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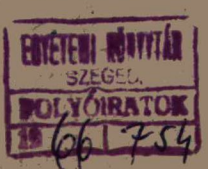

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CONTRIBUTIONS TO THE THEORY OF ABSORPTION AND EMISSION SPECTRA OF FLUORESCENT MOLECULES

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Considering qualitatively the correlation between the electrons and atomic vibrations of fluorescent molecules, it is supposed that in the case of the light absorption one part of the absorbed energy $\hbar(\omega-\omega_0)$ and in the case of a radiative transition between the excited and the ground state of the molecules the resting energy $\hbar(\omega-\omega_0)$ may be converted into heat, $\hbar\omega_0$ being the energy difference between the pure electronic states and $\hbar\omega$ the energy of the photon playing part in the processes mentioned. In this way the temperature of the molecules rises against the temperature of the thermal equilibrium at the beginning of the absorption and emission processes. Owing to this natural supposition, BLOKHINTSEV's theory of absorption and emission spectra can be improved by taking into account the correlation-fluctuations during the transitions and obtained an analytical expression for the absorption and emission spectra previously experimentally found by DOMBI *et al* [1]. Based on the spectra derived, the LEVSHIN's relation of mirror symmetry and the generalized STEPANOV's radiation law can be obtained. Finally, the vibrational specific heat as well as the relaxation time of the thermal interaction process between the fluorescent and the solvent molecules are calculated in good agreement with previous estimations.

§ 1. Introduction

The relation between the absorption spectrum $\alpha(\omega)$ and the emission spectrum $\varepsilon(\omega)$ of fluorescent molecules have recently been investigated by several authors from experimental as well as from theoretical point of view. The present investigation was inspired by a more recent investigation of J. DOMBI, I. KETSKEMÉTY and L. KOZMA [1], who observed that considering LEVŠHIN's relation of the mirror symmetry of the absorption and emission spectra as well as the generalized STEPANOV's law [2, 3]

$$\varepsilon(\omega)/\alpha_{act}(\omega) = d(\theta)n^2(\omega)\omega^2 \exp\{-\hbar\omega/\theta^*\} \tag{1,1}$$

with

$$\alpha_{act}(\omega)=\alpha(\omega)\eta^*(\omega), \quad \theta^*=kT^* \quad \text{and} \quad \theta=kT, \tag{1,2}$$

the active absorption spectrum $\alpha_{act}(\omega)$ and the emission spectrum can analytically be written in the following from:

$$\alpha_{act}(\omega)=\alpha_0 n(\omega)\omega e^{B\omega}\,\mathrm{ch}^{-1}\{A(\omega-\omega_0)\} \tag{1,3}$$

and

$$\varepsilon(\omega) = \varepsilon_0 n^3(\omega)\omega^3 e^{-B\omega}\,\mathrm{ch}^{-1}\{A(\omega-\omega_0)\}. \tag{1,4}$$

Here $d(\theta)$ is a constant independent of the frequency $\omega=2\pi\nu$, but it depends on

the temperature θ (in energy units!); $\eta^*(\omega)$ and $n(\omega)$ are the relative quantum yield and referactive index of the solution, respectively; $2\pi\hbar = h$ and k are PLANCK's and BOLTZMANN's constants, finally α_0, ε_0, A and B are constants depending on the temperature which should be experimentally determined. The formulae reproduce excellently the contour of the spectra mentioned if θ^* is a sligthly higher temperature than θ being the temperature of the solution. Due to Eq. (1,1) one can see that $B = \hbar/2\theta^*$ and based on an elementary dimensional reasoning one obtains immediately that $A = \hbar/\theta'$. However, it was, indeed, a fascinating problem to explain the meaning of θ^*, θ' and to derive the formulae (1,3) and (1,4).

It will be presented in the following that based on obvious suppositions, considering some time-correlation and fluctuation effects in the course of the radiative processes, the formulae (1,3) and (1,4) can easily be obtained by a straightforward generalization of BLOKHINTSEV's method [4] used for the derivation of LEVSHIN's relation of mirror symmetry of absorption and emission spectra, furthermore it will be proved that $\theta' = 2\theta$ and θ^* may be interpreted as the vibrational temperature of the molecules at the moment of absorption and emission, respectively. Finally, if θ^* is experimentally determined (based, *e. g.* on the experiments of DOMBI *et al.* [1]) the vibrational specific heat of the molecules and (based on the knowledge of the mean life time of the excited state) the relaxation time of the interaction process between the fluorescent molecules and the solvent can be calculated in very good agreement with earlier results.

§ 2. General remarks to the theory of absorption and emmission spectra and fundamental assumptions on the structure of fluorescent molecules

As it is well known, the emission and absorption of light by an atom or molecule can easily be understood by referring to the theory of perturbation. A molecule and the radiation field from two quantum mechanical systems with an interaction energy

$$\mathbf{H}_{\text{int}} = -\frac{e}{mc}(\mathfrak{v}\cdot\mathfrak{A}). \tag{2,1}$$

This interaction, regarded as a perturbation, will cause transitions of the unperturbed system (molecule + radiation field) in general consisting of a transition of the molecule from one quantum state to another and of an absorption or emission of photon. Here e and m are the charge and mass of the electrons of the molecule, $\mathfrak{v}$ means the velocity of the electron responsible for the radiative transition, finally $\mathfrak{A}$ represents the vector potential of the radiation field.

Based on the very common method [5], if the transition proceeds between two non-degenerate quantum states ($E_a < E_b$) of the molecule and the induced emission of radiation can be neglected, in the case of dipole radiation one obtains for the absorption and emission spectra [4]:

$$\alpha(\omega) = Nn(\omega)\frac{4\pi^2}{c}\omega|\langle a|\mathfrak{D}|b\rangle|^2\delta(E_b - E_a - \hbar\omega) \tag{2,2}$$

and

$$\varepsilon(\omega) = \frac{4}{3}n^3(\omega)\frac{\omega^3}{\hbar c^3}|\langle a|\mathfrak{D}|b\rangle|^2\delta(E_b - E_a + \hbar\omega), \tag{2,3}$$

where $\langle a|\mathfrak{P}|b\rangle = e\langle a|\mathfrak{r}|b\rangle$ represents the matrix element of the transition dipole moment for the transition $b \to a$ and N is the number of absorbing molecules per unit volume.

Considering the absorption and emission spectra of fluorescent molecules one meets rather complicated situation than in the special case mentioned above. The mean point of the difficulties emerged are not reduced to the facts that

(*i*) the quantum states of such molecules are strongly degenerated, owing to which the principle of correspondence cannot be rigorously applied (or at least the results of the argumentations based on the classical quantum theory of radiation may be very questionable),

(*ii*) considerable interactions exist between the fluorescent and solvent molecules, but it is due to the complexity of the structure of the fluorescent molecules as well.

An exact or at least an approximately acceptable theory of fluorescent molecules based on the common methods of quantum chemistry seems to be even nowdays hopeless in this case. Nevertheless, owing to the very abundant experimental material in this field [6, 7], just the complexity of the fluorescent molecules makes possible to formulate some natural assumptions about the structure and the enrgy spectrum of these molecules, based thereon the general features of the absorption and emission spectra as well as the validity of this reasoning can be obtained.

Of course, the Hamiltonian of the molecules can be formally written in the form:

$$\mathbf{H}^{(m)} = \mathbf{H}_{\mathrm{el}}^{(m)} + \mathbf{H}_{\mathrm{v}}^{(m)} + \mathbf{H}_{\mathrm{int}}^{(m)}, \tag{2,4}$$

where $\mathbf{H}_{\mathrm{el}}^{(m)}$ and $\mathbf{H}_{\mathrm{v}}^{(m)}$ represent the parts of the Hamiltonian corresponding to the electrons and atomic vibrations of the molecules, respectively, and $\mathbf{H}_{\mathrm{int}}^{(m)}$ is the interaction between them. This is just the usual decomposition of the Hamiltonian.

Considering the general feature of the absorption and emission spectra it seems — as it has been suggested by several authors — that the fluorescent molecules differ from the simple two- and simple many-atomic molecules especially in the structure of $\mathbf{H}_{\mathrm{v}}^{(m)}$. In the latter case the harmonic approximation is an adequate description for the atomic vibrations. This means that the vibrational field can be regarded as a system of non-interacting normal vibrations. However, in the case of fluorescent molecules the harmonic approximation breaks down and it has to be assumed that strong interaction among the normal vibrations takes place, so far that the energy absorbed by one of the normal vibrations, dissipates very quickly among the vibrational degrees of freedom. Owing to this reasoning it may be assumed that the energy distribution on the vibrational levels is approximately independent of the electronic states, at least in the case of the two lowest electronic quantum states, important in the processes of fluorescence. Bearing in mind the chemical structure of the fluorescent molecules, the quasi-continuity of the vibrational energy spectrum, due to the very closely placed vibrational levels, as a further natural assumption can be regarded.

The interaction part of the Hamiltonian between the electrons and molecular vibrations depends on the strength of the coupling between these two essentially different degrees of freedom.

Even should we not try to suggest an explicit expression for $\mathbf{H}_{\mathrm{int}}^{(m)}$, it can be supposed that one part — say $\hbar\omega_0$ (being the energy difference between the two

electronic states treated) — of the energy $\hbar\omega$ absorbed excites the system of electrons and the remaining part of the absorbed energy $\hbar(\omega-\omega_0)$ dissipates on the vibrational degrees of freedom. Namely, the magnitude of the energy dissipated depends on the coupling constant contained by $\mathbf{H}_{\text{int}}^{(m)}$ being a characteristic quantity of the fluorescent molecules. Due to the inertia of the atomic vibrations in comparison with the excitations of the electrons, it can be assumed that (at least in the Stokesian domain of the spectrum) $\hbar(\omega-\omega_0) \ll \hbar\omega_0$. However, we have to emphasize that the expectation value of the energy dissipated on the vibrational levels depends last of all on the energy state of the molecules and actually it makes a slight fluctuation, if the time-evolution of the system is taken into account. Indeed, in the following we shall observe that the consideration of this fluctuation will be very important if one treats the derivation of the absorption spectrum (1,3) found experimentally by DOMBI and co-workers.

In the case of emission of the light (of an energy $\hbar\omega$) by fluorescent molecules, one part of the emitted energy (say $\hbar\omega_0$) originates again from the transition between two quantum states of the system of electrons and the remaining second part $\hbar(\omega-\omega_0)$ is added to the first one by changing the vibrational state. The fluctuational effect in this case has to be considered, too.

At this point it seems worthwile to mention a well known analogy with the absorption and emission processes of the atoms. If the motion of atoms interacting with the radiation field is taken into account, a part of the absorbed and emitted energy is, respectively, consumed and increased by the kinetic energy of the atoms. Such a dissipation or gaining of the radiation energy on or from the translational "mechanical degrees of freedom", respectively, appears in the case of considerable $\hbar\omega$ in the broadening of the line width as well as in the separation of the maxima of the absorption and emission spectra and causes a mirror symmetry between them. Such effect in the case of the heavy fluorescent molecules can completely be neglected, but the mirror symmetry of the absorption and emission spectra observed, if the dissipated or the gained energy is attributed to the vibrational mechanical degrees of freedom, can be understood in a very similar way.

For the sake of simplicity we consider radiative transitions of the fluorescent molecules only between the two lowest electronic states (being in a distance $\hbar\omega_0$) and we suppose that these electronic levels are not degenerated. It is well known that such a reasoning has previously been very common in the theory of fluorescence, too. This means, however, that the degeneration of the corresponding quantum states of the molecules is only due to the energy of vibrations. Let us denote the lowest electronic energy state by E_0, the corresponding energy of the molecule by E_a, and the energy of the upper quantum state of the molecule by E_b, then we have

$$E_a = E_0 + W_a \quad \text{and} \quad E_b = E_0 + \hbar\omega_0 + W_b, \tag{2,5}$$

where W_a and W_b mean the energy of the vibrational levels, respectively. Owing to the energy conservation, a transition $a \rightarrow b$ can be induced by the absorption of a photon of energy $\hbar\omega$ fulfilling the relation:

$$E_b - E_a = \hbar\omega \tag{2,6}$$

and it is immediately seen, that

$$W_b - W_a \equiv \hbar\omega_{ba} = \hbar(\omega-\omega_0). \tag{2,7}$$

The corresponding ket vectors fulfilling the time-independent SCHRÖDINGER equations

$$\mathbf{H}^{(m)}|a\rangle = E_a|a\rangle \text{ and } \mathbf{H}^{(m)}|b\rangle = E_b|b\rangle, \tag{2,8}$$

respectively, depend on the co-ordinates of the electrons ($\mathfrak{r}_i$) and on the normal co-ordinates (q_r) of the atomic vibrations. We have to emphasize that — due to the considerable interaction between the electrons and vibrations — the two kinds of co-ordinates cannot be separated, *i. e.*, the kets cannot be decomposed into the product of two kets depending only on the electronic and vibrational co-ordinates, respectively. In this respect we cannot agree with B. J. STEPANOV, who in his excellent monography [7], *e. g.*, on the occasion of a simplified deduction of the mirror symmetry introduced such a separation.

As a matter of fact, under real experimental circumtances we have to investigate a system of fluorescent molecules embedded into a system of another sort of molecules alike in the vapour, fluid and solid state of the system. Let us suppose for simplicity that only thermal intractions between the fluorescent and the extraneous molecules must be taken into account. At the first instant is perhaps surprising, but it seems that just the dilute solutions of the fluorescent molecules would represent the simplest systems from theoretical point of view. Its reason can be given by the argumentation that in dilute solutions — at least in the case when the radiationless energy transfer among the fluorescent molecules is sufficient to be considered — the direct (even thermal) interaction among them can be neglected. Namely, as the number of fluorescent molecules is negligible against the number of the solvent molecules, collisions among the fluorescent molecules practically do not take place. This means, however, that the system of the fluorescent molecules — as a component-system of the solution — from statistical point of view can be regarded as a perfect gas in the heat-bath of the solvent molecules, because the very lack of direct interactions is the mean point of the definition of a perfect gas. As a matter of fact, the system of the fluorescent molecules may satisfactorily be repredensed by a Gibbsian ensemble and the number of molecules having the quantum state E_n is proportional to $\exp\{(\Psi_n - E_n)/\theta\}$, where Ψ_n represents the free energy of the electrons at the temperature θ, furthermore the interaction between the system of fluorescent molecules and the solvent molecules may be described with the phenomenological method of heat conduction. In the case of vapours as a consequence of the more considerable diffusion and in solid state due to the phonon excitation rather complicated effects may occur, too.

Having in mind the theoretical foundation of the experimental spectra, in the form as they can actually be observed, one has — *e. g.*, in the case of the absorption spectrum — to average formula (2,1) over all vibrational levels of the initial and of the excited electronic states as well; finally, one has to multiply with the number of fluorescent molecules in the different vibrational states having the energies $E_a = E_0 + W_a$. If we suppose that the molecules in the initial state are in thermal equilibrium with their surroundings (*i. e.*, with the solvent molecules) at a temperature θ, this means — as it was otherwise discussed, *e. g.*, by BLOKHINTSEV [6] in details — that we have to average over the statistical ensemble, too, and one has to calculate the expression

$$\sum_a \sum_b \exp\{(\Psi_1 - E_a)/\theta_1\} g(E_a) g(E_b) |\langle a|\mathfrak{P}|b\rangle|^2 =$$
$$= \int dW_a \int dW_b \exp\{(\Psi_1 - E_a)/\theta\} g(E_a) g(E_b) F(E_a, E_b), \tag{2,8}$$

where Ψ_1 denotes the free energy of the molecules in the initial state; $g(E_a)dW_a$ and $g(E_b)dW_b$ are the number of vibrational levels in the energy intervals $(E_0+W_a,\ E_0+W_a+dW_a)$ and $(E_0+\hbar\omega_0+W_b,\ E_0+\hbar\omega_0+W_b+dW_b)$, respectively; finaly, $F(E_a, E_b) \equiv F(E_a, E_a+\hbar\omega)$ is an abbreviation of the square of the transition matrix element for the transition $a \rightarrow b$. Owing to the densiteness, *i. e.*, quasi-continuity of the vibrational levels, the summations over the vibrational states are approximated by integrals.

It is well known that this method, being very common in spectroscopy, gives excellent results for the absorption and emission spectra in the case of atoms and simple manyatomic molecules as well. Furthermore, BLOKHINTSEV showed that also the mirror symmetry of the absorption and emission spectra can be obtained in this way. Nevertheless, it seems that in the case of fluorescent molecules one would have slightly to modify the way of thinking. Namely, due to the lack of the explicit knowledge of the operators $\mathbf{H}_{\text{int}}^{(m)}$ and $\mathbf{H}_{\text{v}}^{(m)}$ containing the interaction rules of the electronic motions with the molecular vibrations and among the vibrational modes as well, it is so far undetermined that in the case of the absorption of a photon with energy $\hbar\omega$ how large is the energy $\hbar(\omega-\omega_0)$ exciting the molecular vibrations and in which way is it distributed between the vibrational degrees of freedom? Therefore, as matters stand, we have to formulate a reasonable supposition to overcome this difficulty. Since the energy exciting the molecular vibrations can reach the vibrational modes in different phases, consequently the vibrations can be both increased and damped, it may be concluded that one has every reason to suppose that from a definite initial state E_a every excited states E_b can be reached with equal probability. Of course, the number of the excited molecules cannot depend on this indefiniteness, therefore one has to average also in the states b over the statistical ensemble; this means, however, that before the summation over b we have to multiply by a factor $\exp\{(\Psi_2-E_b)/\theta_2\}$, where Ψ_2 denotes the free energy of the molecules in the excited states. Instead of the temperature θ_1 we have written here any temperature θ_2, because the molecules due to the excitation of their vibrational degrees of freedom "warm up" and they will be in thermal equilibrium at any temperature $\theta_2 > \theta_1$. If this reasoning can be accepted, BLOKHINTSEV's formula (2,8) has to be replaced by

$$\sum_a \sum_b \exp\{(\Psi_1-E_a)/\theta_1\} \exp\{(\Psi_2-E_b)/\theta_2\} g(E_a) g(E_b) |\langle a|\mathfrak{D}|b\rangle|^2 =$$

$$= \int dW_a \int dW_b \exp\{(\Psi_1-E_a)/\theta_1\} \exp\{(\Psi_2-E_b)/\theta_2\} g(E_a) g(E_b) F(E_a, E_b). \quad (2,9)$$

Finally, we have to find the relations between the fictive temperatures θ_1 and θ_2 as well as the temperature θ of the solution (measured experimentally) and the temperature θ^* of excited molecules (predicted by the supposition that one part of the energy absorbed by the mechanical degrees of freedom is converted into the heat of the ensemble of the excited molecules). One can qualitatively argue as follows: We considered in the Hamiltonian (2,3) — as it is usual — only the energies due to the electronic motions and molecular vibrations, but neglected the translational energy of the molecules. This means, however, that the energy E_a (in the exponent of the Gibbsian weight factor) is smaller than the real energy of the molecules in the initial state; therefore in the quotient E_a/θ_1 the temperature θ_1 ues to be also smaller than the real temperature of the solution in order that the

value of the ratio may not undergo a change. Conversely, in the case of excited states we have „distributed" (in our approximation) the energy reached the mechanical degrees of freedom only between the vibrational degrees of freedom (due to the neglection of the translational motion again); this means, however, that in this way "more energy has reached" the vibrational degrees of freedom than it happens in reality, therefore W_b and E_b, respectively, are higher than the real energy of the excited states. In order that the value of the ratio E_b/θ_2 may not change, θ_2 has to be higher than the real temperature θ^* of the excited molecules. Consequently, it can be concluded that $\theta_1 < \theta < \theta^* < \theta_2$. This is, of course, only a qualitative relation, but — based on a reasonable semi-empirical way — it can be converted into a quantitative one as it is obtained in the next paragraph [Eq. (3,12)].

