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THE SELECTION OF THE ATOMIC ORBITALS PLAYING A DETERMINING ROLE IN THE GROUPS FORMING COMPLEXES

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(Received March 21, 1960)

For bonding of the complexes formed by the transition metals the electrons d of the central ion, as well as the outer electrons ($n = 2$) of the complex forming groups are responsible. By means of a half empiric version of the LCAO—MO method it was investigated which states of the electrons of the radicals mentioned above must be taken into account. It was found that the significance of the $2p\sigma$ orbitals is dominating, nevertheless, the $2p\pi$ orbitals cannot be neglected either. The $2s\sigma$ states are, however, of secondary importance.

§ 1. Introduction

The theory of the complexes with covalent bonds was found by PAULING [1] who assumed that the complexes are formed by the localization of the electrons of the radicals into the empty states of the central ion. On the basis of PAULING's suggested theory KIMBALL [2] elaborated all the combinations of atomic orbitals which have to be considered at the bond. WOLFSBERG and HELMHOLZ [3] already deal with some complex ions taking the atomic orbitals of the radicals into consideration, too. The latter authors use the most simple version of the LCAO—MO method and the occuring integrals are calculated from the ionization energies. This method has been used by other authors [4]—[7] too. In the following the methods of WOLFSBERG and HELMHOLZ will be employed. It will be attempted to establish which of the possible orbitals ($2s\sigma$, $2p\sigma$, $2p\pi$) are the dominating ones in the case of complexes of type $\mathrm{Me(CN)}_6^{z-}$ ($\mathrm{Me} = \mathrm{Mn}^{3+}, \mathrm{Fe}^{3+}, \mathrm{Co}^{3+}$).

§ 2. The method of the calculation

The molecular orbitals (MO) of the complex are composed by the linear combinations (LC) of atomic orbitals (AO). The five $3d$, one $4s$ and three $4p$ orbitals of the central ion contribute to this LC. The radicals which turn with their C atoms towards the central ion in the complex contribute pro radical at most with the orbitals one $2s\sigma$, one $2p\sigma$ and two $2p\pi$ of the atomic orbitals of their C atom to the MO's of the complex. In each case the symmetry O_h will be considered and the combinations of the AO's mentioned above belonging to each irreducible representation of the group O_h. Owing to the variation principle the best MO's can be determined by these basic functions. At the calculations the integrals

$$\int \Phi_i^* \Phi_j dt = \mathcal{G}_{ij}, \quad \int \Phi_i^* \mathbf{H} \Phi_i dt = \mathcal{H}_{ii}, \quad \int \Phi_i^* \mathbf{H} \Phi_j dt = \mathcal{H}_{ij} \tag{1}$$

appear, where Φ_i is one of the basic functions mentioned and **H** the Hamiltonian of the problem. Among the integrals (1) $\mathcal{H}_{ii}$ are determined from the ionization energy of the corresponding atomic states and the $\mathcal{H}_{ij}$ are calculated by the formula of WOLFSBERG and HELMHOLZ

$$\mathcal{H}_{ij} = F \mathcal{G}_{ij} \frac{\mathcal{H}_{ii} + \mathcal{H}_{jj}}{2}. \tag{2}$$

In this expression F means a correction parameter which was determined by the calculations concerning the complex of $Me = Cr^{3+}$ so that the empiric results are obtained in the best possible manner and the complexes mentioned in § 1 were calculated with the F values mentioned. The overlap integrals $\mathcal{G}_{ij}$ of the group were determined by means of a previously used approximation [7] assuming a uniform bond intervall 2,00 Å between the central ion and the C atom of the radical.

With the procedure briefly described above three different calculations were carried out. In all three calculations the atomic orbitals mentioned were taken into account.

(a) Taking the three $2p$ orbitals of the atom C among the orbitals of the radicals into account we have altogether 27 orbitals. In the functional space of these 27 atomic orbitals the representation of the group O_h can be decomposed in form

$$\Gamma_{27} = 2A_{1g} + 2E_g + T_{1g} + 3T_{1u} + 2T_{2g} + T_{2u} \tag{3}$$

(as regards denotation see *e.g.* [8]). The calculations relating to $Me = Cr^{3+}$ show that acceptable results can be obtained if the parameter F has the following values

$$F = \begin{cases} 2{,}20 & \text{for } \sigma \text{ bond} \\ 2{,}65 & \text{for } \pi \text{ bond.} \end{cases} \tag{4}$$

The transitions obtained in this manner are collected in cm^{-1} in the columns *a* of the Table.

(b) Among the orbitals of the C atoms of the radicals only taking the orbital $2p\sigma$ into account we have 15 atomic orbitals. The adequate representation of the O_h group in the 15-dimensional functional space can be decomposed in the form

$$\Gamma_{15} = 2A_{1g} + 2E_g + 2T_{1u} + T_{2g}. \tag{5}$$

As in this case only σ bonds appear for the corresponding value of the parameter F in (2)

$$F=2{,}20 \tag{6}$$

can be used. The number of the transitions obtained in this manner decreases and are summarized in the column b of the Table.

Table

Mn^{3+}

a	*b*	*c*	*d*
7340	9370		5600
	12750	14840	
16701		17440	
	25800	21530	
28000		30070	(27000)
29690		30630	30500
33160			(33000)
33400			
37030	37030		(37000)
44700	44700	40430	41000
46750	46750		46000

Fe^{3+}

a	*b*	*c*	*d*
7500		9130	5000
16940	15200		
	19240	18430	
		20880	
23560		23740	
24450	24450	24650	24000
27430	28600	25240	(25000)
31710			(31000)
36150			33000
39210	39210		39000
46310			45500

Co^{3+}

a	*b*	*c*	*d*
7580		7750	6340
		9080	
10890			
15010			
18500	18510		
24290		23740	
		25220	(25000)
31140		30170	
34530			32000
42120	42120		38500
46150	46150		50000

(c) Finally, the orbitals $2s\sigma$ and $2p\sigma$ of the C atoms of the radicals were considered. In this case we have 21 atomic orbitals. The corresponding 21-dimensional representations of the O_h group can be decomposed in the following form

$$\Gamma_{21}=3A_{1g}+3E_g+3T_{1u}+T_{2g}. \tag{7}$$

Now again only the σ bonds play a role but they have now increased in number. For F a value below that of (6) must be taken. According to the calculations concerning $Me = Cr^{3+}$ the value

$$F = 1,50 \tag{8}$$

seems to be the best. The transitions yielded by these calculations are summarized in the columns *c* of the Table.

§ 3. *Discussions*

On the Table it can be seen that in the case of the results of the calculations (b) the transitions corresponding to middle wave numbers (about 30.000 cm^{-1}) are missing, whereas in the case of the results of the calculations (c) the transitions of the higher wave number (about 40.000 cm^{-1}) are lacking. Thus the neglecting of the $2p$ orbitals (calculation (b)) causes the elimination of the transition of middle wave number. If the orbitals $2s$ are taken into consideration (calculation (c)) the transitions of middle wave number appear again but the transitions of higher wave number are shifted from the measurable range. Column *d* of the Table contains the empiric data [9]. The values in brackets show the localization of the inflection points of the absorption curve, the rest of the data that of the maxima of the curve in cm^{-1}. Owing to the observations the complexes in the range 10.000—20.000 cm^{-1} are highly transparent, in spite of this in this range the occurrence of bonds cannot be experimentally ruled out.

Finally, it can be established that the best results are yielded by the calculations (a). Thus the $2s$ orbitals of the radicals are of secondary importance as compared with that of the $2p$ orbitals.

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ИССЛЕДОВАНИЯ ИГРАЮЩИХ ВАЖНУЮ РОЛЬ АТОМНЫХ ОРБИТ ЛИГАНДОВ КОМПЛЕКСНЫХ ИОНОВ

Ф. Й.. Гилде

Ковалентные связы комплексов переходных металлов образуются d-электронами центрального иона и внешними электронами лигандов. С помощью полуэмпирического метода МО-ЛКАО было исследовано, какие орбиты лигандов должны быть расчитаны. По расчетам $2p\sigma$-орбиты оказываются более важными, а $2p\pi$-орбиты также не могут быть оставлены вез внимания. Роли $2s$-орбит не существенны.

CONTRIBUTIONS TO THE GENERAL THEORY OF LCAO-MO METHOD

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The coefficients of the AO's in different MO's belonging to degenerate energy states and the physical quantities dependent on these coefficients, as well, are not unequally determined, but are dependent on diophantic parameters of uncertainty. It will be proved that: (*i*) the diophantic parameters of uncertainty refer to rotations in the eigenspace of MO's belonging to degenerate energy states; (*ii*) in the case of closed shells of MO's the physical quantities are independent of the diophantic parameters of uncertainty; (*iii*) the physical quantities in the case of non-closed electron shells of MO's are only independent of the diophantic parameters of uncertainty if the "number of electrons" is the same on the different MO's corresponding to the same energy.

§ 1. Introduction

Owing to the great success of the molecular orbital (MO) method — particularly if one considers the MO's as linear combinations of atomic orbitals (LCAO-MO method) — in dealing with the practical problem of quantum chemistry, the general theory of the LCAO-MO method has been investigated in detail by several authors [1]—[5]. Nevertheless, in order to solve an actual problem of quantum chemistry by the LCAO-MO method, one of us (M. I. B.) has suggested a practical problem which may also be of interest from the point of view of the general theory, especially in the case of non-closed electron shells (in terms of ROOTHAAN [5]). It is well-known on the one hand that the coefficients of atomic orbitals (AO) in different MO's belonging to degenerate energy states are not unequally determined and on the other hand that such important quantities as the electron densities and the bond orders, respectively, are dependent on these coefficients of the AO's. As a matter of fact, it should be of interest in which cases these quantities are not influenced by the uncertainty of the coefficients of AO's in MO's. It will be proved below that (*i*) the uncertainty of the electron density as well as that of the bond order due to the uncertainty of the coefficients of AO's in MO's for closed shells are automatically eliminated; (*ii*) in the case of

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non-closed shells in order to remove the same difficulty the equalization of the "number" of electrons among the MO's belonging to the same energy will be proposed.

§ 2. *Reinvestigation of benzene as a model*

To prepare the general treatment let us briefly investigate the well-known problem of benzene. Taking only the π electrons of the C atoms of benzene into account, the MO's of the π electrons will be denoted by

$$\psi=\sum_{r=1}^{6} c_r \Phi_r, \tag{2, 1}$$

where the index r of the AO's refers to atom r $(r=1,2,\ldots,6)$. The energy of the MO's as well as the coefficients of the AO's in these MO's can be obtained by solution of the system of linear equations:

$$\sum_{r=1}^{6} c_r(\mathcal{H}_{sr}-E\mathcal{S}_{sr})=0, \qquad (s=1,2,\ldots,6) \tag{2, 2}$$

with

$$\mathcal{H}_{sr}=\int \Phi_s^* H \Phi_r d\tau, \quad \mathcal{S}_{sr}=\int \Phi_s^* \Phi_r d\tau, \tag{2, 3}$$

where H denotes the Hamiltonian of the system. Without any essential specialization of the problem suggested, one can only deal with the well-known approximation of the LCAO-MO method:

$$\mathcal{S}_{sr}=\delta_{sr}, \quad \mathcal{H}_{sr}=\begin{cases}\alpha & \text{for} \quad s=r,\\ \beta & \text{for} \quad s=r\pm 1,\\ 0 & \text{otherwise.}\end{cases} \tag{2, 4}$$

The solution of equation (2, 2) leads to four energy values, two of which belong to doubly degenerated energy states. For sake of perspicuity of the following paragraphs the energy values as well as the MO's, *i. e.* electron shells, will be denoted as follows:

$$E_{i,\varrho}: \quad \begin{matrix} E_{1,1}=\alpha+2\beta, & E_{2,1}=E_{2,2}=\alpha+\beta, \\ E_{3,1}=E_{3,2}=\alpha-\beta, & E_{4,1}=\alpha-2\beta, \end{matrix} \tag{2, 5}$$

$$\psi_{i,\varrho}=\sum_{r=1}^{6} c_{ri,\varrho}\Phi_r. \qquad (i=1,\ldots,4;\ \varrho=1,2) \tag{2, 6}$$

Note that the first index of $c_{ri,\varrho}$ (as well as in the following s, t, u) refers to the AO's, the second one (as in the following j, k, l) to the MO's; by the third one (as in the following by σ, τ) the different MO's are denoted belonging to the degenerated energy $E_{i,\varrho}$ and $\varrho=1,2,\ldots,f_i$, where f_i refers to the order of degeneracy of energy $E_{i,\varrho}$.

Owing to the orthonormality of the MO's belonging to different electron shells:

$$\int \psi^*_{i,\sigma}\psi_{j,\varrho}\,d\tau = \delta_{ij} \tag{2, 7}$$

and (2, 4), we have

$$\sum_{r=1}^{6} c^*_{ri,\varrho}c_{rj,\sigma} = \delta_{ij}\,. \tag{2, 8}$$

In order to determine the MO's *i. e.* the coefficients of the AO's in the MO's explicitly, one can proceed by the following two methods:

2. 1. Taking the equations (2, 2) and (2, 8) into account in the cases $i=1$ and $i=4$ the coefficients $c_{ri,\varrho}$ can be immediately obtained. However, in the case of the degenerated energy states $i=2$ and $i=3$ our equations (2, 2) and (2, 8) do not provide equations enough for the determination of $c_{ri,\varrho}$'s. As matters stand, one can use [6], *e g.*, for $i=2$ the following method:

Due to (2, 2) for the $c_{r2,\varrho}$ the relations

$$c_{12,\varrho} = -c_{42,\varrho}; \quad c_{22,\varrho} = -c_{52,\varrho}; \quad c_{32,\varrho} = -c_{62,\varrho} = -c_{12,\varrho} + c_{22,\varrho} \tag{2, 9}$$

can be obtained. Considering also the equations (2, 8) we have 10 equations for the 12 unknown coefficients ($\varrho = 1, 2$). Let the uncertainty be expressed by the diophantic parameters λ_2 and μ_2:

$$\begin{aligned} c_{12,1} &= -c_{42,1}, & c_{12,2} &= -c_{42,2} = (1-\mu_2)c_{22,2}, \\ c_{22,1} &= -c_{52,1} = \lambda_2 c_{12,1}, & c_{22,2} &= -c_{52,2}, \\ c_{32,1} &= -c_{62,1} = (\lambda_2 - 1)c_{12,1}; & c_{32,2} &= -c_{62,2} = \mu_2 c_{22,2}. \end{aligned} \tag{2, 10}$$

Table I*

r	$i=1$	$i=2$		$i=3$		$i=4$
		$\varrho=1$	$\varrho=2$	$\varrho=1$	$\varrho=2$	
1	$6^{-1/2}$	k	$3^{-1/2}(2\lambda_2-1)k$	$-3^{-1/2}(2\lambda_3+1)k'$	k'	$6^{-1/2}$
2	$6^{-1/2}$	$\lambda_2 k$	$3^{-1/2}(\lambda_2-2)k$	$3^{-1/2}(\lambda_3+2)k'$	$\lambda_3 k'$	$-6^{-1/2}$
3	$6^{-1/2}$	$(\lambda_2-1)k$	$-3^{-1/2}(\lambda_2+1)k$	$3^{-1/2}(\lambda_3-1)k'$	$-(1+\lambda_3)k'$	$6^{-1/2}$
4	$6^{-1/2}$	$-k$	$-3^{-1/2}(2\lambda_2-1)k$	$-3^{-1/2}(2\lambda_3+1)k'$	k'	$-6^{-1/2}$
5	$6^{-1/2}$	$-\lambda_2 k$	$-3^{-1/2}(\lambda_2-2)k$	$3^{-1/2}(\lambda_3+2)k'$	$\lambda_3 k'$	$6^{-1/2}$
6	$6^{-1/2}$	$-(\lambda_2-1)k$	$3^{-1/2}(\lambda_2+1)k$	$3^{-1/2}(\lambda_3-1)k'$	$-(1+\lambda_3)k'$	$-6^{-1/2}$

* In Table I $k = (4\lambda_2^2 - 4\lambda_2 + 4)^{-1/2}$ and $k' = (4\lambda_3^2 - 4\lambda_3 + 4)^{-1/2}$

Since, the different MO's belonging to the same electron shell can be orthonormalized one can replace (2, 8) by

$$\sum_{r=1}^{6} c^*_{ri,\sigma} c_{rj,\varrho} = \delta_{ij}\delta_{\sigma\varrho}, \qquad (2, 11)$$

therefore, our system of equations is completed by

$$c_{12,1}c_{22,2}[1-\mu_2+\lambda_2+\mu_2(\lambda_2-1)]=0 \qquad (c_{12,1}c_{22,2}\neq 0) \quad (2, 12)$$

and, finally, we have

$$\mu_2 = -\frac{\lambda_2+1}{\lambda_2-2}. \qquad (2, 13)$$

This means that the coefficients of the AO's in the MO's are only dependent on λ_i. (Table I.)

2.2. For sake of simplicity one can use the method of group theory. Taking, *e.g.*, the C_{3V} symmetry of benzene into consideration, then the 6-dimensional representation Γ in the linear space of AO's is splitting into

$$\Gamma = 2A_1 + 2E. \qquad (2, 14)$$

(Concerning the notation cf. *e.g.* [7]). The corresponding new basic vectors are

$$\begin{aligned} \varphi^{(A_1)} &= 1/\sqrt{3}(\Phi_1+\Phi_2+\Phi_5); & \varphi^{(A_1')} &= 1/\sqrt{3}(\Phi_2+\Phi_4+\Phi_5); \\ \varphi_1^{(E)} &= 1/\sqrt{2}(\Phi_2-\Phi_6), & \varphi_2^{(E)} &= 1/\sqrt{6}(2\Phi_4-\Phi_3-\Phi_6); \quad (2, 15) \\ \varphi_1^{(E')} &= 1/\sqrt{2}(\Phi_2-\Phi_5), & \varphi_2^{(E')} &= 1/\sqrt{6}(\Phi_3+\Phi_5-2\Phi_1). \end{aligned}$$

Naturally, the energy values are the same ones as in (2. 5). As to the determination of $c_{ri,\varrho}$ one can use our equation (2, 2) and (2, 8) again, but, of

Table II

r	$i=1$	$i=2$		$i=3$		$i=4$
		$\varrho=1$	$\varrho=2$	$\varrho=1$	$\varrho=2$	
1	$6^{-1/2}$	$3^{-1/2}$	0	0	$3^{-1/2}$	$6^{-1/2}$
2	$6^{-1/2}$	$12^{-1/2}$	-2^{-1}	2^{-1}	$-12^{-1/2}$	$-6^{-1/2}$
3	$6^{-1/2}$	$-12^{-1/2}$	-2^{-1}	-2^{-1}	$-12^{-1/2}$	$6^{-1/2}$
4	$6^{-1/2}$	$-3^{-1/2}$	0	0	$3^{-1/2}$	$-6^{-1/2}$
5	$6^{-1/2}$	$-12^{-1/2}$	2^{-1}	2^{-1}	$-12^{-1/2}$	$6^{-1/2}$
6	$6^{-1/2}$	$12^{-1/2}$	2^{-1}	-2^{-1}	$-12^{-1/2}$	$-6^{-1/2}$

course, the AO's have to be replaced by the basic vectors (2, 15). The $c_{ri,\varrho}$ are in this case unambiguous (Table II), and the relations of orthonormality (2, 11) are automatically fulfilled.

Taking other symmetry groups of benzene into account (*e.g.* C_{2V}, D_{6h} [8]) for $c_{ri,\varrho}$ exactly the same table as Table II can be obtained.

One observes immediately that Table II with $\lambda_2 = 1/2$ and $\lambda_3 = -1/2$ can be derived from Table I.

§ 3. *Electron density and bond order*

As is well-known based on the LCAO-MO method several quantities characterizing the physical and chemical properties of molecules (in the following *physical quantities*) can be dealt with. Owing to a previous investigation of C. A. Coulson and H. C. Longuet-Higgins [4] all of these physical quantities can be derived from the *electron density at the atom r*

$$q_r = \sum_i \sum_{\varrho=1}^{f_i} n_{i,\varrho} c^*_{ri,\varrho} c_{ri,\varrho} \tag{3, 1}$$

and from the *bond order between the atoms r and s*

$$p_{rs} = \sum_i \sum_{\varrho=1}^{f_i} n_{i,\varrho} c^*_{ri,\varrho} c_{si,\varrho}, \tag{3, 2}$$

where $n_{i,\varrho}$ refers to the number of electrons in MO $\psi_{i,\varrho}$ and the sum has to be extended over all electron shells of the MO's.

Owing to the fact that the coefficients of AO's in MO's with $f_i > 1$ are depending on λ_i, *i. e.*

$$c_{ri,\varrho} = c_{ri,\varrho}(\lambda_i), \tag{3, 3}$$

one may generally expect that the electron density as well as the bond order are also dependent on λ_i's:

$$q_r = q_r(\lambda_1, \lambda_2, \ldots) \quad \text{and} \quad p_{rs} = p_{rs}(\lambda_1, \lambda_2, \ldots), \tag{3, 4}$$

respectively.

In spite of this one can observe that, *e. g.*, for benzene

$$q_r = 1 \quad \text{and} \quad p_{rs} = \frac{2}{3} \qquad (s = r+1,\ r = 1, 2, \ldots, 6). \tag{3, 5}$$

This means that the electron density and the bond order do not depend on the diophantic parameter of uncertainty introduced.

However, for the positive molecule-ion of benzene having a π-electron system of only five electrons on suggesting the occupation of the energy states by electrons as

$$n_{1,1} = 2, \quad n_{2,1} = 2, \quad n_{2,2} = 1, \quad n_{3,1} = n_{3,2} = n_{4,1} = 0, \tag{3, 6a}$$

and as

$$\tilde{n}_{1,1}=2, \quad \tilde{n}_{2,1}=1, \quad \tilde{n}_{2,2}=2, \quad \tilde{n}_{3,1}=\tilde{n}_{3,2}=\tilde{n}_{4,1}=0, \qquad (3,6b)$$

respectively, the electron densities at the different atoms

$$q_1=q_4=\frac{1}{12}\,\frac{8\lambda_2^2-8\lambda_2+11}{\lambda_2^2-\lambda_2+1}, \quad q_2=q_3=q_5=q_6=\frac{1}{12}\,\frac{11\lambda_2^2-8\lambda_2+8}{\lambda_2^2-\lambda_2+1}, \qquad (3,7a)$$

and

$$\tilde{q}_1=\tilde{q}_4=\frac{1}{4}\,\frac{4\lambda_2^2-4\lambda_2+3}{\lambda_2^2-\lambda_2+1}, \quad \tilde{q}_2=\tilde{q}_3=\tilde{q}_5=\tilde{q}_6=\frac{1}{4}\,\frac{3\lambda_2^2-4\lambda_2+4}{\lambda_2^2-\lambda_2+1}, \qquad (3,7b)$$

respectively, can be obtained, without having any physical reason to distinguish among the two distributions proposed. Fig. 1 refers to both models (3, 6a) and (3, 6b), respectively, for $\lambda=1/2$.

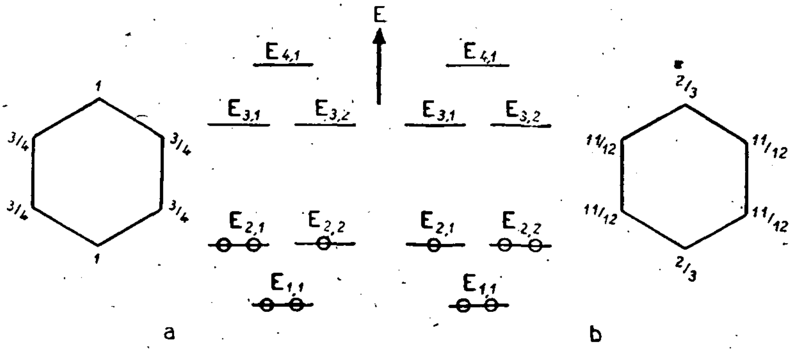

Fig. 1

Concerning the bond orders one can obtain similar results for benzene as well as for the molecule-ion of benzene too.

It seems as if in the case of the electron shells of MO's filled up by electrons and in that of electron shells of MO's without electrons (benzene), respectively, the electron density as well as the bond order are independent of the diophantic parameters of uncertainty introduced; however, in the case of electron shells of MO's which are not filled up by electrons (molecule-ion of benzene) both quantities are dependent on the diophantic parameters of uncertainty without any physical reason. Whether these conclusions can be generally suggested will be discussed in the next paragraph.

§ 4. Investigation and removal of the uncertainty

In order to really understand the meaning of the uncertainty mentioned in the previous two paragraphs let us consider the functional space of MO's. First, it seems suitable to formulate the problem in the case of benzene for $i=2$ again.

4. 1. The functional space of the corresponding MO's — being the eigenspace of energy $E_{2,\varrho}$ — is in this case a two-dimensional subspace of all the MO's. One can use arbitrary pairs of functions of this eigenspace as basic vectors fulfilling (2, 11). Let us consider the MO's

$$\begin{aligned}\psi_{2,1} &= 1/\sqrt{3}\left(\Phi_1+\frac{1}{2}\Phi_2-\frac{1}{2}\Phi_3-\Phi_4-\frac{1}{2}\Phi_5+\Phi_6\right),\\ \psi_{2,2} &= 1/2(-\Phi_2-\Phi_3+\Phi_5+\Phi_6),\end{aligned} \tag{4, 1}$$

which can be obtained by the method mentioned in *2. 1.* In view of fact that the basic vectors (4, 1) are real, by a rotation with angle α another arbitrary basis system

$$\begin{aligned}\psi'_{2,1} &= \psi_{2,1}\cos\alpha+\psi_{2,2}\sin\alpha\\ \psi'_{2,2} &= -\psi_{2,1}\sin\alpha+\psi_{2,2}\cos\alpha\end{aligned} \tag{4, 2}$$

can be derived from the basis system (4, 1).

One may observe, of course, a correspondence between the diophantic parameter of uncertainty λ_2 and the angle α of rotation and it can be proved that

$$\lambda_2=\frac{1}{2}(1\pm\sqrt{3}\,\mathrm{tg}\,\alpha) \tag{4, 3}$$

is valid for all values of α. By the usual limiting process one can easily see that the coefficients of the AO's in MO's are finite also for the case $\alpha=\pi/2, 3\pi/2$.

Due to these considerations the diophantic parameter of uncertainty gets an immediate geometrical meaning.

4. 2. Now, the question has to be investigated in which cases the diophantic parameters of uncertainty occur? Taking the considerations of *4. 1.* into account it looks as *if and only if the quantum mechanical problem has degenerated energy states*. Namely, on the one hand, only the eigenspace of degenerated energy states are multi-dimensional and on the other hand, only in this case can different orthonormal basis systems in the eigenspace of MO's — connected by orthogonal transformations — be introduced. Finally, these orthogonal transformations may be characterized by diophantic parameters of uncertainty.

In the course of our above considerations we have only explicitly considered the double-degenerated energy state $E_{2,\varrho}$ $(\varrho=1, 2)$ of benzene. One can readily see that in the case of a f_i-dimensional eigenspace of energy $E_{i,\varrho}$ $(\varrho=1, 2, \ldots, f_i)$ the number of diophantic parameters of uncertainty is the same as the number of parameters of the f_i-dimensional rotational group.

Let us consider the f_i-dimensional eigenstate of the f_i-fold-degenerated energy state $E_{i,\varrho}$ $(\varrho=1, 2, \ldots, f_i)$ as well as two different basis systems $\{\psi_{i,\varrho}\}$ and $\{\psi'_{i,\varrho}\}$, respectively. They are connected by orthogonal transformations $\mathbf{S}=(S_{\varrho\sigma})$:

$$\psi'_{i,\varrho}=\sum_{\sigma=1}^{f_i} S_{\varrho\sigma}\psi_{i,\sigma} \tag{4, 4}$$

with

$$\sum_{\varrho=1}^{f_i} S_{\sigma\varrho} S_{\tau\varrho} = \delta_{\sigma\tau}. \tag{4, 5}$$

Considering that on the one hand due to (2, 6) and (3, 3) one can generally write

$$\begin{aligned} \psi_{i,\sigma} &= \sum_{r=1}^{N} c_{ri,\sigma}(\lambda_i)\,\Phi_r, \\ \psi'_{i,\varrho} &= \sum_{r=1}^{N} c_{ri,\varrho}(\lambda'_i)\,\Phi_r \end{aligned} \tag{4, 6}$$

and on the other hand taking (4, 4) into account one has

$$\psi'_{i,\varrho} = \sum_{\sigma=1}^{f_i} S_{\varrho\sigma} \sum_{r=1}^{N} c_{ri,\sigma}(\lambda_i)\,\Phi_r = \sum_{r=1}^{N} \sum_{\sigma=1}^{f_i} S_{\varrho\sigma} c_{ri,\sigma}(\lambda_i)\,\Phi_r. \tag{4, 7}$$

Thus one can immediately obtain:

$$c_{ri,\varrho}(\lambda'_i) = \sum_{\sigma=1}^{f_i} S_{\varrho\sigma} c_{ri,\sigma}(\lambda_i), \tag{4, 8}$$

where N refers to the number of the AO's of the problem considered, furthermore λ_i and λ'_i denote the set of diophantic parameters of uncertainty. It may be observed in this way in what manner the uncertainty can be represented by the matrix instead of the diophantic parameters.

4. 3. Owing to the definitions of the electron density (3, 1) and that of bond order (3, 2), for investigation of the dependence of physical quantities on the diophantic parameters of uncertainty it will be enough to deal with the bond order:

$$\begin{aligned} p'_{rs} &= \sum_i \sum_{\varrho=1}^{f_i} n_{i,\varrho} c^*_{ri,\varrho}(\lambda'_i) c_{si,\varrho}(\lambda'_i) = \\ &= \sum_i \sum_{\sigma=1}^{f_i} \sum_{\tau=1}^{f_i} c^*_{ri,\sigma}(\lambda_i) c_{ri,\tau}(\lambda_i) \sum_{\varrho=1}^{f_i} n_{i,\varrho} S_{\varrho\sigma} S_{\varrho\tau}. \end{aligned} \tag{4, 9}$$

It can be proved that *the bond order and the physical quantities are only independent of the diophantic parameters of uncertainty if the number of electrons* $n_{i,\varrho}$ *does not depend on* ϱ, *i. e. if the "number" of electrons is the same on the different MO's corresponding to the same energy* E_i.

