed appendices on mathematical and other fundamentals such as measures, probability, vectors, matrices, tensors; Fourier analysis, vector analysis; differential and integral equations; calculus of variations; laws of thermodynamics; units and dimensions close the volume.

The more than hundred references at the end of each chapter are collected from monographs, conferences and symposia, and from journals.

The style of this work of basic importance is clear, concise but well readable. The publishers contributed to the succes by a pleasant presentation.

L. GÁTI (Institute of Experimental Physics,
Attila József University, Szeged)

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1971
A kézirat a nyomdába érkezett: 1971. szeptember. Megjelenés: 1971. december
Példányszám: 480 Ábrák száma: 55 Terjedelem: 8,4 (A/5) iv
Készült monó szedéssel, íves magasnyomással, az MNOSZ 5601—54 és az MNOSZ 5602—50 A szabványok szerint

71-4873 — Szegedi Nyomda