It seems that the heuristic argumentation detailed above can be replaced by a more rigorous method based on the BORN's approximation, if one adopts the perturbational procedure being well known in the theory of rearrangement collisions. This method will be exposed in a next paper.

Finally, due to the fluctuations in the interaction between the system of electrons and the atomic vibrations of the fluorescent molecules, on calculating (2,9), it has to be considered the time-correlation effect in course of the time-evolution of the system, too, as it will be discussed in the next paragraph.

§ 3. Mean square of the fluctuating dipole moment

In order to calculate the mean square of the fluctuating dipole moment, let us consider its matrix elements in HEINSENBERG-picture:

$$\langle a|\mathfrak{D}(t)|b\rangle = \langle a|\exp\{i\mathbf{H}^{(m)}t/\hbar\}\mathfrak{D}\exp\{-i\mathbf{H}^{(m)}t/\hbar\}|b\rangle$$
$$= \langle a|\mathfrak{D}|b\rangle\exp\{i(E_a-E_b)t/\hbar\} = \langle a|\mathfrak{D}|b\rangle\exp\{i(\omega_{ab}-\omega_0)t\} \tag{3,1}$$

and their FOURIER-amplitudes

$$\langle a|\mathfrak{D}(\omega)|b\rangle = \frac{1}{2\pi}\int_{-\infty}^{+\infty}\langle a|\mathfrak{D}(t)|b\rangle e^{i\omega t}dt =$$

$$= \frac{1}{2\pi}\int_{-\infty}^{+\infty}\langle a|\mathfrak{D}|b\rangle e^{i(\omega-\omega_0+\omega_{ab})t}dt = \langle a|\mathfrak{D}|b\rangle\delta(\omega-\omega_0+\omega_{ab}), \tag{3,2}$$

respectively. The operators $\mathfrak{D}(t)$ and $\mathfrak{D}(t')$ for different instants of time do not, in general, commute, therefore the corresponding time-correlation function must be defined [8] as

$$\Phi(t'-t) \equiv \frac{1}{2}\overline{\{\mathfrak{D}(t)\mathfrak{D}(t')+\mathfrak{D}(t')\mathfrak{D}(t)\}}, \tag{3,3}$$

where the bar denotes averaging by means of the quantummechanical probabilities. Owing to the inversion theorem of the FOURIER transformation

$$\mathfrak{D}(t) = \int_{-\infty}^{+\infty}d\omega\,\mathfrak{D}(\omega)e^{-i\omega t}, \tag{3,4}$$

one obtains

$$\Phi(t'-t)=\frac{1}{2}\int_{-\infty}^{+\infty}d\omega\int_{-\infty}^{+\infty}d\omega'\overline{\{\mathfrak{D}(\omega)\mathfrak{D}(\omega')+\mathfrak{D}(\omega')\mathfrak{D}(\omega)\}}\,e^{-i(\omega t+\omega' t')}. \tag{3,5}$$

The integral on the right-hand side will be a function of the difference $(t'-t)$ only if the integrand contains a δ-function of $\omega+\omega'$. This requires that the spectral density of the mean square fluctuation of the dipole moment has to be defined as

$$\frac{1}{2}\overline{\{\mathfrak{D}(\omega)\mathfrak{D}(\omega')+\mathfrak{D}(\omega')\mathfrak{D}(\omega)\}}\equiv\mathfrak{D}_\omega^2\delta(\omega+\omega'). \tag{3,6}$$

It is well known that, in particular, $\Phi(0)$ is just the mean square of the fluctuating quantity itself, therefore we have to calculate $\mathfrak{D}_\omega^2$. Since

$$\frac{1}{2}\overline{\{\mathfrak{D}(\omega)\mathfrak{D}(\omega')+\mathfrak{D}(\omega')\mathfrak{D}(\omega)\}}=$$

$$\frac{1}{2}\sum_n\sum_m\{\langle n|\mathfrak{D}(\omega)|m\rangle\langle m|\mathfrak{D}(\omega')|n\rangle+\langle n|\mathfrak{D}(\omega')|m\rangle\langle m|\mathfrak{D}(\omega)|n\rangle\}=$$

$$=\frac{1}{2}\sum_n\sum_m|\langle n|\mathfrak{D}|m\rangle|^2\times$$

$$\times\{\delta(\omega-\omega_0+\omega_{nm})\delta(\omega'+\omega_0+\omega_{mn})+\delta(\omega'-\omega_0+\omega_{nm})\delta(\omega+\omega_0+\omega_{mn})\}=$$

$$=\frac{1}{2}\sum_n\sum_m|\langle n|\mathfrak{D}|m\rangle|^2\{\delta(\omega-\omega_0+\omega_{nm})+\delta(\omega-\omega_0+\omega_{mn})\}\delta(\omega+\omega'),$$

we have, in general,

$$\mathfrak{D}_\omega^2=\frac{1}{2}\sum_n\sum_m|\langle n|\mathfrak{D}|m\rangle|^2\{\delta(\omega-\omega_0+\omega_{nm})+\delta(\omega-\omega_0+\omega_{mn})\}. \tag{3,7}$$

Now, beside the quantum-mechanical average, we have to calculate the ensemble-average, too. As a matter of fact, one obtains

$$\frac{1}{2}\sum_a\sum_b\exp\left\{\frac{\Psi_1-E_a}{\theta_1}\right\}\exp\left\{\frac{\Psi_2-E_b}{\theta_2}\right\}|\langle a|\mathfrak{D}|b\rangle|^2\times$$

$$\times\{\delta(\omega-\omega_0+\omega_{ab})+\delta(\omega-\omega_0+\omega_{ba})\}=$$

$$=\frac{1}{2}\sum_a\sum_b\exp\left\{\frac{\Psi_1-E_a}{\theta_1}\right\}\exp\left\{\frac{\Psi_1-E_b}{\theta_2}\right\}\left[1+\exp\left\{-(W_b-W_a)\left(\frac{1}{\theta_1}-\frac{1}{\theta_2}\right)\right\}\right]\times$$

$$\times|\langle a|\mathfrak{D}|b\rangle|^2\delta(\omega-\omega_0+\omega_{ab})=$$

$$=\exp\left\{-\frac{\varkappa\hbar(\omega-\omega_0)}{2\theta_1}\right\}\mathrm{ch}\left\{\frac{\varkappa\hbar(\omega-\omega_0)}{2\theta_1}\right\}\sum_a\sum_b\exp\left\{\frac{\Psi_1-E_a}{\theta_1}\right\}\exp\left\{\frac{\Psi_2-E_b}{\theta_2}\right\}\times$$

$$\times|\langle a|\mathfrak{D}|b\rangle|^2, \tag{3,8}$$

with

$$\varkappa = \frac{\theta_2 - \theta_1}{\theta_2}. \tag{3,9}$$

This means, however, that Eq. (2,10) has to be replaced by

$$\sum_a \sum_b \exp\left\{\frac{\Psi_1 - E_a}{\theta_1}\right\} \exp\left\{\frac{\Psi_2 - E_b}{\theta_2}\right\} g(E_a) g(E_b) |\langle a|\mathfrak{P}|b\rangle|^2 =$$

$$= \exp\left\{\frac{\Psi_1}{\theta_1} + \frac{\Psi_2}{\theta_2} + \frac{\varkappa\hbar(\omega-\omega_0)}{2\theta_1}\right\} \mathrm{ch}^{-1}\left\{\frac{\varkappa\hbar(\omega-\omega_0)}{2\theta_1}\right\} \times$$

$$\times \int dW_a \int dW_b e^{-E_a/\theta_1} e^{-E_b/\theta_2} g(E_a) g(E_b) F(E_a, E_b). \tag{3,10}$$

Inserting the last relation in Eq. (2,2) instead of $|\langle a|\mathfrak{P}|b\rangle|^2$ for the absorption spectrum

$$\alpha_{\mathrm{act}}(\omega) = \alpha_0' n(\omega)\omega \exp\left\{\frac{\hbar(\omega-\omega_0)}{2\theta^*}\right\} \mathrm{ch}^{-1}\left\{\frac{\hbar(\omega-\omega_0)}{2\theta}\right\} I_\alpha(\omega-\omega_0) \tag{3,11}$$

can be obtained with the abbreviations (1,2) and

$$\theta^* \equiv \theta_1/(3\varkappa - 2), \quad \theta \equiv \theta_1/\varkappa = (3\varkappa-2)\theta^*/\varkappa \tag{3,12}$$

$$I_\alpha(\omega-\omega_0) \equiv \int dW_a \exp\left\{\frac{(\varkappa-2)W_a}{\theta_1}\right\} g(E_0 + W_a) \times$$

$$\times g(E_0 + \hbar\omega_0 + W_a + \hbar(\omega-\omega_0)) F(E_0 + W_a, E_0 + \hbar\omega_0 + \hbar(\omega-\omega_0)). \tag{3,13}$$

The constant α_0' introduced in (3,11) is independent of ω and contains all the further factors originatig from Eqs. (2,2) and (3,10).

Similarly, the results for the emission spectrum is

$$\varepsilon(\omega) = \varepsilon_0' n^3(\omega)\omega^3 \exp\left\{-\frac{\hbar(\omega-\omega_0)}{2\theta^*}\right\} \mathrm{ch}^{-1}\left\{\frac{\hbar(\omega-\omega_0)}{2\theta}\right\} I_\varepsilon(\omega-\omega_0) \tag{3,14}$$

with

$$I_\varepsilon(\omega-\omega_0) \equiv \int dW_b \exp\left\{\frac{(\varkappa-2)W_b}{\theta_1}\right\} g(E_0 + W_b + \hbar(\omega-\omega_0) \times$$

$$\times g(E_0 + \hbar\omega_0 + W_b) F(E_0 + \hbar\omega_0 + W_b, E_0 + W_b + \hbar(\omega-\omega_0)). \tag{3,15}$$

In order to compare the formulae (1,3) and (3,11) as well as (1,4) and (3,14), we have to study the properties of the integrals $I_\alpha(\omega-\omega_0)$ and $I_\varepsilon(\omega-\omega_0)$, respectively.

§ 4. General relations between the absorption and emission spectra

Bearing in mind the absorption and emission spectra determined in the last paragraph, one obtains the important relation

$$\frac{\varepsilon(\omega)}{\alpha_{\mathrm{act}}(\omega)} = \frac{\varepsilon_0'}{\alpha_0'} n^2(\omega)\omega^2 \exp\left\{-\frac{\hbar(\omega-\omega_0)}{\theta^*}\right\} \frac{I_\varepsilon(\omega-\omega_0)}{I_\alpha(\omega-\omega_0)} \tag{4,1}$$

being a new generalization of STEPANOV's radiation law (1,1). Unfortunately this relation is only an implicit one, because the solution of the SCHRÖDINGER-equations (2,8) and simultaneously $F(E_a, E_b)$ as well as the functions $g(E_a)$ and $g(E_b)$ are unknown, so the integrals cannot be explicitly evaluated.

One observes, however, on the one hand that

$$\varepsilon(\omega_0)/\alpha_{\text{act}}(\omega_0) = \frac{\varepsilon_0'}{\alpha_0'} n^2(\omega_0)\omega_0^2 \tag{4,2}$$

and on the other that with the abbreviations

$$\varepsilon_0 \equiv \varepsilon_0' \exp\{-\hbar\omega_0/2\theta^*\} I_\varepsilon(\omega-\omega_0) \approx \varepsilon_0' \exp\{-\hbar\omega_0/2\theta^*\} I_\varepsilon(0), \tag{4,3}$$

$$\alpha_0 \equiv \alpha_0' \exp\{+\hbar\omega_0/2\theta^*\} I_\alpha(\omega-\omega_0) \approx \alpha_0' \exp\{+\hbar\omega_0/2\theta^*\} I_\alpha(0),$$

Eq. (4,1) is the same as the generalized STEPANOV's radiation law (1,1) which has been experimentally proved by KETSKEMÉTY *et al.* [3] for a small, but practically considerable frequency interval $(\omega_0-\omega, \omega_0+\omega)$. So BLOKHINTSEV's assumption [4], can be accepted whereby — whenever $\hbar(\omega-\omega_0)$ is negligible against E_0 — both integrands are slowly varying functions of ω, so far that more precisely

$$I_\varepsilon(\omega \mp \omega_0) \approx I_\alpha(\omega \pm \omega_0), \quad \text{if} \quad \hbar|\omega-\omega_0| \ll \overline{E(2\theta)} \tag{4,4}$$

being $\overline{E(2\theta)}$ the mean value of the energy of the molecules at the temperature 2θ. This frequency interval approximately agrees with the domain, where the absorption and emission spectra are overlapped.

Owing to the relation (4,4), we have

$$[\alpha_{\text{act}}(\omega)/n(\omega)\omega]_{\omega\pm\omega_0} = \text{const}\,[\varepsilon(\omega)/n^3(\omega)\omega^3]_{\omega\pm\omega_0}. \tag{4,5}$$

As to the experimental evidence in the frequency interval considered $n(\omega) \approx$ const., the relation (4,5) is essentially just the analytical from of LEVSHIN's law of mirror symmetry.

§ 5. Concluding remarks

One observes that in the suggested theory the assumption was very important that in the case of absorption one part of the energy absorbed and in the case of emission the remaining energy, respectively, rises the vibrational energy of the molecule. However, our reasoning — owing to Eq. (3,12) — can only be accepted, if $\varkappa > \frac{2}{3}$, namely, the sign of the temperature cannot be changed. Using the experimental values given by DOMBI *et al* [1], the temperatures calculated by Eqs. (3,12) and (3,9) are summarized in Table I. It has to be mentioned that DOMBI *et al.* looking for the parameters A and B have used a fixed value for B and determined the best value for A. In fact, we have, however, understood above, that the parameter A contains the temperature θ being the temperature of the solution which means that the parameter A must be fixed. Therefore, we recalculated their curves varying the parameter B in good agrement with their results. Table I contains the temperatures of our calculations.

It is, however, a real problem whether the temperature θ^* introduced would have an experimental evidence? Of course, θ^* cannot be directly checked experi-

mentally. However, if the preceding arguments may be accepted, the energy $\hbar(\omega-\omega_0)$ is converted into heat, and the relation

$$T^*-T=\frac{\gamma\hbar(\omega-\omega_0)N}{MC} \tag{5,1}$$

could be obtained (where $N = 6{,}02486\cdot10^{23}$ $(\text{g}\cdot\text{mol})^{-1}$, $\gamma = 4{,}184\cdot10^{-8}$ cal/erg; M and C denote the molar weight and vibrational specific heat of the solute „gas", respectively) and the unknown specific heat can be determined. Indeed, having used the parameters determined by DOMBI *et al.* [1], we calculated T^* — characteristic of the coupling between the electrons and atomic vibrations of the molecules treated — and the specific heat. The results are summarized in Table I being in good agreement with the data given by N. A. BORISSEVICH [9] and with the estimations of L. KOZMA, L. SZALAY and J. HEVESI [10].

Table I

	T °K	T* °K	C cal/degree·g	τ 10^{-9}s	T_f^* °K	τ* 10^{-9}s
Fluorescein	298,1	377,7	0,323	5,05	331	8,55
Rhodamine B	298,1	407,2	0,033	5,6	332,6	6,89
Trypaflavine	298,1	396,2	0,186	4,0	325,6	4,70

As a further checking the following consideration may be useful. Since the system of excited molecules as a component-system of temperature θ^* is in thermal interaction with the component-system of the solvent molecules of temperature $\theta<\theta^*$, applying DE GROOT's considerations [11] we have

$$\frac{d}{dt}\Delta T=-\frac{1}{\tau^*}\Delta T \qquad (\Delta T\equiv T^*-T) \tag{5,2}$$

τ^* being the relaxation time of the interaction process. This means that

$$\Delta T(\tau)=\Delta T(0)\exp\{-\tau/\tau^*\}, \tag{5,3}$$

where $\Delta T(0)$ and $\Delta T(\tau)$ denote the temperature difference of the component-system $t=\tau$ (*i. e.* at the moment of emission), respectively. We have calculated T^* at the moment of absorption, so $\Delta T(0)$ is a known difference of temperature, therefore using the fluorimetrically measured [12] values of τ and $\Delta T(\tau)=T_f^*-T$, the relaxation time can be calculated. The results summarized in Table I. are in good agreement both with the dielectric relaxation time and the estimations of KOZMA *et al* [10]. The similar order of magnitude of the dielectric relaxation time and that of introduced in Eq. (5,3) seems to be very probable, since both processes are governed by weak thermal interaction.

* * *

I am very much indebted to Dr. I. KETSKEMÉTY, who called my attention to this problem as well as to Dr. L. SZALAY, Dr. J. DOMBI and Dr. L. KOZMA for several valuable discussions, furthermore for communicating their experimental results prior to publication.

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ПРИМЕЧАНИЯ К ТЕОРИИ СПЕКТРОВ АБСОРБЦИИ И ЭМИССИИ ФЛУОРЕСЦЕНТНЫХ МОЛЕКУЛ

Я. И. Хорват

Качественно имея в виду корреляцию электронов и атомных колебаний флуоресцентных молекул предполагается, что в случае абсорбции света часть абсорбированной энергии, $\hbar(\omega-\omega_0)$, и в случае лучевого перехода между основным и возбужденным положением, остаточная энергия, $\hbar(\omega-\omega_0)$, превращается в тепло, так как $\hbar\omega_0$ является разницей энергии между чистыми электронными положениями и $\hbar\omega$ является энергией фотона, играющего роль в процессе абсорбции или эмиссии. Таким образом температура молекулы увеличивается относительно той температуры, которая сформировалась в термическом равновесии в начале процесса абсорбции и эмиссии. На основе этого естественного предположения можно обобщить теорию *Блохинцева*, относящуюся к спектрам абсорбции и эмиссии, из расчета корреляционной флуктуации во время перехода, и вывести для спектра абсорбции и эмиссии аналитическое выражение [1], экспериментально определенное *Домби* и его сотрудниками. На основе выведенных спектров получается закон зеркальной симметрии по *Левшину* и обобщенный лучевой закон по *Степанову*. Наконец, вычисляется удельная теплота колебаний, а также и релаксационное время термического взаимодействия, происходящего между флуоресцентными молекулами и молекулами растворителя, причем получается хорошее соответствие с прежними оценками.

EFFECT OF SOLVENT ON THE ABSORPTION AND FLUORESCENCE SPECTRA OF ALCOHOLIC SOLUTIONS OF TRYPAFLAVINE

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The validity of STEPANOV-relation concerning the connection of absorption and emission spectra has been proved for solutions of trypaflavine in different alcohols of the homologous series.

1. An equation connecting the absorption spectrum $\varepsilon(\nu)$ and the emission energy spectrum $f_e(\nu)$ has been derived by STEPANOV [1]

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

where ν and T denote the frequency and the temperature of the solution, respectively; h and k are PLANCK's and BOLTZMANN's constants, d is a constant independent of frequency. KETSKEMÉTY and co-workers [2] have pointed out, that instead of eq. (1) a modified form of it can be considered more reliable:

$$\frac{f_e(\nu)}{\varepsilon(\nu)} = D\eta^*(\nu)n^2(\nu)\nu^3 \exp(-h\nu/kT), \tag{2}$$

where $\eta^*(\nu)$ and $n(\nu)$ denote the relative yield of fluorescence and the refractive index of the solution, respectively. In case of $\eta^*(\nu) = \text{const}$ and $n(\nu) = \text{const}$ (practically in a smaller spectral region) eq. (2) is identical with eq. (1). Eq. (1) may be rewritten in terms of the wavelength, λ: $F(\lambda) \equiv \log f(\lambda) + 4\log\lambda - \log\varepsilon(\lambda) = -hc/2{,}30\,kT\lambda + \text{const}$; $f(\lambda)$ is the emission quantum spectrum as a function of the wavelength λ. If eq. (1) is valid $F(\lambda)$ is a linear function of λ and the slope of the straight is determined by the temperature T of the solution. The temperature T^* obtained from the slope of the straight was found to be $T^* > T$ is most cases.