Namely, for

$$n_{i,\varrho} = n_i = \text{const (dependent on } i) \tag{4, 10}$$

due to (4, 9) and (4, 5)

$$p'_{rs} = \sum_i \sum_{\sigma=1}^{f_i} \sum_{\tau=1}^{f_i} c^*_{ri,\sigma}(\lambda_i) c_{si,\tau}(\lambda_i) n_i \delta_{\sigma\tau} = \\ = \sum_i \sum_{\sigma=1}^{f_i} n_i c^*_{ri,\sigma}(\lambda_i) c_{si,\sigma}(\lambda_i) = p_{rs} \qquad (4, 11)$$

can be obtained.

4. 4. In order to summarize the physical conclusions of the above results it looks as if the guess suggested at the end of *§ 3.* would be generally proved:

(*i*) *in the case of closed electron shells of MO's the physical quantities are independent of the diophantic parameters of uncertainty, i. e. of the choice of the basis systems in the different subspaces of MO's.*

Namely, in this case the $n_{i,\varrho}$'s are either 2 or 0 and, of course, the condition (4, 10) is fulfilled.

Owing to this result, a remark of Appendix 2 of COULSON and LONGUET-HIGGINS's paper [4] seems to be unnecessary, since, that paper refers only to closed shells.

(*ii*) *in the case of non-closed electron shells of MO's to render possible the independence of physical quantities from the diophantic parameters of uncertainty the "number" of electrons must be the same on the different MO's corresponding to the same energy.*

Consider the example of benzene again. In spite of (3, 6a) and (3, 6b) we have

$$n_{1,1} = 2, \quad n_{2,1} = n_{2,2} = 1{,}5, \quad n_{3,1} = n_{3,2} = n_{4,1} = 0. \qquad (4, 12)$$

One can immediately see that in this case

$$q_i = 5/6 \qquad (i = 1, 2, \ldots, 6). \qquad (4, 13)$$

It looks as if the suggested solution of the problem might be accepted also from the physical point of view, namely, in the case of unperturbed systems one has not any argument to expect some asymmetry in the electron density of the molecules *etc.*, except if the asymmetry mentioned would be based on any physical reason.

Furthermore, it is well known that — according to MCCONNEL's theory of paramagnetic resonance for aromatic systems — the distances of hyperfine structure lines of protons are dependent on the electronic densities at the C atoms. However, in such cases it was not observed so far that any difference between the hyperfine structure lines would have occured. As a matter of fact, our proposal based on quite other arguments is supported by these experimental evidences too.

4. 5. Finally, we have to consider the generalizations of the version of the LCAO-MO method mentioned. The generalization means, *e. g.*, that at the approximation of higher orders some of our suppositions (2, 4) have to be changed. Due to WIGNER's results [9] — although the energy values and the coefficients of AO's in MO's as well can be modified — the degeneration induced by the symmetry of the molecules, the so-called *normal degeneration*, cannot be eliminated. This means, however, that the problem treated above occurs in general cases too and it can immediately be proved that our above considerations can be repeated without any difficulty.

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ЗАМЕЧАНИЯ ОБ ОБЩЕЙ ТЕОРИИ МЕТОДА МО-ЛКАО

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Коэфициенты атомных орбит в различных молекулярных орбитах, относящихся к вырожденному значению энергии, и физические величины, зависящие от этих коэфициентов, неоднозначны, а они зависят от параметров неопределенности *Диофанта*. Было показано: что (I) эти параметры *Диофанта* связаны с поворотами собственного поля, относящегося к вырожденному значению энергии; и что (II) физические величины, в случае занятых МО, не зависят от параметров *Диофанта*; и что (III) физические величины, в случае не совсем занятых МО, только тогда независимы от параметров *Диофанта*, когда число электронов является тождественным для различных МО, относящихся к вырожденному значению энергии.

ÜBER DIE BOSE-STATISTIK IN DER RELATIVITÄTSTHEORIE

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Es wird das relativistische, entartete, idealisierte Korpuskelgas in der BOSE-Statistik behandelt. In den Fällen verschiedener Entartungen — $A<1$ und $A=1$ — werden die gesamte Energie des Systems und die Zustandgleichung angegeben. Es wurde weiterhin festgestellt, daß die bekannte Formel für den Gasdruck in der EINSTEINschen Gastheorie: $p=\frac{2}{3}\frac{u-u_0}{V}$ beim relativistischen, entarteten Gase nicht gültig ist.

1. *Einleitung*

W. GLASER [1] und D. S. KOTHARI—B. N. SING [2] haben sich mit der Untersuchung eines der BOSE-Statistik unterliegenden, relativistischen Korpuskelgases beschäftigt. Sie haben festgestellt, daß bei vollständiger Entartung die Teilchendichte eines idealen Gases von relativistischen Korpuskeln verschwindender Ruhmasse einen maximalen Wert annimmt und beim Überschreiten dieses maximalen Wertes sich der Überschuß des Gases nach der EINSTEINschen Annahme kondensiert und mit seinem Kondensat in thermodynamischen Phasengleichgewicht stehen wird. Die Gesetze des Dampfdruckes dieses gesättigten idealen Gases gehen in die Gesetze der Hohlraumstrahlung über.

Beim Angeben der Zustandgleichung benutzen diese Verfasser HANKELsche Funktionen als Lösungen der BESSELschen Differentialgleichung. In dieser Arbeit wird die gesamte Energie und die Zustandgleichung des Systems in der Form einer Potenzreihe angegeben. Diese Gleichungen werden in den Fällen $A<1$ und $A=1$ für endliche und verschwindende Ruhmasse aufgeschrieben und so wird festgestellt, daß die bekannte Formel für den Gasdruck in der EINSTEINschen Gastheorie: $p=\frac{2}{3}\frac{u-u_0}{V}$ beim relativistischen, entarteten Gase nicht gültig ist.

2. *Die relativistische* BOSE-*Statistik*

Betrachten wir ein idealisiertes Korpuskelgas von Volumen V und der Temperatur T. Die relativistische BOSEsche Zustandgleichung hat nach den obigen Verfassern die folgende Form:

$$dn=n(\varepsilon)d\varepsilon=\frac{4\pi V}{h^3c^3}\frac{\varepsilon(\varepsilon^2-\varepsilon_0^2)^{1/2}d\varepsilon}{\dfrac{\exp(\varepsilon/kT)}{A}-1}, \tag{1}$$

wo ε die Energie eines Teilchens, ε_0 die Ruhenergie und $A=\exp(-\alpha)$ den Entartungsparameter bedeuten. (1) gibt übrigens die Anzahl der Teilchen im V mit Energien zwischen ε und $\varepsilon+d\varepsilon$ an. Da dn immer positiv sein muß und ε/kT beliebig kleine Werte annehmen kann, darf A sich zwischen null und 1 ändern. Wenn $A=1$ erreicht wird, sagt man, das Gas ist vollständig entartet.

Wenn man annimmt, daß zwischen den Gasmolekeln keinerlei Kräfte wirken, ist die gesamte Energie des betrachteten Systems:

$$U=\frac{4\pi V}{h^3c^3}\int_{\varepsilon_0}^{\infty}\frac{\varepsilon^2(\varepsilon^2-\varepsilon_0^2)^{1/2}d\varepsilon}{\dfrac{\exp(\varepsilon/kT)}{A}-1}=\frac{4\pi V}{h^3c^3}\int_{\varepsilon_0}^{\infty}\frac{\varepsilon^2(\varepsilon^2-\varepsilon_0^2)^{1/2}A\exp(-\varepsilon/kT)d\varepsilon}{1-A\exp(-\varepsilon/kT)}. \tag{2}$$

Da die Ruhenergie im allgemeinen einen sehr kleinen Wert hat, kann man annehmen, daß $\frac{\varepsilon_0}{\varepsilon}\ll 1$ ist und so kann man die $(\varepsilon^2-\varepsilon_0^2)^{1/2}=\varepsilon\left(1-\frac{\varepsilon_0^2}{\varepsilon^2}\right)\sim\varepsilon-\frac{\varepsilon_0^2}{2}$ Substitution vollenden:

$$U=\frac{4\pi V}{h^3c^3}\int_{\varepsilon_0}^{\infty}\frac{\varepsilon^3d\varepsilon}{\dfrac{\exp(\varepsilon/kT)}{A}-1}-\frac{2\pi V\varepsilon_0^2}{h^3c^3}\int_{\varepsilon_0}^{\infty}\frac{\varepsilon d\varepsilon}{\dfrac{\exp(\varepsilon/kT)}{A}-1}. \tag{3}$$

Im Falle $A\leqq 1$ läßt sich der Integrand in folgende Potenzreihe entwickeln:

$$\begin{aligned}U=\frac{4\pi V}{h^3c^3}\sum_{l=1}^{\infty}A^l\int_{\varepsilon_0}^{\infty}\varepsilon^3\exp\left(-\frac{l\varepsilon}{kT}\right)d\varepsilon-\\-\frac{2\pi V\varepsilon_0^2}{h^3c^3}\sum_{l=1}^{\infty}A^l\int_{\varepsilon_0}^{\infty}\varepsilon\exp\left(-\frac{l\varepsilon}{kT}\right)d\varepsilon=\\=\frac{4\pi V}{h^3c^3}(kT)^4\sum_{l=1}^{\infty}\frac{A^l}{l^4}B_l'-\frac{2\pi V\varepsilon_0^2}{h^3c^3}(kT)^2\sum_{l=1}^{\infty}\frac{A^l}{l^2}B_l'',\end{aligned} \tag{4}$$

wo

$$B_l' = \exp\left(-\frac{l\varepsilon_0}{kT}\right)\left[\left(\frac{l\varepsilon_0}{kT}\right)^3 + 3\left(\frac{l\varepsilon_0}{kT}\right)^2 + 6\left(\frac{l\varepsilon_0}{kT}\right) + 6\right], \tag{5}$$

$$B_l'' = \exp\left(-\frac{l\varepsilon_0}{kT}\right)\left[\left(\frac{l\varepsilon_0}{kT}\right) + 1\right]$$

sind.

Im Falle verschwindender Ruhmasse ist:

$$U = \frac{24\pi V}{h^3c^3}(kT)^4 \sum_{l=1}^{\infty} \frac{A^l}{l^4}. \tag{6}$$

Zur Bestimmung der relativistischen Zustandgleichung gehen wir von der BERNOULLIschen Gleichung des Gasdruckes aus [3]:

$$p = \frac{1}{3}\varrho m \overline{v^2}, \tag{7}$$

wo ϱ die Anzahl der Teilchen pro cm^3 bedeutet. Auf Grund $V\varrho d\varepsilon = dn$ kann (7) in folgender Weise verallgemeinert werden:

$$pV = \frac{1}{3}\int m v^2 dn. \tag{8}$$

Aber

$$m v^2 = \frac{m_0 v^2}{(1-\beta^2)^{1/2}} = \frac{\varepsilon^2 - \varepsilon_0^2}{\varepsilon} \tag{9}$$

und so ist:

$$p = \frac{4\pi}{3h^3c^3}\int_{\varepsilon_0}^{\infty} \frac{(\varepsilon^2-\varepsilon_0^2)^{3/2} d\varepsilon}{\frac{\exp(\varepsilon/kT)}{A} - 1} = \frac{4\pi}{3h^3c^3}\int_{\varepsilon_0}^{\infty} \frac{(\varepsilon^2-\varepsilon_0^2)^{3/2} A \exp(-\varepsilon/kT) d\varepsilon}{1 - A\exp(-\varepsilon/kT)}. \tag{10}$$

Mit partieller Integration erhält man

$$p = -\frac{4\pi kT}{h^3c^3}\int_{\varepsilon_0}^{\infty} \log[1 - A\exp(-\varepsilon/kT)]\varepsilon(\varepsilon^2-\varepsilon_0^2)^{1/2} d\varepsilon, \tag{11}$$

da

$$\left[(\varepsilon^2-\varepsilon_0^2)^{3/2} kT \log(1 - A\exp(-\varepsilon/kT))\right]_{\varepsilon_0}^{\infty} = 0 \text{ ist.} \tag{12}$$

Gemäß der Gleichung

$$\log[1 - A\exp(-\varepsilon/kT)] = -\sum_{l=1}^{\infty} \frac{A^l}{l}\exp\left(-\frac{l\varepsilon}{kT}\right) \tag{13}$$

folgt:

$$\begin{aligned} p &= \frac{4\pi}{h^3c^3}(kT)\sum_{l=1}^{\infty}\frac{A^l}{l}\int_{\varepsilon_0}^{\infty}\varepsilon^2\exp\left(-\frac{l\varepsilon}{kT}\right)d\varepsilon - \\ &\quad - \frac{2\pi\varepsilon_0^2}{h^3c^3}(kT)\sum_{l=1}^{\infty}\frac{A^l}{l}\int_{\varepsilon_0}^{\infty}\exp\left(-\frac{l\varepsilon}{kT}\right)d\varepsilon = \\ &= \frac{4\pi}{h^3c^3}(kT)^4\sum_{l=1}^{\infty}\frac{A^l}{l^4}C_l' - \frac{2\pi\varepsilon_0^2}{h^3c^3}(kT)^2\sum_{l=1}^{\infty}\frac{A^l}{l^2}C_l'', \end{aligned} \tag{14}$$

wo

$$C_l' = \exp\left(-\frac{l\varepsilon_0}{kT}\right)\left[\left(\frac{l\varepsilon_0}{kT}\right)^2 + 2\left(\frac{l\varepsilon_0}{kT}\right) + 2\right], \tag{15}$$

$$C_l'' = \exp\left(-\frac{l\varepsilon_0}{kT}\right)$$

sind.

Im Falle verschwindender Ruhmasse ergibt sich:

$$p = \frac{8\pi}{h^3c^3}(kT)^4\sum_{l=1}^{\infty}\frac{A^l}{l^4}. \tag{16}$$

Mit vergleichen (6) mit (12) erhalten wir die folgende Gleichung

$$p = \frac{U}{3V}. \tag{17}$$

Wenn das Gas vollständig entartet ist, nehmen dieselben Gleichungen die folgende Form an:

$$U = \frac{4\pi V}{h^3c^3}(kT)^4\sum_{l=1}^{\infty}\frac{1}{l^4}B_l - \frac{2\pi V\varepsilon_0^2}{h^3c^3}(kT)^2\sum_{l=1}^{\infty}\frac{1}{l^2}B_l'', \tag{18}$$

$$p = \frac{4\pi}{h^3c^3}(kT)^4\sum_{l=1}^{\infty}\frac{1}{l^4}C_l' - \frac{2\pi\varepsilon_0^2}{h^3c^3}(kT)^2\sum_{l=1}^{\infty}\frac{1}{l^2}C_l''. \tag{19}$$

Wegen

$$\sum_{l=1}^{\infty}\frac{1}{l^4} = \frac{\pi^2}{90} \quad \text{und} \quad \sum_{l=1}^{\infty}\frac{1}{l^2} = \frac{\pi^2}{6} \tag{20}$$

erhalten wir, wenn die Ruhmasse außerordentlich klein ist, folgende Gleichungen:

$$U = \frac{4\pi^5 V}{15h^3c^3}(kT)^4, \tag{21}$$

$$p = \frac{4\pi^5}{45h^3c^3}(kT)^4, \tag{22}$$

das heißt

$$p=\frac{U}{3V}. \tag{23}$$

Auf Grund unserer Gleichungen können wir feststellen, daß die bekannte Formel für den Gasdruck in der EINSTEINschen Gastheorie: $p=\frac{2}{3}\frac{U-U_0}{V}$ beim relativistischen, entarteten Gase nicht gültig ist.

* * *

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ЗАМЕЧАНИЯ О РЕЛЯТИВИСТИЧЕСКОЙ СТАТИСТИКЕ БОЗЕ

Ф. Беренц

Был исследован вырожденный идеальный газ по статистике *Бозе*. В случае различных вырожденный, т. е. $A < 1$ и $A = 1$, были даны уравнение состояния и энергия системы. Кроме того было установлено, что закон газа $p=\frac{2}{3}\frac{u-u_0}{V}$, известный по теории газа *Эйнштейна*, для релятивистического вырожденного газа недействителен.

MEASUREMENT OF DIFFUSIVITY, LIFETIME AND SURFACE RECOMBINATION VELOCITY IN SEMICONDUCTORS BY THE FLYING SPOT METHOD*

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Detailed discussion of the solution of the continuity equation with surface recombination is given, when generation by a flying light spot takes place. The solution is of a convenient form for experimental studies and renders possible the simultaneous determination of bulk lifetime, ambipolar diffusivity and surface recombination velocity. The reliability of the method is proved by measurements carried out on Ge specimens.

Photoelectric measurements in semiconductor investigations are very widespread. Both steady-state and non-stationary effects may give a number of important informations concerning the behaviour of electrons and holes injected. One of the non-stationary methods is the so-called Flying Spot Method, proposed by ADAM [1]. This method renders possible to measure simultaneously both bulk-lifetime (τ) and ambipolar diffusivity (D_0)[1] in a semiconducting crystal, even, as ADAM did, neglecting end effects, *i. e.* considering the case of zero surface recombination velocity ($s=0$). To avoid this restriction SOROKIN [2] has given a more general solution of the corresponding continuity equation (1) (see below). As this solution in reference [2] has the form of FOURIER-series and requires the knowledge of the imaginary roots of a trigonometric equation, it seemed to be reasonable to find a solution of a more convenient form when generating by a flying light spot.

In the present work the solution is obtained by using a generalization of the well-known integral transform of LAPLACE, the generalization for RIEMANN—STIELTJES integrals, as is described by van ROOSBROECK [3]. The physical picture of the present investigation is also similar to that of van ROOSBROECK.

According to this a semi-infinite semiconductor is assumed ($z \leqq 0$).

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* This work is a part of a doctoral dissertation submitted by one of the authors (J. Gy.) to the University of the Szeged [9].

[1] $D_0 = \frac{n_0 + p_0}{p_0/D_e + n_0/D_h}$, here D_e, D_h are diffusion constants and n_0, p_0 are the equilibrium concentrations of electrons and holes, respectively.

The source of excess carriers is a normalized[2], steady line source (at x_s, z_s) moving along the x-axis with uniform velocity c. The small signal differential equation describing the carrier concentration added (δp) has the following form (trapping neglected):

$$\partial \delta p/\partial t = D_0 \text{ divgrad } \delta p - \delta p/\tau. \tag{1}$$

To take end effects into consideration, the fulfilment of the condition

$$D_0 \partial \delta p/\partial z = s \delta p \qquad \text{(in the plane } z = 0) \tag{2}$$

is required.

In order to simplify Eqs. (1) and (2) we introduce dimensionless variables

$$\delta P = \delta p/(n_0 - p_0),\ U = t/\tau,\ X = x/L,\ Y = y/L,\ Z = z/L,\ L = (D_0 \tau)^{1/2}$$

and $S = s/v_D$, $v_D = L/\tau$ (denoting the drift velocity by v_D).

The continuity equation has then the form:

$$\partial \delta P/\partial U = \text{divgrad } \delta P - \delta P \tag{3}$$

with

$$\partial \delta P/\partial Z = S \delta P, \quad \text{when} \quad Z = 0. \tag{4}$$

The solution of (3) for an infinite semiconductor (ignoring for a moment the motion of the source) is, as follows:

$$\delta P = (4\pi U)^{-1} \exp[-U - (X - X_s)^2/4U] \exp[-(Z - Z_s)^2/4U], \tag{5}$$

where the co-ordinates X_s and Z_s correspond to x_s and z_s.

The solution of the semi-infinite problem with surface recombination differs from (5) only in its Z-dependence, thus the condition (4) may be fulfilled when conveniently altering the last term in (5).

The method applied makes use of the following RIEMANN—STIELTJES integral representation of (5):

$$\delta P = (4\pi U)^{-1} \exp[-U - (X - X_s)^2/4U] \int_{-\infty}^{+\infty} \exp[-(Z - \zeta)^2/4U] dF(\zeta), \tag{6}$$

in which the integrator function, $F(\zeta)$, is chosen that, for $\zeta \geqq 0$, (6) is equivalent to (5) and for other ζ values, $F(\zeta)$ is determined that (4) should be fulfilled. The solution so determined has the form, [3] (written as the GREEN's function corresponding to the system of equations (3), (4)):

$$\begin{aligned} G(X, Z, U; X_s, Z_s) & \\ = (4\pi U)^{-1} \exp[-U - (X - X_s)^2/4U] \{ & \exp[-(Z - Z_s)^2/4U] \\ & + \exp[-(Z + Z_s)^2/4U] - 2S \int_0^{\infty} \exp[-S\zeta - (Z + Z_s + \zeta)^2/4U] d\zeta \}. \end{aligned} \tag{7}$$

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[2] $(n_0 - p_0)L^2$ carrier pairs per length L (L denotes the diffusion length).

Solution of continuity equation in the system of co-ordinates fixed to the source, determination of D_0 and τ

To obtain the solution in the case of the Flying Spot Method, we introduce a new system of co-ordinates, moving together with the source, on the base of $\bar{x}=x-ct$, $\bar{y}=y$, $\bar{z}=z$, $\bar{x}_s=\bar{z}_s=0$:

$$\bar{X}=X-(c/L)t=X-(c\tau/L)U\equiv X-\alpha U,\ \bar{Y}=Y,\ \bar{Z}=Z,\ \bar{X}_s=\bar{Z}_s=0. \quad (8)$$

In this system of co-ordinates (7) has the following form:

$$\begin{aligned} &G(\bar{X},\bar{Z},U;0,0)\\ &\quad=(2\pi U)^{-1}\exp[-U-(\bar{X}+\alpha U)^2/4U]\\ &\qquad\cdot\{\exp[-\bar{Z}^2/4U]-S\int_0^\infty\exp[-S\zeta-(\bar{Z}+\zeta)^2/4U]d\zeta\}\\ &=(2\pi U)^{-1}\exp[-(1+\alpha^2/4)U-(\alpha/2)\bar{X}-\bar{X}^2/4U]\\ &\qquad\cdot\{\exp[-\bar{Z}^2/4U]-S\int_0^\infty\exp[-S\zeta-(\bar{Z}+\zeta)^2/4U]d\zeta\}. \end{aligned} \quad (9)$$

In this new system of co-ordinates we evidently encounter the conditions of a steady state. Thus, to obtain steady-state solutions from (9) we have to integrate (9) respect to U from zero to infinity. The integration results in the following expression, having a detector in the $Z=0$ plane:

$$\begin{aligned} &\bar{G}(\bar{X},0;0,0) \quad (10)\\ &=\pi^{-1}\exp[-\alpha/2)\bar{X}]\{K_0[|\bar{X}|(1+\alpha^2/4)^{1/2}]-S\int_0^\infty e^{-S\zeta}K_0[(\bar{X}^2+\zeta^2)^{1/2}(1+\alpha^2/4)^{1/2}]d\zeta\} \end{aligned}$$ [3]

The form (10) is the generalization of the solutions of Adam and van Roosbroeck, as, for $S=0$ it is reduced to the result of Adam and, for $\alpha=0$ (*i. e.* $c=0$) to that of van Roosbroeck.

Equation (10) may be simplified on integrating it by parts as the integrated term vanishes at the boundaries:

$$\begin{aligned} &\bar{G}(\bar{X},0;0,0)\\ &=\pi^{-1}\exp[-(\alpha/2)\bar{X}]\int_0^\infty e^{-S\zeta}K_1[(\bar{X}^2+\zeta^2)^{1/2}(1+\alpha^2/4)^{1/2}]\frac{\zeta}{(\bar{X}^2+\zeta^2)^{1/2}}d\zeta. \end{aligned} \quad (11)$$

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[3] Using the $(1+\alpha^2/4)U=V$ substitution and the integral representation

$$K_\nu(z)=\frac{1}{2}(z/2)^\nu\int_0^\infty V^{-(\nu+1)}\exp[-V-z^2/4V]dV$$

of the Bessel functions of the second kind for imaginary argument [4].

For the cases of S sufficiently large, the integral in (11) will converge rapidly, thus the approximation $(\bar{X}^2+\zeta^2)^{1/2}\approx\bar{X}$ and $\zeta(\bar{X}^2+\zeta^2)^{-1/2}\approx\zeta/\bar{X}$ is valid, and (11) will be of the following simple form:

$$\bar{G}(\bar{X},0;0,0)\approx(\pi\bar{X}S^2)^{-1}\exp\,[-(\alpha/2)\bar{X}]\,K_1[|\bar{X}|(1+\alpha^2/4)^{1/2}],$$

or using an approximation for $K_1(z)\approx(\pi/2z)^{1/2}e^{-z}$ (independently of ν) [5], valid for large z, and rewriting the quantities having dimensions, δp will be proportional to

$$\delta p\sim(\bar{x})^{-3/2}\exp\,[-(c/2D_0)\bar{x}+|\bar{x}|((c/2D_0)^2+1/(D_0\tau))^{1/2}]. \tag{12}$$

This equation, just as the corresponding one in reference [1], renders possible the simultaneous determination of D_0 and τ, as the logarithmic derivative of (12) at a great distance before and behind the source has the following form[4]:

$$1/L_1\equiv\left|\frac{d(\log\delta p)}{d\bar{x}}\right|_1=c/2D_0+[(c/2D_0)^2+1/(D_0\tau)]^{1/2}$$

and

$$1/L_2\equiv\left|\frac{d(\log\delta p)}{d\bar{x}}\right|_2=-c/2D_0+[(c/2D_0)^2+1/(D_0\tau)]^{1/2}.$$

The quantities D_0,τ (and also L) then may be calculated, as is well known, on base of the simple relations:

$$L=(D_0\tau)^{1/2}=(L_1L_2)^{1/2},$$
$$D_0=\frac{c}{1/L_1-1/L_2},\qquad \tau=\frac{L_2-L_1}{c}. \tag{13}$$

According to these, the quantities in interest may be calculated by measuring the slopes before and behind the source of the curve *logarithm of detector response* versus $\bar{x}=x-ct$.

Figures 1a and 1b show the theoretical curves for several light spot velocities and surface recombination velocities cerresponding to Eq. (11). The numerical values of D_0 and τ (also in the forthcoming Fig. 2.) were chosen as $10^2\,\mathrm{cm}^2\,\mathrm{sec}^{-1}$ and 10^{-4} sec. (f denotes the rate of generation per unit length.)

Solution of continuity equation in the system of co-ordinates fixed to the crystal, determination of S

As the problem is essentially not a steady-state one, it is useful to return to the laboratory system of co-ordinates. In this system the state is time-dependent. On the base of (7) the corresponding solution is of the form

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[4] log $(\bar{x})^{-3/2}$ is supposed to be approximately constant.

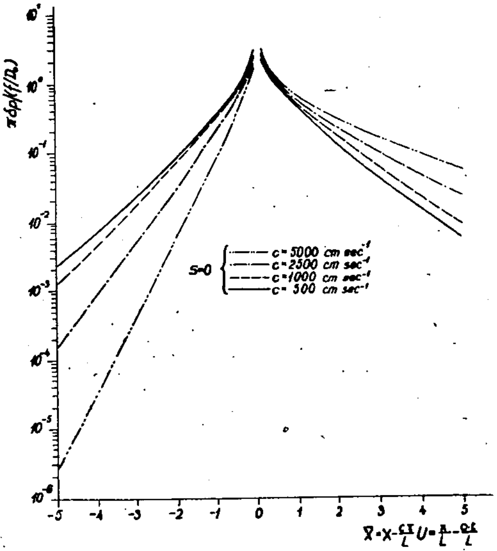

Fig. 1a. Theoretical curves, corresponding to Eq. (11)

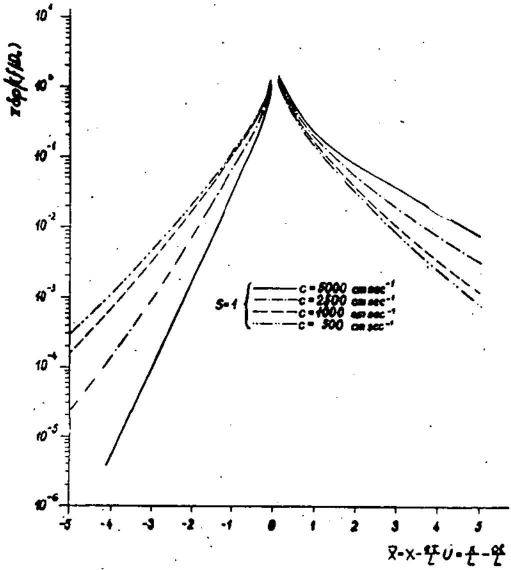

Fig. 1b. Theoretical curves, corresponding to Eq. (11)

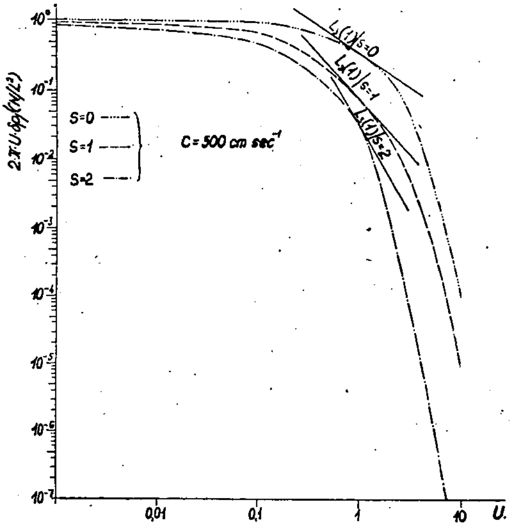

Fig. 2a. Theoretical curves, corresponding to Eq. (14)

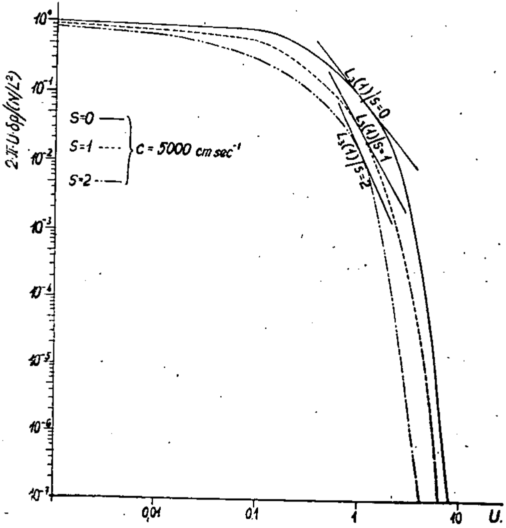

Fig. 2b. Theoretical curves, corresponding to Eq. (14)

(with a detector at $X=Z=0$):

$$\delta p/(N/L^2)=G(0,0,U;\ \alpha U,0)$$

$$=(4\pi U)^{-1}\exp[-U-\alpha^2 U^2/4U]\cdot\{2-2S\int_0^\infty \exp[-S\zeta-\zeta^2/4U[d\zeta\} \quad (14)$$

$$=(2\pi U)^{-1}\exp[-(1+\alpha^2/4)U]\cdot\{1-S\pi^{1/2}U^{1/2}e^{S^2U}[1-\operatorname{erf}(SU^{1/2})]\},$$

where N the number of pairs generated and $\operatorname{erf}(x)=2\pi^{-1/2}\int_0^x e^{-\beta^2}d\beta$. Eq. (14) has been obtained by using integral tables to evaluate the integral $\int_0^\infty \exp[-S\zeta-\zeta^2/4U]dU$, [6].

It is convenient to calculate the derivative of the function $UG(0,0,U;\alpha U,0)$, as the slope of this curve can be easily obtained from oscillograms. To get a curve, independent of scale factors, for the determination of S it is useful to plot the *product of U and detector response* versus U, both in logarithmic scale, as the slope of this curve, $L_3(V)$, at $V=\log U$ has the form (for $Se^{V/2}>1$) [7]:

$$L_3(V)\equiv\frac{\partial\log[e^V G(0,0,e^V;\alpha e^V,0)]}{\partial V}$$

$$=-\left\{(1+\alpha^2/4)e^V+\frac{\pi^{1/2}Se^{V/2}e^{S^2e^V}[1-\operatorname{erf}(Se^{V/2})]\left(\frac{1}{2}+S^2e^V\right)-S^2e^V}{1-\pi^{1/2}Se^{V/2}e^{S^2e^V}[1-\operatorname{erf}(Se^{V/2})]}\right\}$$

$$=-(1+\alpha^2/4)e^V-\frac{4S^4e^{2V}-12S^2e^V-15/2}{4S^4e^{2V}-6S^2e^V+15}, \quad (15)$$

when using the first four terms of the asymtotic expansion of $\operatorname{erf}(x)$ for large arguments [8][5]. This simple form makes possible to calculate S by help of the slope $L_3(V)$, as the root of (15), having physical significance, is of the following form:

$$S=\left\{\frac{3a+[9a^2+60(a-1)b]^{1/2}}{4e^V(a-1)}\right\}^{1/2},$$

where $a=L_3(V)+(1+\alpha^2/4)e^V+2$ (16)

and $b=-L_3(V)-(1+\alpha^2/4)e^V+\frac{1}{2}$.

Figures 2a and 2b show theoretical curves for some light-spot velocities and for several surface recombination velocities corresponding to (14). The

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[5] The expansion is valid for $Se^{V/2}\gg 1$, but when already $Se^{V/2}=2$ it gives rise of an error less then 5 *per cent.*

slopes, $L_3(V)$, at $V=0$, belonging to different surface recombination velocities, show that the quantity $L_3(V)$ — as demanded in the experimental work — depends on S appreciably.

Experimental part

Measurements on Ge samples has been carried out to prove the reliability of the method. The apparatus used has been analogous to the one described by ADAM. For the sake of consistency, the apparatus is sketched here also, as follows (Fig. 3).

A micromanipulator served for holding the specimen and the point contact detector. The light of an incandescent lamp (L_1) falls on a rotating metal-mirror, driven by a synchron motor, the flying image of the slit (S) is thus produced on the surface of the specimen. The photocell (C_1) served for time-scale calibration and the revolution of the motor has been controlled by a stroboscope. The amplifier is followed by a suitably synchronized (by the lamp L_2 and photocell C_2) cathode ray oscilloscope (CRO).

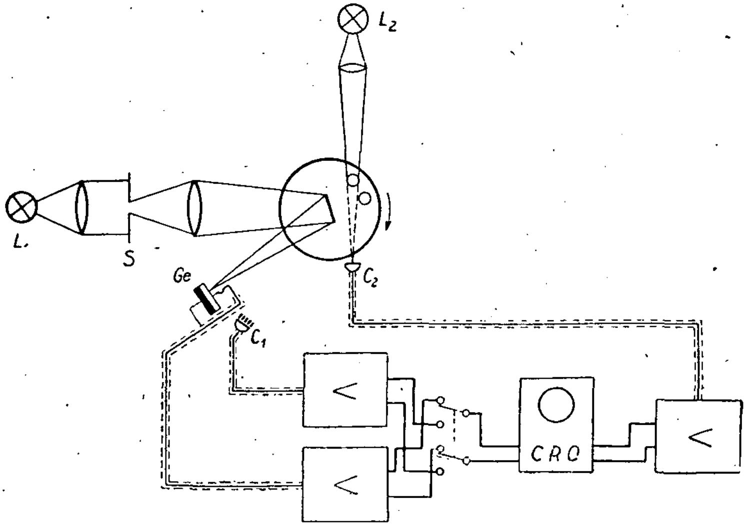

Fig. 3. Measuring apparatus

Oscillograms were taken for several light spot velocities and for several samples (Fig. 4).

The results calculated on the base of (13) and (16) for samples 1 and 2 (surface polished and etched with H_2O_2+NaOH) are to be seen on tables I and II.

The $S(\bar{L}/\bar{\tau})$ [and $s(\bar{L}/\bar{\tau})$] are calculated on using the average values $(\bar{L}, \bar{\tau})$ of L and τ, respectively.

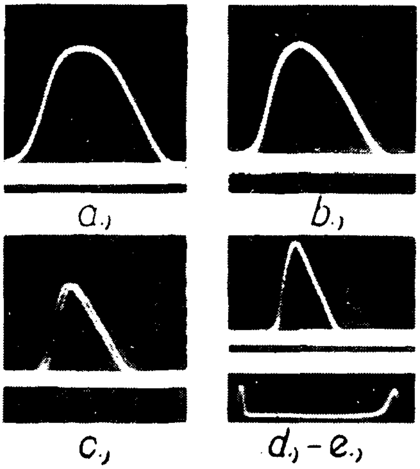

Fig. 4. Oscillograms taken on sample 1. a) $c = 785$ cm sec^{-1}; b) $c = 1000$ cm sec^{-1}; c) $c = 1500$ cm sec^{-1}; d) $c = 2000$ cm sec^{-1}; e) oscillogram for time-scale calibration (the distance of peaks covers a time-interval of 434 μsec)

Table I

Sample 1

c cm sec^{-1}	D_0 cm^2 sec^{-1}	τ μsec	L cm	μ_p cm^2 volt^{-1} sec^{-1}	S	s cm sec^{-1}	$S(\bar{L}/\bar{\tau})$	$s(\bar{L}/\bar{\tau})$ cm sec^{-1}
785	47	103	0,071	1838	0,953	656	1,077	892
1000	65	100	0,081	2512	1,153	934	1,066	883
1500	81	133	0,104	3134	1,573	1230	1,573	1302
2000	83	62	0,071	3219	1,560	1811	4,011	3321
mean values	69,6	99,5	0,081	2677	1,310	1158	1,932	1600

Table II

Sample 2

c cm sec^{-1}	D_0 cm^2 sec^{-1}	τ μsec	L cm	μ_p cm^2 volt^{-1} sec^{-1}	S	s cm sec^{-1}	$S(\bar{L}/\bar{\tau})$	$s(\bar{L}/\bar{\tau})$ cm sec^{-1}
785	96	83	0,089	3692	1,976	2118	1,771	1849
1000	107	70	0,087	4115	2,719	3380	1,813	1893
1500	101	94	0,097	3884	2,026	2091	1,853	1935
2000	97	114	0,105	3730	1,485	1368	2,232	2330
mean values	100,2	90,2	0,094	3855	2,051	2239	1,917	2002

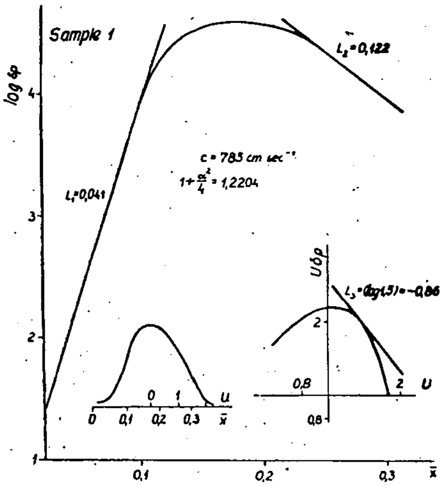

Fig. 5. The determination of the three slopes needed in calculations of D_0, τ and S, sample 1

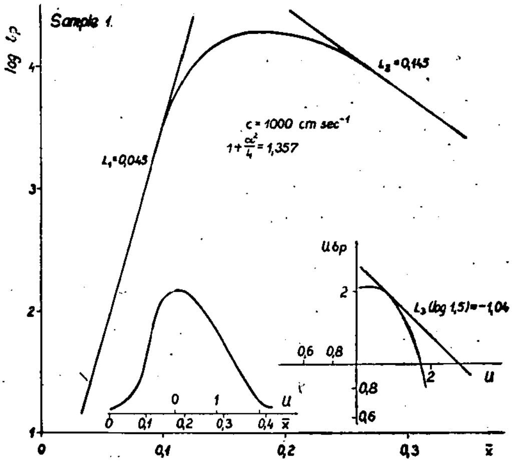

Fig. 6. The determination of the three slopes needed in calculations of D_0, τ and S, sample 1

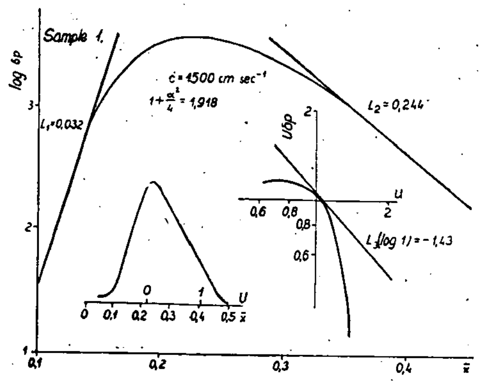

Fig. 7. The determination of the three slopes needed in calculations of D_0, τ and S, sample 1

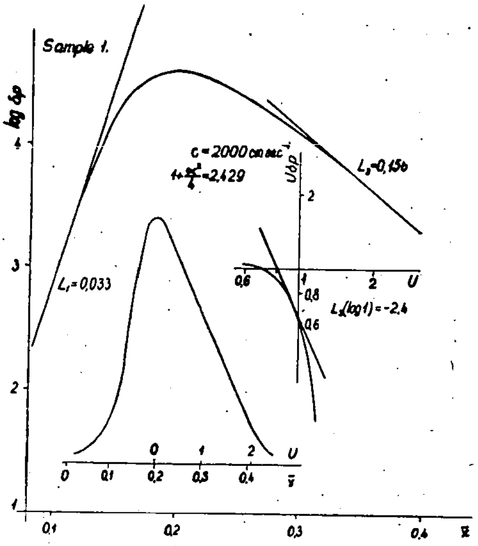

Fig. 8. The determination of the three slopes needed in calculations of D_0, τ and S, sample 1

The determination of D_0', τ and L is evidently seen on Figs. 5—8. *The oscillogram curves*, in the middle of the figures, *were plotted* logarithmically on the one hand *versus* $\bar{x}=ct$, *for the determination of* D_0, τ, etc. [Eq. (13)], then, on the other hand, *against* $\log U=\log t-\log\tau$, *which rendered possible the determination of* S [Eq. (16)]. The mobilities (μ_p) were calculated by using the EINSTEIN relation.

The present investigations show that the solution of the continuity equation in the case of the flying spot method may be succesfully extended for surface recombination velocities differing from zero, giving thus a method for the simultaneous determination all the characteristic parameters occurring in continuity equation (1) and boundary condition (2), and, as dates of the tables show, this determination involves a rather little uncertainty, the deviations from the mean values did not amount in average 30 *per cent.*

* * *

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ОПРЕДЕЛЕНИЕ КОЭФФИЦИЕНТА ДИФФУЗИИ, ВРЕМЕНИ ЖИЗНИ, А ТАКЖЕ СКОРОСТИ ПОВЕРХНОСТНОЙ РЕКОМБИНАЦИИ В ПОЛУПРОВОДНИКАХ, ПОСРЕДСТВОМ ДВИЖУЩЕГОСЯ СВЕТОВОГО ПУЧКА

Й. Дьюлаи и *Й. Ланг*

В статье содержится подробное обсуждение решения уравнения непрерывности в случае генерации носителей тока движущимся световым пучком. Простая форма решения пригодна к применению её к экспериментальной работе и к одновременному определению коеффициента диффузии, времени жизни и скорости поверхностной рекомбинации. Пригодность метода обоснована измерениями над Ge-кристаллами.

BEITRÄGE ZUR CHEMIE DER VANADIUM(V)-KOMPLEXE, MIT BESONDERER RÜCKSICHT AUF IHRE ABSORPTIONSSPEKTREN

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(Eingegangen am 31. Mai 1960)

Die Absorptionsspektren von 8-OH-Chinolin und Salizylaldoxim, ferner die ihrer V-Komplexe wurden, mit besonderen Rücksicht der Lösungsmittelwirkung, untersucht. Es wurde festgestellt:

1. Die Intensität der langwelligen Elektronenübersprungsbande in der Spektren der Ester des V(V)-Komplexes von 8-OH-Chinolin wächst in der Reihenfolge: methyl-äthyl-buthyl-propyl-amyl.
2. In Pyridin wandeln sich die Ester mit verschiedener Geschwindigkeit in eine Additionsverbindung um. Die Geschwindigkeit ändert sich in der Reihenfolge: methyl-äthyl-propyl-buthyl.
3. In Eisessig tritt bei 610 mμ eine sehr intensive Bande auf, deren Intensität mit Erhöhung der Wasserkonzentration linear abnimmt.
4. Das Absorptionsspektrum des Salicylaldoxim-Komplexes hat dieselbe Struktur, wie die des Spektrums des gebundenen Radikals.
5. Im Falle des V(V)-Komplexes von Salizylaldoxim konnte keine Esterbildung nachgewiesen werden; in Eisessig zersetzt sich der Komplex.

1. *Einleitung*

Es ist eine große Anzahl der Komplexverbindungen des Vanadiums als zweiten Gliedes der ersten Übergangsgruppe bekannt. Die physikalisch-chemischen Eigenschaften der V(II)-, V(III)-, V(IV)- und V(V)-Komplexe, ferner — mit Ausnahme der V(V)-Komplexe — auch ihre Absorptionsspektren, bzw. die Mechanismen ihrer Lichtabsorption wurden schon aus verschiedensten Gesichtspunkten untersucht.

Im Absorptionsspektrum des Aquo-Komplexes des V(II) Ions $|3d^3|$ sind drei Banden bei 12600, 18200 und 26500 K zu finden. Der Grundterm ist ^4F. Wird die Wechselwirkung zwischen den F- und P-Termen vernachlässigt, so gibt eine Berechnung mit dem Wert $D_q = 1260$ die Lagen der anderen zwei Banden in guter Näherung wieder [1].

Das Absorptionsspektrum der V(III)-Komplexe $|3d^2|$ enthält gleichfalls drei Banden [2], [3]; die ersten zwei Banden erscheinen bei 17200 bzw. 25000 K [4]—[7].

Mit der Lichtabsorption der V(IV)-Komplexe befaßte sich eingehend JÖRGENSEN, der festgestellt hat, daß z. B. sich die Symmetrie des Tartaratkomplexes in einem so großen Maße von der regelmäßigen kubischen Symmetrie abweicht, da alle vier mögliche Banden auftreten (K = 11000, 17100, 18800 und 25300). Das Spektrum der säurigen Lösung des VO^{++}-Ions enthält bei 13100 K ein Maximum und bei 16000 K eine Inflexion [8].

Man befaßte sich mit den Absorptionsspektren der V(V)-Komplexe $|3d^0|$ aus solchem Gesichtspunkte bisher noch nicht. Mit Berücksichtigung der Elektronenanordnung des Zentralions, wird der Grundterm ^1S bei keiner Symmetrieart sich aufspalten, und im Absorptionsspektrum werden keine Termaufspaltungsbanden auftreten. In der vorliegenden Arbeit handelt es sich um die physikalisch-chemischen Eigenschaften zweier Chelatkomplexe des V(V)-Ions, mit besoderer Rücksicht auf ihre Absorptionsspektren bzw. auf die beiden Spektren vorkommenden Lösungsmittelwirkungen.

2. *Beschreibung der experimentellen Ergebnissen*

A) *Absorptionsspektren der gebundenen Liganden.* Da das Absorptionsspektrum des Komplexes unter Anwendung verschiedenster Lösungsmitteln ausgemessen wurde, war es zweckmäßig, auch im Falle der gebundenen Liganden ähnlicher Weise zu verfahren.

Tabelle I

Ligand	Lösungsmittel	mμ und log ε		
Oxin	Äthylalkohol	—	315 (3,39)	242 (4,59)
	Äthylalkohol + 0,5 M HCl	365 (3,29)	315 (3,19)	253 (4,72)
	Äthylalkohol + 0,5 M NaOH	354 (3,73)	—	257 (4,60)
	Pyridin	—	320 (3,43)	—
	Äthylendiamin	385 (3,26)	342 (3,38)	—
	Eisessig	350 (3,18)	315 (3,20)	254 (4,53)
SaOx	Äthylalkohol	—	308 (3,69)	257 (4,14)
	Äthylalkohol + 0,5 M HCl	—	307 (3,60)	257 (4,10)
	Äthylalkohol + 0,5 M NaOH	340 (4,00)	—	268 (4,04)
	Pyridin	—	308 (3,69)	—
	Äthylendiamin	362 (3,88)	[325 (3,65)]	—
	Eisessig	—	308 (3,59)	258 (4,09)

Die Absorptionskurve der alkoholischen Lösung des 8-OH-Chinolins (Oxin) enthält bei 315, 242 und 217 mμ drei Banden [9], die auf Grund der Theorie der orientierten Lichtabsorption erklärt [10] und den y-, x'- und y'-Erregungen zugeordnet werden können [11]. In säurer Lösung bindet das N-atom ein Proton, die Ionisation der OH-Gruppe wird zurückgedrängt, weswegen die Mesomerie des O-Atoms weniger wahrscheinlich ist [11]; die x- (365 mμ) und y- (315 mμ) Banden treten getrennt auf [9]. In basischer Lösung ist die Trennung sehr gering [9] und die Banden verschieben sich in Richtung der längeren Wellen (Tabelle 1). Im Wesentlichen kann ähnliches auch bezüglich der in Eisessig, Pyridin und Äthylendiamin ausgemessenen Spektren festgestellt werden (Fig. 1, Kurven 1, 2 und 3).

Die Absorptionskurve der alkoholischen Lösung des Salizylaldoxims (SAO) enthält bei 308 und 257 mμ zwei scharfe Banden [12], deren Lage bei säurer Lösung und auch im Pyridin praktisch ungeändert bleibt (Fig. 2, Kurven 4, 5, 7 und 9). Die kurzwellige Bande verschmelzt sich stark in NaOH mit einer gleichzeitigen Extinktionsverminderung, wahrscheinlich wegen der Bildung von Na-Salz oder Na-Chelat [13].

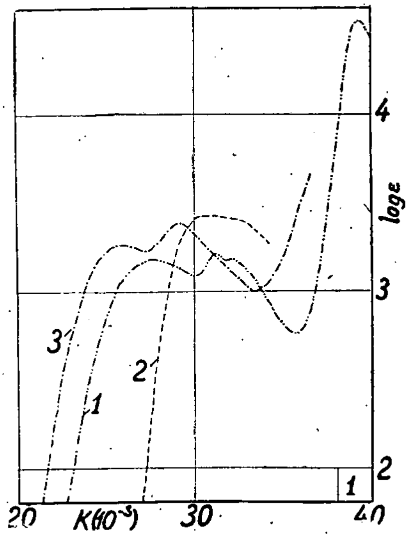


Fig. 1. Kurve 1: Oxin in Eisessig (cc = 0,000552); Kurve 2: Oxin in Pyridin (cc = 0,000552); Kurve 3: Oxin in Äthylendiamin (cc = 0,000552)

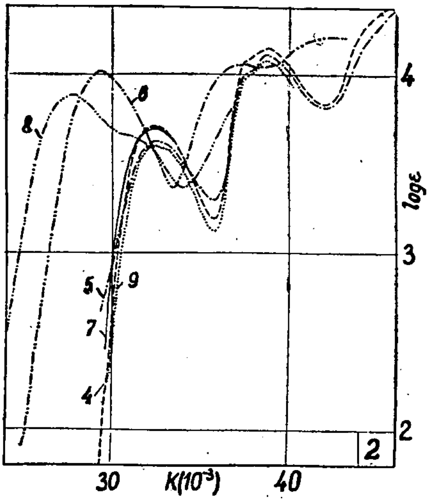
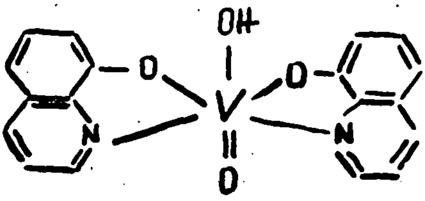


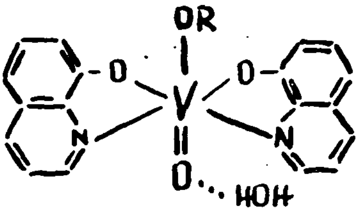
Fig. 2. Kurve 4: SAO in Äthylalkohol (cc = 0,000175); Kurve 5: SAO in Äthylalkohol + 0,5 M HCl (cc = 0,0000875); Kurve 6: SAO in Äthylalkohol + 0,5 M NaOH (cc = 0,0000875); Kurve 7: SAO in Pyridin (cc = 0,000583); Kurve 8: SAO in Äthylend.amin (cc = 0,000583); Kurve 9; SAO in Eisessig (cc = 0,000583)

Bezüglich des Mechanismus der Lichtabsorption dieser Verbindungen in Ermangelung quantenmechanischer Berechnungen können natürlich keine konkreten Feststellungen gemacht werden, hinsichtlich der gefundenen Banden des Komplexes können aber gewisse Folgerungen gezogen werden.

B) *Absorptionsspektren der Komplexe.* In alkoholischen Lösungen des Komplexes bis-(8-OH-Chinolin)VO.OH |I| durch Esterbindung kommen neue Verbindungen zustande [14], die mit der Vergrößerung der Zahl der C-Atome der Alkoholen in Form je besser definierter Kristallen isoliert werden können (Fig. 3—7) und im Gegensatz zur Ausgangsverbindung in allen organischen Verbindungen gut lösbar sind. Die Struktur des Komplexes |I| bzw. die seiner Ester kann wie folgt angegeben werden:



|I|



|II|—|VI|

|II| R = CH_3
|III| C_2H_5
|IV| C_3H_7
|V| C_4H_9
|VI| C_5H_{11}

Die Absorptionsspektren der Ester haben von cca 350 mμ an einen ähnlichen Verlauf. Bei 240—243 mμ findet man die charakteristische hohe e-Bande des gebundenen Radikals. Die Inflexionen bei 315 bzw. 256 mμ sind wahrscheinlich der ebenda liegenden e-Bande des Oxins oder einem Elektronenübersprungsprozeß zuzuordnen. Eine wesentliche Abweichung zeigt sich auf dem längerwelligen Gebiete des Spektrums (Tabelle 2). Die Intensitäten der Absorptionskurven des in dem entsprechenden Alkohol gelösten Methyl- |II|, Äthyl- |III|, Propyl- |IV|, Buthyl- |V| bzw. Amylesters |VI| des Komplexes |I| wachsen in der Reihenfolge |II| - |III| - |V| - |IV| - |VI|, (Fig. 8, Kurven 10—14). In Dioxan haben alle Verbindungen Absorptionsspektren mit praktisch identischem Verlauf; man findet bei cca 470, 375, 320 und 270 mμ flache Inflexionen und bei 246 mμ die charakteristische Bande des Oxins (Tabelle 2).

Tabelle 2

No	Lösungsmittel	mμ und log ε				
[II]	Methylalkohol	490 (2,95)	367 (3,58)	315 (3,71)	256 (4,42)	240 (4,72)
[III]	Äthylalkohol	485 (3,35)	366 (3,56)	310 (3,78)	256 (4,36)	242 (4,72)
[IV]	Propylalkohol	485 (3,49)	376 (3,65)	312 (3,76)	260 (4,30)	243 (4,66)
[V]	Buthylalkohol	480 (3,44)	370 (3,63)	310 (3,75)	260 (4,34)	242 (4,68)
[VI]	Amylalkohol	480 (3,52)	372 (3,69)	310 (3,78)	260 (4,35)	242 (4,71)
[I]	Äthylalkohol-HCl	—	370 (3,66)	310 (3,70)	256 (5,01)	—
[I]	Äthylalkohol-NaOH	—	363 (3,74)	335 (3,72)	256 (4,78)	—
[I]	Pyridin	—	390 (3,45)	312 (3,66)	—	—
[II]	„	—	388 (3,50)	310 (3,73)	—	—
[III]	„	—	390 (3,49)	310 (3,72)	—	—
[IV]	„	—	387 (3,49)	310 (3,71)	—	—
[V]	„	—	392 (3,51)	315 (3,74)	—	—
[VI]	„	—	396 (3,48)	315 (3,72)	—	—
[I]	i-Propylamin	—	400 (3,25)	335 (3,97)	258 (4,37)	—
[I]	n-Amylamin	—	392 (3,62)	335 (3,59)	262 (4,58)	—
[I]	Benzylamin	—	405 (3,71)	330 (3,62)	—	—
[I]	Äthylendiamin	—	385 (3,69)	342 (3,82)	260 (4,71)	—
[II]	Dioxan	~ 465 (3,51)	~ 375 (3,66)	~ 318 (3,69)	~ 268 (4,26)	246 (4,64)
[I]	Eisessig	610 (3,54)	~ 345 (3,67)	~ 305 (3,72)	—	253 (4,67)

Fig. 3. Mikrophotographie der Esterkristalle |II|

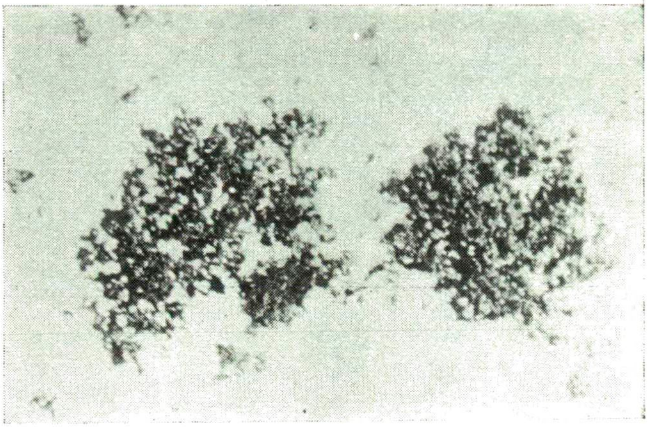
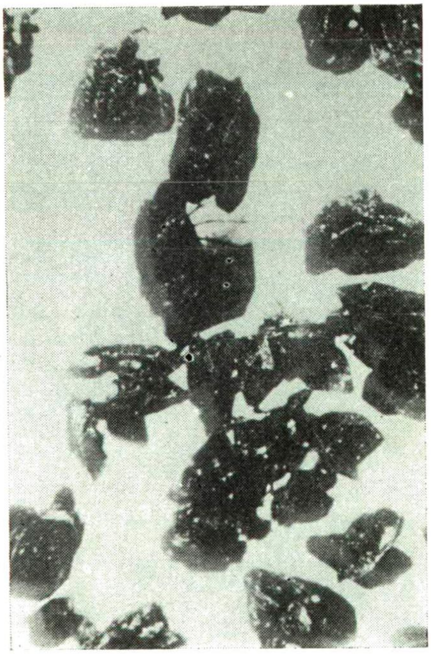


Fig. 4. Mikrophotographie der Esterkristalle |III|

Fig. 5. Mikrophotographie der Esterkristalle |IV|



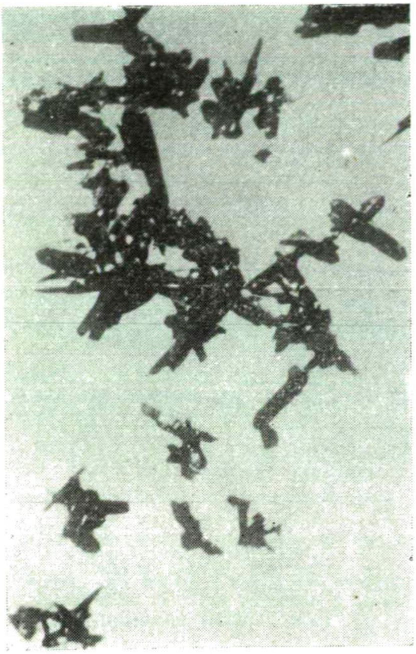


Fig. 6. Mikrophotographie der Esterkristalle |V|

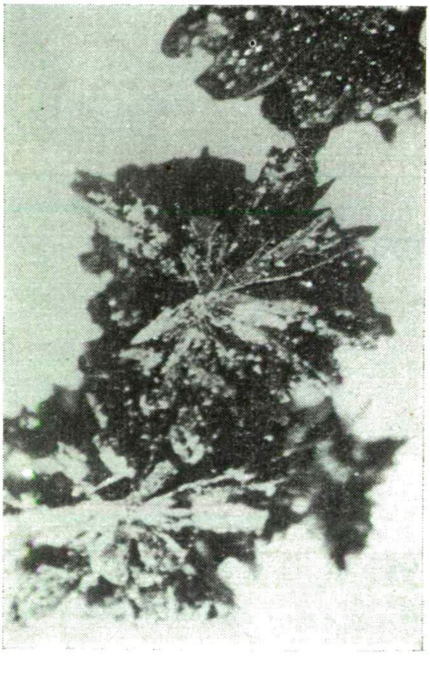
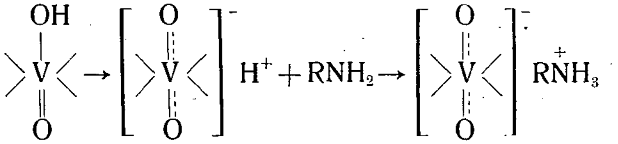


Fig. 7. Mikrophotographie der Esterkristalle |VI|

In Anwesenheit von verschiedenen Aminen wandelt sich die lila-rötlich Farbe in gelb um, dementsprechend ändert sich wesentlich auch das Absorptionsspektrum [15]. Hier muß man folgender Umwandlung Rechnung tragen [14]:



Die Banden und Inflexionen die wahrscheinlich dem gebundenen Liganden und dem Elektronenübersprungsprozeß zwischen Metall und Ligand zugeordnet werden können, erscheinen nur unterhalb 400 mμ (Tabelle 2).