STEPANOV [3], ALENTSEV [4], ALENTSEV and PAHOMITCHEVA [5], KRAVTSOV and RUBINOV [6], KETSKEMÉTY and co-workers [2], HEVESI and KOZMA [7], RHAZANOVA and co-workers [8], further BORISSEVICH and GRUZINSKII [9] and GRUZINSKII and BORISSEVICH [10] carried out experiments in order to control the validity of STEPANOV's equation in luminescent solid, liquid and vapour systems. In all the investigated systems eq. (1) — in a given spectral region where $\eta^*(\nu)$ and $n(\nu)$ are approximatly constant — has been found to be valid, and temperatures of $T^* \cong T$ were obtained.

There is no doubt temperatures of $T^* > T$ may be derived from the slope of the STEPANOV's straights in many cases, however, the nature of this higher temperature is not clear enough. Though the excess of the exciting energy — the source of the increase of temperature — could easily be degraded in condensed (solid and liquid) systems on account of the strong interaction of solute and solvent, T^* was found to be higher than T even in many of these systems. In order to clear up the nature of this interaction the effect exerted by the solvent on the same solute ought to be known. The aim of the present paper is to contribute to a better understanding of the phenomena in liquid systems.

In order to explain some phenomena found in the polarization of fluorescence of solutions, JABŁONSKI [11] suggested a mechanism for degradation of the excess of exciting energy. According to this mechanism a part of the excess-energy is converted into the energy of elastic waves by an "initial shock" and the other part is converted into heat ("slow effect") in the neighbourhood of the excited particles

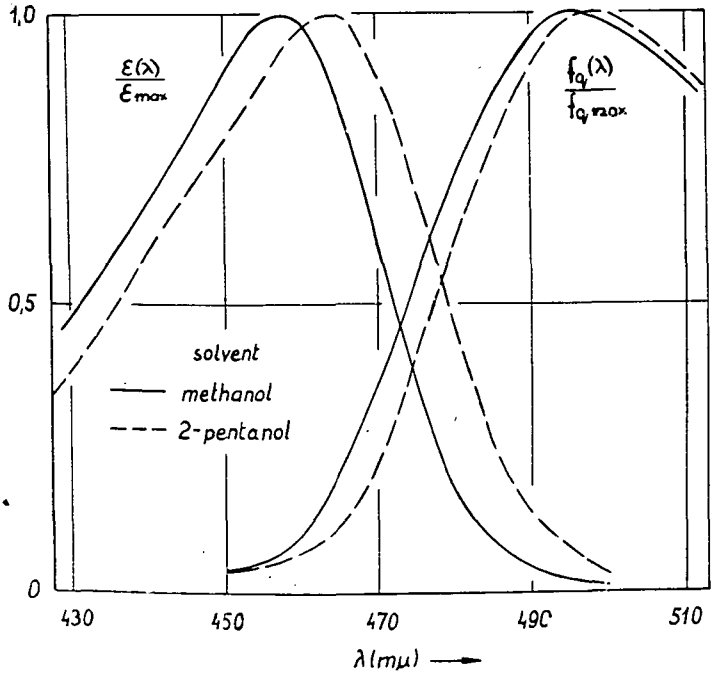

Fig. 1

thus causing a depolarization of fluorescence. JABŁONSKI's investigations seem to furnish further reasons to carry out experiments referring to the problem of T^*.

2. Trypaflavine purified by repeated crystallization was dissolved in different monohydric alcohols (see Table 1) of spectroscopic purity[1] in a concentration of $c_M = 3 \cdot 10^{-4}$ mole/l. The absorption and emission spectra have been determined

[1] Authors are indebted to dr. *J. Hires* for making available some purified solvents.

by means of a spectrophotometer (Optica Milano CF4) at a temperature of $T = 293 \pm 2°$ K. Fig. 1 exhibits two examples of these spectra, the main characteristics of absorption and emission for all solutions investigated are shown in Table I ($k(\lambda)_{max} = 2{,}3026 \cdot c_M \cdot \varepsilon(\lambda)_{max}$).

Table I

1	2	3	4	5	6
Solvent	absorption		emission	T^* obtained from spectra corrected to	
	λ_{max} ($m\mu$)	$k(\lambda)_{max}$	λ_{max} ($m\mu$)	reabsorption	secondary fluor.
methanol	457,6	14,40	496,9	352,3	324,0
ethanol	462,0	19,35	493,8	356,8	326,6
1-propanol	462,8	15,05	495,0	375,0	336,7
2-propanol	463,0	12,99	495,4	380,1	338,1
1-butanol	463,2	14,14	495,4	390,5	345,2
2-pentanol	463,8	13,62	498,6	445,9	373,9

The excitation was carried out at a wavelength of 436 mμ with a high pressure mercury lamp. The directions of excitation and observation were approximately parallel. The layer thickness of solutions was $l = 0{,}1$ cm. The spectral influence of reabsorption (a) of primary fluorescence and the spectral influence of secondary fluorescence (b) on emission spectra were eliminated according to a method given by BUDÓ and KETSKEMÉTY [12]. Both the emission spectra corrected taking into account of effect (a) and those corrected taking the effect (b) into consideration were used for the determination of T^* in all solutions; the results are shown in Table 1. Some examples of the fulfilment of eq. (1) is to be seen in Fig. 2. (The straight lines were constructed by the method of "least squares".)

As for the experimental results, the following remarks should be made. The elimination of influence (b) (of secondary fluorescence) seems to be very important, because the temperatures T^* obtained from the emission spectra corrected taking into account reabsorption (*i. e.* influence (a)) only are much greater than those obtained from spectra corrected taking the effect (b) into consideration (see Table I, columns 5 and 6)[2]. The temperature T^* increases when we go over to a higher alcohol. This phenomenon is similar to that found by HEVESI and KOZMA [7] in case of fluorescein dissolved in glycerol-water mixtures. In both systems T^* increases with the viscosity.

3. A rather rough model — as an alternative of that given in [13] — can be constructed for an illustration of the processes taking place after excitation — provided there exists a microregion of a temperature $T^* > T$. The excess of the

[2] *Ketskeméty* and co-workers give a value of $T^* = 321°$ K for an ethanolic solution of trypaflavine in a good accordance with the present value of 326,6° K obtained from an emission spectrum corrected to secondary fluorescence. According to *Alentsev* and *Pahomitcheva* [4] effect (b) should cause an increase of T^*. As a matter of fact, the spectral influence of secondary fluorescence depends on the conditions of excitation and observation and on the exciting wavelength as well and may change (either increase or decrease) the value T^*.

exciting energy is converted into heat during the process of excitation and is distributed in a sphere of radius r' and it causes a local temperature of $T_0^* > T$. The temperature difference may be estimated as follows:

$$T_0^* - T = \frac{3k'h(\nu_a - \nu_{e\,max})}{4\pi r'^3 \varrho c}, \tag{3}$$

where $k' = 2{,}39 \cdot 10^{-8}$ cal/erg, $h(\nu_a - \nu_{e\,max}) = 5{,}4 \cdot 10^{-13}$ erg (the excess of the exciting energy estimated from the frequencies of excitation and emission maximum),

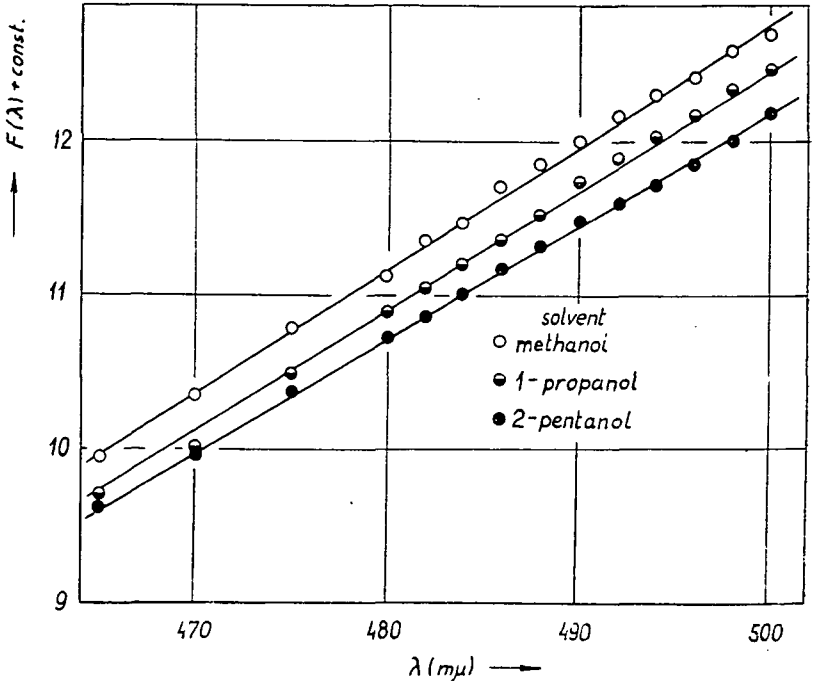

Fig. 2

$\varrho c \approx 0{,}5$ (ϱ and c are the density in g/cm^3 and the specific heat in cal/g grad of the alcohols, respectively. On assuming a value of $r' = 3$ Å, $T_0^* - T \approx 250°$. Making use of the data in Tab. 1 eq. (3) yields a series of values of the order of 5 Å for r (5,8 Å in methanol and 4,3 Å in 2-pentanol). This seems to be a reliable value because the avarage distance of the neigbouring excited solute particles is obviously much greater.

* * *

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ВЛИЯНИЕ РАСТВОРИТЕЛЯ НА СПЕКТРАХ ПОГЛОЩЕНИЯ И ЛЮМИНЕСЦЕНЦИИ СПИРОВЫХ РАСТВОРОВ ТРИПАФЛАВИНА

И. Кечкемети, Л. Салаи, З. Варкони

В случае разных спритовых растворов трипафлавина исследовалось выполнение соотношение Степанова, описывающие связь между спектрами поглощения и люминесценции.

SELF-DEPOLARIZATION AND SELF-QUENCHING IN FLUORESCENT SOLUTIONS

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The validity of JABŁOŃSKI's theory of self-depolarization has been studied for solutions of fluorescein in water-glycerol mixtures of different viscosity. A phenomenon of rotational repolarization has been found and explained in solutions of extreme high concentration.

1. Self-depolarization has already been treated theoretically by many authors [1]. A simple sphere-model was given by JABŁOŃSKI [2]: the primarily excited luminescent particle A^* is surrounded by an "active sphere". If an unexcited particle of the same kind A exists within the sphere, the probability of radiative deactivation of A^* is equal to the probability of radiationless transfer of exciting energy to A, independently on the distance between A^* and A. In terms of emission anisotropy [5] the calculations led to the result

$$\frac{r_0}{r} = \frac{\sum_{k=1}^{\infty} \frac{v^{k-1}}{k!} \frac{k}{\gamma + W_k + W_f}}{\sum_{k=1}^{\infty} \frac{v^{k-1}}{k!} \left(\frac{1}{\gamma + W_k + W_f} + \frac{k-1}{\gamma + W_k + W_f + k\mu} \right)}, \tag{1}$$

where the notations are as follows: r — emission anisotropy of fluorescence; γ, W_k, W_f and μ — the probability of emission, self-quenching, inner quenching + foreign quenching and radiationless transition, respectively; v — the number of luminescent particles in the active sphere of a volume v ($v = 6{,}02 \cdot 10^{20} v c_M$; c_M is the concentration of the solution in mole/l); r_0 — the limiting value of emission anisotropy ($r \to r_0$, if $c_M \to 0$).

For $W_k = W_f = 0$ (*i. e.*, no self-quenching and foreign quenching exist) and $\gamma = \mu$, the relation

$$\frac{r_0}{r} = \frac{v^2}{2(v - 1 + e^{-v})} \tag{2}$$

is obtained and found to be valid in the range of small concentrations, where the assumption $W_k = 0$ is reliable. Under special assumptions a formula for higher

concentrations has been derived from eq. (1) by BOJARSKI [3].

$$\frac{r_0}{r} = \frac{v^2 \frac{s}{s+1} g_s(v)}{\left[v - 1 + e^{-v} - \frac{v^2}{s+1} g_s(v)\right]} \tag{3}$$

where $s \equiv \mu/W_1 \gg 1$, *i. e.*, the probability of inner quenching (W_1) is much smaller, than that of radiationless energy transfer (μ), and $g_s(v) \equiv {}_1F_1(1, s+2, -v)$, a given value of the confluent hypergeometric series [20]. Though for small v and large s $g_s(v)$ is rapidly convergent, in cases of the most important highest concentrations the convergency is very slow.

A refinement of the sphere-model (introducing shells of the same volume and a dependence of the radiationless transfer of energy on the distance of the particles) given by BOJARSKI [4] yields a more complex expression even for the case of $W_k = 0$:

$$\frac{r_0}{r} = \frac{1 + \sum_{k=1}^{z} \frac{k_l}{l^2}}{2e^{-vz} \sum_{l_1 \ldots l_z} \frac{v^{k_1 - 1}}{(k_1 - 1)!} \prod_{l=z}^{z} \frac{v^{k_l}}{k_l!}}, \tag{4}$$

where z denotes the number of shells considered. Though the cases when $z \geqq 4$ may be practically neglected, the calculations with eq. (4) are tedious and the results are not in good agreement with the experiments for higher concentrations.

2. An approximation for high concentrations may be given as follows. Let eq. (1) be rewritten with the notations $W \equiv \gamma + W_k + W_f$ and $M \equiv \mu/W$:

$$\frac{r}{r_0} = \frac{\sum_{k=1}^{\infty} \frac{v^{k-1}}{k!} k \frac{M+1}{kM+1}}{\sum_{k=1}^{\infty} \frac{v^{k-1}}{k!} k}. \tag{5}$$

Since $\sum_{k=1}^{\infty} \frac{v^{k-1}}{k!} k = e^{-v}$,

$$\frac{r}{r_0} = (M+1)e^{-v} \sum_{k=1}^{\infty} \frac{v^{k-1}}{(k-1)!} \frac{1}{kM+1}. \tag{6}$$

Supposing there is no foreign quenching ($W_f = 0$) $M = \mu/(\gamma + W_k)$. For $\mu = \gamma$ (as before in eq. (2)) and using the relations $\mu = 1/\tau_0$ and $\gamma + W_k = 1/\tau$ (where τ_0 and τ denote the fluorescence in unquenched and quenched solutions) $M = \tau/\tau_0$. Substituting this value of M into eq. (6), the relation

$$\frac{r}{r_0} = \left(\frac{\tau}{\tau_0} + 1\right) e^{-v} \sum_{k=1}^{\infty} \frac{v^{k-1}}{(k-1)!} \frac{1}{k \frac{\tau}{\tau_0} + 1} \tag{7}$$

holds.

A simple lower limit may be given for r/r_0. Apparently

$$\frac{r}{r_0} = e^{-\nu} \sum_{k=1}^{\infty} \frac{\nu^{k-1}}{(k-1)!} \frac{1}{1+(k-1)\frac{M}{M+1}} > e^{-\nu} \sum_{k=1}^{\infty} \frac{\nu^{k-1}}{(k-1)!} \frac{1}{\left(1+\frac{M}{M+1}\right)^{k-1}} =$$

$$= e^{-\nu} \sum_{k=1}^{\infty} \frac{\left[\frac{\nu}{1+\frac{M}{(M+1)}}\right]^{k-1}}{(k-1)!} = e^{-\nu} \cdot e^{\frac{\nu}{1+M/(M+1)}} = e^{-M\nu/(1+2M)},$$

i. e.

$$\frac{r}{r_0} > e^{-\frac{\tau/\tau_0}{1+2\tau/\tau_0}\nu}. \tag{8}$$

Instead of inequality (8) — as it will be seen — eq. (7) may be more satisfactorily approximated by the equation

$$\frac{r}{r_0} = \frac{\tau/\tau_0+1}{(\tau/\tau_0)^2} \frac{\nu\tau/\tau_0-1+e^{-\nu}}{\nu^2} \tag{9}$$

or, if $\tau/\tau_0 = \eta/\eta_0$ (the relative quantum yield)

$$\frac{r}{r_0} = \frac{\eta/\eta_0+1}{(\eta/\eta_0)^2} \frac{\nu\eta/\eta_0-1+e^{-\nu}}{\nu^2}. \tag{10}$$

For unquenched solutions ($\tau/\tau_0 = \eta/\eta_0 = 1$) eqs. (9) and (10) become identical with eq. (2).

3. Fluorescein solutions containing glycerol and water in different proportions and 2 per cent NaOH were studied. The concentration of dye was varied between $1{,}0\cdot10^{-5} - 5{,}0\cdot10^{-2}$ mole/l. The photoelectric apparatus used for measuring the degree of polarization is described in [6]. The wavelength of the exciting light was 510 mμ, the temperature of the samples was maintained at a value of $30{,}0 \pm 0{,}1$ centigrade by means of a Höppler ultrathermostat. The viscosity was measured at the same temperature by a Höppler viscosimeter. The degree of polarization of fluorescence obtained experimentally was corrected for secondary fluorescence according to an equation and method given in [7]. For this correction the absorption and emission spectra were measured by a photoelectric spectrophotometer Optica Milano CF-4. The absolute quantum yield of fluorescence was determined by a method given in [8].

Fig. 1 exhibits the depolarization curves for solutions of different viscosities. As it is to be seen a considerable repolarization occurs in the concentration range of $1{,}0\cdot10^{-2} - 5\cdot10^{-2}$ mole/l. The repolarization increases with decreasing viscosity. An opposite behaviour would be expected because of the enhanced rotational possibility of particles in solutions of small viscosity. If, however, the self-quenching curves shown in Fig. 2 for glycerol and (after [8]) for water solvent are considered, it may be concluded that in water a shorter mean life time of the excited state should prevail than in glycerol, consequently — in spite of the high rotational

mobility of fluorescent particles — is solutions of small viscosity a higher repolarization may appear than in solutions of higher viscosity.

As for the quantitative agreement of eq. (10) and the experiment Fig. 3 shows the self-depolarization curve for the whole range of concentration and in the case of the solution of highest viscosity. The empirical parameter v, the volume of the active sphere, was determined by fitting the experimental values of r to eq. (10) in the range of small concentrations. The radius of the active sphere was found to

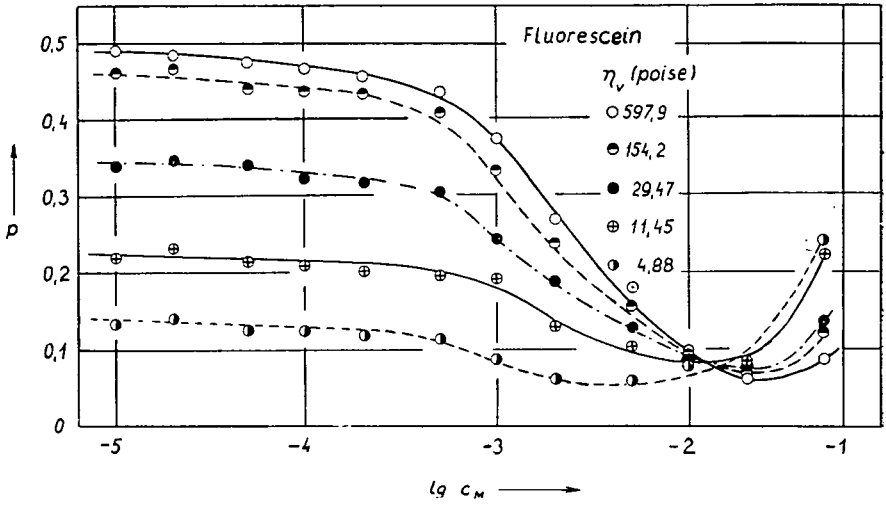

Fig. 1

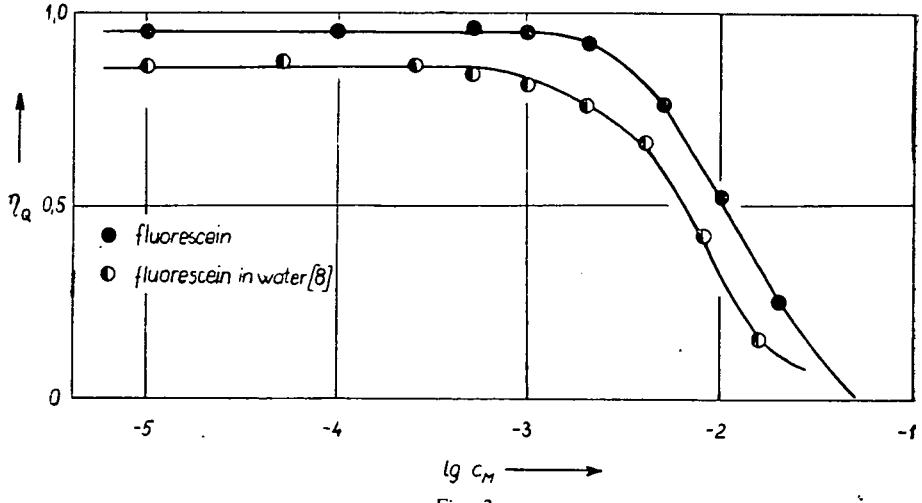

Fig. 2

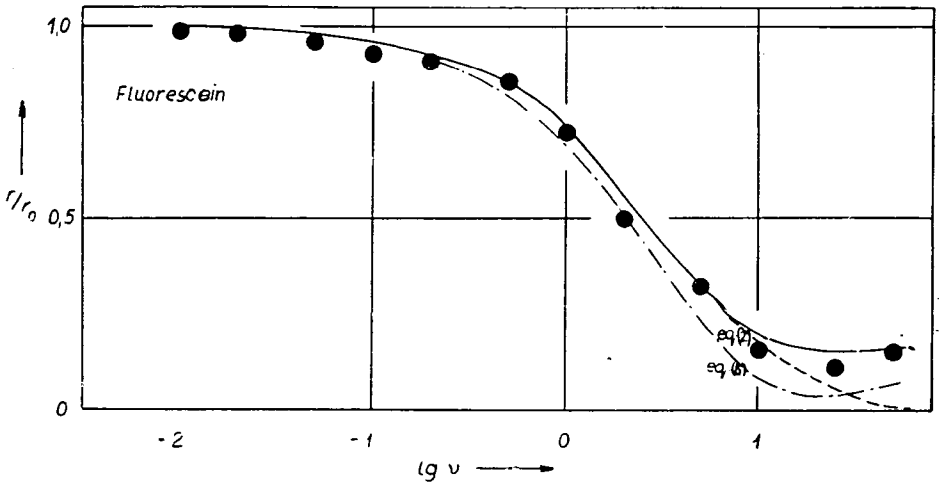
1,0
Fluorescein
r/r0
0,5
0
-2
-1
0
1
lg ν
eq (2)
eq (6)

Fig. 3

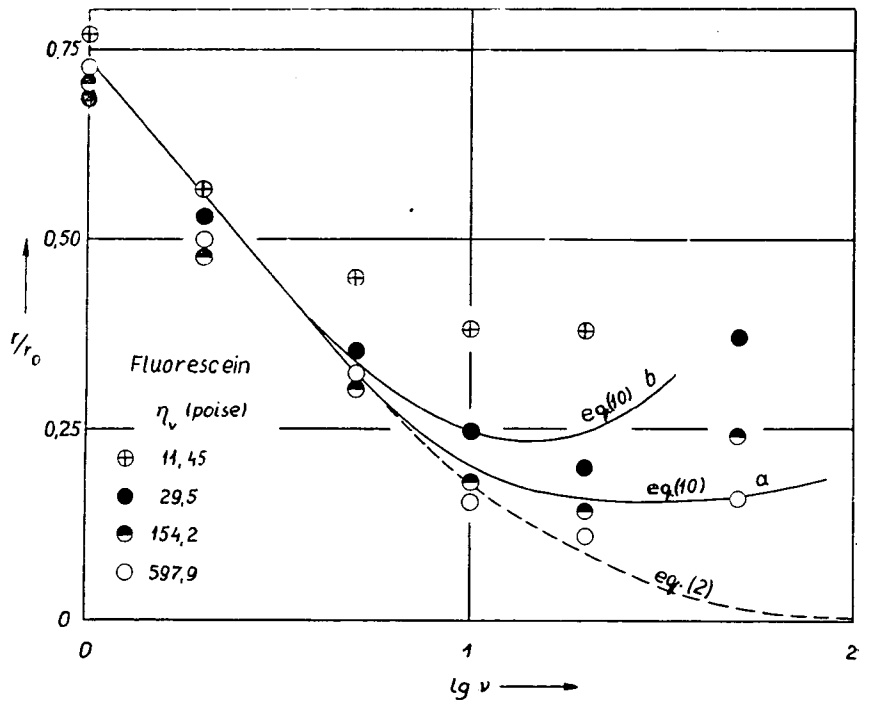
0,75
0,50
r/r0
0,25
0
Fluorescein
ην (poise)
11,45
29,5
154,2
597,9
eq (10) b
eq (10) a
eq. (2)
0
1
2
lg ν

Fig. 4

be $R_J = 72{,}0$ Å (a value near to 70,8 Å given in [9] and 79 Å given in [10] for the same system). The broken line, dotted line and the solid line were calculated by eq. (2), (8) and (10), respectively. The best agreement of experiment and theory is given by eq. (10). Fig. 4. represents the theoretical curves of self-depolarization calculated by eq. (2) (broken line) and by eq. (10) (solid lines) for the concentration range of $1{,}0 \cdot 10^{-3} - 5 \cdot 10^{-2}$ mole/l. The relative yield values were taken from the data in Fig. 2. The upper and lower depolarization curves (solid lines) in Fig. 4. belong to water and glycerol solutions, respectively. The experimental points lie near to these curves which can account — at least partly — for the repolarization as well.

In case of trypaflavine dissolved in a mixture of glycerol-ethanol and containing 2 per cent acetic acid the data for self-depolarization and self-quenching have already been published [11]. Fig. 5 shows how eqs. (2), (8) and (10) are fulfilled for this system. The radius of active sphere was found to be $R_J = 42{,}8$ Å (in [10] $R_J = 40$ Å), with this parameter and with $\eta/\eta_0 = 0{,}90$, 0,25 and 0,16 for the three highest concentrations we obtain the broken, dotted and solid line by eqs. (2), (8) and (10), respectively. According to [11] these quantum yields are too high, probably, eq. (7) should give a better agreement, because usually $\tau/\tau_0 < \eta/\eta_0$ for higher concentrations. Because of lack of experimental τ/τ_0-values it was not possible to check eq. (7).

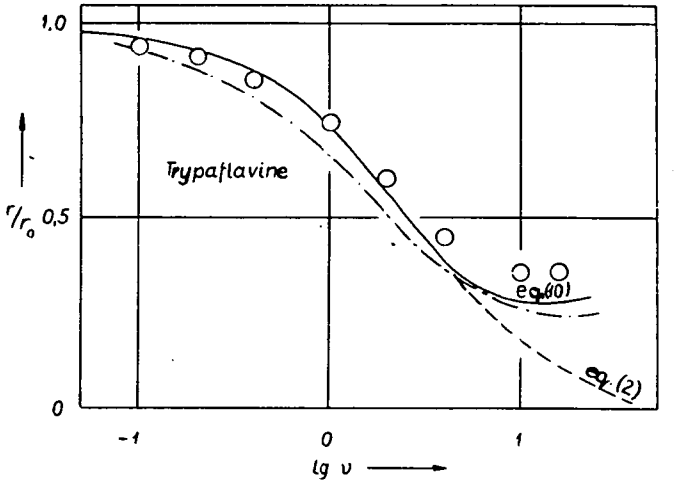

Fig. 5

The recent measurements referring to the fluorescein solutions of different η_v viscosities corroborate the statements given in [14] about the independence of the processes determining the rotational depolarization and the self-depolarization. As Fig. 6 shows the self-depolarization curves belonging to different concentrations get nearer to each other, if the viscosity is decreased, since in the competition of the two processes of depolarization the role of rotational depolarization becomes prevailing. However, in solutions of very high concentration this regularity is no

longer to be found. The increase of degree of polarization of fluorescence with the decrease of the viscosity of solution (shown by broken line for a concentration of $5 \cdot 10^{-2}$ mole/l in Fig. 6) — some kind of rotational repolarization — is not in contradiction with the well-known PERRIN—LEVSHIN equation (see *e. g.* in [15]). Namely, according to this equation the increase of the degree of polarization of fluorescence — *ceteris paribus* — is expected, when τ/η_v is decreased and this quantity may decrease — due to the dependence of self-quenching on the viscosity shown in Fig. 2 — even if η_v decreases.

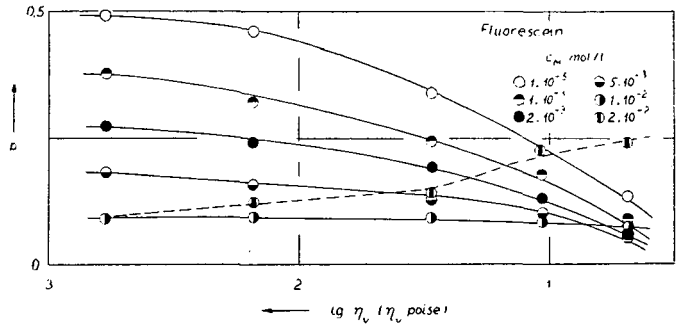

Fig. 6

The independence of the two mentioned depolarization processes led to the reasoning that PERRIN—LEVSHIN equation must no be applied to self-depolarization [14]. In [16], however, a formula was derived from this equation for the self-depolarization. This formula implies a mean life time of the excited state obtained by a relation for self-quenching and yield an increase of the degree of polarization of fluorescence with the increase of concentration in the range of low concentrations, a result inconsistent with the experimental results obtained hitherto. (The alone case mentioned in [17], except that in [16], could not be corroborated in [18].) Consequently, our results referring to the independence of rotational depolarization and self-depolarization show that the formula given in [16] may not be considered as reliable in principle. The experimentally obtained rise of the degree of polarization of fluorescence at small concentrations should be carefully controlled for the systems mentioned in [16].

* * *

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КОНЦЕНТРАЦИОННАЯ ДЕПОЛЯРИЗАЦИЯ И КОНЦЕНТРАЦИОННОЕ ТУШЕНИЕ ФЛУОРЕСЦЕНЦИРУЮЩИХ РАСТВОРОВ

Л. Салаи, Б. Шаркань, Э. Томбац

Исследовалось выполнение концентрационной деполяризованной теории Яблонского на разных вязких глицеринно- водных растворах флуоресцениа. В случае больших концентрационных растворов обнаруживается явление вращательной реполяризации.

К ВОПРОСУ СООТНОШЕНИЯ МЕЖДУ СПЕКТРАМИ ПОГЛОЩЕНИЯ И ЛЮМИНЕСЦЕНЦИИ УРАНИЛОВЫХ СОЕДИНЕНИЙ

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Результаты настоящей работы показывают, что соотношение, описывающее связь между спектрами поглощения и люминесценции, выполняется и в случае жидких и твердых растворов ураниловых соединений. В исследованных случаях температура опыта и вычисленная температура из соотношения (1) совпадают.

Соотношение

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

выведенное *Кечкемети* и его сотрудниками [1], которое описывает связь между спектрами поглощения $[k(\nu)]$ и люминесценции $[f_e(\nu)]$ при температуре T, или прежднее соотношение *Степанова* [2], из которого модифицировано получили (1), многие авторы проверяли и подтверждали на основе экспериментальных данных в случае растворов и паров [3—9]. Здесь h и k постоянные *Планка* и *Больцмана*, D — постоянный, практически независящий от частоты, $\eta(\nu)$ — квантовый выход, зависящий от частоты возбуждающего света. Исследования показывают, что температура T^*, вычисленная из наклона прямых

$$F(\nu) = \ln f_e(\nu) - \ln k(\nu) - \ln\eta(\nu) - 3\ln\nu = \frac{h}{kT}\nu + c \tag{2}$$

в большинстве случаев больше чем T. Разницу $\Delta T = T^* - T$ связали с частотой возбуждающего света [1, 3, 7], тушением люминесценции [8], строением люминесценцирующего центра и ходом функции $\eta(\nu)$ [6, 9].

Так как до сих пор в первую очередь исследовали жидкие и газовые системы, состоящие из сложных органических люминесценцирующих молекул, мы считали целесообразным исследовать и системы, которые состоят из простых неорганических люминесценцирующих молекул. Можно ожидать, что и в случае больших времен жизни применимо соотношение (1), даже и в том случае когда вязкость среды много раз больше, чем в раннее исследованных случаях. В настоящих исследованиях предметами служили урановое стекло и водные растворы уранилсульфата. Сравнивая с веществами,

исследованными раньше с точки зрения выполнения соотношения (1), время затухания флуоресценции иона $UO_2^{++}(\tau \approx 10^{-4} s^{-1})$ больше на нескольких порядков.

При температурах 263, 298, 318, 338, 363 °К спектр поглощения измерили на спектрофорометре СФ—4 Оптика Милано (решеткой), спектр люминесценции с методом разработанным в [10], и $\eta(\nu)$ описанным методом

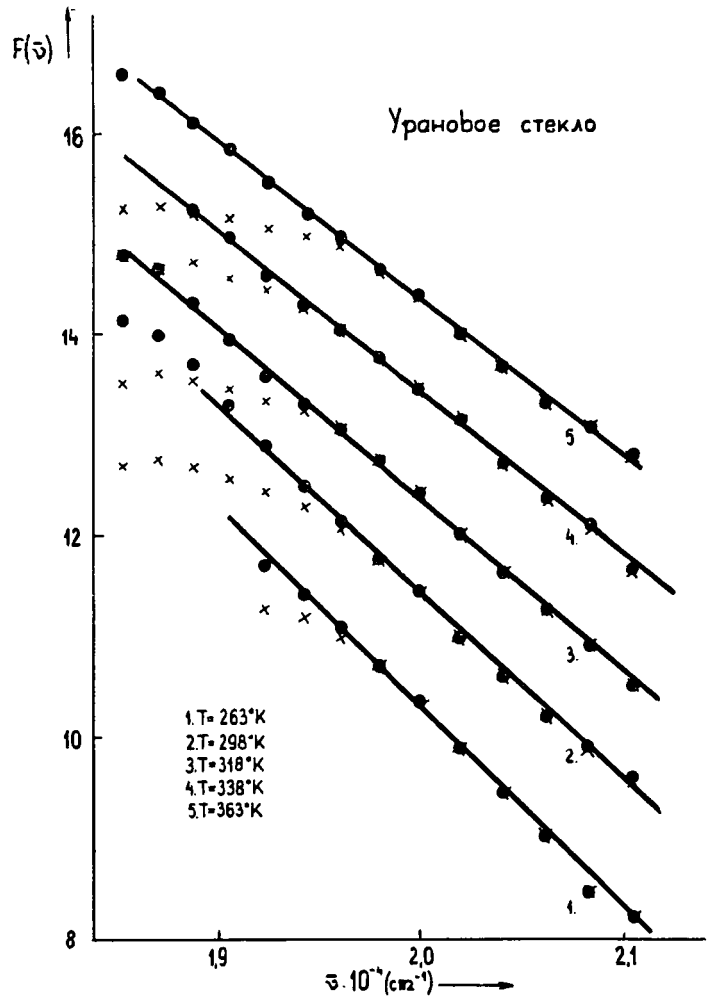

Рис. 1

в [11]. (У раствора уранилсульфата длинновольновую часть функции $\eta(\nu)$ не измерили из-за трудностей, выступающих вследствие малого выхода и сильного температурного тушения.) Спектры поглощения и люминесценции мало пересекаются, но все-таки мы должны были считать влияние втарич-

ной люминесценции, разроботанным методом в [12] на основе соотношения (37), так как из-за малой интенсивности люминесценции, толстые слои исследовали. Ход спектров поглощения и излучения, полученных нами, и их изменение с температурой совпадают с результатами, полученными в [13, 14].

На рисунке 1 черными кружками изображали значения $F(\nu)$ уранилого стекла, вычисленные из формулы (2), а крестики представляют те значения, которые получили из соотношения *Степанова*. Рисунка 2 представляет значения $F(\nu)$ раствора уранилсульфата, полученные из формулы *Степанова*,

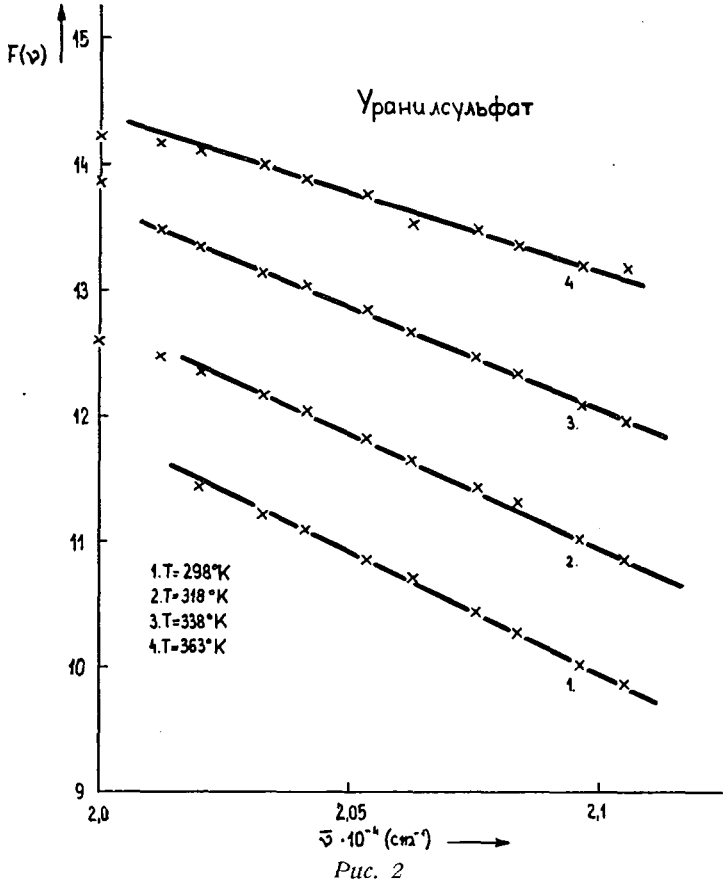

Рис. 2

которая не содержит функцию $\eta(\nu)$. Из рис. 1 видно, что соотношение (1) выполняется в широкой частотной области, содержащей частоту электронного перехода, для спектров поглощения и излучения уранилого стекла, в то же время соотношение *Степанова* применяется только в более узкой полосе.

Из наклона прямых рисунков 1 и 2 вычислили значения температуры T^*, и представили их в таблице 1, где в первом ряде приведенны температуры опыта, во втором и третьем рядах вычисленные знчения T^*. Из данной таблицы видно, что так у мало вязкого водного раствора уранилсульфата, как и у большого вязкого уранилового стекла, при каждой нами исследованной температуре $T^* \approx T$. Это означает, что до акта испускания избыток возбуждающей энергии $h(\nu_B - \bar{\nu}) \approx 5{,}8 \cdot 10^{-13}$ эрг ($\nu_B = 6{,}88 \cdot 10^{14}\, s^{-1}$ частота возбуждающего света, $\bar{\nu}$ — средняя частота первой полосы люминесценции) полностью передается среде, в независимости от вязкости среды, и от колебательной энергии молекул.

Таблица 1.

Вещество \ T (°K)	263	298	318	338	363
Ураниловое стекло	275	302	321	347	366
Уранилсульфат	—	305	322	349	365

Наши результаты показывает, что соотношение (1) выполняется и в случае жидких и твердых растворов ураниловых соединений, состоящие из малочисленных атомов, которые характеризуются структурными спектрами. Связь между расчитанными температурами T^* и характеристиками люминесценцирующих систем (время возбужденного состояния, вязкость и температура среды и т. д.) полученные в случае ураниловых соединений, подтверждают более ранные опыты, которые относятся к сложным молекулам.