Der Komplex [I] löst sich in organischen Säuren mit blau-lila Farbe. Im Falle von Eisessig als Lösungsmittel tritt bei 610 mμ eine breite, intensive Bande (Fig. 9, Kurven 15—19), deren Intensität sich linear mit der Konzentration des dem System zugesetzten Wassers vermindert [15]. Von der Konzentration cca 2,2 Mol H_2O an hat das Spektrum denselben Verlauf, wie die in säurer Lösung aufgenommene Kurve des Oxins, der Komplex zersetzt sich. Im Falle starker Säuren soll man wahrscheinlich der von Bielig und Bayer [16] angenommenen Additionsverbindung Rechnung tragen. Die (roten) alkoholischen Lösungen der Verbindungen [II]—[VI] zeigen in Anwesenheit von Eisessig keine Änderung. Wird Alkohol den blauen Lösungen dieser Komplexe in Eisessig zugesetzt, so kann eine Farbenumwandlung blau-rot beobachtet werden, in Anwesenheit von Alkohol kommen also stärkere Bindungen zustande, als im Falle der Ausbildung des Säuren-Adduktes. Bei wachsender Wasserkonzentration tritt eine sich vergrößernde Dissoziation des Eisessigs und damit die Zersetzung des Komplexes auf. Die Erhöhung der Zahl der C-Atome des Alkohols verursacht eine geringfügige Verschiebung der Bande in Richtung der längeren Wellen. In Anwesenheit von HCl bzw. NaOH erhält man wegen der Zersetzung des Komplexes, das insäurer bzw. alkalischer Lösung aufgenommene Spektrum des Oxins (Tabelle 2).

Nach der Auflösung der Verbindungen [II]-[VI] in Pyridin kann eine Farbenumwandlung rot-gelb beobachtet werden. Die Umwandlung geht bei den einzelnen Komplexen mit verschiedener Geschwindigkeit vor sich (Tabelle 3) [15], das Endprodukt ist aber — auf Grund der Identität der Spektren — in allen Fällen als identisch anzusehen (Tabelle 2). Die Werte

Tabelle 3

No	$k \cdot 10^3$			ΔH kcal/Mol	$-\Delta S$ cal/Grad	ΔF kcal/Mol
	25°	35°	45°			
[II]	6,56	14,22	27,01	13,3	23,9	20,8
[III]	4,91	10,30	21,57	13,9	22,4	20,7
[IV]	2,39	6,08	14,13	16,7	14,7	21,1
[V]	2,49	6,15	13,00	15,5	15,3	20,2

Tabelle 4

No	0°	10°	20°	30°	40°
[II]	0,055	0,059	0,065	0,071	0,078
[III]	0,400	0,397	0,390	0,386	0,384
[IV]	0,557	0,542	0,518	0,493	0,477
[V]	0,540	0,537	0,510	0,479	0,450
[VI]	0,615	0,602	0,578	0,545	0,502

der Geschwindigkeitskonstanten wachsen in der Reihenfolge |II|-|III|-|IV|-|V|; die Abhängigkeit des Wertes log k von $1/T$ ergibt in guter Näherung eine Gerade [15].

Die Extinktion der Komplexe |II|-|VI| zeigt eine interessante Temperaturabhängigkeit. Wie es in Tabelle 4 ersichtlich ist, vergrößert sich die Extinktion in Falle der Verbindung |II| nur wenig, in der Reihenfolge |III|-|VI| zeigt sie dagegen eine Verminderung, in wachsendem Maße. Die beobachteten Änderungen überschreiten die Wirkung der von Volumerhöhung der Lösung herrührenden Konzentrationsabnahme und sind unseres Erachtens

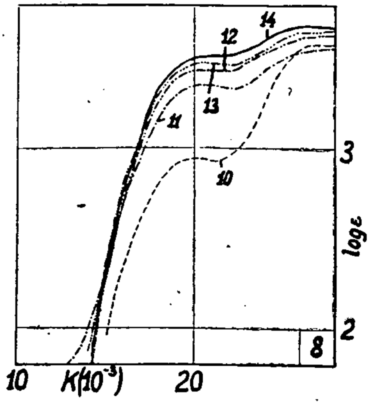


Fig. 8. Kurve 10: |II| in Methylalkohol (cc = 0,000207); Kurve 11: |III| in Äthylalkohol (cc = 0,0001995); Kurve 12: |IV| in Propylalkohol (cc = 0,000193); Kurve 13: |V| in Buthylalkohol (cc = 0,000187); Kurve 14: |VI| in Amylalkohol (cc = 0,000180)

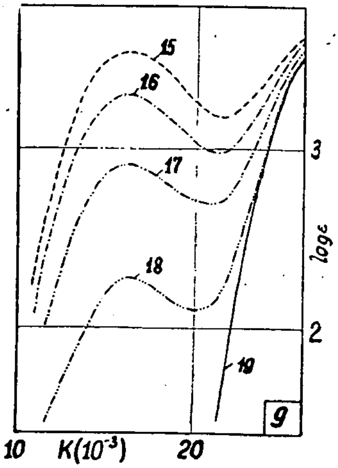
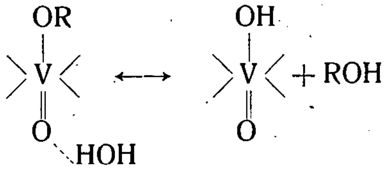


Fig. 9. |I| in Eisessig. Kurve 15: + 0 M H_2O (cc = 0,000215); Kurve 16: + 0,425 M H_2O (cc = 0,000210); Kurve 17: + 0,875 M H_2O (cc = 000206); Kurve 18: + 1,75 M H_2O (cc = 0,0001935); Kurve 19: + 2,25 M H_2O (cc = 0,0001935)

in erster Reihe auf den Prozeß

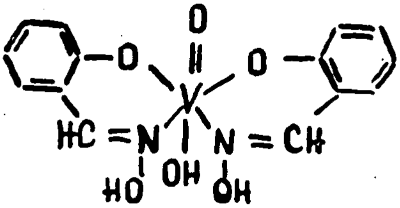


$$\begin{array}{c} OR \\ | \\ >V< \\ \| \\ O\cdots HOH \end{array} \longleftrightarrow \begin{array}{c} OH \\ | \\ >V< \\ \| \\ O \end{array} + ROH$$

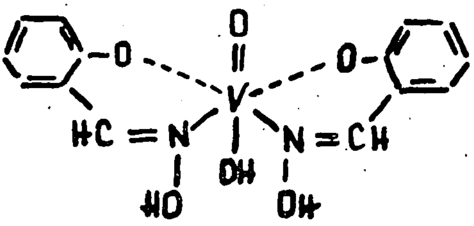
zurückzuführen.

JÖRGENSEN |17| hat beim Komplex Ir (III)-Pyridin eine neue Bande um 29000—35000 K beobachtet, die er dem Elektronenübersprung vom Zentralion auf die π-Bahn des Pyridins zuschreibt. Mit Betrachtnahme auch des hohen Valenzzustandes des Zentralions kann der Gedanke auch bei den hier untersuchten Verbindungen, bezüglich des Ursprungs der hohen Banden auf dem sichtbaren Spektralgebiete, auftauchen, daß auch diese Banden einem ähnlichen Elektronenübersprungsprozeß zugeordnet werden können, der zwischen dem entsprechenden Atom der gebundenen Liganden und dem Zentralion vor sich geht.

Die Struktur des V(V)-Komplexes von SAO |VII| kann folgendermaßen angegeben werden [18]:



|VII|



|VII/a|

Die Farbenumwandlung von lila in rötlich-braun schreibt man dem Übergang von |VII| in |VII/a| zu, welcher im Falle eines apolaren Lösungsmittels beobachtet wurde. Es wurde angenommen [18], daß |VII/a| ein sogenannter normaler Komplex, |VII| dagegen ein Eindringungskomplex ist. Gleichgewichtsmessungen nach ist die Form |VII| an Energie ärmer und ihre Umwandlung in die Form |VII/a| ist ein endothermer Prozeß.

Im Gegensatz zu den Komplexen |I|-|VI|, haben die Absorptionsspektren der alkoholischen Lösungen von |VII| denselben Verlauf, wie die Kurve von SAO (Tabelle 5; Fig. 10, Kurve 20). Die charakteristischen Banden des gebundenen Radikals erschneinen um 305 und 256—260 mμ, ungefähr mit den zu erwartenden Höhen. Um 400 mμ findet man gleichfalls eine sich von $\log \varepsilon = 2,2$ bis $\log \varepsilon = 2,7$ ändernde Vorbande, die aber keine solchartige Regelmäßigkeit aufweist, die wir bei den Komplexen |II|-|VI| beobachtet haben. Als Resultat einer Behandlung in Alkohol, konnten wir keine Esterbildung ausweisen. Die Verbindung ist oberhalb etwa 500 mμ ganz lichtdurchlässig.

Tabelle 5

VO.OH $(SaOX)_2$ in verschiedenen Lösungsmitteln

Lösungsmittel	mμ und log ε			
Methylalkohol	—	397 (2,72)	305 (3,89)	256 (4,35)
Äthylalkohol	—	395 (2,22)	355 (4,03)	258 (4,47)
Propylalkohol	—	[395 (2,38)]	305 (3,94)	257 (4,39)
Butylalkohol	—	[400 (2,44)]	305 (3,94)	258 (4,38)
Amylalkohol	—	405 (2,22)	305 (4,00)	260 (4,40)
Äthylalkohol-HCl	—	—	308 (3,75)	258 (4,20)
Äthylalkohol-NaOH	—	—	340 (4,17)	270 (4,40)
Pyridin	525 (2,63)	[355 (3,45)]	310 (3,95)	—
Äthylendiamin	—	367 (4,19)	—	—
i-Propylamin	—	356 (3,43)	310 (4,11)	—
n-Amylamin	—	350 (3,25)	311 (4,03)	—
Benzylamin	—	345 (3,36)	310 (3,96)	—
Dioxan	[550 (2,76)]	—	302 (4,15)	259 (4,45)
Eisessig	—	—	308 (3,96)	258 (4,43)
Kloroform	—	[380 (2,90)]	320 (3,95)	262 (4,41)

Die längerwellige Bande des in Pyridin, i-Propylamin (Fig. 10, Kurve 21), Benzylamin und n-Amylamin gelösten Komplexes findet man verschoben auf 310 mμ, in der Umgebung von 350 mμ tritt aber in allen Fällen eine ausgeprägte Inflexion auf. In Pyridin ist auch die schon erwähnte Vorbande stark verschoben zu finden (Tabelle 5). Es ist interessant, daß die Ligandbande in Äthylendiamin (Fig. 10, Kurve 22) stark verschoben, bei 367 mμ erscheint.

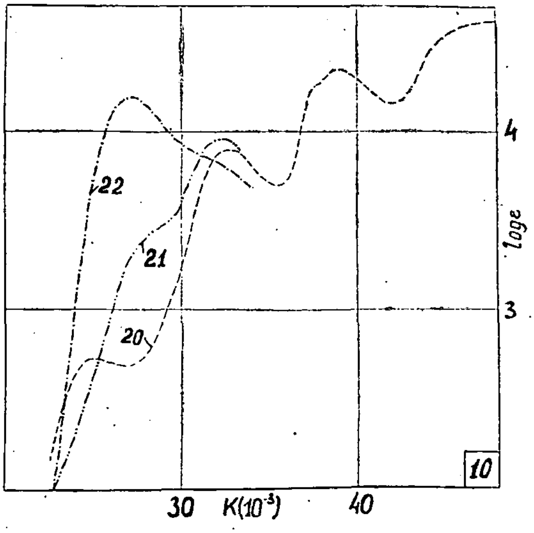


Fig. 10.

Kurve 20: |VII| in Methylalkohol (cc = 0,000241);
Kurve 21: |VII| in i-Propylamin (cc = 0,000241);
Kurve 22: |VII| in Äthylendiamin (cc = 0,000241)

Die Lagen der in Eisessig, in HCl, bzw. NaOH enthaltenden Lösungen auftretenden Banden sind beinahe identisch mit denen der Banden von SAO (Tabelle 5). In diesem Falle bildet sich also keine dem Komplex |I| ähnliche Additionsverbindung; der Komplex zersetzt sich in allen drei Fällen gänzlich. Die Entscheidung der Frage, warum die Verhaltung dieser zwei Komplexe so verschieden ist, erfordert noch eine weitere eingehende Untersuchung.

3. *Experimentelles*

Die Komplexe wurden nach Literaturangaben [14], [16]—[18] hergestellt, ihre Reinheit wurden durch N-Analyse kontrolliert. Die Absorptionsspektren wurden unter Anwendung von Quarzküvetten der Dicke 10, 1,0 und 0,1 cm, mit Hilfe eines Beckmanschen DU-Spektralphotometers aufgenommen. Die Lösungsmitteln wurden auf die gewöhnte Weise gereinigt.

Der Ablauf der Reaktion zwischen Pyridin und den Estern wurde spektralphotometrisch untersucht; die Messungen ereigneten sich bei 25, 35 und 45°C, 480 mμ und bei konstanter Esterkonzentration. Die Geschwindigkeitskonstanten berechneten sich aus den spezifischen Extinktionen der in den entsprechenden Alkoholen und in Pyridin gelösten Ester, bzw. in Kenntnis der während der Umwandlung gemessen Extinktionen und der Ausgangskonzentrationen.

* * *

Herrn Prof. Dr. Á. Kiss, korrespondierendem Mitglied der Akademie, für die stetige Förderung unserer Arbeit sei auch hier der beste Dank ausgesprochen. Wir sagen Dr. J. Hires für die wertvollen Diskussionen und Dr. Gy. Grasselly für die Fertigstellung der Mikrophotographie vielen Dank.

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ДАННЫЕ О ХИМИИ КОМПЛЕКСОВ ВАНАДИЯ (V) В ЧАСНОСТИ, ОБ ИХ АБСОРПЦИОННЫХ СПЕКТРАХ

Й. Часар и *Й. Балог*

Были рассмотрены абсорпционные спектры 8-ОН-хинолина и альдоксима салицила, а также их комплексов ванадия, в часности действие растворителя. Было установлено:

1) Интенсивность длинноволновой полосы перескакивания электрона, наблюденной в спектре эфиров комплекса 8-OH-хинолина-V(V), поднимается в ряде метил-этил-бутил-пропил-амила.

2. В пиридине эфиры превращаются в аддитивное соединение с разной скоростью. Значение постоянных скоростей изменяется в ряде метил $>$ этил $>$ пропил $\cong$ бутила.

3. В ледяном уксусе при 610 mμ появляется полоса большой интенсивности, интенсивность которой линейно уменьшается в возрастанием концентрации воды.

4. Спектр комплекса альдоксима салицила имеет такое же строение, как связанный радикал.

5. В случае комплекса альдоксима салицила-V(V) образования эфира не удалось обнаружить; в ледяном уксусе комплекс распадает.

EFFECT OF SOLVENTS ON THE ELECTRONIC ABSORPTION SPECTRUM OF 2-OXY-QUINOXALINE

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(Received May 15, 1960)

A specific effect of the solvent in dioxan and diethyl-ether was found at the ultraviolet absorption spectra of 2-oxy-quinoxaline. This effect seems to be due to the formation of the complex or to the proton migration between the solvent and the 2-oxy-quinoxaline.

A great deal of theoretical and experimental work has already been devoted to the elucidation of the effect of solvents on the electronic absorption spectra of organic molecules. In earlier papers the band displacement relative to the vapour state was considered as a function of the refractive index [1], in later papers more complex formulae were given taking into account both the refractive index and dielectric constant of the solvent [2]. According to the formula derived by MC RAE and used in a simplified form by R. POPOVICH and B. ROGERS the absorption band displacement

$$\Delta\bar{\nu} = a\frac{n^2-1}{2n^2+1} + b\left(\frac{D-1}{D+2} - \frac{n^2-1}{n^2+2}\right),$$

where $\Delta\bar{\nu}$ means the displacement of the absorption maximum relative to an arbitrary solvent in wave numbers, n and D denote the refractive index (referring to the D-line of Na) and the dielectric constant of the solvent, respectively, a and b are constants, which for a given class of solvents depend only on the solute. By means of this equation R. POPOVICH and B. ROGERS investigated the effect of solvents on the absorption spectra of 8-quinolinol and its Zn-chelate. Recently I. A, ZHMYREVA, V. V. ZELINSKY and their coworkers carried out similar researches on 4-aminophtalimide [3]. The aim of this paper is to investigate the influence of solvent on 2-oxy-quinoxaline by means of the equation given above.

The ultraviolet absorption spectra of 2-oxy-quinoxaline were obtained with a Beckman DU spectrophotometer in nine different solvents shown in the first column of the table. All the solvents were specially purified for spectroscopical purposes according to the usual methods (see *e. g.* in [4]). The compound to be investigated was carefully purified, and according to [5] it was found to be sufficiently pure. Characteristic properties of the solvents used are seen in the second and third column of the table and were taken from the literature [6]. The values of ν_{max} in cm^{-1} for different solvents and for the band of greatest wavelength are included in the fourth column and the error in the determination of the position of the band maximum is estimated to be about ± 25 cm^{-1}. Considering the highest value of $\bar{\nu}_{max}$ at chloroform as reference solvent, the measured values of $\Delta\bar{\nu}_{max}$ relative to the reference $\bar{\nu}_{max}$ are tabulated in the fifth column. The constants a and b were calculated by substituting two measured $\Delta\bar{\nu}$ values into the equation; the data for two pairs of solvents (ethanol and 2-pentanol, water and propanol) yielded the mean values for the constants: $a = -8410$ cm^{-1}, $b = 3170$ cm^{-1}. By means of these empirical constants the band displacements were calculated for all the solvents used are tabulated as $\Delta\bar{\nu}_{calc.}$ values in the sixth column.

Table I

1	2	3	4	5	6
Solvent	n	D	$\bar{\nu}_{max}$	$\Delta\bar{\nu}_{meas}$	$\Delta\bar{\nu}_{calc}$
			in cm^{-1}		
Water	1,332	81,0	28 570	1010	971
Methanol	1,331	35,7	28 820	760	804
Ethanol	1,363	26,8	28 950	630	600
Propanol	1,385	22,2	29 180	400	436
Butanol	1,399	19,2	29 280	300	302
2-pentanol	1,409	14,3	29 440	140	138
Chloroform	1,44	5,14	29 580	0	—791
Diethyl ether	1,354	4,4	29 280	300	—605
Dioxane	1,442	3,0	29 410	170	—1242

A comparison of $\Delta\bar{\nu}_{meas.}$ and $\Delta\bar{\nu}_{calc.}$ shows that these values are in a good agreement at water and alcohols, the difference between measured and calculated band displacements is within the range of the estimated error. A very great discrepancy is to be observed at chloroform, diethyl ether and dioxane. In order to clear up the cause of this discrepancy the whole absorption spectra were investigated. For the sake of a better survey the figure shows only four selected spectra. Comparing all the spectra it is easy to observe that these fall into two groups, the one group exhibits a maximum or shoulder at a wave number 40 000 cm^{-1} (similarly to curves 1 and 2), the second group, however, shows no sign of such a maximum or shoulder (similarly to curves 3 and 4). The band displacements of all the absorption curves belonging to the one group may be calculated by the Mc Rae equation, while those of the second group may not be given by calculation.

This behaviour of the spectra may be explained by an alteration of the character of interaction between solvent and solute molecules when turning from the one group of solvents to the second group. Water and alcohols behave predominantly as a continous polarizing medium and suppress the specific interaction, if it exists at all, therefore the measured and calculated band displacements coincide. Chloroform, diethyl ether and dioxane have a considerable smaller polarizing effect, consequently these solvents give a possibility for the developing of specific interactions between solvent and solute molecules. The disappearance of the maximum or shoulder at a wave number of 40 000 cm^{-1} at the latter solvents is a sign of this specific interaction, which may consist in a proton donation to the solvent molecule.

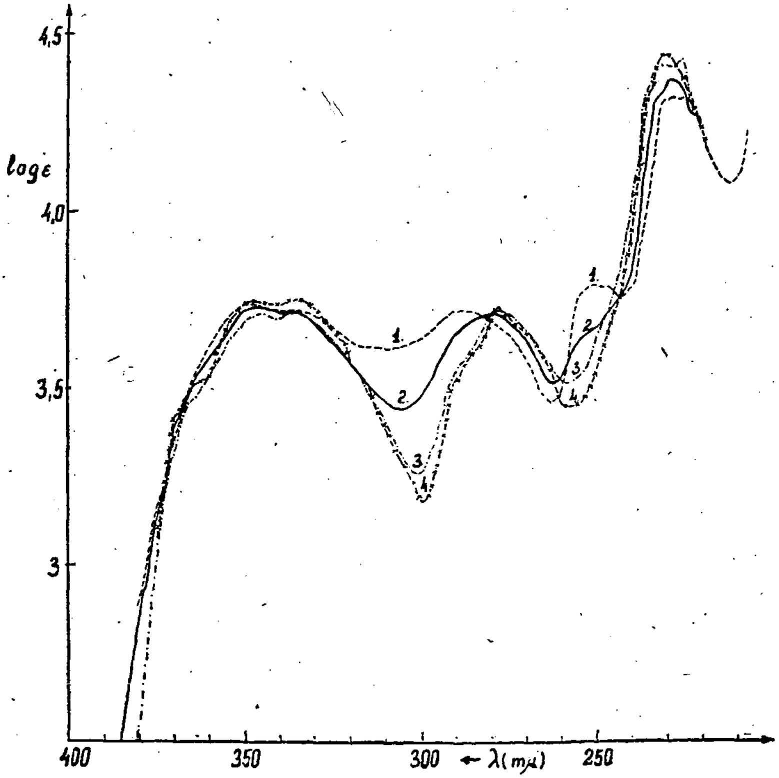

Fig. 1

This supposition seems to be verified by the results of [5]. Though nitrogen has proton-acceptor properties, the N-atom in 2-oxy-quinoxaline is not saturated but capable for proton acception or donation according to its surroundings. Even in water pH-values were to be found at which the maximum or shoulder at a wave number of 40 000 cm^{-1} could not be detected and this change in the spectrum undoubtedly seemed to be in connection with a proton acception or donation. It is not excluded either, that the specific interaction is due to a complex formation between the solute and solvent molecules; the free electron pairs of chloroform, diethyl ether and dioxane may cause a formation of assotiation complexes of 2-oxy-quinoxaline with the solvent molecules.

* * *

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ВЛИЯНИЕ РАСТВОРИТЕЛЕЙ НА ЕЛЕКТРОННЫЕ СПЕКТРЫ ПОГЛОЩЕНИЯ 2-ОКСИ-КИНОКСАЛИНОВ

Е. Томбац

У ультрафиолетового спектра поглощения 2-окси-хиноксалина найден в диоксане и диэтилэфире специфический эффект растворителя. Повидимому этот эффект заключается в образовании комплексов или в миграции протонов между 2-окси-хиноксалином и растворителем.

ON THE PROBLEM OF THE IONIC CHARACTER AND THE POLARITY OF THE CHEMICAL BOND

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A general survey of the literature on the ionic character and the degree of polarity of the chemical bonds is given. With this consideration the concept of the effective electric field strength of free atoms and ions and their constituents is introduced. To calculate this was possible by using the ionisation potentials of atoms and ions and by clearing up the exponential dependence of the effective field strength of ions on their charge. In equilibrium, on the basis of the virial-theorem the effective electric field strength of the cationic constituent must be equal to that of the anionic constituent. This equality renders possible to calculate the degree of bond polarity without using experimental degrees of bond polarity or arbitrarily chosen adjusting parameters. In the whole range between ideal ionic and pure covalent bonds there is a fair agreement between degrees of bond polarity calculated by us and experimentally found. The deviation is not greater than $\pm 5\%$. The shortcomings of this method lay in the fact that the properties of the bonded constituents are approximated by the properties of free atoms and ions.

On the basis of our investigations on the periodicity of the physical and chemical properties of the elements [1]—[6] it has been established that the physics and chemistry of elements are ruled by two opposite factors. One of them is the *effective principal quantum number* of the outermost electronic shell of constituent atoms and ions. resp., while the other is the *effective nuclear charge* of the constituents, *i. e.* the screening and shielding numbers (parameters), resp., of electrons subtracted from the positive nuclear charge number. After clearing up this qualitative connection a further aim of our investigations presented itself, namely, to investigate quantitatively the relation between the two main factors and the chemical and physical properties of elements determined by these. Within the scope of this programme the calculation of the degree of polarity and ionic character resp., closely connected with the "electropositive" and "electronegative" character of the atoms was considered to be the most important aim.

The overwhelming majority of the types of the bonds in inorganic compounds is placed between two limiting cases, forming a gradual transition from pure polar (ideal ionic) to pure non-polar (normal covalent) bonds. These are the so called compounds with transition type of bond. *E. g.* in gas-phase molecule Cl_2, the Cl—Cl bond is an ideal non-polar one, in solid KCl it is nearly ideal ionic, while TlCl and AgCl are compounds with transition type of bond. The amount of the ionicity is already a function of the different states of aggregation. Unfortunately, we know only very little about the extent of ionicity of compounds in the solid and liquid phases.

The measure of the ionicity of transition type of bonds in gas phase compounds, that is, where does the type of bond of the given compound take place between two limiting cases, is described with diverse expressions by the different authors [7].

One of them is the concept and the amount of the ionic character (β) [9] of the bond, which can be estimated with the nuclear quadrupole coupling constants [8] and theoretically can be calculated by methods of quantum mechanics (MO—LCAO). According to the LCAO approximation of the molecular orbitals, the wave function of the *binding electron* between atoms A and B is represented by Eq. $\Psi = a\psi_A + b\psi_B$ where ψ_A and ψ_B are the wave functions of the atomic orbitals of atoms A and B. If ψ is normalized, then $a^2 + b^2 + 2abS = 1$ where S is the so called overlap integral, $S = \int \psi_A \psi_B \cdot d\tau$. Then the measure of the ionic character is:

$$\beta = b^2 - a^2 \tag{1}$$

where $b^2 - a^2$ is the difference of the probability that the electron is found at atoms A und B. The ionic character is the function of the ratio of the effective nuclear charges and of the difference between the electronegativities of atoms A und B, respectively, and can be regarded as an absolute measure of the iónicity of the compounds [9].

Another, widely used concept the *polarity*, of the chemical bond had been introduced by K. FAJANS [10a, 10b]. Later PAULING called this the "ionic character of the bond", what cannot be mistaken for the previous concept defined by quantum mechanics. Taking into consideration the experimentally determined electric dipole moment and the internuclear distance of AB binary compound:

$$\text{degree of polarity } (p) = \frac{\mu_{\text{exp.}}}{\mu_{\text{calc.}}} = \frac{\mu_{\text{exp.}}}{e \cdot R_{AB}} \tag{2}$$

$$\text{degree of polarity in p. c.} \quad (p)\text{p.c.} = 100 \frac{\mu_{\text{exp.}}}{e \cdot R_{AB}} \tag{2'}$$

where $\mu_{\text{exp.}}$ and $\mu_{\text{calc.}}$ are electric dipole moments experimentally determined and calculated for the assumed idealized binding of rigid ions, e is the ionic charge, R_{AB} the interatomic distance accurately determined in an experimental way, $e \cdot R_{AB}$ the calculated bond dipole moment of a hypothetic A^+B^- molecule with an assumed ideal ionic bond. Using the above mentioned concept of the degree of polarity the real charge distribution of molecule AB can be written in the following form: $A^{+p}B^{-p}$, where p (degree of polarity) gives the partial ionic charge, too. Generally the charge distribution of molecule A_iB_j can be written by the following formula: $(A^{+\delta^{(A)}})_i(B^{-\delta^{(B)}})_j$, where $\delta^{(A)}$ is the number of partial charges on atom A, and $\delta^{(B)}$ that on atom B. The relation between δ partial charge number and p degree of polarity:

$$\delta = p \cdot \delta_{\max} \tag{2''}$$

where, if $p = 1$ then $\delta_{\max} = \delta$, therefore $\delta_{\max}$, in a hypothetical molecule

$\left(A^{+\delta^{(A)}_{\max}}\right)_i \left(B^{-\delta^{(B)}_{\max}}\right)_j$ with idealized ionic bond, means the ionic charge, in FAJANS's "quanticule" formula [10c] the overall ionic charge. Thus the charge distribution of molecule A_iB_j can also be written in the following form: $\left(A^{+p\cdot\delta^{(A)}_{\max}}\right)_i \left(B^{-p\cdot\delta^{(B)}_{\max}}\right)_j$.* (*E. g.* in the case of an ideal ionic bond, that is $p=1$ and 100% resp., the formula of molecule SO_2 would be $O^{2-}S^{4+}O^{2-}$, while FAJANS's approximating quanticule formula: $(e)_2S^{6+}\genfrac{}{}{0pt}{}{O^{2-}}{O^{2-}}$ therefore $\delta^{(S)}_{\max}=4e$ and $\delta^{(0)}_{\max}=-2e$ mean the ionic charge and in FAJANS's formula the overall ionic charge, resp. The real charge distribution $O^{p(-2)}S^{p(+4)}O^{p(-2)}$, thus if the degree of polarity *e.g.* $p=0{,}25$ *i.e.* of 25% then $O^{-0{,}5}S^{+1}O^{-0{,}5}$ or shortly $S^{+}(O^{-1/2})_2$ reflects the real charge distribution.) According to the principle of electroneutrality:

$$|+\delta^{(A)}_{\max}\cdot i| = |-\delta^{(B)}_{\max}\cdot j|$$

and

$$|+\delta^{(A)}\cdot i| = |-\delta^{(B)}\cdot j|.$$

On dividing these two equations:

$$+\delta^{(A)}/+\delta^{(A)}_{\max} = -\delta^{(B)}/-\delta^{(B)}_{\max}$$

and taking into consideration Eq. $\delta = p\cdot\delta_{\max}$

$$p^{(A)} = p^{(B)}$$

is given, thus it can be stated that the concept of bond polarity is applicable for the bonds of an arbitrary A_iB_j molecule.