* * *

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NOTE ON THE CONNECTION BETWEEN THE ABSORPTION AND LUMINESCENCE SPECTRA OF URANIUM COMPOUNDS

By L. Kozma

A formula concerning the absorption and luminescence spectra was found to be valid for liquid and rigid solutions of uran compounds. The temperature of measurement and that of calculated from the formula exhibited a good agreement.

ИЗУЧЕНИЕ ХИМИЧЕСКИХ ПРЕВРАЩЕНИЙ ДИОЛОВ ИОРГАНИЧЕСКИХ ОКИСЕЙ. IX

Реакция двупервичных 1,3-диолов с ацетилхлоридом

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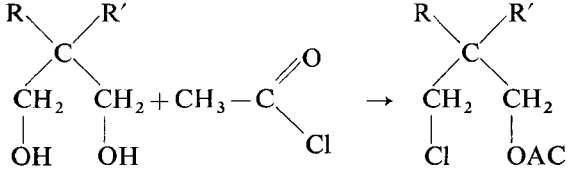
В настоящей работе изучаются реакции пропандиола-1,3, 2-метил-, 2-этил-, 2-н. пропил-, 2-и. пропил-, 2-н. бутил-, 2-т. бутил-, 2-ц. гексил-, 2-фенил-, 2-бензил-, 2,2-диметил-, 2,2-диэтил-, 2-метил-2-н. пропил- и 2-этил-2-н. бутилпропандиола-1,3 под воздействием ацетилхлорида. Превращения приводят к соответствующим 1,3-хлороацетатам с выходом 60—80%. Имея в виду простоту метода и хороший выход, эти реакции могут быть употреблены для выгодного производства производных 2-моно- и 2,2-двузамещенных пропана. В результате работы над синтезом описывается простой метод производства а также структура и физические константы двенадцати до сих пор в литературе неописанных соединений.

Изучая химические реакции диолов мы изучаем их превращения с ацилгалоидами, в результате которого и ацильная группа и анион галоида вступают в молекуль диола. В ведении одной из наших предыдущих работ мы обсудили обзор, значение для препаративной и теоретической органической химии реакций диолов под действием ацетилхлорида [1]. В литературе мало работ найдено о таком типе превращений диолов.

Настоящая работа занимается результатами препаративного осуществления превращения следующего типа:



где R R′: CH_3 H, C_2H_5 H, н. C_3H_7 H, и. C_3H_7 H, н. C_4H_9 H, т. C_4H_9 H, C_6H_{11} H, C_6H_5 H, C_7H_7 H, CH_3 CH_3 C_2H_5 C_2H_5, CH_3 н. C_3H_7, C_2H_5 н. C_4H_9.

Выводы предыдущей работы [1] стоят и для механизма этих превращений. Экспериментальное оправдывание этих ожидается путем изучения соединений асиметрической структуры.

2-монозамещенные производные пропандиола-1,3 были приготовлены исходя из диэтилового эфира малоновой кислоты. Под действием алкилгалоидов из диэтилового эфира малоновой кислоты алкилзамещенные малоновые эфиры были получены с хорошим выходом (~80%). Диэтиловый эфир фенилмалоновой кислоты был получен из этилового эфира фенилуксусной кислоты путем конденсации диэтиловым эфиром щавелевой кислоты, методом уже ранее описанным [2]. Реакцией малоновых эфиров гидридом лития алюминия соответствующие диолы [3] были приготовлены. Гидрирование может быть осуществлено соответственно *Адкинс* и *Билика* [4] просто и хорошим выходом (80%) в автоклаве гидрированием на меднохромовом катализаторе.

Реакция моно- и двузамещенных производных пропандиола-1,3 под действием хлористого ацетила была изучена методом описанным *Богерт* и *Слокум* [5] в запаянной трубке. Реакция может быть осуществлена и без давления [6]. При диолов с меньшим молекулярным весом влияние давления на направления реакции и на выход совсем незначительно. А в случае диолов с большим молекулярным весом давление увеличивает выход хлороацетата. Давление ускоряет реакцию OH → Cl таким образом что увеличивается концентрация HCl. Скорость реакции уменьшается с повышениен молекулярного веса. Сама собой разумеется, применение давления не вредно и у диолов с меньшим молекулярным весом, но в этом случае выход хлороацетата может быть около 80 процентов и без давления. Настоящая работа не пытает установить оптимальные параметры реакции оформления хлороацетата. В этом смысле данные о выходе в Таблице V не окончательные так как только одно исследование было осуществлено с одним диолом в приблизительно аналогичных условиях.

Таким рядом экспериментов мы хотели доказать что у двупервичных 1,3-диолов реакция хлороацетилирования имеет место и в то же время простой и дешевый синтез нескольких исходных веществ, применяемых в медицинской индустрии осуществлен (выход 60—80%). В будущее мы намерены изучать химические превращения хлороацетатов.

Полученные продукты были проанализированы методом газожидкостной хроматографии. Из этих результатов и из микроанализа видно что при реакциях диолмоноацетат получается. Появление последнего находится в соответсвии с нашим представлением о механизме процесса хлороацетилирования [1].

В данной работе даются в таблицах литературные данные о приготовлении и физических константах соответствующих малоновых эфиров, 1,3-диолов, 1-хлор-2,2-диметил-3-ацетоксипропана (Таблица I) и также приведены экспериментальные данные настоящей работы (Таблицы II, III и IV).

Экспериментальная часть

Алкильные- и арильные малоновые эфиры приготовлялись по методам описанным в литературе из диэтилового эфира малоновой кислоты. Диметилсульфат [29], бромистый и. пропил [30], бромистый этил [30], хлористый н. пропил [30], бромистый н. бутил [30], хлористый т. бутил, [15], бромистый

Таблица I

Данные в литературе о приготовлении и физических константах эфиров малоновой кислоты, 1,3-диолов и 1,3-хлористых ацетатов описанных в экспериментальной части

№	Название	Выход %	Температура кипения С° (рт. мм.)	d г/см³	n_D (t °C)	Литература
1.	диэтиловый эфир метилмалоновой кислоты		74 (3) 196 (773)	$1{,}0131_{25}^{25}$ $1{,}0225_4^{20}$	1,4126 (20)	7 8
2.	диэтиловый эфир этилмалоновой кислоты	62	98 (12) 109 (24)	$1{,}005\ _4^{20}$ $1{,}0047_4^{20}$	1,4171 (20) 1,4166 (20)	9 8
3.	диэтиловый эфир н. пропилмалоновой кислоты		222 (760) 221,5 (767)	$0{,}9914^{20}$ $0{,}9873_4^{20}$	1,4197 (20)	10 8
4.	диэтиловый эфир и. пропилмалоновой кислоты	29	103—7 (15) 110—12 (20)	$0{,}9850_{25}^{25}$	1,4190 (25)	11,7 12
5.	диэтиловый эфир н. бутилмалоновой кислоты	91	132 (17) 127 (23)	$0{,}9764_4^{20}$	1,4218 (25) 1,4229 (20)	13 14
6.	диэтиловый эфир т. бутилмалоновой кислоты		110 (17)	$0{,}9828_4^{28{,}5}$	1,4200 (28,5)	15
7.	диэтиловый эфир ц. гексилмалоновой кислоты	44	122—3 (4) 95—8 (1)	$1{,}0228_4^{25}$	1,4478 (25) 1,4550 (25)	16 4
8.	диэтиловый эфир фенилмалоновой кислоты	85	155—160 (18) 142 (22)	$1{,}0950_4^{20}$ $1{,}0959_4^{20}$	1,4977 (20) 1,4913 (20)	2,17 14
9.	диэтиловый эфир бензилмалоновой кислоты		163 (14) 176 (21)	$1{,}0750_4^{20}$ $1{,}0749_4^{20}$	1,4872 (20) 1,4871 (20)	18 14
10.	2-метилпропан-диол-1,3	~80	83,5—4 (3) 123,5 (20)		1,4430 (25)	4 19
11.	2-этилпропан-диол-1,3	71 ~80	124—7 (16) 83—6 (1—2)	$0{,}9970^{20}$	1,4480 (20)	3 4

Таблица I

№	Название	Выход %	Температура кипения °С (рт. мм.)	d г/см³	n_D (t °С)	Литература
12.	2-пропилпропандиол-1,3	~80	96—8 (3)	$0{,}9636^{25}$	1,4480 (25)	4
13.	2-и. пропилпропандиол-1,3	65—70	130—5 (18)			20
14.	2-н. бутилпропандиол-1,3	~80	98—100 (2)	$0{,}9461^{25}$	1,4492 (25)	4
15.	2-т. бутилпропандиол-1,3		т. п. 59—61			21
16.	2-ц. гексилпропандиол-1,3					
17.	2-фенилпропандиол-1,3	50—56	130—2 (5) 136—7 (2) т. п. 48,5—49	$1{,}1161_4^{20}$	1,5863 (20) 1,5348 (25)	22 4,23
18.	2-бензилпропандиол-1,3	~80	155—6 (3) т. п. 68			4 24
19.	2,2-диметилпропандиол-1,3		т. п. 126—8 206 (760) т. п. 106			19,25 26
20.	2,2-диэтилпропандиол-1,3		110—3 (5) 240 (760) т. п. 60,5			27 26
21.	2-метил-2-пропилпропандиол-1,3		т. п. 62—3 234 (760) т. п. 56,6			27 26
22.	2-этил-2-бутилпропандиол-1,3		110 (2) 262 (760) т. п. 43,8		1,4587 (25)	4 26
23.	1-хлоро-2,2-диметил-3-ацетоксипропан	83	68 (10)		1,4325 (20)	28

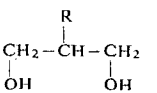
Таблица II

Физические константы R-замещенных диэтиловых эфиров малоновой кислоты

№	R	Выход %	Формула	Молекулярный вес	Т. кип. °С (рт. мм.)	d_4^{20} г/см³	n_D^{20}	MR		C%		H%	
								найд.	выч.	найд.	выч.	найд.	выч.
1.	метил	75	$C_8H_{14}O_4$	174,19	76—7 (4)	1,023	1,4126	42,42	42,45	55,28	55,16	7,98	8,10
2.	этил	76	$C_9H_{16}O_4$	188,22	88—90 (10)	1,005	1,4172	47,12	47,07	57,56	57,43	8,51	8,57
3.	пропил	82	$C_{10}H_{18}O_4$	202,24	114—16 (25)	0,989	1,4195	51,69	51,74	59,22	59,38	9,03	8,97
4.	и. пропил	83	$C_{10}H_{18}O_4$	202,24	86—88 (4)	0,988	1,4196	51,80	51,74	59,26	59,38	9,02	8,97
5.	бутил	80	$C_{11}H_{20}O_4$	216,27	110—12 (4)	0,976	1,4230	56,43	56,35	61,25	61,08	9,36	9,32
6.	т. бутил	12	$C_{11}H_{20}O_4$	216,27	88—90 (8)	0,978	1,4232	56,32	56,35	60,86	61,08	9,24	9,32
7.	ц. гексил	52	$C_{13}H_{22}O_4$	242,31	122—4 (4)	1,026	1,4497	63,44	63,38	64,45	64,44	9,28	9,15
8.	фенил	74	$C_{13}H_{16}O_4$	236,26	134—6 (4)	1,096	1,4936	62,77	62,64	66,23	66,09	6,95	6,83
9.	бензил	70	$C_{14}H_{18}O_4$	250,28	140—2 (10)	1,075	1,4872	66,98	67,28	67,32	67,18	7,23	7,25

Таблица III

Физические константы 2-монозамещённых пропандиолов-1,3



№	R	Выход %	Формула	Молекулярный вес	Т. кип. °С (рт. мм.)	d_4^{20} г/см³	n_D^{20}	MR		C%		H%	
								найд.	выч.	найд.	выч.	найд.	выч.
1.	метил	73	$C_4H_{10}O_2$	90,12	86—7 (4)	1,009	1,4450	23,76	23,72	53,18	53,30	11,22	11,18
2.	этил	68	$C_5H_{12}O_2$	104,15	85—6 (2)	0,982	1,4482	28,41	28,34	57,54	57,66	11,68	11,62
3.	пропил	82	$C_6H_{14}O_2$	118,17	100—2 (4)	0,960	1,4494	33,02	32,96	61,04	60,98	12,05	11,94
4.	и. пропил	75	$C_6H_{14}O_2$	118,17	114—16 (6)	0,961	1,4495	33,00	32,96	61,06	60,98	12,08	11,94
5.	бутил	72	$C_7H_{16}O_2$	132,20	148—50 (8)	0,950	1,4514	37,51	37,58	63,46	63,60	12,35	12,20
6.	т. бутил	76	$C_7H_{16}O_2$	132,20	т. пл. 61	—	—	—	37,58	63,59	63,60	12,24	12,20
7.	ц. гексил	81	$C_9H_{18}O_2$	158,23	т. пл. 94	—	—	—	44,61	68,35	68,31	11,38	11,47
8.	фенил	56	$C_9H_{12}O_2$	152,19	138—40 (1) т. пл. 49	1,132	1,56	43,46	43,21	71,08	71,03	7,81	7,95
9.	бензил	64	$C_{10}H_{14}O_2$	166,21	т. пл. 68	—	—	—	47,83	72,35	72,26	8,33	8,49

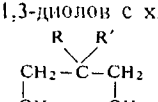
Таблица IV

Физические константы 1-хлор-2,2-R,R′-3-ацетоксипропанов

№	R	R′	Формула	Молекулярный вес	Т. кип. °C (рт. мм.)	d_4^{20} г/см³	n_D^{20}	MR		C%		H%		Cl%	
								найд.	выч.	найд.	выч.	найд.	выч.	найд.	выч.
1.	H	H	$C_5H_9ClO_2$	136,72	68—70 (20)	1,112	1,4327	31,90	31,81	44,02	43,97	6,61	6,64	25,84	25,96
2.	метил	H	$C_6H_{11}ClO_2$	150,76	85—86 (22)	1,080	1,4329	36,28	36,43	47,92	47,85	7,32	7,36	23,41	23,54
3.	этил	H	$C_7H_{13}ClO_2$	164,63	80—82 (6)	1,048	1,4338	40,91	41,05	51,24	51,07	8,02	8,02	21,42	21,53
4.	пропил	H	$C_8H_{15}ClO_2$	178,66	87—88 (6)	1,038	1,4420	45,53	45,66	53,88	53,79	8,41	8,46	19,74	19,85
5.	и. пропил	H	$C_8H_{15}ClO_2$	178,66	110—2 (22)	1,033	1,4400	45,59	45,66	53,85	53,79	8,33	8,46	19,62	19,85
6.	бутил	H	$C_9H_{17}ClO_2$	142,68	120—2 (22)	1,014	1,4406	50,14	50,28	56,28	56,10	8,93	8,89	18,15	18,40
7.	т. бутил	H	$C_9H_{17}ClO_2$	192,68	116—7 (22)	1,016	1,4422	50,21	50,28	56,02	56,10	8,75	8,89	18,28	18,40
8.	ц. гексил	H	$C_{11}H_{19}ClO_2$	218,72	124—5 (3)	1,074	1,4744	57,26	57,32	60,64	60,41	8,83	8,75	16,41	16,18
9.	фенил	H	$C_{11}H_{13}ClO_2$	212,54	156—8 (18)	1,153	1,5180	55,85	55,92	62,36	62,12	6,24	6,16	16,34	16,68
10.	бензил	H	$C_{12}H_{15}ClO_2$	226,56	160—2 (5)	1,129	1,5140	60,41	60,53	63,74	63,60	6,61	6,67	15,38	15,65
11.	метил	метил	$C_7H_{13}ClO_2$	164,63	72—3 (9)	1,045	1,4335	40,98	41,05	51,27	51,07	7,90	8,00	21,35	21,53
12.	метил	пропил	$C_9H_{17}ClO_2$	192,68	89—90 (8)	1,013	1,4403	50,16	50,28	56,38	56,10	8,76	8,89	18,28	18,40
13.	этил	этил	$C_9H_{17}ClO_2$	192,68	96—8 (7)	1,023	1,4457	50,22	50,28	56,44	56,10	8,74	8,89	18,34	18,41
14.	этил	бутил	$C_{11}H_{21}CO_2$	220,73	127—8 (15)	0,995	1,4483	59,45	59,52	59,76	59,85	9,65	9,59	15,83	16,06

Таблица V

Условия реакций 1,3-диолов с хлористым ацетилом



№	R	R′	Температура °C	Время реакции в часах	Выход %	№	R	R′	Температура °C	Время реакции в часах	Выход %
1.	метил	H	100	8	84	8.	фенил	H	160	24	64
2.	этил	H	100	8	79	9.	бензил	H	160	24	54
3.	пропил	H	110	10	74	10.	метил	метил	120	12	80
4.	и-пропил	H	110	10	82	11.	метил	пропил	140	20	80
5.	бутил	H	120	12	78	12.	этил	этил	140	20	82
6.	т-бутил	H	120	12	72	13.	этил	бутил	150	24	66
7.	ц-гексил	H	140	14	70						

циклогексил и хлористый циклогексил [31], бромистый фенил [2] и хлористый бензил [32] были употреблены по методам описанным в литературе. Полученные малоновые эфиры были очищены на колонке ректификации наполненной стекланными спиралями (15 теоретических тарелок) а потом степень чистоты проверена была газожидкостной хроматографией (колонна: термолит содержащий 20% силиконовое масло). Процентный выход полученных продуктов, главные физические константы и данные микроанализа приведены в Таблице II.

Получение 2-моноалкильных и арильных производных пропандиола-1,3. Названные диолы были приготовлены редукцией гидридом лития алюминия из соответствующих малоновых эфиров следующим методом. 500 мл абс. эфирный раствор 2М малонового эфира прибавляется по каплям к 2500 мл абс. эфирному раствору 2 М (76 г) гидрида лития алюминия в течение 2 часа при охлаждении льдом и перемешивании. После этого смесь перемешивается при комнатной температуре в течение часа. Продукт был охлажден при помощи смеси льда с солью и далее перемешивание продолжается. 1500 мл 20% соляной кислоты было прибавлено по каплям с целью разлагания. После отделения органического продукта, водистая часть была экстрагирована эфиром в проточной системе в течение полуторадвух дней. После сушения соединенных эфирных частей прокаленным карбонатом натрия эфир перегоняли. Соответствующие диолы были получены после фракционной перегонки остаток при хорошем вакууме (1—5 рт. мм.) (Выход 60—80%). Процентный выход диолов, их главные физические константы и данные микроанализа приведены в Таблице III. Инфракрасным спектром диолов занимался *Шлейер* [33].

2,2-диалкилзамещенные производные пропандиола-1,3 были получены от Chemische Werke Hüls за что мы выражаем благодарность. Самые важные физические константы названных диолов приведены в Таблице I.

Реакция 2-моно- и 2,2-двузамещенных производных пропандиола-1,3 с ацетилхлоридом. Превращения были изучены в запаянной трубке. В запаянной трубке около 100 мл объёма, 30—40 г диола был замещен, охлажден вместе с трубкой смесью ацетона и сухого льда до —50 °С и при охлаждении ацетилхлорид (температура —70 °С) был прибавлен в известном количестве через раструбочное отверстие запаянной трубки. В охлажденной состоянии сосуд был закрыт, стоял сперва в ледяной воде а потом при комнатной температуре через 2—3 часа. В зависимости от молекулярной веси исходного диола вещество положили в печку при различных температурах в течение разного времени (Таблица V).

После нагревания в печке через нужное время сосуд был осторожно открыт и сырой продукт помещен на 50—60 г льда. После отделения органической части водистая часть была экстрагирована дважды 20—20 мл эфиром. Соединенные органические фазы промывали раствором карбоната натрия, сушали прокаленным карбонатом натрия а потом перегоняли в фракционирующей колонке дополненной стекляной спиралью. Выход: 60—80%. Чистота полученных продуктов проверялась газожидкостной хроматографией (колонна: 20% силиконовое масло — термолит). Главные физические константы и данные микроанализа полученных хлороацетатов описываются в Таблице IV.