Relation Between the Degree of Polarity of the Bond and the Amount of Its Ionic Character

Regarding that in the literature the expression of the amount of the ionic character of the bond is used for the degree of polarity determined by experimental dipole moments and bond lengths, and that these two different values are used, named as ionic character, to calibrate the same curve of "electronegativity" against the ionic character, after definying the concepts of the degree of polarity and of the ionic character, it seems necessary to examine their relation, too.

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* Equation 2″ is obtained by the following conversion of Eq. (2) defining the degree of polarity

$$p = \frac{\delta\cdot e\cdot R_{AB}}{\delta_{\max}\cdot e\cdot R_{AB}} = \frac{\delta}{\delta_{\max}} \qquad (2'')$$

where $\delta\cdot e$ is the magnitude of the partial ionic charge on atoms A and B, $\delta_{\max}\cdot e$ is the ionic charge in the case of an assumed ideal ionic bond; e is the elementary charge.

The whole dipole moment contains beside the primary moment determined by the ionic character and the bond length also the deformation caused by the mutual polarization of the constituents, the effect of the hybridization occurring in the bonding atomic orbitals and the overlap of these orbitals [11]—[16]:

$$\mu_{\text{exp}} = e(b^2 - a^2)R_{AB} + \mu_{\text{polarization}} + \mu_{\text{hybridization}} + \mu_{\text{overlap}}. \tag{2a}$$

The first term of the right is the so called *primary dipole moment:*

$$\mu_p = e(b^2 - a^2)R_{AB} = e\beta R_{AB} \tag{2b}$$

which arises from the asymmetrical charge distribution between atoms A and B of the binding electron or electrons. The latter is the function of the difference between the electronegativities of the two atoms. It can be seen from eqns (1), (2) and (2b) that *the ionic character* $\beta = u_p/e \cdot R_{AB}$ *is the "degree of polarity" corresponding to the primary moment,* thus the ionic character can be calculated from experimentally measured dipole moments or the nuclear quadrupole coupling constants, if other terms can be evaluated.

The second term is the so called *polarization or induced or atomic core dipole moment* μ_i, including the polarization, induced by the primary moment of the atomic cores (A^+B^-), *i. e.* of the non-bonding electrons. The polarization moment has a sign always opposite to that of the primary moment. The polarization moment can be evaluated with the classical formula:

$$\mu_i = E_A\alpha_A + E_B\alpha_B \tag{2c}$$

where α_A and α_B are the polarizabilities of ions A^+ and B^-, E_A and E_B are the polarizing electric field strengths. To estimate these latters, *e. g.* E_A; it is assumed that it arises from an effective charge on B and its extent is $\mu_{\text{exp.}}/R_{AB}^3$. Similarly, the field E_B is calculated from the effective pole on A. Thus the value of the polarization moment:

$$\mu_i = \frac{\mu_{\text{exp.}}}{R_{AB}^3}(\alpha_A + \alpha_B). \tag{2d}$$

The third member is the so called *hybridization moment* [17]. It arises from the asymmetry of hybrid atomic orbitals of the valency shell. The correct value of the degree of hybridization is different even referred to the same atom, at present time its reliable evaluation is impossible, as it is proved by the rather different values taken up by several authors. We find quite often strictly opposite views concerning basic problems, *e. g.* in the case of an atom with positive valency state DAILEY and TOWNES [14] do not take up hybridization, since the energy needed for this is more than two times greater than that of an atom in a covalent bond (*e. g.* in the case of molecules FCl and FBr), on the other hand according to GORDY [16], in the case of a constituent with positive charge, especially when this positive charge is great, the extent of hybridization may be very considerable (*e. g.* in the case of molecules FCl, FBr and NF_3). It was possible to make only qualitative conclusions concerning the hybridization and the problem was complicated by the fact that the effect of hybridization on structural data of the bonds experimentally determined, such as *e. g.* bond lengths, bond angles, bond dipole moments, nuclear quadrupole coupling constants etc. may considerably differ. In general the sign of the hybridization moment related to the primary moment depends on the kind of hybridization.

The fourth term is the so called *overlap moment* [18] (homopolar dipole moment), it arises from the overlap of atomic orbitals with different size. Here the fractional part of the charge distribution of the electron shell is considered, which holds the part of atomic orbital in the overlap range:

$$\mu_S = 4abe \cdot S_{AB} \cdot \bar{z}_S \approx \frac{-2eS_{AB}}{1+S_{AB}}\left(r - \frac{R_{AB}}{2}\right) \tag{2e}$$

where $\bar{z}_S$ is a vectorial distance characterizing the overlap range, r is the covalent radius of the smaller atom. If the negative end of the dipole is formed by a constituent with smaller size, then the overlap moment has an opposite sign to the primary moment and vice versa. According to VENKATESWARLU and JASEJA [16a] the overlap factor is an exponentially decreasing function of the difference in the atomic radii:

$$S^2 = A e^{-2|r_A - r_B|} \tag{2f}$$

where r_A and r_B are the radii of atoms forming A_2 and B_2 diatomic molecules, the value of the constant is $A = 0{,}21$.

Unfortunately, the dipole moments and the nuclear quadrupole coupling constants experimentally determined do not make possible an independent evaluation of the different moments [14]. The case is even more complicated by the fact that, according to the recent statements [16], the quadrupole coupling constants are influenced beside the factors above mentioned *i. e.* the primary, hybridization and overlap moments, by the effect of the neighbouring atoms and ions, respectively, and by the distortions of non bonding closed shells of electrons around the nucleus in question. The effect of neighbouring ionic constituents depends on the bond length to the greatest extent [14], [16a], but the quality of the constituents also plays a part. The fact that the curve of the ionic character versus differences in electronegativities turns back at high differences in electronegativity, (*e. g.* $\beta_{\mathrm{LiI}} = 0{,}900$, $\beta_{\mathrm{NaI}} = 0{,}867$; $\beta_{\mathrm{KCl}} = 1{,}000$, $\beta_{\mathrm{CsCl}} = 0{,}968$), is interpreted by the effect of the bond length and of the distortions of the closed shells. The greatest complication in the evaluation of β is that the nuclear quadrupole coupling constant is more sensitive to an electron charge distribution near to the nucleus and not to the electron charge distribution of the overlap range of the valency bond, as the bond dipole moment is [18a].

Mention must be made that the degree of bond multiplicity plays also an important part in forming the value of the dipole moment. Being the problem a complex one, mainly *A—B* molecules with single bonds used to be investigated.

In the case of molecules with pure ionic bond (*e. g.* potassium chloride) the expression $\mu_{\mathrm{exp.}}/e \cdot R_{AB}$ yields the extent of mutual polarization of ions, exerted on each other (beside the primary moment, the polarization moment is the main factor) while in the case of transition types of bond the polarity can be considered as the sum not only of the ionic character of the bond but of the polarization, hybridization and orbital overlap moments, too.

Most recently the following semiempirical method has been elaborated by FAJANS [18b] to calculate the degree of polarity of alkali halides. The dipole moment (μ_p) formed by rigid, spherical, symmetric ions is diminished, by the superposition of an opposite induced dipole moment (μ_i), induced by another ion in the ion with α polarizability. The equation definying the polarizability of the ion yields a connection between the magnitude of α and that of the induced moment (μ_i) and between the strength of the homogeneous, not too strong electrostatical field (E): $\mu_i=\alpha E$. On applying this equation, FAJANS used the following idealized conditions: one of the ions was considered as a polarizing one and its electric field as homogeneous, its strength was given by expression $E=e/R_{AX}^2$, while the polarizability of the other ion (α and R_D, respectively) in bound state was taken to be the same as in free state. Thus in an idealized case $\mu_i=\alpha E=\alpha e/R_{AX}^2$ hence the degree of polarity $p=\mu_{\text{exp.}}/\mu_{\text{calc.}}=\mu_{\text{exp.}}/\mu_{\text{ionic}}=\mu_{\text{exp.}}/\mu_{\text{primary}}=(\mu_{\text{primary}}-\mu_i)/\mu_{\text{primary}}$, from this:

$$1-p=\frac{\mu_i}{\mu_{\text{primary}}}=\frac{\alpha\cdot e/R_{AX}^2}{e\cdot R_{AX}}=\frac{\alpha_{A^+}+\alpha_{X^-}}{R_{AX}^3}. \qquad (2g)$$

Taking into consideration the LORENZ—LORENTZ equation, giving the connection between the mole refraction (R_∞) and the polarizability:

$$1-p=\frac{\alpha_{A^+}+\alpha_{X^-}}{R_{AX}^3}=0{,}3966\,\frac{R_\infty(A^+)+R_\infty(X^-)}{R_{AX}^3}. \qquad (2h)$$

Using the mole refractions of free alkali- and halide-ions in two extreme cases (with lithium iodide and caesium fluoride) extremely great differences were obtained between experimental values and those calculated according to Eq. (2h). At LiI, the small and rigid Li$^+$ cation penetrates the electron shell of I$^-$ anion, which is the most polarizable halide ion. On the contrary at CsF, F$^-$ being only slightly polarizable, it repulses the electronic shell of the easily polarizable Cs$^+$ cation. Since in bound state the refraction of the

Table I.

Degree of Polarity* p for Vapor Molecules

HF	0,433	HCl	0,168	HBr	0,116	HI	0,049
LiBr	0,594 (0,590)	LiI	0,544 (0,544)	NaF	— (0,85)	NaCl	0,794 (0,754)
KCl	0,818 (0,787)	KBr	0,768 (0,768)	KI	0,755 (0,744)		
CsF	0,699 (0,699)	CsCl	0,747 (0,753)	CsI	0,709 (0,746)	TlCl	0,364 (0,540)

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* The values without parentheses, $p=\mu_{\text{exp}}/e\cdot R_{AX}$ obtained from observed μ and R_{AX}, those in parentheses calculated using E_q. (2i).

anion is smaller and that of the cation is greater than in free state, it is reasonable that at LiI the calculated $(1-p)$ value was given too high, while in the case of CsF too small. Therefore FAJANS applied in Eq. (2h) instead of theoretical factor 0,3966 empirical 0,3408 (for anions) and 0,4781 (for cations), both being calculated from the experimental degrees of polarity of LiI and CsF, and the following equation was obtained:

$$1-p=0{,}3408\frac{R_{\infty}(X^{-})}{R_{AX}^{3}}+0{,}4781\frac{R_{\infty}(A^{+})}{R_{AX}^{3}}. \qquad (2i)$$

Data calculated on the basis of Eq. (2i) fairly agree with experimental ones (see Table I.). According to this method of calculation the ideal ionic bond is approximated by sodium fluoride with a calculated value of $p_{NaF}=0.85$. But there are negative p values for hydrogen halides, since the proton penetrates the electronic shell of halide anions, and this makes the application of the approximation Eq. (2i) rather irreal. In the case of thallium chloride molecule the difference between experimental and calculated values is very significant, what indicates a very high polarizing power and polarizability of the Tl^{+} ion with non-noble gas-type configuration. As a close it can be stated that the applicability of this method is very restricted.

Now it is clear that the amount of the ionic character of the chemical bond calculated from the nuclear quadrupole coupling constant, and the numerical value of the degree of bond polarity obtained from the bond dipole moment and bond length may differ from each other even in the case of the same bond, further, being the main factors, the primary and polarization moments always with opposite signs, generally the degree of polarity is smaller than the amount of the ionic character *(I. C.* $=\beta$*)*:

Table II.

Molecule	*I. C.*	*p*	Molecule	*I. C.*	*p*
LiBr	0,944	0,594	KI	0,970	0,755
LiI	0,900	0,578	RbCl	0,992	0,785
NaCl	0,990	0,794	CsCl	0,968	0,747
NaI	0,867	0,716	TlCl	0,831	0,364
KCl	1,000	0,818	ClF	0,259	0,113
KBr	0,985	0,768	BrF	0,329	0,153

A Survey of Methods for the Calculation of the Degree of Polarity of Chemical Bonds

1. PAULING'S *values for electronegativity and different attempts to use these values*

PAULING [19] established a pure empirical connection between the difference in the electronegativities of the constituents $|X_A-X_B|$ and the degree of polarity of the bond of AB binary compound in gas-phase. To this end he made use of FAJANS's values for the degree of polarity (naming it ionic character) and experimental data of HCl, HBr and HI molecules:

$$p = 1 - e^{-\frac{|x_A - x_B|^2}{4}}. \tag{3'}$$

From this formula 0,6 is given for the value of p_{HF}. Later HANNAY and SMYTH [20] obtained 0,43 experimentally for p_{HF} and they modified Eq. (3′):

$$p = 0{,}16|x_A - x_B| + 0{,}035|x_A - x_B|^2. \tag{3}$$

Values of p, belonging to $|x_A - x_B|$, calculated on the basis of Eqs. (3) and (3′) are summarized in Table III. For the calculation of the differencies in electronegativity $|x_A - x_B|$ the following equation is given:

$$|x_A - x_B|^2 = \frac{\Delta(A-B)}{23{,}06} \tag{4}$$

from which

$$|x_A - x_B| = \sqrt{1/23{,}06}\,\sqrt{\Delta(A-B)} = 0{,}208\,\sqrt{\Delta(A-B)} \tag{4'}$$

where

$$\Delta(A-B) = D_{(A-B)} - \tfrac{1}{2}(D_{(A-A)} + D_{(B-B)}) \tag{5}$$

Table III.

Degree of Polarity (p) as a Function of the Differences in Electronegativities, Calculated according to HANNAY and SMITH (3) and PAULING (3′), respectively

$x_A - x_B$	$p(3)$%	$p(3')$%	$x_A - x_B$	$p(3)$%	$p(3')$%
0,0	0	0	1,8	40,14	55,51
0,1	1,635	0,25	1,9	43,035	59,44
0,2	3,34	1,00	2,0	46,00	63,21
0,3	5,115	2,22	2,1	49,035	66,79
0,4	6,96	3,92	2,2	52,14	70,17
0,5	8,875	6,05	2,3	55,315	73,35
0,6	10,86	8,61	2,4	58,56	76,31
0,7	12,915	11,53	2,5	61,875	79,05
0,8	15,04	14,79	2,6	65,26	81,55
0,9	17,235	18,33	2,7	68,715	83,84
1,0	19,5	22,12	2,8	72,24	85,91
1,1	21,835	25,92	2,9	75,835	87,78
1,2	24,24	30,23	3,0	79,50	89,46
1,3	26,715	33,80	3,1	83,256	90,95
1,4	29,26	38,74	3,2	87,04	92,27
1,5	31,875	43,02	3,3	90,915	93,43
1,6	34,56	47,27	3,4	94,86	94,44
1,7	37,315	51,44	3,5	98,875	95,32
1,8	40,14	55,55	3,6		96,084

or

$$\Delta'(A-B)=D_{(A-B)}-\sqrt{D_{(A-A)}\cdot D_{(B-B)}}. \tag{5'}$$

$D_{(A-B)}$, $D_{(A-A)}$, $D_{(B-B)}$ are the bond energies (dissociation energies) of molecules AB, A_2 and B_2 in gas-phase, expressed in *k*cal/mole, while 23,06 is the conversion factor from *k*cal to electron volts. According to PAULING's theorem $\Delta(A-B)$ the so called extra ionic resonance energy term is always positive or at most zero, and the cause of this is the "resonance" between the different ionic and covalent structures formed between atoms A and B. Owing to the complicated eqn (2a) a close correlation between $\mu_{\mathrm{exp}}/e\cdot R_{AB}$ and the electronegativity difference cannot be expected, since these latter are in a close connection only with the primary moment, therefore $\mu_{\mathrm{exp.}}/e\cdot R_{AB}$ is not a measure for the difference in the electronegativity $|x_A-x_B|$ of atoms A and B. However, the fact that $\mu_{\mathrm{exp.}}/e\cdot R_{AB}$ and the corresponding electronegativity differences change near in a parallel way, is an empirical evidence that the contributions of the polarization, hybridization and overlap moments to the primary moment often equalize each other [14], [15], [21].

The heat of formation in the case of gas-phase molecules containing n_N atom of nitrogen and n_O atom of oxygen:

$$Q=23{,}06\Sigma(x_A-x_B)^2-55{,}1\cdot n_N-24{,}2\cdot n_O. \tag{6}$$

HAISSINSKY [22] by introducing the heat of sublimation (L) made use of the heats of formation for solid state, for the calculation of the electronegativities and extended his investigations to most of the elements of the periodic system. He described the following equation for the heat of formation:

$$Q=23{,}0\,\Sigma(x_A-x_B)^2-L-55{,}1\cdot n_N-24{,}2\cdot n_O. \tag{7}$$

Using the recent thermochemical data, the values for electronegativities of the atoms of copper, zinc and the gallium groups were also calculated [23]. Most recently the electronegativities of all the elements of the periodic system were given by GORDY and THOMAS, using recent thermochemical data (see Table IV) [24]. MULLIKEN [25] pointed out that the mean value of the ionization potential (I_A) and of the electron affinity (E_A) of a bounded atom is the measure for PAULING's electronegativity of the atom. Numerically

$$(I_A+E_A)/130=x_A. \tag{8}$$

Recently SKINNER and PRITCHARD [26] have established a connection between the values of Mulliken's scale for electronegativity $x_M=(I_A+E_A)/2$ and Pauling's values (x_P):

$$x_M=3\cdot 15\,x_P$$

NYEKRASOV [27] used the quotient of the ionization works and the corresponding ionization degree in order to calculate the polarity of compound AB on a basis that in general the elements having great electron affinity request greater ionization energy and vice versa, elements demanding small ionization work have small electron affinity (excepting rare gases). He has given the following simple formula for the calculation of the polarity of compound AB:

$$p = g(I_B + I_A)/(I_B - I_A) \tag{9}$$

where g depends on the bond number and shows the bond multiplicity. In a single A—B bond $g = 1$. Essentially Nyekrasov's formula is analogous to Mulliken's one and thus the values for p calculated by Eq. (9) well agree with those calculated from Pauling's electronegativity differences.

Most recently Lehmann and Bähr [28] have used the atomic core charge number Z^*/n to estimate Pauling's values for electronegativity. On the basis of Finkelnburg's connection [29] $Z^*/n = \sqrt{\bar{I}/Rhc}$, where Z^* is the effective nuclear charge number, n the principal quantum number, $\bar{I} = \Sigma I/v$, v being the number of ionization degrees. Essentially this formula, too, takes into consideration the ionization works, but espresses them in hydrogen ionization work units and deduces the problem of calculating the degrees of bond po-

Table IV.

Pauling's Values for Electronegativity as Selected by Gordy

Atomic number	Element	Electronegativity	Atomic number	Element	Electronegativity
1	H	2,15	52	Te	2,1
2	He	—	53	I	2,55
3	Li	0,95	54	Xe	—
4	Be	1,5	55	Cs	0,75
5	B	2,0	56	Ba	0,9
6	C	2,5	57	La	1,1
7	N	3,0	58	Ce	1,1
8	O	3,5	59	Pr	1,1
9	F	3,95	60	Nd	~ 1,2
10	Ne	—	61	Pm	~ 1,2
11	Na	0,9	62	Sm	~ 1,2
12	Mg	1,2	63	Eu	~ 1,1
13	Al	1,5	64	Gd	~ 1,2
14	Si	1,8	65	Tb	~ 1,2
15	P	2,1	66	Dy	~ 1,2
16	S	2,5	67	Ho	~ 1,2
17	Cl	3,0	68	Er	~ 1,2
18	Ar	—	69	Tm	~ 1,2
19	K	0,80	70	Yb	~ 1,1
20	Ca	1,0	71	Lu	~ 1,2
21	Sc	1,3	72	Hf	1,4
22	Ti	1,6	73	Ta	$1,3^{\mathrm{III}}$ $1,7^{\mathrm{V}}$
23	V	$1,4^{\mathrm{III}}$ $1,7^{\mathrm{IV}}$ $1,9^{\mathrm{V}}$	74	W	$1,6^{\mathrm{IV}}$ $2,0^{\mathrm{VI}}$
24	Cr	$1,4^{\mathrm{II}}$ $1,6^{\mathrm{III}}$ $2,2^{\mathrm{IV}}$	75	Re	$1,8^{\mathrm{V}}$ $2,2^{\mathrm{VII}}$
25	Mn	$1,4^{\mathrm{II}}$ $1,5^{\mathrm{III}}$ $2,5^{\mathrm{VII}}$	76	Os	2,0

larity to PAULING's method. AHRENS [30] investigated the problem in a similar way on applying the ionization work, considering it as the measure of the anion affinity of the cation. REED [31] studied the connection between the polarizability of the molecule and its ionization work and established simple and reversed proportions.

GORDY [32] emphasized the empirical connection between the bond stretching force constants calculated from spectroscopical data and PAULING's electronegativity values:

$$f = aN\left(\frac{x_A \cdot x_B}{R_{AB}^2}\right)^{3/4} + b \tag{10}$$

where N is the bond order, R_{AB} the bond length, a and b are constants within a certain group of the molecules. WILLIAMS [32a] pointed out that GORDY's result, Eq. (10), according to which the force constant depends on the product of the electronegativities, is only accidental, since the main factors determining the force constant are the number of valency electrons of

Table IV. Continued

Atomic number	Element	Electronegativity	Atomic number	Element	Electronegativity
26	Fe	1,7^{II} 1,8^{III}	77	Ir	2,1
27	Co	1,7	78	Pt	2,1
28	Ni	1,8	79	Au	2,3
29	Cu	1,8^{I} 2,0^{II}	80	Hg	1,8
30	Zn	1,5	81	Tl	1,5^{I} 1,9^{III}
31	Ga	1,5	82	Pb	1,6^{II} 1,8^{IV}
32	Ge	1,8	83	Bi	1,8
33	As	2,0	84	Po	2,0
34	Se	2,4	85	At	2,2
35	Br	2,8	86	Rn	—
36	Kr	—	87	Fr	0,7
37	Rb	0,8	88	Ra	0,9
38	Sr	1,0	89	Ac	1,1
39	Y	1,2	90	Th	1,0^{II} 1,4^{IV}
40	Zr	1,5	91	Pa	1,3^{III} 1,7^{V}
41	Nb	1,7	92	U	1,4^{IV} 1,9^{VI}
42	Mo	1,6	93	Np	~1,1
43	Tc	1,9^{V} 2,3^{VII}	94	Pu	~1,3
44	Ru	2,0	95	Am	~1,2
45	Rh	2,1	96	Cm	~1,3
46	Pd	2,0	97	Bk	~1,3
47	Ag	1,8	98	Cf	~1,3
48	Cd	1,5	99	Es	~1,3
49	In	1,5	100	Fm	~1,3
50	Sn	1,7^{II} 1,8^{IV}	101	Md	~1,3
51	Sb	1,8	102	No	~1,2

both atoms and their covalent radii (see GUGGENHEIMER's Eq. [32b]). Being the electronegativity a simple function of these, GORDY's equation, expressing force constants includes the product of the electronegativities. It is astonishing since most of the physical and chemical properties depend on the differences in electronegativities.

However, WALSH [33] regards the force constant for the $A—H$ bond to be the measure for the electronegativity of an A atom. Taking into consideration Eq. (10), the bond stretching force constant depends not only on the values for electronegativity, but on the bond distances, too. Therefore WALSH's determination is not unambigous [24]. Similarly to this SIEBERT [34] also investigated the connection between force constants and the type of binding.

GORDY [35a, b] gives as a measure for the electronegativity of a neutral atom in a stabile molecule the potential resulting from effective nuclear charge of the bonded atom, effective on a bonding electron when the electron is at a distance r from the nucleus:

$$x_A = \frac{Z^* e}{r} = \frac{ev - 0,5(v-1)e}{r} = 0{,}5e(v+1)/r = 0{,}31\left(\frac{v+1}{r}\right) + 0{,}50 \qquad (11)$$

where r is the covalent radius, v the number of valency electrons. From the formula it can be seen that, on the basis of PAULING's scheme, the screening number of a valency electron is taken into consideration with 0,5 unit (PAULING had calculated 0,4e) while the right part of the equation expresses the connection between $(v+1)/r$ and x_A empirically found. Similarly to this LI [35c] obtained the following eqn using the ionic radii (R):

$$x_A = 0{,}11\, Z^*/R + 0{,}64. \qquad (11')$$

Soon after we also have dealt with the calculation of PAULING' electronegativity [35d] (see later) a similar treatment by ALLRED and ROCHOW was elaborated [35e]. ALLRED and ROCHOW used PAULING's definition for the electronegativity according to which the electronegativity of a bonded atom is the measure of the force of attraction of an atom, exerted on the electrons. Thus the expression e^2Z^*/r^2 measures the attractive electrostatic force exerted by the atomic core with eZ^* charge to an electron with e charge, being in r distance from the nucleus. In this expression r is the covalent radius, Z^* the value calculated according to SLATER's rule [35g]. ALLRED and ROCHOW obtained empirically an approximation connection between PAULING's value for electronegativity x_A and Z^*/r^2:

$$x_A = 0{,}359 \frac{e^2 Z^*_{A^0}}{r^2} + 0{,}744. \qquad (11a)$$

It is similar to GORDY's empirical Eq. (11). A significant difference, besides the exponent of r is that in Eq. (11) the effective nuclear charge number of the ion with one positive charge is in the numerator, while in formula (11a) the effective nuclear charge of the neutral atom is used. WILMSHURST [35f] applied GORDY's expression for the effective atomic potential (11) to calculate the electronegativities of the radicals.

Recently GORDY and THOMAS [24] have established a simple linear relation between PAULING's electronegativity values and work function of the metals:

$$x_A = a \cdot \varphi + b = 0{,}44 \cdot \varphi - 0{,}15$$

where they used the mean value of data on work functions compiled by MICHAELSON [36] (φ in eV). The relation thus established is valid only for metals, for carbon, silicium *etc.*, for semimetals and non-metals it is not. Previous to GORDY and THOMAS's work STEVENSON [37] had established a similar relation on the basis of a consideration that analogously to MULLIKEN's concept the metal work functions can be regarded partly as surface ionization works and partly as the electron affinities of unfilled eletron energy levels connected with the Fermi-level of the metals. Thus

$$x_A = \frac{23{,}06}{130}(I_A + E_A) = 0{,}1775\,(2\varphi) = 0{,}355$$

where $23{,}06/130 = 0{,}1775$ is an empirical scale factor. STEVENSON's values were as general somewhat lower than GORDY and THOMAS's ones.

There were established relations between the ionic character determined by the differences in the electronegativities and the extent of the overlap of atomic orbitals [38]—[42a]. The greater the extent of the ionic character of the bond is, the smaller the overlap.

Some Critical Remarks on PAULING's *Methods for the Calculation of Electronegativity of Atom and on Other Similar Attempts*

As it can be seen from the previous, the calculation of the degrees of bond polarity by PAULING's electronegativities was only possible when one or more values for the degree of polarity determined by experiments, were applied. The most part of later efforts, instead of a direct calculation of the degrees of polarity, were limited to a possibly accurate calculation of PAULING's values for electronegativity from the physical constants deduced from diverse properties of the atoms and molecules resp., (such as thermochemical data, ionization works, electron affinities, normal covalent radii, force constants, work functions, atomic core charge numbers, *etc.*). All these methods working with fixed values for the electronegativity of an atom have several theoretical difficulties:

1. The electronegativity has the dimensions of force (see later) and so this means the electrostatic attracting force of a bonded atom exerted on the binding electrons described by the expresson $a \cdot e/r^2$, where a is a parameter depending on the positive nuclear charge, on the screening and the interaction of electrons, e is the elementar charge and r the distance from the nucleus to the electron in question. But the differences in electronegativities can be calculated by PAULING's Eq. (4)

$$|x_A - x_B| = 0{,}208\sqrt{\Delta(A-B)}.$$

Thus $\varDelta x = 0{,}208[D_{\{(A-B)-1/2[(A-A)+(B-B)]\}}]^{1/2}$ *i.e.* the electronegativity is proportional to the square root of the potential energy corresponding to the dissociation energy, *i. e.* to the expression $\sqrt{a \cdot e/r^2}$ and not to $a \cdot e/r^2$.

2. The value for electronegativity (x_A) is not a characterizing constant of the atom of an element at all, thus *a constant electronegativity of an element cannot have a definite meaning at least in quantitative respect.* [43]—[45].

a) The x_A value for the parameter determining the „ionic character" of the bond changes depending on the valency-state of an atom (A) with the same partner (*e. g.* the value of x_S considerably differs in $SO, SO_2, S_2O_3, SO_3, SO_4$ etc. molecules).

b) In the same valency-state the electronegativity of an element (x_A) also depends on the electronegativity of the partner (x_B), *i. e.* the partners are in mutual interaction (*e. g.* the value of the electronegativity of the nitrogen atom in the same valency state $x_{N^{III}}$ is considerably different in compounds NF_3 and NI_3). Namely the closely neighbouring atoms in the bonds mutually influence their field of force, therefore electronegativity is concerned with atoms in molecules rather than with atoms in isolation, that is measurement in a precise way is not easy [7].

An atom may exhibit a *range of electronegativity* depending upon the range of valence state available to it and the partner. There remains the problem of choosing from this range the unique value which the atom achieves in a given molecular environments. In the strictest sense one should speak not of the electronegativity of an atom, but rather of *the electronegativity of atomic orbitals* and *of bonding molecular orbitals* [7].

P. Daudel and R. Daudel [45a] pointed out that the extra ionic resonance energy $\varDelta(A-B)$, introduced by Pauling, must relate not to the differences in the electronegativity of the neutral atoms but first to the differences in the electronegativities of the so called ionic constituents *i. e.* bonded atoms with formal charge, being formed on the effect of the differences in electronegativities. Thus in the case of an AB binary molecule instead of Pauling's Eq. (4') they recommended the following:

$$|x_{A^0} - x_{B^0}| = 0{,}208\sqrt{\varDelta(A-B)} + p(\zeta_{A^+} + \zeta_{B^-}) \tag{4a}$$

where x_{A^0} and x_{B^0} are the electronegativities of neutral atoms, p the degree of polarity of the $A-B$ bond and ζ_{A^+} and ζ_{B^-} are changes in the electronegativities of A and B atoms, if A and B receive a formal unit positive or negative charge. So equation

$$0{,}208\sqrt{\varDelta(A-B)} = |x_{A^0} - x_{B^0}| - p(\zeta_{A^+} + \zeta_{B^-}) \tag{4a'}$$

also indicates that the electronegativity of a bonded atom depends on the atoms bonded with it, *i. e.* on the partners and the valency-state of the atom. Unfortunately the value of ζ practically can be estimated only roughly.