В целом ходе работы Willy Giede GCHF 18/2 газхроматограф был употреблен.

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STUDY OF DIOLS AND CYCLIC ETHERS. IX

The Reaction of Diprimary 1,3-Diols with Acetylchlorid

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The paper deals with the reaction of propanediol-1,3, 2-methyl-, 2-ethyl-, 2-n-propyl-, 2-i-propyl-, 2-n-butyl-, 2-t-butyl-, 2-c-hexyl-, 2-phenyl-, 2-benzyl-, 2,2-dimethyl-, 2,2-diethyl-, 2-methyl-2-n-propyl- and 2-ethyl-2-n-butylpropanediol-1,3 on the effect of acetylchloride. The transformations result with a yield of 60–80 *per cent* in the formation of corresponding 1,3-chloroacetates. Regarding the simple method and the very good yield, the reactions can be used for abundant production derivatives of 2-mono- and 2,2-disubstituted propandiol-1,3. As a result of the work on synthesis, a simple method of preparation, structure and main physical constants of 12, so far in the literature undescribed compounds are given.

NEUE NITRO-KALKONE. VIII

Von

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Es wurde eine Reihe der Reaktionsfähigkeit der Substituenten im Falle basenkatalisierte Kalkonbildungsreaktione der Nitro-hydroxy-acetophenone und Benzaldehyde festgestellt und einige neue Kalkone dargestellt.

In der vorliegenden Mitteilung wurden bei Nitro-hydroxy-acetophenonen und mit verschiedenen gearteten Substituenten versehenen Benzaldehyden auf die Wirkung von Natronlauge als Katalysator eintretende Kalkonbildungsreaktionen vollzogen, um in den Besitz neuerer Daten bzgl. der reaktionsbeeinflussenden Rolle der Benzaldehydsubstituenten zu gelangen.

Tabelle I zeigt, daß unter den angewandten, gleichen Reaktionsbedingungen das mit elektronenanziehenden Substituenten versehene p-Nitro-benzaldehyd mit allen Ketonen reagierte, während das Anisaldehyd nur mit zwei Ketonen nicht in Reaktion trat, und das 4-Hydroxy-benzaldehyd mit keinem einzigen Keton das entsprechende Kalkon lieferte. Das 4-Hydroxy-benzaldehyd kondensierte unseren früheren Erfahrungen zufolge auch unter den abwechslungsvollsten Reaktionsbedingungen nur mit einem einzigen Keton zu Kalkon [1, 2].

Das hinsichtlich der Kalkonbildung theoretisch relativ günstige 3-Hydroxybenzaldehyd reagierte unter den obigen Umständen mit drei Ketonen. Auf Grund dieser experimentellen Tatsachen wird also bei Anwesenheit von Natronlauge als Katalysator durch die untersuchten Substituenten der Benzaldehydkomponente die Kalkonbildung in der theoretisch zu erwartenden folgenden Reihenfolge begünstigt:

$$4\text{-}NO_2 > 4\text{-}OCH_3 \quad \text{und} \quad 3\text{-}OH > 4\text{-}OH,$$

bzw. im Falle der Hydroxy-benzaldehyde sind wegen des alkalischen Milieus in der Tat Phenolat-Anionen zugegen.

Im Laufe der mit Benzaldehyd angestellten vergleichenden Kalkonbildungsversuche entstand mit jedem Keton das entsprechende Kalkon, doch war die Ausbeute — von einer Ausnahme abgesehen — niedriger als im Falle des 4-Nitrobenzaldehyds.

Auch die Untersuchung der Rolle der Acetophenonkomponente läßt feststellen, daß die theoretisch zu erwartenden Ergebnisse resultierten, indem das über zwei in meta-Stellung befindliche Nitrogruppen verfügende Keton nur mit schwacher Ausbeute, oder überhaupt nicht reagierte, während die beste Ausbeute die

Tabelle I

Nr	– kalkon	Katalysator	Reaktions-zeit	Reaktions temperatur	Schmp. °C	+ Lit. schmp. °C	Misch. schmp. °C	Aus-beute %	Summenforme	Molge-wicht	N-Gehalt	
											Ber.	Gef.
1	2′-Nitro-3′-hydroxy	2.4% NaOH	1/2 Stunde	Zimmer temp.	135°	135°	135°	52	$C_{15}H_{11}O_4N$	269	5,2	–
2	3′-Nitro-4′-hydroxy	,,	,,	,,	162°	160°	161°	24	$C_{15}H_{11}O_4N$	269	5,2	–
3	4′-Nitro-2′-hydroxy	,,	,,	,,	190°	190°	190°	33	$C_{15}H_{11}O_4N$	269	5,2	–
4	4′-Nitro-3′-hydroxy	,,	,,	,,	135°	135°	135°	58	$C_{15}H_{11}O_4N$	269	5,2	–
5	5′-Nitro-2′-hydroxy	,,	,,	,,	181°	180°	180°	29	$C_{15}H_{11}O_4N$	269	5,2	–
6	6′-Nitro-3′-hydroxy	,,	,,	,,	186°	186°	186°	48	$C_{15}H_{11}O_4N$	269	5,2	–
7	2′, 4-Dinitro-3′-hydroxy	,,	,,	,,	212°	217°	213°	38	$C_{15}H_{10}O_6N_2$	314	8,9	–
8	3′, 4-Dinitro-4′-hydroxy	,,	,,	,,	214°	216°	215°	49	$C_{15}H_{10}O_6N_2$	314	8,9	–
9	4′, 4-Dinitro-2′-hydroxy	,,	,,	,,	210°	211°	210°	47	$C_{15}H_{10}O_6N_2$	314	8,9	–
10	4, 4-Dinitro-3′-hydroxy	,,	,,	,,	207°	208°	207°	6	$C_{15}H_{10}O_6N_2$	314	8,9	–
11	5, 4-Dinitro-2′-hydroxy	,,	,,	,,	226°	230°	227°	58	$C_{15}H_{10}O_6N_2$	314	8,9	–
12	6, 4-Dinitro-3′-hydroxy	,,	,,	,,	205°	202°	204°	57	$C_{15}H_{10}O_6N_2$	314	8,9	–
13	2′-Nitro-3′-hydroxy-4-metoxy	,,	,,	,,	137°	135°	136°	38	$C_{16}H_{13}O_5N$	299	4,6	–
14	3′-nitro-4′-hydroxy-4-metoxy	,,	,,	,,	–	151°	–	–	$C_{16}H_{13}O_5N$	299	4,6	–
15	4′-Nitro-2′-hydroxy-4-metoxy	,,	,,	,,	198°	202°	200°	5	$C_{16}H_{13}O_5N$	299	4,6	–
16*	4′-Nitro-3′-hydroxy-4-metoxy	,,	,,	,,	160°	–	–	27	$C_{16}H_{13}O_5N$	299	4,6	4,8
17	5′-Nitro-2′-hydroxy-4-metoxy	,,	,,	,,	–	165°	–	–	$C_{16}H_{13}O_5N$	299	4,6	–
18	6′-Nitro-3′-hydroxy-4-metoxy	,,	,,	,,	95°	107°	–	14	$C_{16}H_{13}O_5N$	299	4,6	4,5
18*	2′-Nitro-3′, 3-dihydroxy	,,	,,	,,	199°	–	–	30	$C_{15}H_{11}O_5N$	285	4,9	4,8
20	3′-Nitro-4′, 3-dyhydroxy	,,	,,	,,	–	214°	–	–	$C_{15}H_{11}O_5N$	285	4,9	–
21	4′-Nitro-2′, 3-dyhydroxy	,,	,,	,,	–	198°	–	–	$C_{15}H_{11}O_5N$	285	4,9	–
22*	4′-Nitro-3′, 3-dyhydroxy	,,	,,	,,	192°	–	–	36	$C_{15}H_{11}O_5N$	285	4,9	5,0
23	5′-Nitro-2′, 3-dyhydroxy	,,	,,	,,	–	187°	–	–	$C_{15}H_{11}O_5N$	285	4,9	–
24	6′-Nitro-3′, 3-dyhydroxy	,,	,,	,,	170°	179°	–	7	$C_{15}H_{11}O_5N$	285	4,9	5,1

+ Siehe: *Gy. Sipos, T. Széll:* Acta Phys. et Chem. Univ. Szeged, **5**, 70 (1959), *Gy. Sipos, T. Széll, I. Várnai:* Acta Phys. et Chem. Univ. Szeged, **6**, 109 (1959), *Gy. Sipos, I. Dobó, B. Czukor:* Acta Phys. et Chem. Univ. Szeged, **8**, 160 (1962).

* Neue Verbindungen

Ketone mit in meta-Stellung befindlicher Hydroxylgruppe und ortho- oder para-Stellung Nitrogruppe lieferten. Die besseren Produktionsergebnisse wurden auch hier bei der orthogestellten Nitrogruppe erhalten.

Die mit Acetophenon durchgeführten, vergleichenden Kalkonbildungsversuche waren nur im Falle des 4-Nitro-benzaldehyds erfolgreich, die übrigen Aldehyde reagierten nicht. Dieses Ergebnis beweist die reaktionsfördernde, entscheidende Rolle sowohl der Keton-, als auch der Aldehyd-Nitrogruppe [3].

Es wurden auch einige Kalkone hergestellt, deren Acetophenonkomponente außer der Nitro- und Hydroxylgruppe auch Bromsubstituenten enthält (s. Tabelle II).

Experimenteller Teil

Die Ketone und Aldehyde wurden in 2,5 ml Aethanol gelöst — in einigen Fällen mittels Erwärmung — und dann, nach Abkühlen auf Raumtemperatur mit 4 ml 4%-iger NaOH-Lösung versetzt, $^1/_2$ Stunde bei Raumtemperatur stehen gelassen. Nun wurde mit konz. HCl angesäuert und die Lösungen mit dest. Wasser auf etwa das Vierfache verdünnt. Über Nacht stehen gelassen wurde am nächsten Tage die ausscheidende Substanz filtriert, mit dest. Wasser säurefrei gewaschen, getrocknet und aus einem Aceton-Wassergemisch 1:1 oder 1:4 umkristallisiert. Das 2′-nitro-3′-Hydroxy-4-methoxy-kalkon wurde aus Aethanol-Wasser (1:1), und das 4′-Nitro-2′-hydroxy-4-methoxy-kalkon aus Aethanol-Aethylacetat (1:1) umkristallisiert. Bei den Brom-Nitro-Hydroxy-Kalkonen (s. Tabelle II) erfolgte die Umkristallisierung aus einem Aethanol-Aethylacetat-Chloroformgemisch (1:1:1).

Tabelle II

Nr	-kalkon	Katalysator	Reaktionszeit	Reaktionstemperatur	Schmp. °C	Ausbeute %	Summenformel	Molgewicht	C-und H — Gehalt			
									Ber.		Gef.	
									C	H	C	H
1*	3′-Nitro-4′-hydroxy-5′-brom	2,4% NaOH	1/2 Stunde	Zimmer temp.	228°	6	$C_{15}H_{10}O_4NBr$	348	51,7	2,8	51,6	2,7
2*	5′-Nitro-2′-hydroxy-3′-brom	,,	,,	,,	228°	30	$C_{15}H_{10}O_4NBr$	348	51,7	2,8	51,8	2,8
3*	3′-Nitro-4′-hydroxy-5′-brom-5-chlor	,,	,,	,,	188°	9	$C_{15}H_9O_4NBrCl$	382	47,0	2,3	46,7	2,5
4*	5′-Nitro-2′-hydroxy-3′-brom-4-chlor	,,	,,	,,	256°	28	$C_{15}H_9O_4NBrCl$	382	47,0	2,3	46,7	2,3

* Unbekannte Verbindungen

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НОВЫЕ НИТРОКАЛКОНЫ. VIII

Г. Шипош и Т. Селл

Авторами определен порядок реакционной способности заместителей с бензальдегидным компонентом в случае калконобразующих реакций нитрогидроксиацетофенонов и различно замещенных бензальдегидов катализованных щелочью.

PREPARATION OF NITROHYDROXY KETONES BY FRIEDEL-CRAFTS REACTIONS

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Some nitrohydroxy ketones were prepared by FRIEDEL—CRAFTS synthesis from nitrophenols. These processes are compared with the FRIES reaction of the corresponding nitrophenolesters.

1. Introduction

Though nitrohydroxy ketones are synthesized since long by classical methods, the preparation of these compounds by the FRIEDEL—CRAFTS reaction of nitrophenols and acid chlorides is rare. This is doubtlessly due to the retarding effect of the nitro group of the phenyl ring which results in poor yields.

The reaction between phenols and acyl chlorides was studied by ROSEMUND and SCHNURR [1] who found that acylation primarily takes place, instead of the nucleus, actually on the oxygen atom. Similar observations were published later also by other authors [2, 3]. BROWN was the first who succeeded in preparing 3-nitro-4-hydroxy-acetophenone and its homologues in satisfactory yields [33 to 41%] by the FRIEDEL—CRAFTS reaction of the appropriate phenol with acid chloride in the presence of aluminium chloride [4]. Similarly, 5-nitro-2-hydroxy-acetophenone was prepared by the teams of JOSHI [5] and of CHHAYA [6].

As we succeeded earlier [7] in carrying out the FRIES rearrangement of some nitrophenylesters into nitrohydroxy ketones, it appeared to be of interest to compare these FRIES reactions with the corresponding FRIEDEL—CRAFTS reactions.

2. Results and discussion

The reactions between 3-nitrophenol and acetyl chloride, phenyl acetyl chloride, benzoyl chloride, 3-nitrobenzoyl chloride, propionyl chloride, further between 4-nitrophenol and acetyl chloride, 2-nitrophenol and acetyl chloride, respectively, were carried out. The results may be summarized as follows.

The FRIEDEL—CRAFTS and the FRIES reactions yielded in all cases identical products, in accordance with the observations of CULLINANE [8] made with other models. The products were already described earlier by us [7].

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At relatively lower temperatures when no substantial FRIES reaction can be observed, the main product of the reaction is nitrophenolester. This temperature limit depends on the nature of the ester, *e. g.* the FRIEDEL—CRAFTS reaction is getting predominant over 80° in the case of 2-nitrophenol and acetyl chloride and over 140° in that of 3-nitrophenol and benzoyl chloride. FRIEDEL—CRAFTS reactions take place at the temperature of the corresponding FRIES reaction, of nitrophenol-esters

In the case of 2-hydroxy ketones, the yields of the FRIEDEL—CRAFTS reaction are but slight lower than those of the FRIES reactions, while in the case of the 4-hydroxy ketone studied the former are appreciably higher. This observation is not in contrast to the presumption that the mechanism of the FRIEDEL—CRAFTS reaction of phenols is in essence similar to the mechanism of the FRIES reaction in the course of which, subsequent to the equilibral splitting of esters, the products of cleavage react with each other giving hydroxy ketones (and esters again) [3]. The favourable yield of 4-hydroxy ketones, in turn, can be explained by the observation of GERECS according to which the *para* rearrangement is promoted by the presence of hydrogen chloride [2]. This can probably be ascribed to the effect of hydrogen chloride on the equilibral splitting of the ester [3]. Obviously in the FRIEDEL—CRAFTS reaction hydrogen chloride is formed as a by-product of the equilibral formation of the ester.

In FRIEDEL—CRAFTS reactions it is necessary to apply at least as many moles of aluminium chloride as the moles of acid chloride used. Of the latter, it is advisable to use 1,5 moles per mole of phenol.

The FRIEDEL—CRAFTS reactions take place in nitrobenzene. However, the use of a solvent is not indispensable because the reactions can be also carried out in melt. Still, the temperature in this latter case should not attain the decomposition temperature of the corresponding nitrophenols in the presence of aluminium chloride [9].

3. Experimental

As examples characteristic of FRIEDEL—CRAFTS reactions, the preparation of 4-nitro-2-hydroxy acetophenone, 4-nitro-2-hydroxy benzophenone and of 4,3′-dinitro-2-hydroxy benzophenone will be described here.

4-nitro-2-hydroxy acetophenone

14,3 ml (15,8 g; 200 mmoles) of acetyl chloride were added to the mixture of 13,9 g (100 mmoles) of 3-nitrophenol and 13,4 g (100 mmoles) of aluminium chloride. The system was kept 3 hours in an oil bath of 125°. On cooling, the complexes were decomposed by a mixture of 30 ml of water and 10 ml of concentrated hydrochloric acid, the obtained turbid aqueous system extracted with 4×25 ml of carbon tetrachloride and 2×25 ml of benzene. The combined organic phases were then subjected to distillation in order to remove the solvents, and the residue made up to 35 ml with methanol. On adding 40 ml of an ethanolic solution of sodium methylate containing 10% of sodium, the system was kept in an ice box when 1,1 g of 4-nitro-2-hydroxy acetophenone sodium precipitated in red brick-coloured crystals (yield 5,5%). Prior to adding sodium ethylate, 9 g of unchanged 3-nitrophenol acetate could be detected in the solution (40% yield).

On altering the reaction period to 8 hours, the temperature to 130°, and the mole ratios of phenol-aluminium chloride-acetyl chloride to 1:1,5:1,5, the yield increased consecutively to 16,5—18,0%.[1] The free ketone could be liberated from its sodium salt by shaking at 60—70° with a 1,0*N* solution of sulphuric acid. M. p. of the product: 63°, on recrystallization from ethanol: m. p. 67°.

4-nitro-2-hydroxy benzophenone

23 ml (28,1 g=200 mmoles) of benzoyl chloride was added to a mixture of 13,9 g (100 mmoles) of 3-nitrophenol and 13,4 g (100 mmoles) of aluminium chloride, the system kept 2 hours in a 170° oil bath. On cooling, the melt was decomposed with a mixture of 15 ml of concentrated hydrochloric acid and 100 g of ice, affording a brownish aqueous emulsion and a dark sticky paste. On decanting the aqueous emulsion, it was shaken with 2 ×30 ml of carbon tetrachloride. The paste residual on the bottom of the flask was treated with 40 ml of ethanol, and the solvent removed by distillation in order to obtain waterfree residue. The combined organic phases obtained from the above described extraction were dried (Na_2SO_4), poured on the anhydrous paste, and the system refluxed for 12 hours, and extracted with 4 ×40 ml of a 4% solution of sodium hydroxide in order to separate the phenols from the ester. The combined alkaline extracts were acidified with concentrated hydrochlorid acid, shaken with 4 ×40 ml of carbon tetrachloride, the combined extracts dried (Na_2SO_4), and the solvent removed. On cooling, the residue solidified to a brown mass which was extracted with 6 ×10 ml of boiling petroleum ether. Removal of petroleum ether gave 5,3 g of a yellow substance which was recristallized from ethanol to give 2,4 g of crude ketone (9,9% yield)[2] which melted at 90—104°. On recrystallization from ethanol and ligroin m. p. was 108°. The product was identical with that prepared from 4-nitrosalicylic chloride and benzene [10].

When the mole ratio was altered to 1:1,5:1,5 for phenol- aluminium chloride-acyl haloid, the reaction period to 3 hours and the temperature to 125—130°, the amount of crude 3-nitrophenol benzoate crystallizing after decomposition ranged 22,4 g (92% yield) m. p. 80—93° and no ketonic product could be obtained.

When the mole ratio of the last experiment was maintained, and the system was heated 2 hours at 170°, the yield referred to crude ketone was 7,5%.

4,3′-dinitro-2-hydroxy benzophenone

Mode of preparation as in preceding experiment with a mole ratio of 1:1,5:1,5 of 3-nitrophenol (13,9 g=100 mmoles)- aluminium chloride- 3-nitrobenzoyl chloride, at 175—180° for 2,5 hours. On cooling, a partially blistered melt was obtained. This was treated with 170 ml of ethanol, shaken till it almost completely dissolved, then a mixture of 20 ml of concentrated hydrochloric acid and 1000 ml of water was poured to the system. On allowing the reaction mixture to stand overnight, the aqueous solution was decanted and shaken with 4 ×100 ml of carbon tetrachlo-

[1] The corresponding FRIES reaction under similar conditions gave around 20% yield [7].

[2] The FRIES reaction of 3-nitrophenyl benzoate in the presence of equimolar $AlCl_3$ gave 11% yield of crude ketone [10].

ride, and with 6 ×100 ml of benzene. Subsequently 3 ×50 ml of ethanol was poured on the black tar-like mass, the solvent removed by distillation to make it water free, and the combined mixture of tetrachloromentane and benzene previously dried (Na_2SO_4) poured on the residual mass. On refluxing the system 12 hours and filtering the mixture hot, the filtrate was evaporated to dryness, the residue boiled with 3 ×100 ml of petroleum ether and then with 4 ×15 ml of ligroin, the combined extract evaporated, and the residual crystals recrystallized from ethanol: yield 0,15 g, m. p. 150—152°. On recrystallization it melted at 157—158°.

* * *

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ПОЛУЧЕНИЕ НИТРОГИДРОКСИКЕТОНОВ РЕАКЦИЕЙ ФРИДЕЛЬ-КРАФТСА

Т. Селл, З. Хаяш и Ш. Шипош

Были получены некоторые нитрогидроксикетоны из нитрофенолов путём синтеза *Фридель—Крафтса*. Процессы сопоставляются с реакцией *Фриза* соответствующих сложных эфиров нитрофенола.

FRIES REARRANGEMENT OF 3-NITROPHENYL-3-NITROBENZOATE

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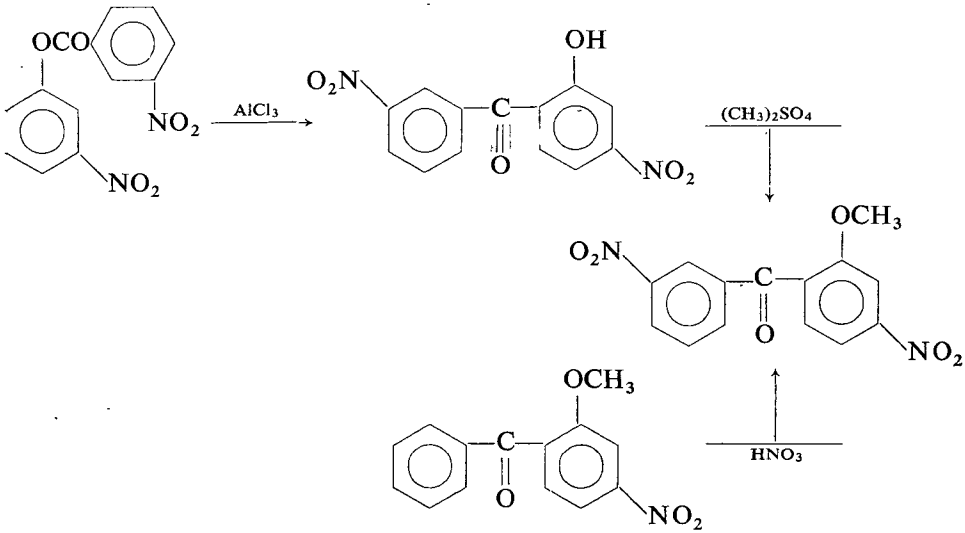
On subjecting 3-nitrophenyl-3-nitrobenzoate to FRIES rearrangement, the so far unknown 3′, 4-dinitro-2-hydroxy-benzophenone was obtained in a poor yield.

In continuation of our earlier work [1, 2], the FRIES rearrangement of 3-nitrophenyl-3-nitrobenzoate was carried out. On keeping the ester and an equivalent amount of aluminium chloride for two hours in an oil bath of 175°, 3,4-dinitro-2-hydroxybenzophenone was formed in a poor yield. The product was characterized by its phenylhydrozone and by its sodium salt.



Though it is known that the successful course of the FRIES raction is inhibited by the presence of a nitro group substituted in the nucleus of the phenol portion of phenylesters [3], several cases were described [2] where nitro-phenylesters have

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undergone FRIES reaction in rather poor yields. To our knowledge, the present work is, however, the first FRIES rearrangement involving dinitrophenylesters. The poor yield observed may be ascribed to the presence of two nitro groups.

In order to prove the structure of the ketone, it was attempted to nitrate 4-nitro-2-hydroxy-benzophenone [4]. However, the mononitro product obtained in this way was not identical with the ketone formed in the FRIES reaction. (Presumably the nitro group entered the phenol portion.) In order to reduce the effect of the phenolic hydroxyl group, 4-nitro-2-hydroxy-benzophenone was first methylated, and the methyl derivative subjected to nitration. The product thus obtained was identical with the methyl derivative of the compound formed in the FRIES reaction examined, proving that in fact 3', 4-dinitro-2-hydroxy-benzophenone was formed in the FRIES rearrangement.

Experimental

Fries rearrangement of 3-nitrophenol-3-nitrobenzoate

A mixture of the ester (17,9 g; 62 mmole) and an equivalent amount (8,25 g; 62 mmole) of aluminium chloride (B. D. H.) was placed in a cold oil bath under reflux equipped with a ground calcium chloride tube. The temperature of the oil bath was slowly raised to 175° and kept two hours at a temperature of 173—177°. A hard black blistered melt was obtained.

The melt was boiled 20 minutes with 60 ml of ethanol, the resulting coffee-coloured suspension containing solid undissolved particles was then poured into a mixture of 12 ml of concentrated hydrochloric acid and 600 ml of water, and the mixture allowed to stand overnight. The system separated into two phases: a sharp, slightly brownish aqueous phase and a tar-like organic phase. The aqueous phase was shaken with 6×50 ml of carbon tetrachloride, then with 2×50 ml of benzene of a temperature of 34—40°. The combined carbon tetrachloride-benzene fractions were washed with 6×100 ml of water (in order to remove 3-nitrobenzoic acid), and dried with sodium sulphate. Then a suspension was made of the above mentioned tar-like phase in 50 ml of hot ethanol mixed with the carbon tetrachloride-benzene solution, and the whole system refluxed for 12 hours. After filtering the warm suspension through cotton 200 ml of solvent were removed from the filtrate by distillation, the phenols were extracted from the residue with 4×40 ml of 1*N* sodium hydroxide, the alkaline solution acidified with concentrated hydrochloric acid, the system allowed to stand overnight in an ice box, the separated asphalt-like sticky substance filtered through filter paper, dried at room temperature and ground (7,25 g). Subsequently, the product was transferred into a 250 ml round-bottomed flask, boiled with 2×100 ml of petroleum ether then with 4×15 ml of ligroin (b. p. 112—113°). The combined petroleum ether-ligroin extracts were evaporated to a volume of 25—30 ml, and allowed to stand overnight in an ice box to give 0,4 g of a yellow crystalline substance of m. p. 116—125°. On recrystallizing it from 50% ethanol, then from 96% ethanol the yellow keton melted at 158—159°. (Anal.: Calc.: $C_{13}H_8O_6N_2 = 288{,}2$, C 54,17 H 2,8 N 9,72; Found: C 54,06 H 3,08 N 9,62.)

On adding some phenylhydrazine base to a saturated solution of 3,4'-dinitro-2-hydroxybenzophenone in 60% ethanol, the liquid was boiled 4—5 minutes. On allowing the system to stand in an ice box, dark yellow needles of the phenylhydrazone, m. p. 240—242° separated. (Anal.: Calc.: $C_{18}H_{14}O_5N_4$ = 378,3 N 14,81; Found: N 14,80.)

From the solution of the ketone in benzene by adding a methanolic solution of sodium methylate (10% in respect to sodium), the orangered sodium salt of the hydroxy-ketone separated.

Nitration of 4-nitro-2-hydroxybenzphenone

To the analogy of the nitration of similar compound [5] [6], the nitration of 4-nitro-2-hydroxybenzophenone of authentic structure [4] was carried out as follows. The powderized ketone (1,22 g; 5 mmole) was allowed to stand 3 hours at room temperature with 4 ml of nitric acid of sp. gr. 1,43. Then the mixture was heated two hours at 50—55° on the water bath. The heterogeneous system turned homogeneous, then again heterogeneous. By filtration, a substance melting at 96° while by pouring the mother liquor into 80 ml of water a substance melting at 130 were separated. On repeatedly recrystallizing the latter substance from 60% ethanol, its m. p. rose to 144—146°. The product ($C_{13}H_8O_6N_2$ = 288,2) contained 9,72% of N proving that it was a mononitro product. Neither of the products however, were identical with the ketone obtained by the FRIES reaction of 3-nitrophenyl-3-nitrobenzoate.

Methylation of 4-nitro-2-hydroxybenzophenone

The solution of 1,22 g of 4-nitro-2-hydroxybenzophenone (5 mmoles) in 2,5 ml of 2*N* sodium hydroxide was diluted with 7 ml of water. On adding 0,65 g (*i. e.* 0,5 ml) of dimethyl sulphate (5 mmoles) to the bordeaux red solution, its colour gradually turned into dark red, and precipitation of crystals was observed. The system was then strirred for one hour at 40°, its colour turned yellow. Further 0,2 g (1,5 mmoles) of dimethyl sulphate was added to the emulsion and the system allowed to stand overnight. The suspension (pH = 2) was treated with 1,2 ml of 2 N sodium hydroxide, stirred 25 minutes at 40°, then the pH value adjusted with one drop of 2 N sodium hydroxide to 7,5—8,0, the precipitated crystals filtered and washed with water. Yield: 1,18 g (91,4%) of crude methylether, m. p. 112—116°. Recrystallization of the product once from ligroin and once from ethanol gave 0,75 g of white needles, m. p. 130—131°. (Anal.: Calc.: $C_{14}H_{11}O_4N$ = 257,24 C 65,35 H 4,31 N 5,44; Found: C 65,05 H 4,52 N 5,58.)

Nitration of 4-nitro-2-methoxybenzophenone

2 ml of nitric acid of sp. gr. 1,43 was poured on 0,64 g (2,5 mmoles) of 4-nitro-2-methoxy-benzophenone. At first much heat evolved, the substance was intstantaneously dissolved and the nitric acid turned brown. On allowing the mixture to

stand an hour, it was kept for another hour on a 55° water bath, then 15 hours at room temperature, and finally poured into 40 ml of ice water. The precipitated product was filtered, dried at room temperature to give a crude product which was boiled with 10 ml of ethanol and filtered hot. In an ice box, 0,25 g of a substance of m. p. 153—158° crystallized from the filtrate. By recrystallizing it from a 3:1 mixture of ethyl acetate and ethanol, white needles of m. p. 159—160° were obtained. (Anal.: Calc.: $C_{14}H_{10}O_6N_2 = 302{,}24$ C 55,63 H 3,34 N 9,27; Found: C 55,71 H 3,70 N 8,91.)

Methylation of 4,3'-dinitro-2-hydroxy-benzophenone

0,15 g of 4,3'-dinitro-2-hydroxy-benzophenone was suspended in 0,3 ml of 2 *N* sodium hydroxide. The substance was only partially dissolved. Subsequently the suspension was diluted with 0,9 ml of water, 0,1 ml of dimethyl sulphate added, and the suspension stirred at 40° until it turned yellow. On adding 3,3 ml of sodium hydroxide solution and 0,2 ml of dimethyl sulphate, stirring was continued for an hour. The final pH was about 10. White crystals were separated from the yellow solution by filtration, and recrystallized from 8 ml of a 3:1 mixture of ethanol and ethyl acetate. M. p. 158—159°. This white substance proved to be identical with the end product of the preceding experiment.

* * *

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ПЕРЕГРУППИРОВКА ФРИЗА 3-НИТРОФЕНИЛ-3-НИТРОБЕНЗОАТА

Й. Эдед, А. Фурка, и Т. Селл

Подвергая 3-нитрофенил-3-нитробензоат перегруппировке *Фриза*, авторы получили незнакомый до сих пор 3',4-динитро-2-гидрокси-бензофенон в небольшом выходе.

UNTERSUCHUNG DER THERMISCHEN EIGENSCHAFTEN KATALYTISCHER KONTAKT-REAKTOREN MIT NEUER GEOMETRISCHER FORMGESTALTUNG

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(Eingegangen am 15. Dezember, 1964)

Es wurde die analytische Bestimmung der Temperatur-Ortsfunktionen der verschiedenen Reaktorformen, und im Besitze dieser die Feststellung der makroskopischen Ähnlichkeitskriterien gegeben. Bei der Temperaturverteilungsberechnung wurden zwar einige vereinfachende Bedingungen angewandt, die aber beim relativen Vergleich bzgl. der verschiedenen Formen weniger schwer ins Gewicht fallen.

Die Ergebnisse dieses Vergleiches wurden bei der Auswertung der thermischen Eigenschaften der neuen Reaktorformen verwendet.

Im Laufe unserer experimentellen Arbeiten trat die Durchführung der in der stark exothermen Dampfphase ablaufenden katalytischen organischen Reaktionen unter isothermen (oder annähernd isothermen) Verhältnissen in den Vordergrund. Der Durchmesser der zu diesem Zweck allgemein gebrauchten Röhrenreaktoren (Fig. 1) kann wegen der Gefahr des Einbrennens nicht beliebig vergrößert werden, doch ist eines unserer Hauptziele die Erhöhung der Produktionskapazität. Wir haben daher neue geometrische Formen vorgeschlagen. Die Verbesserung der Wärmeübertragung und der aerodynamischen Faktoren durch Verwendung neuer, vom Röhrenreaktor abweichender Formen ist kein neues Problem, und in dieser Richtung sind bereits zahlreiche Versuche unternommen worden [1—3]. Die empfohlenen Lösungen sind: planparallele Form (Fig. 2) mit ebenen Platten begrenzter Strömungsraum. Koaxiale Form (Fig. 2a), wo der Strömungsraum ist ein zwischen zwei Zylindern befindlicher ringförmiger Teil, sowie der Scheibenreaktor [4], mit dem wir uns aber wegen den komplizierteren Strömungsverhältnissen hier nicht befassen wollen. Die Aufgabe der vorliegenden Arbeit ist, die thermischen Eigenschaften der Reaktorformen zu untersuchen und auf Grund dessen die verschiedenen Formen miteinander zu vergleichen. Als wichtigste Vergleichsbasis betrachteten wir die Voraussetzung, daß innerhalb des Reaktors die makroskopische Temperaturdifferenz

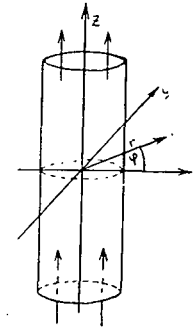

Fig. 1

zwischen der wärmsten und der kältesten Stelle bei den verschiedenen Formen gleich sei. Die mit dieser Bedingung gewinnbaren geometrishcen Daten liefern gewisse Informationen zwischen die im Reaktor herrschender Wärmedifferenzen und die spezifische Abmessung des Reaktors.

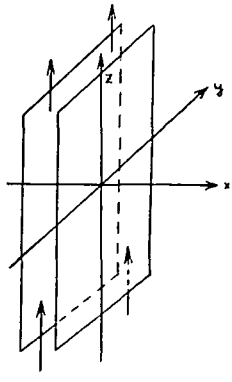

Fig. 2

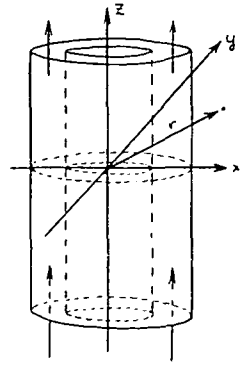

Fig. 2a

Um die Temperaturdifferenzen berechnen zu können, benötigt die Orts- (und Zeit-) abhängigkeit der Temperatur bekannt sein. Die Lösung des Problems ist im allgemeinsten durch Lösung der Grundgleichungen des zwangsströmungsbedingten Wärmeaustausches erreichbar, wie BARON [5] angegeben hat. Diese Gleichungen berücksichtigen die kinetischen Daten und die Wärmetönung der Reaktion, sowie die Verteilung der Konzentration der reagierenden Stoffe; sie enthalten die Differentialgleichungen der Kontinuitäts-, Bewegungs-, Energie- und Konzentrationsverteilung. Die Gleichungen müssen wesentlich gekürzt werden, um als Ergebnis nicht eine unübersehbare, viele Veränderliche enthaltende numerische Integration zu erhalten [6]. Die Vereinfachungen sind folgende: es wird die einfachste Lösung der Kontinuitäts- und Bewegungsgleichung, der eindimensional homogene (orthogonale) Strömungsraum genommen. Dieser bedeutet bei den konkreten Formen die Strömung in Richtung der z-Achse. Die (Wärme-) Energiegleichung für die i-te reagierende Substanz ist folgende:

$$\frac{\partial(C_p \varrho t)}{\partial \tau} + (\upsilon \operatorname{grad}) t + R_i H_i M_i = \operatorname{div}(\lambda \operatorname{grad}) t, \tag{1}$$

wo c_p die spezifische Wärme bei konstantem Druck, ϱ die Dichte, τ die Zeit, υ den Geschwindigkeitsvektor, t die Temperatur R_i die Bildungs- (Verschwindens) Geschwindigkeit der i-ten Substanz, d. h. die Reaktionsgeschwindigkeit, H_i die Reaktionswärme der i-ten Substanz, M_i das Molekülgewicht und λ das Wärmeleitungsvermögen bedeutet.

Unsere Kürzungen sind folgende: nur stationäre Fälle werden untersucht, dann ist das erste Glied der linken Seite Null. (Offensichtlich ist die eine Folge der das Problem richtig beschreibenden Gleichung die Erreichbarkeit oder Unerreichbarkeit des stationären Zustandes, die Schwingungsfähigkeit des Systems.

Die primäre Untersuchung wäre die Untersuchung der Stabilität. Die Praxis befaßt sich aber nicht mit den Wärmeschwingungen der Reaktoren, und so wäre die Untersuchung nur theoretisch interessant, so daß wir hier auf sie verzichten.)

Ziehen wir den oben beschriebenen Strömungsraum in Betracht, so wird der im DESCARTESschen Koordinatensystem aufgeschriebene (v grad) Operator auf ein Glied reduziert: $\left(v_z \frac{\partial}{\partial z}\right)$, da $v_x = v_y = 0$.

Das größte Problem bedeutet das dritte Glied der linken Seite. Im ersten Teil unserer Arbeit nahmen wir konstante Reaktionsgeschwindigkeit, deren Temperatur- und Ortsunabhängigkeit, Unabhängigkeit der Reaktionswärme von der Temperatur und eine einzige reagierende Substanz an. Hiermit haben wir die Aufgabe radikal vereinfacht, da wir hierdurch die von BARON benutzte Differentialgleichung der Konzentrationsverteilung weggelassen haben, die durch das dritte Glied repräsentierte Wärmequellendichte ist vom Ort und Temperatur unabhängig geworden, wir bezeichnen sie im weiteren mit $\varkappa$.

Nehmen wir ferner an, daß die Reaktoren in entsprechend ausgezeichneten Richtungen unendlich lang sind (Rohr: z-Achse, Planparallel: y, z; usw.), das heißt ein Wärmeaustausch in diesen Richtungen ausgeschlossen ist, so ist die Wärmequellendichte konstant, woraus unmittelbar folgt, daß in diesen Richtungen ein Wärmegradient nicht auftreten kann, das heißt: $\left(\frac{\partial t}{\partial z}\right) = 0$, usw.