3. The exchange forces and the resonance, on the basis of which Pauling theoretically deduced the values for electronegativity are without any real basis [46]—[48]. "The concept of the exchange of electrons led to the

incorrect conclusion of the existence of specific exchange forces. In reality there are no exchange forces. In the molecules electric, namely, coulomb forces are acting". [49]. In the conventional explanation of the localized covalent bond formed on the interaction of atoms, the following energy terms are taken into consideration: the kinetic energy of the electrons, the electron — nuclear and nuclear — nuclear potential energies, and the electron-electron potential energy. An adequate discussion of the last of these energy terms requires a consideration of electron correlation on a six-dimensional configuration space. HURLEY [50a, b, c, d] pointed out that the formation and the properties of the localized covalent bond may be understood solely in terms of electrostatical forces of the coulomb type. These forces are completely determined by a single charge distribution function in three-dimensional physical space. This electrostatical treatment of the localized covalent bond, using the term of the optimum orbitals considerably simplifies the question, does not involve any loss of accuracy of the calculation. The electrostatical interpretation of the directed valences of molecular hydrides with a covalent bond established by GRAY and PRITCHARD [50e] indicates, that there is no casual relationship between the mathematical convenience of the orbital approximation and the occurrence of the directed valences. According to FAJANS [50f] and KIMBALL [50g] and Coulson [50h] the nature of the chemical binding forces both in inorganic and organic molecules and complexes, essentially is coulombic, electrostatic.*

As a close *it can be stated that the chemical binding forces can be interpreted even without supposing any specific exchange and resonance forces, resp., as essentially coulombic forces.*

From the point of view of the interpretation of the origin of PAULING's values of electronegativity it is very important that COTTRELL and SUTTON [51] applied the HEITLER—LONDON—SUGIURA treatment for the two-electron diatomic molecule while HURLEY [52] applied LENNARD—JONES and POPLE's approximate wave-function. It had been pointed out that if the calculated dissociation energy of molecule AB is greater than the mean (arithmetic or geometric) value of the calculated dissociation energies of molecules A_2 and B_2, this is not caused by an ionic-covalent resonance. Really, mainly the internuclear repulsion energy is reduced in molecule AB, (or generalizing it can be assumed that that between atomic cores decreases) related to the arithmetic or geometric mean of the internuclear repulsion energies in molecules AA and BB. It also had been established that the extra ionic resonance energy $\Delta(A—A)$ may be not only positive but also negative [52], [53].

4. To establish a relationship between the difference in the electronegativities of the constituents and the polarity of the bond of an AB binary compound in gaseous state, it is not practicable to use the data of hydrogen halides [54] since in this molecules according to experimental data, proton deeply penetrates the electronic shell of the anionic constituent. Overlap of such a great extent is never produced in the case of other cations.

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* See *e. g. Ephraim* f. in his book Inorganic Chemistry (Oliver and Boyd, Edinburgh and London, 1954, 6th Edition) applies FAJANS's polarisation and quanticule theory, respectively.

From practical points of view there are two complications in connection with the electronegativities:

1. Parameters determining the "ionicity" of the chemical bond (x_A, x_B) can be calculated from different empirical data. The inaccuracies and the insufficient number of such data (electron affinities, work functions of metal, heats of dissociation, *etc.*) and the different participation of the electronegativities in the values of diverse physical constants, largely limit the general valadity of the relations.

2. A great part of the different definitions for electronegativity is not simple (*e. g.* PAULING's) [33] or if it is simple as *e. g.* MULLIKEN's definition, then there are complications in its application in simple form. (The author himself admits that because of the dependence of ionization potentials and electron affinities on the valency state, values often related not to the normal state are to be used. [25].)

2. *Critical Review of* SANDERSON's *Method*

SANDERSON's values for the electronegativity, the so called stability ratios]55a—f] considerably differ from PAULING's ones both from point of view of the method and the numerical value. As the measure for the electronegativity of an active atom SANDERSON considers the ratio of the average electron density of an atom (ED) and the average electron density of a real or hypothetical isoelectronic inert atom. This is the so called stability-ratio (SR) for the given element:

$$SR = \frac{(ED)}{(ED)_i} = \frac{Z}{4/3\, r^3 \pi (ED)_i} = \frac{Z}{4{,}19\, r^3 (ED)_i}, \tag{12}$$

where Z is the number of electrons of the active atom in question (non inert-gas), r the nonpolar covalent atomic radius or the ionic radius, (ED) the average electronic density of the atoms *i. e.* the average number of electrons per Å^3; $(ED)_i$ the average electron density of an isoelectronic inert atom real, or hypothetical, determined by linear interpolation between the average real values of two inert-gas atoms placed nearest before and after the atom in question in the periodic system.

During the formation of a chemical bond *i. e.* when the atoms of the active elements combine into molecules, *the attractions of the atoms or atomic cores of the molecules on the valency electrons equalize thus a stabile bond is formed,* their electronegativities (SR) become equal.

SANDERSON had postulated that the SR_m of the molecule is a geometrical mean of the SRs of all the atoms of the molecule before the combination. Thus in the case of a binary compound A_iB_j $SR_m = \sqrt[i+j]{SR_A^i \cdot SR_B^j}$. This postulate was proved so that calculating the the atomic radii within the molecule from its SR_m by formula

$$r = \sqrt[3]{\frac{Z}{4{,}19 \cdot (ED)_i SR_m}}$$

the bond lengths as sums of two radii calculated in this way fairly agree with experimental data in case of near 700 investigated bonds, but also certain corrections were necessary, taking into consideration geometrical points of view at some bonds [55a], [55c].

SANDERSON assumed that *the change in the electronegativity, i. e. in the SR, is linear to that in the charge,* thus $\delta^{(A)}$ partial charge on atom A of the molecule and ions, resp.,:

$$\frac{SR_A - SR_{A^{v+}}}{v} : (SR_m - SR_A) = 1 : \delta^{(A)} \tag{13}$$

from this

$$\delta^{(A)} = \frac{SR_m - SR_A}{(SR_A - SR_{A^{v+}})/v} \tag{13a}$$

where $SR_{A^{v+}} = \dfrac{Z_{A^{v+}}}{4{,}19 \cdot r^3_{A^{v+}} (ED)_i}$ [55e]. Regarding that the value of $\delta^{(A)}$ refers to the partial charge of the constituent atoms of the molecules in gas-phase in order to calculate $SR_{A^{v+}}$ and $SR_{B^{v-}}$ of the electronegativities of the ions, the crystal ionic radii cannot be used. The only experimental values for ionic radii in gas-phase are obtained in case of atoms of alkali metal group, univalent atoms of alkali earth metal and aluminium groups and of halide and hydride ions [56]—[58]. However, it is possible to calculate theoretical values in the case of all the isolated ions with BOHR's formula [59].

Thus for sodium and fluoride ions the following values can be given:

Radius	Experimental Data	Calculated from Polarizability	Theoretically calculated
r_{F^-}	1,04 Å	1,02 Å	1,03 Å
r_{Na^+}	0,89 Å	0,57 Å	0,50 Å

Thus $(SR)_{NaF} = \sqrt{SR_{Na} \cdot SR_F} = \sqrt{0{,}70 . 5{,}75} = 2{,}01$.

Using these data:

$$SR_{F^-} = \frac{10}{4{,}19 (1{,}04)^3 \cdot 1{,}06} = 2{,}00$$

$$SR_{Na^+} = \frac{10}{4{,}19 (0{,}89)^3 \cdot 1{,}06} = 3{,}19$$

$$\delta^{(F)} = \frac{2{,}01 - 5{,}75}{5{,}75 - 2{,}00} = -0{,}997$$

$$\delta^{(Na)} = \frac{2{,}01 - 0{,}70}{3{,}19 - 0{,}70} = 0{,}526.$$

Therefore the so obtained charge distribution $Na^{+0{,}53}F^{-1{,}00}$ contradicts to the principle of electroneutrality and does not correspond to the real charge distribution of sodium fluoride molecule. In our opinion the cause of this discrepancy is that SANDERSON's postulate for the geometrical mean value referring to SR_m does not correspond to the conditions existing in the real charge distribution of the molecule. Thus a considerable difference arises *e. g.* between the bond lengths of sodium fluoride, calculated according to SANDERSON and RITTNER's [56] values:

$$r_{Na^+} = r_{F^-} = \frac{10}{4{,}19 \cdot 1{,}06 \cdot 2{,}01} = 1{,}039 \text{ Å}$$

thus $d_{NaF} = 1{,}039 + 1{,}039 = 2{,}078$ Å, while d_{NaF} from RITTNER's radii: 1,93 Å. In table VI. we give some correct values for bond length of alkali halides determined experimentally, and also those calculated according to SANDERSON. At the methods I and II the corresponding values for inert gas radius and $(ED)_i$ are the following (Table V):

Table V.

Atom	I. method		II. method		Other method	
	Univalent radii	$(ED)_i$	Crystal* ionic radii	$(ED)_i$	Radii after ROWLINSON	$(ED)_i$
He	0,93	0,61	0,93	0,59	1,28	0,23
Ne	1,12	1,70	1,31	1,06	1,39	0,89
Ar	1,54	1,18	1,74	0,82	1,71	0,86
Kr	1,70	1,78	1,89	1,27	1,80	1,45
Xe	1,90	1,87	2,09	1,41	2,0	1,61
Rn	2,2	1,93	2,14*	2,09*	—	—

The above data show that there is a very significant difference between experimental data and those calculated according to SANDERSON, especially at values for $(ED)_i$ recently used in the II group (excepting lithium halides).

In other cases it is true that the principle of electroneutrality is not valid for values of partial charge calculated by using geometrical mean value postulate referring to SR_m and by using the values of experimentally found and theoretically calculated ionic radii in gas-phase. This complication was eliminated by SANDERSON so that he arbitrarily chose a bond, that of the isolated sodium fluoride molecule, and chose it in 90% of "ionic character". (It is to be noted that for isolated sodium flouride molecule there are no experimental data from which the "ionic character" of the sodium fluoride bond could be estimated.) After this, using equation

$$\delta^{(F)} \text{ referring to } \delta^{(F)} = \frac{2{,}01 - 5{,}75}{5{,}75 - SR_{F^-}} = 0{,}90 \text{ and another}$$

$$\delta^{(Na)} = \frac{2{,}01 - 0{,}70}{SR_{Na^+} - 0{,}70} = 0{,}90$$

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* see ref. [60]

the value for SR_{Na^+} and SR_{F^-} can be obtained. Using these values in a successive approximation it becomes possible to calculate the SR of the most different free cations and anions [55b]. *Using the arbitrarily chosen adjustable parameter the method lost its advantage to the previous ones.* However, on comparing it with PAULING—HAISSINSKY's method, it has the merit of a more general applicability *e. g.* it simply can be used to calculate the ionic character of bonds in transition metal compounds, different complexes and organic molecules.

Table VI.

Formula	Experimental value		References	SANDERSON'S I. Method	SANDERSON'S II. Method
	Bond Distance				
LiF	1,51 ± 0,08		[60]	1,92	1,69
LiBr	2,1704	± 0,00006	[58]	2,48	2,35
LiJ	2,3919		[58]	2,77	2,54
KCl	2,6666		[58]	2,82	2,93
KBr	2,8207		[58]	2,98	3,11
RbCl	2,7867		[61]	2,94	3,09
CsF	2,3453		[58]	2,64	2,86
CsCl	2,9062		[58]	3,05	3,31
CsJ	3,3150		[58]	3,46	3,76
TlCl	2,541		[62]		2,47

Recently SANDERSON has taken the "ionicity" of the sodium fluoride bond to be of 75% and so the previous values for the partial charge, calculated with 90%, must be multiplied with 0,833. This change was done in order to obtain for uniatomic anions (fluoride, chloride, etc.) the theoretically expected lower ED value than those obtained for $(ED)_i$ of isoelectronic inert gas atoms with a greater nuclear charge and thus a more compact electronic shell.

In connection with this, mention must be made of the fact that it is possible to calculate the value of δ instead of geometrical mean value postulate with SANDERSON's method using the following less arbitrary method. Supposing that the change of SR is linear to the change in the partial charge and taking into consideration that if the compact, more negative atom takes a partial charge from a more positive atom, the originally more compact shell of the negative atom becomes loose while the less compact shell of the positive atom becomes more compact, supposing that this process lasts until the SR_A of the cationic constituent equals to the SR_B of the anionic constituent, thus in case of AB molecule

$$SR_m = \delta\cdot SR_{B^-} + (1-\delta)SR_B = \delta\cdot SR_{A^+} + (1-\delta)SR_A$$

(autoequivalent equation) from which the value of

$$\delta = \frac{SR_A - SR_B}{(SR_{B^-} - SR_B) + (SR_A + SR_{A^+})}$$

Table VII.

SANDERSON's Values for Electronegativity (SR = stability ratio)

A	log SR_A	SR_A	$(SR_A - SR_{A^{v+}})/v$	A	log SR_A	SR_A	$(SR_A - SR_{A^{v+}})/v$
H	0,5502	3,55	3,919	As	0,5922	3,91	4,112
Li	—0,1308	0,74	1,789	Se	0,6284	4,25	4,289
Be	0,2810	1,91	2,923	Br	0,6561	4,53	4,426
B	0,4533	2,84	3,545	Rb	—0,2757	0,53	1,514
C	0,5786	3,79	4,050	Sr	0,0414	1,10	2,267
N	0,6523	4,49	4,408	Y	0,2430	1,75	2,752
O	0,7168	5,21	4,749	Zr	0,3541	2,26	3,126
F	0,7597	5,75	4,988	Ag	0,3617	2,30	3,155
Na	—0,1549	0,70	1,741	Cd	0,4133	2,59	3,347
Mg	0,1931	1,56	2,661	In	0,4564	2,86	3,517
Al	0,2878	1,94	2,968	Sn	0,4914	3,10	3,663
Si	0,4183	2,62	3,418	Sb	0,5276	3,37	3,819
P	0,5238	3,34	3,802	Te	0,5587	3,62	3,958
S	0,6138	4,11	4,216	I	0,5843	3,84	4,077
Cl	0,6929	4,93	4,618	Cs	—0,3098	0,49	1,456
K	—0,2518	0,56	1,556	Ba	0,0086	1,02	2,189
Ca	0,0864	1,22	2,376	La	0,2923	1,96	2,912
Sc	0,2742	1,88	2,852	Au	0,4518	2,83	3,500
Ti	0,3560	2,27	3,272	Hg	0,4669	2,93	3,584
Cu	0,3856	2,43	3,243	Tl	0,4800	3,02	3,646
Zn	0,4533	2,84	3,529	Pb	0,4857	3.06	3,679
Ga	0,5092	3,23	3,772	Bi	0,4969	3,14	3,727
Ge	0,5551	3,59	3,942				

calculated from this eqn is between the values calculated with a reference standard of 90% and 75% ionic character for NaF (see Table VIII).

The *ED* values of the elements give the mean value of the compactness of the electron shell around the atomic nucleus. It can be expected that in case of atoms with compact electronic shell the expression $ED = Z/4{,}19 \cdot r^3$ well approximates this, *i. e.* in case of atoms with loose electronic shell the approximation is very poor. Really, especially in the case of alkali metal and alkaline earth metal atoms one does not obtain even the order qualitatively expected, therefore SANDERSON, taking into account the ionization works, modified the *ED* and *SR* values of these elements. However, there is only a slight difference between the revised values for lithium and sodium related to those between the values of potassium and sodium. Thus the "ionic character" of lithium compounds differs only with 1% from those of sodium compounds while the difference between the "ionic character" of sodium and potassium compounds is with 5% greater. Really, lithium compounds, due to the small size and great polarizing force of lithiumion, have considerably smaller "ionic character" and polarity, respectively, than other alkali metal compounds.

Table VIII.

Compound	$p_{\text{NaF}} = 90\%$	Autoequ. with Experim. Radii	$p_{\text{NaF}} = 75\%$
NaF	0,90	0,817	0,75
NaCl	0,798	0,69	0,665
NaBr	0,74	0,667	0,62
NaI	0,648	0,60	0,54
KF	0,95	0,817	0,793
KCl	0,85	0,695	0,71
CsF	0,9795	0,83	0,816
BrCl	0,053	0,048	0,0442

The values for degrees of bond polarity calculated according to SANDERSON's method considerably differ from the experimental ones, in general they are smaller, especially those obtained by most recently used $p_{\text{NaF}} = 0{,}75$ standard calibration value (see later Table IX).

It can be proved that SANDERSON' *SR* values are directly proportional to the attractive forces exerted by the atom on the valence electrons:

$$SR = \frac{Z}{4{,}19 \cdot r^2 \cdot r(ED)_i}$$

is converted, on substituting BOHR's formula for atomic radius, into

$$r = \frac{a_{\text{H}} \cdot n^2}{Z - S} = \frac{a_{\text{H}} \cdot n^2}{Z^*}$$

where $a_{\text{H}} = 0{,}5292$ Å is BOHR's radius of the hydrogen atom n the principal quantum number of the orbit for electrons detached during ionization of the atom in question, S the screening number of electrons remained after ionization. Thus, $Z-S=Z^*$ expresses the so-called effective nuclear charge number of the remained atomic core

$$SR=\frac{ZZ^*}{4{,}19\cdot r^2 a_{\mathrm{H}} n^2 (ED)_i}\,.$$

Introducing the notation

$$\frac{Z}{4{,}19\cdot a_{\mathrm{H}} n^2 (ED)_i}=C,$$

where C is constant in the case of isoelectronic ions, or approximately constant by elements of the same period. Thus

$$SR=C\cdot\frac{Z^*}{r^2}\,.$$

This term expresses the magnitude of attractive forces exerted by one atom of the molecule on the electrons.

The exact form of the correlation between the difference of PAULING's electronegativity and bond energy as evolved by P. DAUDEL and R. DAUDEL yields for the degree of ionic character and polarity, respectively, the following formula:

$$p=\frac{|x_A^0-x_B^0|-0{,}208\sqrt{\varDelta(A-B)}}{\zeta_{A^+}+\zeta_{B^-}}$$

which greatly resembles to SANDERSON's equation

$$\delta^{(A)}=p\cdot\delta_{\max}^{(A)}=\frac{SR_m-SR_A}{(SR_A-SR_{A^{+v}})/v}$$

$$\delta^{(B)}=p\cdot\delta_{\max}^{(B)}=\frac{SR_m-SR_B}{(SR_B-SR_{B^{-v'}})/v'}$$

in them we find in both cases the difference between the electronegativities of the neutral atom and the ionic constituent with partial charge of the molecule in the numerator, or an amount directly proportional to it, whilst the denominator measures the changes in electronegativity in A and B when they acquire unit positive and unit negative formal charge, respectively. This close similarity indicates that the terms in P. DAUDEL's and R. DAUDEL's equation also correspond to SANDERSON's definition of electronegativity.

PRITCHARD and SKINNER [7] pointed out that calculating the $(ED)_i$ values for the inert gas atoms, there are some complications when choosing the normal covalent radii of the inert gas atoms, since they form no compound. Such radii can be interpolated only from univalent crystal radii of isoelectronic ions or from crystal ionic radii. In Table V it can be seen that SANDERSON's and ROWLINSON's [63] recent values considerably differ from each other. But PRITCHARD and SKINNER's opinion, according to which the origin of alternations in electronegativity (SR) found in the major groups of the periodic system can be found in the values for normal covalent radius and $(ED)_i$ of inert gas atoms chosen by SANDERSON, is faulty. Really this alternation can be found already in the normal covalent atomic radii of the elements of the major groups, while its interpretation is yielded by *transition metal* contraction and the *double (transition metal + lanthanide) contraction* [64a].

Both SANDERSON's and ROCHOW's values for electronegativity well show the alternation within one column of the major group of the periodic system. Therefore it is rather odd and without sense to bring this into correlation with PAULING's values for electronegativity, which do not show this alternation, *i. e.* plotted against each other on the same curve (see *e. g.* [35e], [64b]). Thus it is reasonable that sometimes there is a difference of about 0,5 electronegativity units between correlated and original values.

Another practical complication of SANDERSON's method had already been pointed out by DOERFFEL, according to him the inaccuracy of the radius is more emphasized, since it takes place at its third power [64c]. At last the linear relation between the stability ratio and the partial charge cannot be proved.

3. RITTNER'*s Method*

On the basis of the classical electrostatical model, by introducing certain simplifications, RITTNER has elaborated a semiempirical method for the calculation of the bond energy and the degree of polarity and dipole moments, resp., of alkali halides solely [56]. This method has been applied by KLEMPERER and MARGRAVE [56a] for the calculation of the dipole moments and binding energies of alkali hydrides. This application was criticized by ALTSHULLER [56b] on the basis that the penetration of alkali metal anions into hydride anions is of considerably greater extent than that into halide anion, therefore the simplified model applied to alkali halides is not suitable for alkali hydrides. According to KLEMPERER and MARGRAVE there was a great difference between calculated and experimental values already in the case of alkaline-earth-metal oxides. Generally RITTNER's method was to be applied only for alkali halides of high degrees of polarity, and even here the agreement between the most recent experimental values for the degree of polarity and those calculated with this method is very poor.

New Ways for Calculating the Degree of Polarity

On the basis of the above critical review of these semiempirical methods it is clear that the task of further investigations is not to seek new values for the electronegativity, reflecting more exactly the chemical character of the elements, or to deduct and calculate more useful values for PAULING's electronegativities from other physical constants of atoms and molecules. The aim is to elaborate such a *new method,* in which we can start from data experimentally obtained independently of the bond length and of the bond dipole moment to be evaluated, theoretically calculated with methods of the quantum mechanics, and it is desired that these data precisely can be measured and we have many of them. The further task is to elaborate a method of calculation which takes into consideration actual forces, based on a resonable structure, without using any other experimentally determined degree of polarity or any other adjustable parameters arbitrarily chosen. Naturally the polarity of the ionic character of a given molecule must be yielded precisely by this method of calculation considering each case as a special one.

The present paper starts from FAJANS's approach to the chemical binding forces, supported experimentaly and quantum mechanically. FAJANS's approach is the so called "quanticule and polarization theory" of the chemical bond. [10c], [50f]. According to FAJANS's quanticule theory, the nature of chemical binding forces is coulombic, *i. e.* the interactions in molecules, crystals, melts and solutions can be traced back to the electrostatic interactions between nuclei and electrons. In first approximation, these may be investigated as electrostatic interactions of quanticules: namely, of atomic nuclei or atomic cores, further of binding electron groups and of antibinding electron groups (molecular or atomic quanticules). The qualitative results of these interactions on the bond polarity are summarized in FAJANS's polarization rules, according to which the degree of polarity is the smaller, the stronger the field of the deforming ion (the atomic core quanticule) and the larger the polarizability of the deformed ion (anionic quanticule) are. Both depend on the charge, size and electron configuration of the ion in question.

Starting from FAJANS's quanticule and polarization theory, as a first step it is necessary to take into consideration quantitatively the polarizing power of the cation. Several attempts of this kind can be found in literature. In 1926 GOLDSCHMIDT [65] introduced ve/r^2 and ve/R_{AB}^2 resp., as the measure for the field strength of the cation [66a, b], where v is the valency and charge, respectively, of the ion, e the elementary charge and r the cationic radius, R_{AB} the distance between the anion and the cation. Yet CARTLEDGE [67] in 1928 used the expression ve/r to take quantitatively into consideration the polarizing power of the cation. A common inadequacy both of the magnitude of the field strength and the ionic potential is that owing to the use of macroscopic ionic charge, v, does not reflect the difference between the polarizing power of ions with the same charge and size but with different electronic configuration [68, 69], as it had been pointed out already by FAJANS [10a]. The measure for the attraction force of the cations with the same size and charge but with different electronic configuration, exerted on a given anion, or simplifying the question, on an outer electron, is the ionization work needed for the detachment of this electron. That is why a more general applicability of the ionic potential and the electric field strength expressions was attempted by several authors, when they introduced the ionization work (I). AHRENS [70a, 70b] introduced the expression of the "electric intensity" and the "field strength" ($F=I/r$), resp., measuring anion affinity of a cation, with the same charge and the same size in volt per Å. GOLDSCHMIDT in his recent book [71] takes as the measure for the polarizing force the value of the ionization work needed for the detachment of the last electron during the forming of the cation in question, referred to unit ionic charge:

shortly the potential per unit charge (I/v). Regarding, that the shielding and screening effects (Se) of electrons with different configuration (having different principal, azimuthal, magnetic and spin quantum numbers) exerted on the nucleus with $+Ze$ charge, are very different, and this difference has some effect on the ionization work needed for the detachment of the outermost electron, the endeavour to use the so called effective nuclear charge $Z^{*}\cdot e = e(Z-S)$ proposed by some authors [28, 35a, b, 72] can be regarded quite obvious. So GORDY has applied the term $Z^{*}e/r$, while LEHMANN and BÄHR Z^{*}/n, as a measure for PAULING's electronegativity of the atoms. The values of Z^{*} used by GORDY and LEHMANN considerably differ from each other, since GORDY used PAULING's scheme for the estimation of the screening number (the screening number 0,5 *per* one valency electron). LEHMANN and BÄHR used FINKELNBURG's [73] screening number and Z^{*} values, resp., on the basis of $Z^{*}/n = \sqrt{I/Rhc}$. GORDY's $Z^{*}e/r$ values were calculated again by PRITCHARD and SKINNER [74], using SLATER's rule [75]. Most recently AHRENS has introduced $S_{eff} = 5v^{1,27}/I\sqrt{r}$ under the name "shielding efficiency of the cations" [76].

The method essentially already described by us [35d] has been applied by FERREIRA [77] for PAULING's and P. DAUDEL and R. DAUDEL's equation respectively, where he used KOHLRAUSCH's [59] screening constants for the calculation of the degrees of polarity. With his method he succeeded only to calculate the degree of polarity of hydrogen halides, in the case of other bonds he could not make calculations for them due to complications in choosing the screening constants for the different hybridization states.

ALLRED and ROCHOW calculate in the expression $P^{*} = \frac{Z_A^{*}e^2}{r^2}$, the effective nuclear charge number of the constituent atom on the basis of the SLATER-rule, while r is the covalent atomic radius experimentally obtained.

Mention must be made that GOLDSCHMIDT doubted [78] the real physical meaning of the ionic potential, and according to CRAIG [79] in complex compounds the "relative capacity of attraction" for a metal ion, exerted on the ligands can be measured better with the expression of the field strength than with that of the ionic potential.

After all, considering all these attempts we thought that the most suitable is to introduce the concept of the *"effective electric field strength"* (F^{*}) where the absolute value of the effective electric field strength is $F^{*} = Z^{*}\cdot e/r^2$ and $Z^{*}\cdot e/R_{AB}^2$. (In the expression r, depending on the problem to be investigated may be a value theoretically calculated, the true radius of the free atoms or ions, or a radius obtained from the interionic or interatomic distances in crystal lattices, or ionic radius deduced from the bond length of molecules in gas-state while R_{AB} is the bond length of compounds in gas or solid state, *i. e.* the anion-cation distance and in the case of elements the shortest bond length.)

The polarizability of the anions can be calculated from mole refractions precisely determined experimentally (R_∞) by the LORENZ—LORENTZ equation:

$$\alpha = \frac{3}{4\pi N}\frac{n^2-1}{n^2+2}\cdot\frac{M}{s} = \frac{3}{4\pi N}R_\infty$$

where n is the refractive index for $\lambda = \infty$, M the molecular weight, s the density, and N AVOGADRO's number. Theoretically, on the basis of the BORN—HEISENBERG relationship $\alpha = \frac{C}{Z^{*3}}$ where C is an amount proportional to the sixth power of the effective principal quantum number, thus α is proportional to r^3. According to RICE [80] the polarizability $\alpha = 0{,}76\ vr^3$ where v is the valence of the anion, *i. e.* the negative charge number. Most recently the concept of the anionic potential v/r has been introduced by SZÁDECZKY [81] analogously to the cationic potential (v the valence of the negative ion, or its charge number). Considering that strongly polarizable anions have small positive effective electric field strength (actually it may be negative) and *vice versa*, so we can introduce the expression $F^* = Z^* e/r^2$ of the effective electric field strength for anions, too as measure of its polarizability.

In a common quantitative treatment of the polarizing force and polarizability, taking into consideration all the previous attempts (see *e. g.* reference [81]) a difficulty arises that the polarizing force is inversely proportional to the size of the constituent ion or atom, while the polarizability is directly proportional to it. SZÁDECZKY's method is a common treatment, where the potential of the compound combines from the anionic and cationic potentials, and the atomic potentials, resp. In accordance with the experimental results, a larger cationic potential shows always greater polarizing force. But regarding the question from the side of the polarizability of the anions, the following contradiction arises: in the case of an ions with the same charge but with difference size, the decrease of the anionic potential means an increasing polarisability (*e. g.* F^-, Cl^-, Br^- and I^- anionic row), while at anions with near the same size but having different charge, the polarizability decreases together with the decrease of the anionic potential (*e. g.* OH^- and O^{2-}). To avoid this the problem of the polarizability was deduced to the problem of the polarizing force, whenever both was quantitatively taken into consideration with the effective electric field strength. This attempt involves no contradiction, since in the comparison we must take into consideration that FAJANS's approximating formules represent limiting cases with ideal ionic bond, and FAJANS's polarization rules refer to the same, what informs us to what an extent does the real charge distribution of the molecule in question differ from the ideal ionic bond state. With FAJANS's own words: "In my theory Li^+H^- and $S^{6+}(O^{2-})_4$ express correctly the quantization, while the continuous polarization which automatically follows from these formulations and from the polarization properties of the ions, leads to the charge distribution $Li^{p+}H^{p-}$ etc. [82]". However, the effective electric field strength value of the anionic and cationic constituents considerably differs from that of the corresponding free, ideal, rigid ions, *i. e.* from the polarizing force and the polarizability, too. To understand this the following must be considered. According to SANDERSON's definition, the electronegativity of an atom is represented by the force, with which the atom in the molecule affects the electron. A molecule being formed, if in the beginning the attraction force of the constituents differed, it must be equalized by a charge shift (see *e. g.* SANDERSON's concept), *i. e.* the more electronegative atom expands thereby lessening its attraction for the valence electrons, and the less electronegative atom contracts, thereby increasing its attraction for the valence electrons, shortly on the other side the cation deforms the electronic shell of the anion until the *effective electric field strength of the cationic constituent becomes equal to that of the anionic component.* The extent of the charge shift, calculated on the basis of the equality of the effective electric field strength, gives us information about the degree of polarity of the bond. According to our investigations the effective electric field strength of the constituent, in equilibrium, is always in the positive range during the formation of the most diverse molecules and never becomes negative (a negative value, as a rule, would correspond to a limit case, to the effective electric field strength of the free anion). At last the polarizability of the anion was substituted by the polarizing force of the anionic constituent. Now, we must emphasize that there is an important difference between our concept of the "effective electric field strength" and the concept of the "field strength" widely used by FAJANS and others. *E. g.* the electrostatic field strength of the fluoride ion, effective in macroscopical dimension (in $d \gg r$ distance), is a negative value $-e/r^2$ and $-e/d^2$, at the same time the electrostatic field strength of the fluoride ion formed just around itself, *i. e.* the absolute value of an electrostatic attraction force exerted on a unit negative charge placed at a distance of the radius of the isolated fluoride ion (0,954 Å) from the fluoride-nucleus, the so called "effective electric field strength" the absolute value of which is $F^*_{F^-} = +0{,}3426 \cdot e/\text{Å}^2$ positive value, since the ten electrons of the fluoride ion do not perfectly screen the nuclear charge with the magnitude of $Z = +9e$. The nuclear charge screened by ten electrons of fluoride ion with neon configuration $8{,}6882 \cdot e$ and so the effective nuclear charge of the fluoride ion $(9-8{,}6882)e = 0{,}3118 \cdot e$, therefore the effective electric field strength: $e \cdot Z^*/r^2 = e \cdot 0{,}3118/(0{,}954)^2\text{Å}^2 = 0{,}3426 e/\text{Å}^2$. In our investigations the charge shift in question within a molecule was to be calculated by taking into consideration quantitatively these power ratios with microscopical character. In order to calculate the effective nuclear charge number, the screening number, the effective principal quantum number and the radius of the atomic or ionic constituents of the bond, the method of approximation using the properties of free, isolated atoms and ions was applied [35d]. Here GLOCKLER—LISITZIN's equation for ionization works of free, isoelectric ions:

$$I = aZ^2 + bZ + c$$

was taken into consideration together with KOHLRAUSCH's equation for the ionization works:

$$I = Rhc \frac{(Z-S)^2 e^2}{(n^*)^2} - \gamma .$$

From these equations the following results were deducted:

$$S = -b/2a$$

$$(n^*)^2 = Rhc/a = 13{,}595/a$$

$$\gamma = \frac{b^2}{4a} - c .$$

These two main factors determine the average distance of the electron and maximum electron charge-density, respectively, from the nucleus, *i. e.* the radius of the atomic or ionic constituent in question:

$$r = a_H(n^*)^2/Z^* = 0{,}529172(n^*)^2/Z^* \qquad (\text{in Å}).$$

When carrying out calculations for elements of the fields *S* and *P* by using the most reliable data for the ionization potentials we have the values of the effective nuclear charge number, screening number, effective principal quantum number, contraction work (γ) and radius of all the atoms and ions with whole number positive or negative charges. Afterwards the amount of the microscopic effective electric field strength of these free ions and atoms was calculated ($F^* = Z^* e/r^2$). This can be regarded as an absolute measure of the electronegativity of free, isolated ions and atoms and fully consistent with SANDERSON's original definition of electronegativity for the free ions and atoms. Further investigations proved that the effective electric field strength of free ions and atoms is an exponential function of their charge. When a molecule forms, a charge shift will occur as compared to the charge distribution of the free ions. As a consequence of this charge shift, the value of the effective charge on ions and together with this their dimensions change and accordingly the effective electric field strength around the ions changes, too. The extent of this charge shift is determined at the equilibrium state by the classical *virial-theorem,* according to which the effective electric field strength of the cationic constituent must be equal to that of the anionic constituent:

$$\frac{Z^*_{A^{+p\delta^{(A)}_{\max}}}}{r^2_{A^{+p\delta^{(A)}_{\max}}}} = \frac{Z^*_{B^{-p\cdot\delta^{(B)}_{\max}}}}{r^2_{B^{-p\cdot\delta^{(B)}_{\max}}}}$$

where p is the degree of polarity of the bond in question, $\delta_{\max}$ is the maximal charge on the constituents *A* and *B*, when supposing an ideal ionic bond. The extent of the charge shift obtained this way determined the degree of the bond polarity or using PAULING's term, the degree of the ionic character of the bond:

$$p = \frac{\log F^*_B - \log F^*_A}{(\log F^*_{A^+} - \log F^*_A)\cdot\delta^{(A)}_{\max} + (\log F^*_B - \log F^*_{B^-})\cdot\delta^{(B)}_{\max}}$$

where F^*_A and F^*_B are the effective electric field strengths of free, isolated *A* and *B* atoms, while $F^*_{A^+}$ and $F^*_{B^-}$ are those of the isolated, free A^+ and B^- ions. On comparing the results obtained by using this equation and those obtained by the methods so far common in literature with the experimental values, ours are in a considerably better agreement (Table IX). Greater differences occur only in the case of molecules where FAJANS's approximation formula differs from the more simple formula applied by us. The cause of this can be found in the shortcomings of the method of calculation, namely by this method the properties of bonded constituents were approximated with the properties of free atoms and ions. In case of great number of bonds the numerical values of the degrees of bond polarity calculated in the *S, P, D*-fields

Table IX.

Molecular formula	Fajans's approximation formula	Degree of bond polarity (p)			
		Experimental	Pauling (Hannay and Smyth)	Samderson ($p_{NAF}=0{,}75$)	Present paper
ClF	Cl^+F^-	0,113	0,195	0,085	0,157
BrF	Br^+F^-	0,153	0,24	0,130	0,168
$BrCl$	Br^+Cl^-	0,056	0,03	0,044	0,016
ICl	I^+Cl^-	0,100	0,007	0,125	0,149
IBr	I^+Br^-	0,110	0,03	0,081	0,133
ClF_3	$(e)_4\,Cl^{7+}(F^-)_3$	0,090	—	0,044	0,121
BrF_3	$(e)_4\,Br^{7+}(F^-)_3$	0,127	—	0,067	0,129
BrF_5	$(e)_2\,Br^{7+}(F^-)_5$	0,125	—	0,045	0,105
IF_5	$(e)_2\,I^{7+}(F^-)_5$	0,178	—	0,075	0,173
SO_2	$(e)_2\,S^{6+}(O^{2-})_2$	0,116	0,195	0,042	0,119
NO_2	$(e)\,N^{5+}(O^{2-})_2$	0,042	0,09	0,027	0,047
PCl_3	$(e)_2\,P^{5+}(Cl^-)_3$	0,073	0,17	0,099	0,176
$P=O$	$P^{5+}\cdots O^{2-}$	0,105	0,29	0,066	0,133
AsF_3	$(e)_2\,As^{5+}(F^-)_3$	0,259	0,46	0,106	0,212
$AsCl_3$	$(e)_2\,As^{5+}(Cl^-)_3$	0,139	0,195	0,060	0,128
$AsBr_3$	$(e)_2\,As^{5+}(Br^-)_3$	0,110	0,15	0,037	0,118
$SbCl_3$	$(e)_2\,Sb^{5+}(Cl^-)_3$	0,197	0,24	0,097	0,202
$SbBr_3$	$(e)_2\,Sb^{5+}(Br^-)_3$	0,155	0,195	0,073	0,193
CO	$C^{4+}(e)_{10}\,O^{6+}$	0,011	0,20	0,080	0,155
CO_2	$O^{2-}\,C^{4+}\,O^{2-}$	0,105	0,195	0,056	0,107
CS_2	$S^{2-}\,C^{4+}\,S^{2-}$	0,030	0,00	0,013	0,024
SiF_4	$Si^{4+}(F^-)_4$	0,307	0,52	0,168	0,272
$SnCl_2$	$(e)_2\,Sn^{4+}(Cl^-)_2$	0,267	0,28	0,153	0,267
BF_3	$B^{3+}(F^-)_3$	0,273	0,47	0,186	0,244
$TlCl$	$(e)_2\,Tl^{3+}\,Cl^-$	0,364	0,32	0,158	0,306
$LiCl$	$Li^+\,Cl^-$	0,608	0,46	0,650	0,601
$LiBr$	$Li^+\,Br^-$	0,594	0,40	0,610	0,594
LiI	$Li^+\,I^-$	0,544	0,35	0,528	0,556
KF	K^+F^-	0,703	0,87	0,793	0,716
KCl	$K^+\,Cl^-$	0,818	0,52	0,708	0,818
KBr	$K^+\,Br^-$	0,768	0,46	0,664	0,809
KI	$K^+\,I^-$	0,755	0,40	0,582	0,768
CsF	$Cs^+\,F^-$	0,699	0,91	0,816	0,685
$CsCl$	$Cs^+\,Cl^-$	0,747	0,55	0,731	0,747
$CsBr$	$Cs^+\,Br^-$	0,711	0,49	0,687	0,740

of the periodic table were published in a set of publications appearing in Acta Chim. Hung. [83] and [35d].

The effective electric field strength of the anionic and cationic constituents was measured with the expression $F^{*} = Z^{*}\cdot e/r^{2}$, and this or the other $Z^{*}\cdot e/R_{AB}^{2}$ expression is generally used when investigating a force or physical chemical constants being in close connection with the effective forces. In energetical calculations or in a quantitative treatment of constants connected with these we shall use the expression of the "effective ionic potential" $Z^{*}\cdot e/r$, and $Z^{*}\cdot e/R_{AB}$. Both expressions truly reflect the dependence of the field strength and potential, resp., of the questioned atoms or ions not only on its size and charge but on its electron configuration, too. The reality and the usefulness of the concept of the "effective electric field strength" is proved by that it had been used with success during the quantitative investigations of the physical properties of elements and metals, together with the derivative of the effective electric field strength. We succeeded in developing a connection between force constants calculated from the values for melting points, compressibility and specific heat at low temperature of metals, and the effective electric field strength of metal ions placed in the lattice point, namely it was given as a linear function of the derivative of the force constant of the effective field strength in distance.

Summarizing these results, the effective ionic potential, effective electric field strength and the derivative of the effective electric field strength opened new ways for the quantitative treatment of the physical-chemical constants of the elements and their compounds, based on a simple and real structure.

* * *

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О ПРОБЛЕМЕ ПОЛЯРНОСТИ И ИОННОГО ХАРАКТЕРА ХИМИЧЕСКОЙ СВЯЗИ

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Автор, изучая проблему полярности и ионного характера попытался рассчитать степень полярности связи определенную *Фаянсом*. Определение степени полярности было возможно только при помощи дифференций в электронегативности *Паулинга*, применяя другие, экспериментально заранее определенные степени полярности. Последние стремления в большей части были ограничены к возможно точнейшему вычислению величин электронегативности *Паулинга* из всевозможных «постоянных» атомов и молекул. Величины электронегативности, так называемые «связи стабильности», вычислены *Сандерсоном* с такой же целью, значительно отличаются от этих же *Паулинга*, но здесь также нужно было употреблять одну величину калибрации: ($P_{NaF} = 0{,}75$).

В настоящей работе для квантитативного подхода к рулям поляризации Фаянса автором была введена концепция «эффективной силы поля» (F^*), абсолютное значение которой $F^* = Z^* \cdot e/r^2$ где Z^* — число эффективных зарядов ядра данной изолированной формации (иона или атома), r—ее радиус. В равновесии, эффективная сила поля катионного компонента равна той же анионного компонента, это дает возможность рассчитать размер смещения заряда или степень полярности связи с 5 процентов точностью.

$Z^* \cdot e/r^2$ — так называемое выражение эффективного ионного потенциала и эффективная сила поля является производным по дистанции предыдущего в энергетических расчетах, так как производное по дистанции эффективной силы поля открыло новые возможности при квантитативном подходе постоянных натяжений связей полученных из разных физических постоянных элементов и металлов.

AN INVESTIGATION OF THE CONNECTION BETWEEN PHYSIOLOGICAL ACTIVITY AND CHEMICAL STRUCTURE OF NEW DRUGS ACTING ON THE CENTRAL NERVOUS SYSTEM

I. The Synthesis of Some Aminoacetates Containing Cyclic Tertiary Nitrogen Atom

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In the course of our work we have prepared some cyclic tertier-amino-acetic-acid-esters and the short series of their quaterner derivatives in order to subject them to pharmacological investigations.

Especially the effect of the mentioned ester-typed compounds on the central nervous system was examined.

This investigations made clear that from this group of compounds only the N-piperidino acetic acid benzyl-ester had, a slight antinicotinic effect that might be increased, to a little extent, by quaternerization.

The problems of the synthesis and pharmacology of β-amino ketones are recently often treated in literature. One of the authors [1]—[5], has devoted extensive studies to the pharmacology of this group of materials. Several of these compounds possess remarkable antinicotinic action, and some of them are known today as well established pharmaceuticals.

The main object of our investigations has been to find some connection between the physiological action and chemical structure. The possibility of such connection appeared to be all the more probable, since there are some other groups of compounds known besides β-amino ketones which have antinicotinic action. An example of such materials is Parpanit (diethylamino-ethyl ester of l-phenylcyclopentane-l-carboxylic acid), which is effective against spasms caused by nicotine, even when it is applied in very small doses, such as 5 mg/kg. Thus, in the course of our initial efforts, compounds having the general formula of $R{>}N(CH_2)_nCOOR'$ were synthesized and their physiological action determined. At the same time also some of the „reversed esters", were prepared. (Fig. 1.)

$$R{>}N(CH_2)_n{\cdot}COOR' \rightarrow R{>}N(CH_2)_nO{\cdot}COR'$$

where R>N represents a piperidino, pyrrolidino or morpholino group, and R′ denotes methyl, ethyl, butyl, benzyl substituents, and $n = 1, 2, 3$.

A study was made of the influence of the number of methylene groups present on physiological activity, and the optimum methylene chain length was determined.

A short survey of the pharmaceutical use of similar N-piperidino and other secondary amine derivatives may be given as follows:

a) As it has been described earlier, different N-piperidino-β-amino ketones are known as compounds possessing antinicotinic action [1]—[6].

b) Some N-piperidino or other N-cyclic amino carboxylic esters or their amides are local anaesthetics or spasmolytic agents [7], [8], whereas some β-piperidino-benzoates have midriatic action [9].

c) Certain piperidine derivatives have been described as inhibitors of spirochetes.

d) Bis-(3-hydroxy dimethyl piperidinium) bromide ethers have been used as neuromuscular blocking agents [11].

e) Some dialkyl aminoalkyloxy-alkyl piperidines and pyrrolidines have been recommended as blood pressure lovering agents [12].

These few examples may show that a great number of various drugs have been derived from the chemical group of secondary cyclic amines.

During the course of the present investigations short series of cyclic N-substituted acetates have been prepared, and an attempt has been made to trace down the physiological properties of the products.

Our method of synthesis was the following:

The simplest way of preparing N-substituted acetates is the condensation of monochloroacetates with secondary amines [8]. In this way, a whole series of aminoacetic acid derivatives could be prepared:

$$2\,R{>}NH + Cl\cdot CH_2COOR' \rightarrow R{>}N\cdot CH_2COOR' + R{>}NH\cdot HCl$$

R>N = piperidino, pyrrolidino or morpholino groups,

R′ = methyl, ethyl, butyl or benzyl groups.

The experiments involved an investigation of the influence of the nature of the halogen substituent in the $X\cdot CH_2COOR'$ aliphatic halogen carboxylic esters on the yield of the final product. When X = I, or Br, or Cl, best yields could be obtained with bromoalkyl carboxylic esters [13]. Decrease of the yield may be explained by the polymerisation of by-products when iodoacetates were used, whereas the sluggish reaction of chloroacetates necessitated more severe reaction conditions producing the same detrimental result on the yield.

For the purpose of identification the picrates and the quaternary derivatives of the N-acetates were always prepared. On the other hand, hydrochlorides were best suitable for pharmacological tests, as a consequence of their solubility in water.

Experimental

A general method of preparing the picrates, quaternary derivatives and hydrochlorides is given as follows:

Picrates were obtained by adding a 5 % picric acid solution in anhydrous ethanol to the material or to its anhydrous alcoholic solution.

Quaternary methiodides were prepared by reacting the materials with the calculated amount of methyl iodide. In several cases the formation of the methiodides failed to occur, mainly due to solubility factors.

The preparation of hydrochlorides was carried out by means of a calculated amount of hydrogen chloride in dry ether solution.

The crystalline products obtained were filtered in all the three cases, they were washed with the appropriate solvent and dried for analysis.

A general description of the preparation of N-cyclic aminoacetic esters is the following: 1 mol. of a chloroacetate was reacted with 2 mol. of the cyclic secondary amine in dry benzene solution, and the formed secondary amine hydrochloride was filtered. If the reaction was too slow, as it was the case especially with morpholino-derivatives, the mixture was refluxed for several hours on the steam bath. The secondary amine hydrochloride was washed with hot anhydrous benzene, the filtrates were combined, and the solvent was evaporated. Finally, the residue was distilled under reduced pressure.

Below are given the empirical formulae, molecular weights, some physical constants and analyses of the compounds prepared.

N-(piperidino) acetic acid methyl ester

$C_8H_{15}O_2N$ · MW: 143,1 · B. p. 69°C at 5 mm.
Calculated C 61,50; H 9,68; N 8,97 %
Found C 61,75; H 9,19; N 8,37 %.
Picrate: $C_{14}H_{18}O_9N_4$. MW: 386,31. M. p. 115°C.
Calculated N 14,51 %. Found N 15,22 %.

N-(piperidinium) acetic acid methyl ester methiodide

$C_9H_{18}O_2NI$ · MW: 285,15 · M. p. 163—164°C.
Calculated C 36,13; H 6,06; N 4,68; I 42,42 %
Found C 36,33; H 6,10; N 4,72; I 42,90 %.
Hydrochloride: $C_8H_{16}O_2NCl$ · MW: 193,66 · M. p. 214°C.

N-(piperidino) acetic acid ethyl ester

$C_9H_{17}O_2N$ · MW: 171,14 · B. p. 68°C at 1 mm.
Calculated C 63,13; H 10,01; N 8,18 %
Found C 63,10; H 10,15; N 8,60 %.
Picrate: $C_{15}H_{20}O_9N_4$ · MW: 400,34 · M. p. 122°C.
Calculated N 13,99 %. Found N 14,30 %.

N-(piperidinium) acetic acid ethyl ester methiodide

$C_{10}H_{20}O_2NI$ · MW: 313,08 · M. p. 160—161°C.
Calculated C 38,35; H 6,44; N 4,47; I 40,53 %
Found C 38,02; H 6,85; N 4,50; I 40,70 %.

Hydrochloride: $C_9H_{18}O_2NCl$ · MW: 207,63 · M. p. 117—117,5°C.

N-(piperidino) acetic acid butyl ester

$C_{11}H_{21}O_2N$ · MW: 185,15 · B. p. 100—101°C at 4 mm.
Calculated C 66,29; H 10,62; N 7,03 %
Found C 66,50; H 9,98; N 6,79 %.

Picrate: $C_{17}H_{24}O_9N_4$ · MW: 428,39 · M. p. 85°C.
Calculated N 13,08 %. Found 13,20 %.

N-(piperidinium) acetic acid butyl ester methiodide

$C_{12}H_{24}O_2NI$ · MW: 341,18 · M. p. 178°C.
Calculated C 42,23; H 7,09; N 4,11; I 37,19 %
Found C 42,51; H 7,49; N 4,20; I 36,38 %.

Hydrocloride: $C_{11}H_{22}O_2NCl$ · MW: 235,74 · M. p. 118°C.

N-(piperidine) acetic acid benzyl ester

$C_{14}H_{19}O_2N$ · MW: 220,14 · B. p. 134—135°C at 1 mm.
Calculated C 72,06; H 8,21; N 6,00 %
Found C 72,15; H 8,30; N 6,25 %.

Picrate: $C_{20}H_{22}O_9N_4$ · MW: 426,41 · M. p. 138°C.
Calculated N 12,12 %. Found 12,81 %.

N-(piperidinium) acetic acid butyl ester methiodide

$C_{15}H_{22}O_2NI$ · MW: 375,20 · M. p. 93°C.
Calculated C 48,10; H 5,87; N 3,73; I 33,59 %
Found C 48,20; H 6,00; N 3,95; I 33,9 %.

Hydrochloride: $C_{14}H_{20}O_2NCl$ · MW: 269,77 · M. p. 133°C.

N-(morpholino) acetic acid methyl ester

$C_7H_{13}O_3N$ · MW: 159,1 · B. p. 77°C at 2 mm.
Calculated C 52,81; H 8,23; N 8,80 %
Found C 59,90; H 8,40; N 9,10 %.

Picrate: $C_{13}H_{16}O_{10}N_4$ · MW: 372,16 · M. p. 143°C.
Calculated N 14,43 %. Found 14,50 %.

N-(morpholinium) acetic acid methyl ester methiodide

$C_8H_{16}O_3NI$ · MW: 301,13 · M. p. 147,5°C.
Calculated C 31,89; H 5,32; N 4,65; I 42,19 %
Found C 32,05; H 5,63; N 5,03; I 42,10 %.
Hydrochloride: $C_7H_{14}O_3NCl$·MW: 194,63·M. p. 150,5°C.

N-(morpholino) acetic acid ethyl ester

$C_8H_{15}O_3N$ · MW: 173,12 · B. p. 86—87°C at 4 mm.
Calculated C 55,47; H 8,73; N 7,72
Found C 55,40; H 8,95; N 7,90 %.
Picrate: $C_{14}H_{18}O_{10}N_4$ · MW: 402,14 · M. p. 163°C.
Calculated 13,93 %. Found 14,29 %.

N-(morpholinum) acetic acid ethyl ester methiodide

$C_9H_{18}O_3NI$ MW: 315,07 · M. p. 132—133°C.
Calculated C 36,47; H 6,08; N 4,26; I 38,60 %
Found C 36,70; H 6,20; N 4,55; I 39,10 %.

N-(morpholino) acetic acid butyl ester

$C_{10}H_{19}O_3N$ · MW: 201,15 · B. p. 105,5—106°C at 3 mm.
Calculated C 59,67; H 9,52; N 6,96 %
Found C 59,80; H 9,40; N 6,60 %.
Picrate: $C_{16}H_{21}O_{10}N_4$ · MW: 429,36 · M. p. 118°C.
Calculated N 13,02 %. Found 13,15 %.

N-(morpholinium) acetic acid butyl ester methiodide

$C_{11}H_{22}O_3NI$ · MW: 343,10 · M. p. 95—96°C.
Calculated C 38,48; H 6,46; N 4,08; I 37,00 %
Found C 38,56; H 6,60; N 4,15; I 36,76 %.
Hydrochloride: $C_{10}H_{20}O_3NCl$ · MW: 237,61 · M. p. 128°C.

N-(morpholino) acetic acid benzyl ester

$C_{13}H_{17}O_3N$ · MW: 236,14 · B. p. 164—165°C at 5 mm.
Calculated C 67,74; H 7,68; N 5,62 %
Found C 67,10; H 7,70; N 5,80 %.
Picrate: $C_{19}H_{20}O_{10}N_4$ · MW: 450,14 · M. p. 144°C.
Calculated N 12,12 %. Found 12,73 %.

N-(morpholinium) acetic acid benzyl ester methiodide

$C_{14}H_{20}O_3NI$ · MW: 376,22.

This compound was not formed.

Hydrochloride: $C_{13}H_{18}O_3NCl$ · MW: 268,60 · M. p. 149°C.

N-(pyrrolidino) acetic acid methyl ester

$C_7H_{13}O_2N$ · MW: 157,12 · B. p. 72°C at 8 mm.
Calculated C 53,50; H 8,46; N 8,89 %
Found C 53,70; H 8,50; N 9,05 %.
Picrate: $C_{13}H_{16}O_9N_4$ · MW: 372,29 · M. p. 104°C.
Calculated N 15,05 %. Found N 15,20 %.

N-(pyrrolidinium) acetic acid methyl ester methiodide

$C_8H_{16}O_2NI$ · MW: 285,12 · M. p. 153°C.
Calculated C 33,68; H 5,65; N 4,91; I 44,44 %
Found C 33,80; H 5,70; N 5,10; I 44,60 %.
Hydrochloride: $C_7H_{14}O_2NCl$ · MW: 193,58 it is very hydroscopic.

N-(pyrrolidino) acetic acid ethyl ester

$C_8H_{15}O_2N$ · MW: 157,12 · B. p. 59—60°C at 2 mm.
Calculated C 61,10; H 9,63; N 8,91 %
Found C 61,20; H 9,71; N 9,10 %.
Picrate: $C_{14}H_{18}O_9N_4$ · MW: 386,31 · M. p. 119,5°C.
Calculated N 14,50; Found 14,98 %.

N-(pyrrolidinium) acetic acid ethyl ester methiodide

$C_9H_{18}O_2NI$ · MW: 299,15.

This compound was not formed.

Hydrochloride: $C_8H_{16}O_2NCl$ · MW: 197,59 · M. p. 133°C.

N-(pyrrolidino) acetic acid butyl ester

$C_{10}H_{19}O_2N$ · MW: 185,25 · B. p. 81—82°C/3 mm.
Calculated C 51,07; H 7,9; N 21,54 %
Found C 51,20; H 7,95; N 21,60 %.
Picrate: $C_{16}H_{22}O_9N_4$ · MW: 414,36 · M. p. 109,5°C.
Calculated N 13,52 %. Found 13,88 %.

N-(pyrrolidinium) acetic acid butyl ester methiodide

$C_{11}H_{22}O_2NI$ · MW: 327,20 · M. p. 104°C.
Calculated C 38,08; H 6,98; N 4,44; I 40,31 %
Found C 39,10; H 7,04; N 4,60; I 39,90 %.
Hydrochloride: $C_{10}H_{20}O_2NCl$ · MW: 235,63 it is very hydroscopic.

N-(pyrrolidino) acetic acid benzyl ester

$C_{13}H_{17}O_2N$ · MW: 219,13 · B. p. 134—135°C at 1 mm.
Calculated C 71,22; H 7,94; N 6,31 %
Found C 71,16; H 8,13; N 6,42 %.
Picrate: $C_{19}H_{20}O_9N_4$ · MW: 488,38 · M. p. 159—160°C.
Calculated N 12,21 %. Found 12,50 %.

N-(pyrrolidinium) acetic acid benzyl ester methiodide

$C_{14}H_{20}O_2NI$ · MW: 361,22 · M. p. 156°C.
Calculated C 43,53; H 5,54; N 3,87; I 35,18 %
Found C 43,60; H 5,60; N 3,95; I 35,42 %.
Hydrochloride: $C_{13}H_{18}O_2NCl$ · MW: 270,62 · M. p. 139°C.

* * *

The authors wish to express their thanks to the Analytical Department of this Institute for carrying out the analyses, to MR. J. FÜLÖP for preparing one part of the compounds, and to Miss M. KOLTAI for her valuable assistance during the experimental work.

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ИССЛЕДОВАНИЕ СВЯЗИ ФАРМАКОЛОГИЧЕСКОГО ЭФФЕКТА И ХИМИЧЕСКОЙ СТРУКТУРЫ В СЛУЧАЕ НОВЫХ ЛЕКАРСТВ, ВЛИЯЮЩИХ ЦЕНТРАЛЬНУЮ НЕРВНУЮ СИСТЕМУ

Б. Маткович, Ш. Фельдеак и *Й. Порсас*

В результате работы был получен краткий ряд различных циклических секундерно-аминовых эфиров уксусной кислоты а также их кватернеров, с целью подвергнуть их фармакологическому исследованию.

Цель исследований состоял в первую очередь в наблюдении действия упомянутых соединений типа эфира на центральную нервную систему.

В результате исследований было установлено, что лишь бензиловый эфир пиперидиноо- и пирролидино-уксусной кислоты обладает небольшой антиникотинной активностью. В упомянутых двух случаях действие было повышено б небольшой степени кватернированием.

CONTRIBUTIONS TO THE SYNTHESIS OF DL-p-NITROPHYENYL ALANINE

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(Received February 25, 1960)

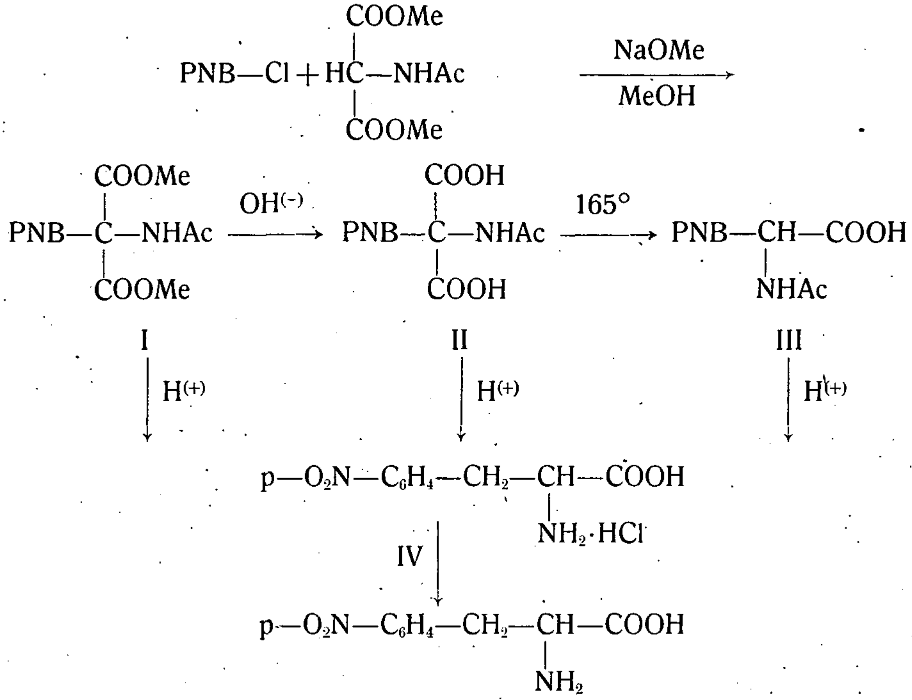
On condensating dimethyl acetylaminomalonate with p-nitrobenzyl chloride, DL-p-nitrophenyl alanine can be prepared. The synthesis can also be carried out in several steps, and the dicarboxylic acid phase can be isolated by the alkaline hydrolysis of the condensate. The thermal decarboxylation of this isolated phase yields N-acetyl-DL-amino-acid which latter affords, on acid hydrolysis, the desired aminoacid. The structure of the intermediates can be proved by acid hydrolysis in that in each case the chlorohydrate of the aminoacid forms. On liberating the aminoacid from its chlorohydrate, it was possible to isolate a stable hydrate.