Setzen wir noch voraus, daß λ vom Ort und Temperatur unabhängig ist, so ergibt sich

$$\vec{\nabla}^2 t = \frac{\varkappa}{\lambda}, \tag{2}$$

das heißt, das Problem ist zu einem potentialtheoretischen Problem, zur POISSONschen Gleichung reduziert. Im weiteren Teil unserer Arbeit haben wir versucht, die Termperaturabhängigkeit der die Wärmequellendichte repräsentierenden Funktion in Betracht zu ziehen. Einerseits haben wir die Temperaturabhängigkeit von H_i und R_i—entsprechend dem KIRCHHOFFschen bzw. ARRHENIUSschen Gesetz — separat berücksichtigt. Die gleichzeitige Berücksichtigung führt jedoch zu mathematischen Schwierigkeiten. Die erste Annäherung entspricht der Voraussetzung einer so schnellen Reaktion, daß diese in jedem Raumpunkt praktisch vollkommen abläuft und die ganze Reaktionswärme frei wird. Im zweiten Falle wird die Geschwindigkeit der Wärmeentwicklung in erster Linie von der Reaktionsgeschwindigkeit bestimmt. Ferner haben wir die Unendlichkeitsbedingungen reduziert.

Die Untersuchung der Verteilung der Temperatur und ihr Vergleich bei verschiedenen Reaktorformen:

Die zylindrischen und flächensymmetrischen Lösungen der POISSONschen Gleichung sind sowohl innerhalb des Wärmequellenraumes, als auch am wärmequellfreien Ort zu erhalten, wenn man den LAPLACEschen Operator zu einer zylindrischen bzw. zur DESCARTESschen Koordinaten transformiert.
Für Röhrenreaktoren:

$$\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial t}{\partial r}\right) + \frac{1}{r^2}\frac{\partial^2 t}{\partial \varphi^2} + \frac{\partial^2 t}{\partial z^2} = \frac{\varkappa}{\lambda}, \tag{3}$$

für Planparallelreaktoren:

$$\frac{\partial^2 t}{\partial x^2}+\frac{\partial^2 t}{\partial y^2}+\frac{\partial^2 t}{\partial z^2}=\frac{\varkappa}{\lambda}. \tag{4}$$

Wenn wir beachten, daß — wie einleitend gesagt — in (3) t nicht eine Funktion von φ und z, und in (4) t nicht eine Funktion von y und z ist, so werden die partiellen Differentialgleichungen zu gewöhnlichen Differentialgleichungen vereinfacht, die mittels Quadratur zu lösen sind.

Innerhalb des Wärmequellraumes sind die Auflösungsfunktionen
für Röhrenreaktoren

$$t=-\frac{\varkappa}{4\lambda}r^2+t_{r=0},$$

für Planparallelreaktoren

$$t=-\frac{\varkappa}{2\lambda}x^2+t_{x=0},$$

wo $t_{r=0}$, bzw. $t_{x=0}$ die Kerntemperaturen sind. (Außerhalb des Wärmequellraumes ist der Temperaturverlauf ein logarithmischer bzw. linearer.) Die Lösungen enthalten auch die Randbedingungen.

Hieraus ist festzustellen, daß — wenn X die Halbschichtdicke des Planparallelreaktors ist — der Radius jenes Röhrenreaktors, in dem die gleiche Temperaturdifferenz herrscht,

$$R=\sqrt{2}X$$

ist.

Bei der koaxialen Form muß z. B., wenn der äußere Radius das Doppelte des Radius (R) des zylindrischen Wärmequellraumes ist, der innere Radius des Wärmequellraumes die Größe $r=\sqrt{3}R$ hat, daß die Temperaturdifferenz übereinstimme. Dann beträgt die koaxiale Schichtdicke eine Wert von $0{,}268R$, sie ist also ziemlich dünn. (Bei dieser Lösung wurde das DIRICHLETsche Problem auf den Kreis angewandt).

Wir haben untersucht, ob die Verhältnisse sich bessern, wenn nicht nur die mittels Leitung entschwindene Wärme, sondern auch die in gewissen nahen Wärmeabsorbent verschwundene Wärme berücksichtigt wird. Bei der mit der Leitung sich entschwindene Wärme nahmen wir nämlich an, daß die Wärmeabsorbenten in unendlicher Entfernung von den Wärmequellen liegen und über die gleichen Symmetrieeigenschaften verfügen, wie die Quellen. Interessant ist die Untersuchung, die sich auf den Fall bezieht, wenn die Wärmeabsorbenten in unmittelbarer Nähe der Wärmequelle sind, was entspricht einer Kühlung des Reaktors. Potentialtheoretisch ist die Lösung der Frage nicht problematisch, nur die Additivität der Potentiale (Temperatur) muß für das fragliche Problem bewiesen werden, und das ist nicht schwer. Eine von innen gekühlte koaxiale Form und ihre Wärmeverteilung ist an (Fig. 3) dargestellt. Ausführliche Diskussion des Problems (Maximumuntersuchung) ließ im Wärmequellraum folgen-

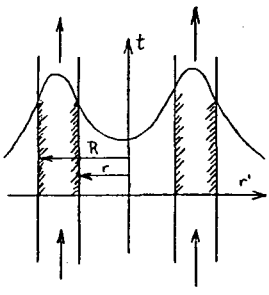

Fig. 3

den Temperaturverlauf feststellen:

$$t(r') = \frac{\varkappa R^2}{2\lambda} \ln \frac{r'}{R} - \frac{\varkappa'}{4\lambda} r'^2 + C, \quad \text{wenn} \quad r \leqq r' \leqq R,$$

wo C = Integrationskonstante, $\varkappa$ = die Wärmequelldichte, und $\varkappa'$ = die Aufnehmerdichte, sowie der Ort des Maximums $r_{\max} = \sqrt{\frac{\varkappa}{\varkappa'}}\, R$.

Das Verhältnis $\varkappa/\varkappa'$ wurde aus der willkürlichen Voraussetzung bestimmt, daß die Temperatur des inneren und äusseren Randes übereinstimmt. Dann ist

$$\frac{\varkappa}{\varkappa'} = \frac{3}{2 \ln 2} \equiv a.$$

Die Differenz der Termperatur zwischen Rand und Maximumort beträgt, wenn der äußere Radius das Doppelte des inneren ist ($R = 2r$):

$$t_{\max} - t_{\text{rand}} = \frac{\varkappa R^2}{2\lambda} \left(\ln \sqrt{a} - \frac{1}{2} + \frac{1}{2a} \right) \cong \frac{\varkappa R^2}{2\lambda} 0{,}0504$$

Ein Vergleich dieser Daten mit denen des Röhrenreaktors, wo $\Delta t = \frac{\varkappa R^2}{4\lambda}$, zeigt, daß — wenn der innere Radius des koaxialen Reaktors R, der äußere $2R$, und der des Zylinder-Reaktors ebenfalls R ist — die Temperatur der koaxialen Form — bei dem gleichen Wärmeleitungsvermögen — viel ausgeglichenerer ist. Ähnliche Berechnungen wurden auch mit Bezug auf die planparallele Form durchgeführt.

In weiteren Untersuchungen sollte festgestellt werden, welche Wirkungen auftreten, wenn der planparallele Reaktor nicht unendlich breit, sondern in der Richtung y endlich ist, das heißt, seine Grundfläche ein Rechteck bildet. Gleichzeitig damit kann natürlich nicht nur die Untersuchung der Temperaturverteilung in Reaktoren mit quadratischer Grundform erfolgen, sondern auch die Reaktoren mit abgerundeten Rechteck-Grundformen (zur Ausschaltung der Eck-wirkungen) erfolgen (es ist zweckmäßig, einfache Formen, z. B. eine Ellipse zu wählen (Fig. 4)).

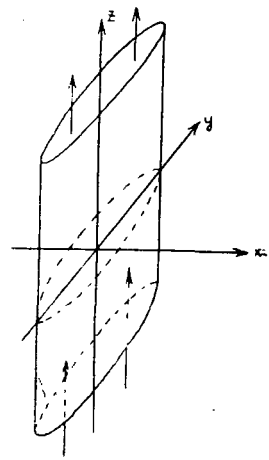

Fig. 4

In diesem Falle muß die POISSONsche Gleichung für den gegebenen Flächenbereich — als Wärmequelle — gelöst werden. Hier sind zweckmäßig zwei Fälle zu unterscheiden, je nach dem, ob die Temperatur innerhalb des Wärmequellenraumes, oder außerhalb gesucht wird. Im Falle des inneren Punktes zeigt das folgende Integrandus — dessen Integral die Lösung der POISSONschen Gleichung für den Flächenbereich bildet [7], — Singularität:

$$t(x, y) = C \iint_{\Omega} \varkappa(x, y) \ln \frac{1}{\sqrt{(x-\xi)^2 + (y-\eta)^2}}\, d\xi\, d\eta.$$

In Analogie zu dem in der Potentialtheorie angewandten Verfahren [7] können wir die Temperatur in jedem inneren Punkt erhalten.

So z. B. im Falle des Quadratbereiches nach der Integration (abgesehen von dem konstanten Multiplikator) erhalten wir:

$$t(m) = 2(1-m)\ln\sqrt{(1-m)^2+1} + 2(1+m)\sqrt{(1+m)^2+1} + \frac{1}{2}(1-m)^2 \operatorname{arc\,tg}\frac{1}{1-m} +$$

$$+\frac{1}{2}(1+m)\operatorname{arc\,tg}\frac{1}{1+m} + \frac{1}{2}\operatorname{arc\,tg}(1-m) + \frac{1}{2}\operatorname{arc\,tg}(1+m),$$

wo m die an der Medianlinie des Quadrats gemessene Entfernung vom Mittelpunkt ist. Im Falle eines äußeren Punktes empfiehlt sich Reihenentwicklung des Integrandus. Auf Grund der entsprechenden Eigenschaften der Integrandusreihe (gleichmäßige Konvergenz) ist die Integrierung durchführbar, die Temperaturverteilung wird dabei in einer Reihenentwicklung nach momentartigen Quanten erhalten. Die auf die verschiedenen Flächen bezüglichen Momente wurden auf Quadrat, Rechteck und Ellipse bestimmt. Die ausführliche Diskussion dieser Untersuchung ergab, daß der Verlauf der Temperatur stets parabolischer ist (die eingehende Untersuchung des Eck-effektes verlangte jedoch eine große numerische Arbeit). Im weiteren haben wir die Verminderung der eingangs erwähnten Idealisierungen untersucht. Wird die Temperaturabhängigkeit von H_i nach dem KIRCHHOFFschen Zusammenhang

$$\Delta H_i = \Delta H_i^\circ + \int_{t^\circ}^{t} \Delta C_p\, dt$$

berücksichtigt und geht man in der Potentialreihe von Δc_p nur bis zur ersten Annäherung vor, so ist die Wärmequelldichte

$$\varkappa_t = \varkappa + mt,$$

wo m konstant ist. Die Wärmetönung ist durch das Vorzeichen von m angezeigt. Für die Lösung ergibt sich bei Flächensymmetrie

$$t = -2C_1 \operatorname{ch}\sqrt{\frac{|m|}{\lambda}}\, x - \frac{\varkappa}{2\lambda}x^2 + C_2, \quad \text{wenn} \quad m > 0,$$

und

$$t = -2C_1 \cos\sqrt{\frac{|m|}{\lambda}}\, x - \frac{\varkappa}{2\lambda}x^2 + C_2, \quad \text{wenn} \quad m < 0;$$

bei Zylindersymmetrie

$$t = -C_1' I_0\left(\sqrt{\frac{|m|}{\lambda}}\, r\right) - \frac{\varkappa}{2\lambda}r^2 + C_2', \quad \text{wenn} \quad m > 0,$$

und

$$t = -C_1' J_0\left(\sqrt{\frac{|m|}{\lambda}}\, r\right) - \frac{\varkappa}{2\lambda}r^2 + C_2', \quad \text{wenn} \quad m < 0,$$

wo I_0 und J_0 die BESSELschen Funktionen darstellen, und C_1, C_1', usw. die aus Randbedingungen zu ermittelnden Konstanten sind. Aus den Lösungsfunktionen — wenn $m < 0$ — geht hervor, daß periodische Funktionen in beiden Fällen die

ursprünglichen nichtperiodischen Lösung ($\varkappa = \text{konst}$) überlagern. In diesem Falle sind die Systeme wahrscheinlich schwingungsfähig, die Erreichbarkeit des stationären Zustandes könnte mittels besonderer Stabilitätsuntersuchung entschieden werden. Wenn $m > 0$, dann liegt die Stabilität auf der Hand. Will man die ARRHENIUSsche Form der Temperaturabhängigkeit der Reaktionsgeschwindigkeit berücksichtigen, so kann die Lösung nicht mit elementaren Funktionen in geschlossener Form gegeben werden.

Wir haben bei der Lösung graphische Methoden herangezogen, diese bedürfen aber noch weitere Diskussionen. Die Untersuchung der Berücksichtigung der Temperaturabhängigkeit von R_i und H_i kann nicht als abgeschlossen betrachtet werden.

* * *

Die Verfasser sind Herrn Dozenten Dr. F. J. GILDE für seine prinzipiellen Ratschläge zu aufrichtigem Danke verpflichtet.

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ИЗУЧЕНИЕ ТЕРМИЧЕСКИХ СВОЙСТВ КОНТАКТ-КАТАЛИТИЧЕСКИХ РЕАКТОРОВ НОВОЙ ГЕОМЕТРИЦЕСКОЙ ФОРМЫ

С. Фени и Л. Месарош

В настоящей работе описаны результаты изучения термических свойств контактно-каталитических реакторов в новой геометрической форме. Самым значительным в этом отношении является аналитическое определение зависимости температуры и места. Имея эти данные критерии макроскопической подобности определены для различных реакторов. Результаты полученные теоретическим путем употребляются для экспериментов.

HETEROGENEOUS CATALYTIC OXIDATION OF FURFURYL ALCOHOL AND BENZYL ALCOHOL IN THE GAS PHASE IN A REACTOR FILLED WITH LEAD OXIDE

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The oxidative decarboxylation reaction of furfuryl and benzyl alcohols in the presence of lead oxide has bean studied. It has been established that in the course of oxidative decarboxylation of furfuryl alcohol, furane and pyrophoric lead are formed. The oxidative decarboxylation of benzyl alcohol at different temperatures resulted in benzene, benzaldehyde and toluene. The increase of temperature favours benzene formation while the amount of toluene decreases.

In our previous papers [1—4] it has been shown that lead oxide is a suitable catalyst for realizing the oxidative decarboxylation of furfurol to furane. The decarboxylation of benzoic acid to benzene is known [5, 6] and several authors have dealt with the heterogeneous catalytic preparation of benzyl alcohol and furfuryl alcohol in gas phase. SABATIER and his coworkers [7, 8] observed that on aluminium oxide catalyst benzyl alcohol yields a resinous product, however, the formed substances have not been studied yet. The formation of dibenzyl ether on the former catalyst has been described as well as the decomposition of this product into toluene and benzaldehyde by ADKINS and FOKERS [9]. According to BARTÓK's [10, 11] investigations benzyl alcohol at lower temperatures yields dibenzyl ether, which undergoing intramolecular dehydrohydrogenation at higher temperature results in toluene and benzaldehyde. The decomposition of dibenzyl ether has been first described by CANNIZZARO, LOWE and ODDO [12—14]. In the course of reaction of furfuryl alcohol and benzyl alcohol on metal catalysts, SULTANOV and his coworkers [15] isolated aldehydes and hydrocarbons.

In the present investigation experiments were carried out to study the oxidative decarboxylation of furfuryl alcohol and benzyl alcohol in the reactor shown in [4]. For the experiments the reactor was filled with lead oxide catalyst and the temperature was 300 °C. By a charging pump furfuryl alcohol was bubbled through the foreheater — where it was vaporized — than the reactor filled with lead oxide. On the surface of the catalyst oxidative decarboxylation occured. Isolation of the formed products was realized partly in coolers connected with the reactor, and partly in the absorption column and gasometer, respectively, joined to the coolers. Separation of the condensed products was carried out by fractionation and by

Table I

Percentage amount and physical constants of products formed during the oxidation of benzyl alcohol. Experiments at different temperatures.

Reactor C°		B.p.	Amount %	n_D^{20}	C %	H %	Products
320—330	1	90	30	1,4989	92,02	7,52	benzene
320—330	4	110—115	25	1,4969	91,00	8,54	toluene
320—330	10	112—114	15	1,5459	79,08	6,18	benzaldehyde
300—310	1	—90	10	1,4985	91,83	7,60	benzene
300—310	4	111—114	35	1,4968	91,42	8,75	toluene
300—310	8	110—114	28	1,5446	79,83	6,49	benzaldehyde
				Physical Constats			
benzene		80,1		1,5014	92,3	7,68	
toluene		110,8		1,4978	91,24	8,76	
benzaldehyde		179,5		1,5463	82,42	5,87	

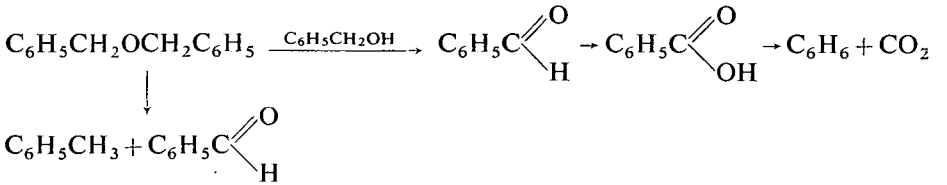
steam desorption of the absorbed products steam.

Study of the oxidative decarboxylation of furfuryl alcohol on lead oxide showed that furane, water and carbon dioxide were formed. Water and unchanged furfuryl alcohol were condensed in the coolers. Furane and carbon dioxide moved in the absorption column and gasometer, respectively. After steam desorption the furane vapors were condensed at −15 °C.

The first step of the reaction is the oxidation of furfuryl alcohol into furfurol. At a considerable rate furfurol can be isolated. The formed furfurol is further transformed according to the known mechanism. Simultaneously with the oxidative decarboxylation pirophorous lead is formed.

Benzyl alcohol was oxidized at a temperature ranging from 300—310 and 320—330 °C. From the separation of the condensed products it was established that at both temperatures the isolated organic phases contained benzene, toluene, benzaldehyde and unchanged benzyl alcohol, while water formed in the course of the reaction in a separate phase. It was further experienced that on raising the temperature the relative amount of toluene and benzaldehyde decreased and the quantity of benzene increased. The supposed mechanism of the reaction involves the formation of benzene in a way similar to the furfuryl alcohol — furane transformation. This is supported by the fact that from the reaction products we have succeeded in isolating

benzaldehyde which may be considered the first product of the oxidation. Chemical reactions are shown by the following scheme.



Quantitative data and physical constants of products formed at different temperatures are shown in Table I. It can be seen in the Table that the amount of toluene is considerable and its formation is the main direction of the reaction at lower temperatures. For the interpretation of the reaction mechanism it is reasonable to suppose that lead oxide, in the first step of the reaction catalyzes the formation of dibenzyl ether in a similar way as aluminium oxide does. On the surface of electrophilic lead oxide toluene and benzaldehyde are formed from dibenzyl ether, likely by a thermal disproportionation of ionic mechanism. As a final result, toluene is formed during the cleavage of an intermediate resulting from intermoleculer anionothropy.

It may also be supposed that in the presence of pirophorous lead there is a reductive cleavage of dibenzyl ether to give toluene. This supposition has to be experimentally proved, sonce it has not been studied so far whether the hydrogenolysis can be catalyzed by pirophorous lead under the given experimental conditions.

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ГЕТЕРОГЕННОЕ КАТАЛИТИЧЕСКОЕ ОКИСЛЕНИЕ ФУРФУРИЛОВОГО И БЕНЗИЛОВОГО АЛКОГОЛЕЙ В РЕАКТОРЕ НАПОЛНЕННОМ ОКИСЬЮ СВИНЦА

Л. Месарош и П. Агоч

Авторами изучалось окислительное декарбоксилирование фурфурилового и бензилового алкоголей в присутствии окиси свинца. Установлено, что в окислительном декарбоксилировании фурфурилового алкогодя получаются фуран и пирофорный свинец. В окислительном декарбоксилировании бензилового алкоголя при различных температурах бензол, альдегид бензола и толуол были изолированы. Увеличивая температуру получается больше бензола и меньше толуола.

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