The synthesis of DL-p-nitrophenyl alanine from diethyl acetylaminomalonate by condensation with p-nitrobenzyl chloride was described by BURCKHALTER and STEPHENS [1]. The condensation product (of m. p. 193—194° C) was converted into aminoacid by hydrolysis with strong acid. However, it is also possible to conduct hydrolysis in an alkaline medium so as to isolate the intermediate phases as well, in a way already observed by TISHLER and associates [2] at the synthesis of N-acetyl-DL-triptophane. Thus, it is possible to isolate N-acetyl-DL-p-nitrophenyl alanine. This latter product is expected to be resolvable [3] and to be suited for use in an active form as a resolving agent, due to its possible capability of readily crystallizing. In the present experiments dimethyl acetamino-malonate was applied, accordingly, the obtained condensate (I) consisted of the dimethylate.

The alkaline hydrolysis of I afforded a dicarboxylic acid (II) which latter, on heating in an aqueous solution, decarboxylated and yielded N-acetyl-DL-p-nitrophenyl alanine (III). On determining the m. p. of the dicarboxylic acid it was observed that the compound melts at 152—153°C under foaming, then solidifes at about 160°C to melt again at 194—196°C. The phenomenon was subjected to examinations in detail with preparative quantities and was identified as thermal decarboxylation. The product melting at 194—196°C proved to be identical with compound III. It must be mentioned that thermal decarboxylation was carried out in excellent yields.

The hydrolysis of N-acetyl-DL-p-nitrophenyl alanine (III) with hydrochloric acid afforded the chlorohydrate of DL-p-nitrophenyl alanine (IV). The same product was obtained under similar conditions by the hydrolysis of the dicarboxylic acid (II) and of the condensate (I), respectively, with hydrochloric acid, confirming the validity of the presumed structure of the intermediates.

The hydrolysis by hydrogen bromide as described by Burckhalter and Stephens [1] proved to be more suited for hydrolyzing the condensate than the hydrolysis by hydrochloric acid. Namely, the latter is in this case an agent not strong enough.



$PNB = p—O_2N—C_6H_4—CH_2—$ (p-nitrobenzyl)

The aminoacid can be liberated from the chlorohydrate with the use of sodium acetate buffer. On allowing the solution with aminoacid liberated in form of a fluffy precipitate to stand for some days, it recrystallized as well developed crystals of a stable hydrate. On determining its m. p., water was liberated as drops. On drying weighed amounts of the substance, defined weight decrease was experienced. On the basis of these observations and of the analytical data, the composition of the compound corresponds to that of a monohydrate. The m. p. of the monohydrate differs from that of the product previously dried, this latter being of a less elongated nature. The hydrate showed a point of decomposition of 227—238°C against 242—244°C of the aminoacid previously dried under decreased pressure at the b. p. of xylene. It must be noted, however, that Burckhalter and Stephens [1] recorded a point of decomposition of 222—240°C.

Experimental

Dimethyl p-nitrobenzyl-acetylaminomalonate (I)

On adding 20 g (0,105 mole) of dimethyl acetylaminomalonate to a solution of 3 g of metallic sodium in 250 ml of anhydrous methanol, the solution was slightly heated to facilitate dissolution, then heated to gentle reflux and 20 g (0,127 mole) of p-nitro-benzyl chloride added at this temperature in about 15 minutes. Subsequently, the reaction mixture was gently refluxed for 8 hours, then the solution evaporated to dryness under reduced pressure, the residue extracted hot with 5×50 ml of chloroform, the combined filtrates evaporated to dryness under reduced pressure and the residue (33,2 g) recrystallized from 200 ml of anhydrous ethanol. On cooling, 26,04 g brilliant white crystals of the condensate were obtained. Yield 82%, referred to dimethyl acetylamino malonate. M. p. 162°C. On repeatedly recrystallizing from 120 ml of anhydrous ethanol, 20,4 g (64%) of product, m. p. 164—165°C.

Analysis: $C_{14}H_{16}O_7N_2$. Calcd. C: 51,97 H: 4,97 N: 8,64%
Found C: 52,20 H: 4,82 N: 8,78%.

p-Nitrobenzyl acetylaminomalonic acid (II)

On adding 5 g (0,0154 mole) of I to 20 ml of a 10% solution of sodium hydroxide, the mixture was refluxed for 2 hours. On cooling and filtering, 10 ml of concentrated hydrochloric acid was dropwise added, the precipitated yellow crystals were filtered and washed with water. On drying, yield 3,4 g (74%), m. p. 152—153°C under foaming, solidifying at 160°C and again melting at 194—196°C.

Analysis: $C_{12}H_{12}O_7N_2$. Calcd. C: 48,65 H: 4,08 N: 9,45%
Found C: 48,63 H: 4,00 N: 9,40%.

N-acetyl-DL-p-nitrophenyl alanine (III)

a) On adding 1 g of II to 20 ml of water, the mixture was refluxed for 3 hours, slightly clarified and filtered hot. During cooling, fine yellow crystals appeared. On filtering and drying: 0,62 g (72%), m. p. 193—196°C.

Analysis: $C_{11}H_{12}O_5N_2$ Calcd. C: 52,37 H: 4,79 N: 11,10%
Found C: 52,57 H: 4,60 N: 11,43%.

b) On cautiously heating 2 g of II, it was melted in an oil bath at 165°C, kept at this temperature for further 10 minutes and allowed to cool. On solidification, it was dissolved hot in 30 ml 50% aqueous ethanol, clarified and filtered. During cooling, orange crystals appeared. On filtering and drying: 1,48 g (86%), m. p. 194—196°C.

Analysis: C: 52,48 H: 4,82 N: 11,32%.

DL-p-Nitrophenylalanine chlorohydrate (IV)

a) On adding 15 ml of concentrated hydrochloric acid to 3,24 g (0,01 mole) of I, the mixture was boiled under reflux for 6 hours, rapidly filtered while hot and allowed to cool when fine needles crystallized. On filtering and drying: 2,3 g (93%). Recrystallized from 50% aqueous ethanol or from a mixture of anhydrous ethanol and anhydrous ether: m. p. 227—230°C (decomp.).

Analysis of substance dried over P_2O_5, at the b. p. of xylene under a pressure of 5 mm Hg

$C_9H_{11}O_4N_2Cl$ Calcd. C: 43,82 H: 4,49 N: 11,35 Cl: 14,37%
Found C: 44,02 H: 4,30 N: 11,50 Cl: 14,22%.

b) On hydrolyzing 2,96 g (0,01 mole) of II with concentraced hydrochloric acid in the way described under a), and recrystallizing the product, yield 1,91 g (78%), m. p. 227—230°C (decomp.).

Analysis: C: 43,98 H: 4,41 N: 11,57 Cl: 14,09%.

c) On hydrolyzing 2,52 g (0,01 mole) of III with concentrated hydrochloric acid in the way described under a) and recrystallizing the product, yield 1,69 g (69%), m. p. 227—230°C (decomp.).

Analysis: C: 43,65 H: 4,51 N: 11,43 Cl: 14,11%.

DL-p-Nitrophenylalanine (V)

On dissolving 1 g of DL-p-nitrophenylalanine chlorohydrate in 10 ml hot water, 1 g of pulverized sodium acetate was added to the solution while hot, the precipitated crystalline substance was filtered, washed with some water, ethanol and finally with ether. On drying, yield 0,68 g (80%), m. p. 242—244°C (decomp.).

Analysis of substance dried over P_2O_5 for 3 hours at the b. p. of xylene under a pressure of 5 mm Hg

$C_9H_{10}O_4N_2$ Calcd. C: 51,42 H: 4,79 N: 13,32%
Found C: 51,21 H: 4,90 N: 13,23%.

DL-p-Nitrophenylalanine hydrate

On adding 5 ml of a solution of sodium acetate saturated at room temperature to a solution of 1 g of DL-p-nitrophenylalanine chlorohydrate in 5 ml of water, the mixture was allowed to stand for two days. The flocculated substance which appeared at the beginning, slowly converted into well developed fine platelets-needles. On filtering and washing the crystals with some water, ethanol and ether, and drying, yield: 0,78 g (83%), m. p. 227—238°C (decomp.).

Analysis: $C_9H_{12}O_5N_2$ (monohydrate) Calcd. C: 47,20 H: 5,28 N: 12,23%
Found C: 47,18 H: 5,04 N: 12,30%.

Dehydration

On drying 0,1132 g of DL-p-nitrophenylalanine hydrate over P_2O_5 for 6 hours at the boiling point of xylene under a pressure of 5 mm Hg, the actually weighed decrease of weight amounted to 0,101 g, against 0,0090 g calculated with respect to monohydrate.

* * *

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ДАННЫЕ К СИНТЕЗУ DL-p-НИТРОФЕНИЛАЛАНИНА

М. Гальмош

Конденсацией диметилого эфира ацетиламиномалоновой кислоты и хлористого p-нитробензила может быть получен DL-p-нитрофенилаланин. Синтез может быть разложен на этапы: щелочным гидролизом конденсата может быть изолирована дикарбоно-кислотная фаза, последняя может быть декарбоксилирована термически в N-ацетил-DL-аминокислоту. Аминокислота получается из последней кислотным гидролизом. Структура промеждуточных продуктов может быть доказана кислотным гидролизом, из каждого из них образуется соляно-кислотная соль аминокислоты. При освобождении аминокислоты из ее соляно-кислотной соли удалось изолировать устойчивый гидрат.

ISOLATION OF ARISTOLOCHIC ACID FROM *ARISTOLOCHIA CLEMATITIS* NATIVE IN HUNGARY. THE PREPARATION OF PHYSIOLOGICALLY ACTIVE ARISTOLOCHIA DERIVATIVES

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(Received April 10, 1960)

A material of strong physiological activity with the composition of $C_{17}H_{11}O_7N$ has been isolated from *Aristolochia clematitis* native in Hungary. The same compound had been found in other species of *Aristolochia*. An interesting property of the compound is that its nitrogen function is contained in a nitro group. Several derivatives have been prepared for pharmacological investigation.

Species of *Aristolochia* are native mostly in countries around the Mediterranean, however, a number of them is to be found also in other parts of Europe. The active principle of the plant is a stimulative poison, and several experiments have been made to find a use for it in the medical practice. Some species of *Aristolochia* have been used as popular drugs to produce abortion. The chief active principle in the *Aristolochia* species is aristolochic acid, a yellow and extremely bitter material, having an acidic character. In 1892 POHL [1] isolated a yellow crystalline solid from the seeds of *Aristolochia rotunda,* and from the result of combustion analysis he established the empirical formula $C_{32}H_{22}O_{13}N_2$. The material showed acidic properties, and it gave a well defined barium salt. POHL called the active principle obtained by him aristolochine, and he was the first to make pharmacological experiments with it. In 1895 HESSE [2] isolated three acidic substances from *Aristolochia argentina,* namely aristinic acid ($C_{18}H_{13}O_7N$), aristidinic acid (which is considered by him as an isomer of aristinic acid), and aristolic acid ($C_{15}H_{11}O_7N$); all the three materials showed rather similar properties. A yellow crystalline and very bitter solid was isolated in 1922 by CASTILLE [3] from *Aristolochia sipho l'Hérit;* its properties were similar to those of the material obtained by POHL, however, it had the empirical formula $C_{17}H_{11}O_7N$. The compound gave off ammonia when fused with potassium hydroxide. The residue showed the characteristics of antrachinone, from which it was concluded that the material had an anthracene sceletal structure, probably with a tertiary nitrogen atom on it. In 1943 ROSENMUND and REICHSTEIN [4] investigated the material isolated from *Aristolochia sipho.* An active principle of the composition $C_{17}H_{11}O_7N$ could be isolated by extraction, which was identical with the material obtained by CASTILLE. The compound could be sublimed under reduced pressure, however, not without decomposition. Treatment with diazomethane gave a derivative with the empirical formula $C_{18}H_{13}O_7N$ which was found to be very stable againts hydrolysis. The parent compound as well as its derivatives were optically inactive. Hydrogenation in the presence of platinum oxide resulted in the formation of a light yellow material, which was shown by analysis to have the composition $C_{18}H_{13}O_7N \cdot 0{,}5\,H_2O$. Decarboxylation with copper in quinoline afforded $C_{16}H_4O_5N$, and the reaction confirmed the assumption that aristolochic acid was a monobasic acid, and the acidic character was not derived from the presence of phenolic hydroxyl, as it was thought formerly. However, this investigation did not elucidate the character of the nitrogen atom and of the other functional groups of the molecule. PAILER *et all.* [5] started a research in 1956, and found that aristolochic acid isolated from *Aristolochia clematitis* L. was identical with the material of Rosenmund and Reichstein. They pointed out that the various acids of *Aristolochia* as described by different authors were not uniform preparations, and this fact rendered the investigations very difficult. The aristolochic acid isolated by them showed the empirical formula $C_{17}H_{11}O_7N$ which had been considered most probable also previously. The usual method of methoxyl determination gave but very little CH_3J, which had led earlier researchers to erroneous conclusions concerning the functional groups of the molecule. When the method was developed to be come more punctual, the presence of one methoxyl group was demonstrated. Catalytic hydrogenation of aristolochic acid permitted the isolation of a material having neutral character. Hydrogenation of the decarboxylated acid gave rise to a basic material from which a hydrochloride, picrate and acetate could be prepared. Diazotation followed by hydrolysis gave a red material. These different experimental results suggested the presence of a nitro group in aristolochic acid which could be reduced to an amino group, when the amine obtained will form a lactam. This assumption has been substantiated also by the evidence of infrared spectra. The presence of the methylenedioxy group was demonstrated by the method of PAVOLINI [6]. Distillation of the compound with zinc dust gave phenanthrene. After having established the nature of the functional groups, PAILER *et al.* found out their relative positions by oxidative degradation. This investigation gave the structure of aristolochic acid as 3,4-methylenedioxy-8-methoxy-10-nitrophenanthrene-1-carboxylic acid. The formula was proved by synthesizing 3,4-methylenedioxy-10-acetamidophenanthrene, which was also obtained from the degradation of aristolochic acid. The synthesis was carried out by condensing homopiperonylic acid with o-nitrobenzaldehyde, followed by PSCHORR [7] ring closure.

We have found that the active principle of the *Aristolochia clematitis* native in Hungary was in all respects identical with the material isolated by ROSENMUND and REICHSTEIN and it had the formula as given by PAILER. It is interesting that the nitrogen atom of the molecule is contained in a nitro group, which fact suggested further pharmacological investigation. There are only very few nitrogen containing compounds occurring in nature which possess nitro group. Such rare compounds are chloramphenicol, isolated in 1947, and β-nitropropionic acid found not much later. A detailed pharmacological study of aristolochic acid has been carried out recently by MÉHES *et al.* [8, 9].

The chemical investigation of aristolochic acid presented two problems. First, a method was to be developed for the extraction of aristolochic acid from *Aristolochia clematitis* native in Hungary; second, the isolated acid had to be modified in various ways. To prepare derivatives for pharmacological study, first of all we wanted to eliminate the action of the acidic carboxyl group of the molecule. This was partly done by decarboxylation, partly by preparing various esters of the acid. Esterification could not be carried out in the conventional way, thus the acid chloride was prepared first, which gave the desired ester on alcoholysis. Ethyl, n-propyl and n-butyl esters have been prepared in this way. The methyl ester was obtained by means of diazomethane. (Fig. 1.)

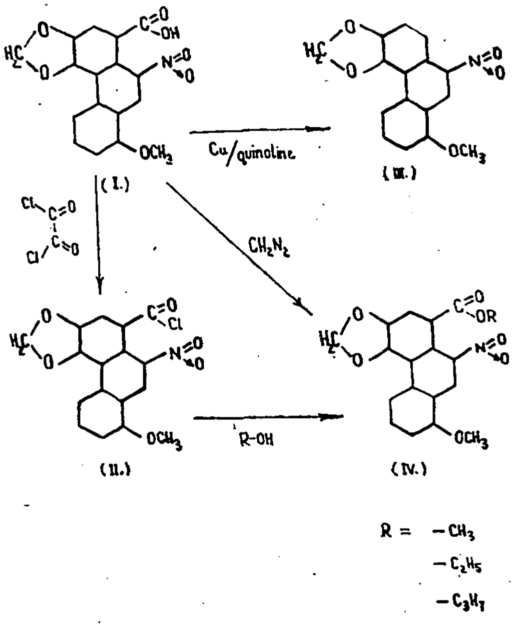

Fig. 1

Experimental

Isolation and purification of aristolochic acid (I)

Roots of *Aristolochia clematitis,* collected during the autumn season, were cleansed and dried under reduced pressure at 60° C. After drying, the material was ground in a beating mill. The pulverized substance was extracted with cold petroleum ether to dissolve fatty components. The material was then extracted with ethanol, until the solvent ceased to show a brown colour. The extraction was finished by employing ethanol containing 1 % sodium ethoxide. The ethanol and sodium ethoxide extracts were combined and evaporated at 50° C under reduced pressure. The residue was a mobile, brown, oily liquid which was dissolved in 1 % sodium hydroxide, and acidified with 1 % sulphuric acid. A brownish-yellow precipitate was obtained which was centrifuged, washed free of sulphate ions and dried at room temperature over phosphorus pentoxide to give a brown powder which had an extremely bitter taste. The crude aristolochic acid obtained this way was extracted with petroleum ether in a Soxhlet apparatus. The extraction was then continued using diethylether. After having performed the operation for several days, aristolochic acid separated as a yellow solid in the extraction flask. The crust of crystals was dissolved in dioxane, treated with decolourizing carbon, and crystallized by the addition of a small amount of water. Orange-yellow plates were obtained. Aristolochic acids crystallized from dioxane gave no exactly reproducible analyses, because varying amounts of dioxane may be bound by the acid. Material for analysis was crystallized from butyl alcohol. M. p. 283—285° C (decomposition). (The determination of the melting point was carried out according to the microanalytical method of A. KOFFLER.) Analysis: $C_{17}H_{11}O_7N$ requires C 59,82; H 3,25; N 4,11; OCH_3 9,09%. Found C 59,94; H 3,24; N 4,17; OCH_3 9,12%.

Sodium salt of aristolochic acid

Aristolochic acid (200 mg) was dissolved in anhydrous ethanol containing a calculated amount of sodium ethylate, and the solution was evaporated to dryness. The residue was dissolved in butyl alcohol. The sodium salt crystallized from this solution in long, bright red needles, m. p. 275—278° C (decompn.). Analysis: $C_{17}H_{10}O_7N\,Na$ requires C 56,19; H 2,77; N 3,85 %. Found C 56,27; H 2,68; N 3,89%.

Decarboxylated aristolochic acid (III)

Aristolochic acid (80 mg) was dissolved in 10 ml of quinoline, 50 mg of copper powder was added, and the material refluxed for 15 minutes. After cooling it was diluted with chloroform, filtered from copper, washed with diluted hydrochloric acid, then with $NaHCO_3$ solution and water. The chloroform solution was dried, and the chloroform distilled. The residue was recrystallized from a mixture of chloroform and methanol, to give long yellow needles, m. p. 212° C. Found: C 64,74; H 3,78; N 4,85%. Calculated for $C_{16}H_{11}O_5N$: C 64,65; H 3,73; N 4,71%.

Chloride of aristolochic acid (II)

Aristolochic acid (500 mg) was dissolved in 50 ml of anhydrous dioxane and a great excess of oxalyl chloride (8 ml) was added. The solution was allowed to stand at room temperature for one day, and it was evaporated under reduced pressure. A greenish-yellow crystalline material was obtained which was recrystallized from chloroform. M. p. 275—278° C (decompn.) Found: C 56,80; H 2,89; N 3,72; Cl 9,68%. Calculated for $C_{17}H_{11}O_6N\,Cl$: C 56,76; H 2,80; N 3,89; Cl 9,63%.

Methyl ester of aristolochic acid (IV)

Aristolochic acid (100 mg) was dissolved in 20 ml of anhydrous dioxane and an excess of diazomethane dissolved in ether (20 ml) was added. A crystalline precipitate was obtained in an hour. After evaporating the ether, the material was dissolved in chloroform, and the solution was washed with $NaHCO_3$, dried, and evaporated to dryness. Recrystallization from methanol gave thin needles, m. p. 280—283° C. Found: C 60,72; H 3,75; N 3,97; OCH_3 17,60%. Calculated for $C_{18}H_{13}O_7N$: C 60,85; H 3,68; N 3,94; OCH_3 17,46%.

Lower homologous esters of aristolochic acid (V)

The chloride of aristolochic acid (50 mg) was dissolved in 10 ml of chloroform, and a large excess of the esterifying alcohol added. The mixture was refluxed for one hour. After cooling, the solution was evaporated, the residue dissolved in chloroform, washed with $NaHCO_3$ solution, dried, and concentrated to small volume which resulted in the crystallization of the ester.

M. p. of ethyl ester: 282—283° C (decompn.). Found: C 61,92; H 4,15; N 3,86%. Calculated for $C_{19}H_{15}O_7N$: C 61,79; H 4,09; N 3,79%.

M. p. of n-propyl ester 286—288° C (decompn.). Found: C 62,59; H 4,54; N 3,76%. Calculated for $C_{20}H_{17}O_7N$: C 62,67; H 4,47; N 3,65%.

M. p. of *n*-butyl ester 286—290° C (decompn.). Found: C 63,55; H 4,93; N 3,58%. Calculated for $C_{21}H_{19}O_7N$: C 63,47; H 4,81; N 3,52%.

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ИЗОЛИРОВАНИЕ АРИСТОЛОКИА-КИСЛОТЫ ИЗ ARISTOLOCHIA CLEMATITIS РАСТУЩЕЙ В ВЕНГРИИ. ИЗГОТОВЛЕНИЕ АРИСТОЛОКИА-ПРОИЗВОДНЫХ, ЕФФЕКТИВНЫХ ФАРМАКОЛОГИЧЕСКИ

Дь. Шнейдгр

Из *Aristolochia clematitis* растущей в Венгрии было изолировано вещество, соответствующее составу $C_{17}H_{11}O_7N$ которое обладает сильным фармакологическим действием. Такое же вещество содержится и в других породах Aristolochia. Соединение представляет собой интерес, потому что функция азота носится в нем нитрогруппой. Для фармакологических исследований были изготовлены некоторые из его производных.

CONVERSION OF FURFURAL INTO FURAN BY VAPOUR-PHASE OXIDATIVE DECARBOXYLATION ON METAL OXIDE CATALYSTS

Preliminary Communication

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(Received June 15, 1960)

Two catalyctic methods are known for converting furfural into furan in the vapour-phase. When furfural vapours are passed over the surface of metal turnings in the complete absence of air (1) and water at about 300—500°C, furan and CO are obtained with a low conversion. The second process (2) consists of passing furfural together with a fivefold excess of steam over a metal chromite or soda-lime catalyst, in the presence of hydrogen but carefully excluding oxygen. The products are furan, CO_2 and hydrogen. The latter type of process should be carried out between 200 and 500°C. Therefore, the employed catalysts are prepared by heating the higher oxides of metals in hydrogen atmosphere.

We have found (3) that furfural may readily be converted to furan carboxylic acid at 300—500°C, on the surface of any higher oxide of heavy metals in the presence of oxygen or air, and the acid is spontaneously decarboxylated at the reaction temperature to give furan. The working hypothesis leading to this result was based mainly upon the fact that pyromucic acid decomposes at about 200°C, furthermore that even the so-called decarbonylation of furfural was presumed (4) to occur by way of pyromucic acid, and finally that furfural is easily oxidised in the vapour-phase to maleic anhydride (5) involving the formation of furan — carboxylic acid and furan, respectively MILAS and WALSH (6) and CALNIN *et al.* (7).

We succeeded in isolating this second assumed intermediate under strictly controlled experimental conditions which rendered possible to stop the oxidation at that stage.

The first precaution we have taken was diluting the oxygen by a neutral gas, *e. g.*, by using air or a mixture of CO_2 and oxygen. Useful catalysts are very simple and many, such as silver oxide, vanadium pentoxide, zinc oxide, lead oxide, tin oxide, titanium oxide, etc. All these catalysts may be employed alone or mixed or even precipitated on aluminium. The catalysts are not sensitive and they have long service lives. For example, by using a 100 cm long tube of 190 ml useful volume filled with vanadium-pentoxide on aluminium and administering 5,5 g furfural at 350°C together with 0,75 mol of oxygen, 0,83 g of furfural was recovered and 3,0 g of furan (77% yield) was obtained.

Isolation of furan from the end-gases could be effected by adsorption towers as well as by compression and cooling to low temperatures. The heat of reaction is at least 10:1 compared with that of converting furfural into furan in the presence of water. In the latter method namely, the heat of decomposition of water which necessarily takes place in te first step of the process, consumes a considerable part of the energy of formation of furancarboxylic acid.

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ДЕКАРБОКСИЛИРОВАНИЕ В ГАЗОВОЙ ФАЗЕ ФУРФУРОЛА В ФУРАН НА КАТАЛИЗАТОРЕ ОКИСИ МЕТАЛЛА

Л. Месарош

Согласно литературным данным получение фурана из фурфурола газофазным гетерогенным каталитическим путем осуществлено в условиях освобожденных ос следов кислорода. Реакция поводится автором оксидативным декарбоксилированием.

THE ADDITION COMPOUND OF N,N-DIMETHYLFORMAMIDE AND HYDROGEN CHLORIDE

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(Received March 1, 1960)

A hydrogen chloride addition compound of N, N-dimethylformamide has been prepared, and showed to be the monohydrochloride. The compound can be distilled without decomposition, other properties being similar to those of like known products.

It is known that carboxylic acid amides are neutral compounds, or in any case, the basic character of their amino group is very weak. A few addition compounds of amides with mineral acids, reported in the literature, are rather unstable materials, and suffer an instantaneous hydrolysis when exposed to water. The crystalline adduct of formamide with hydrogen chloride is stable only at lower temperatures, otherwise it undergoes violent decomposition to give carbon monoxide and ammonia [1]. There have been several studies [2, 3] on the preparation of the hydrogen chloride adduct of acetamide; a crystalline product is, in general, obtained when gaseous hydrogen chloride is introduced into a cooled ethereal solution of the acid amide. In some cases, mineral acid adducts of amides may be prepared also by treating the corresponding nitriles with mineral acids, as it was found in the case of propionitrile by HEULE and SCHUPP [4]. WERNER [5] surveyed the methods of preparing hydrogen bromide and hydrogen iodide adducts of various acid amides and discussed their composition, since this group includes addition compounds not only of the molar ratio of 1:1, but also of different compositions. WERNER was the first to describe a hydrogen bromide adduct of formamide having the composition $(HCONH_2)_3 \cdot (HBr)_2$.

In the series of acid-amides alkylated on the nitrogen atom, N-methylacetamide semi-hydrochloride was described by BLICKE (6); this compound could be recrystallized from acetone. A systematic study of N-methyl amides was made by D'ALELIO and REID (7). They observed the formation of two types of hydrogen chloride addition compounds, namely $R \cdot CONHCH_3 \cdot HCl$ and $(R \cdot CONHCH_3)_2 \cdot HCl$. The first type is formed in nonpolar solvents, the second in the absence of solvents.

In the course of the present work we succeeded in preparing the hydrogen chloride addition compound of N, N-dimethylformamide which has not been described in the literature so far. There is but one reference concerning this compound published by DAWSON *et al.* (8); these authors carried out conductivity measurements in the dimethylformamide — hydrogen chloride system and found diversions both from the ONSAGER equation and the OSTWALD dilution rule. These findings have been interpreted by assuming a strong interaction between the components even at low hydrogen chloride concentrations.

In our experiments, the hydrogen chloride adduct was prepared in the usual way, by introducing hydrogen chloride into dimethylformamide. The reaction gave a crystalline compound. Analysis showed the product to consist of monohydrochloride, at variance with the assumption of D'ALELIO, according to which the semi-hydrochloride was to be expected in the absence of solvents. The hydrogen chloride adduct had a surprisingly high stability; it could be distilled under reduced pressure without decomposition. The boiling point is apparently identical with that of dimethylformamide. When the adduct is treated with water or alkali, the amid can be recovered. The acid content of the adduct is very slowly lost, even when the compound is stored in an exsiccator over sodium hydroxide.

Furthert investigations are intended to study the basic dissociation constants of non-substituted and substituted amides also in non-aqueous solvents, and to establish the composition and properties of their addition compounds formed wit various acids.

Experimental

N, N-Dimethyl-formamide monohydrochloride

Dry hydrogen chloride was passed for several hours into a solution of 94,84 g freshly distilled N, N-dimethyl-formamide cooled in ice-water. 47,17 g hydrogen chloride was absorbed. (Theory requires 47,42 g HCl for the monohydrochloride.) At the end of the reaction the solution solidified to a crystalline mass. The crystals were washed on a filter with a small amount of anhydrous ether, and the material was distilled, b. p. 76° at 40 mm. The product was a colourless syrupy liquid which soon solidified. Yield 102,5 g (72 %).

For analysis, 6,25 g was dissolved in water in a 10 ml volumetric flask, and an aliquot part titrated. The solution contained 2,07 % calculated as free hydrochloric acid, which gave a hydrogen chloride content of 33.20 % for the compound. The formula of monohydrochloride requires 33,34 % HCl.

Recovery of the amide

19,53 g of crystalline N, N-dimethylformamide monohydrochloride was ground with 18,9 g anhydrous Na_2CO_3 in a mortar. The material was filtered from the salt. The filtrate was distilled to give a main fraction boiling at 152—154° (760 mm), yield 6,8 g, $n_D^{25} = 1,4270$. The literature (9) records for N, N-dimethyl formamide b. p. 153°, $n_D^{25} = 1,4269$.

* * *

The authors' thanks are due to Miss K. L. LÁNG and to Miss G. B. BOZÓKI for the analyses.

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СОЛЯНО-КИСЛОТНОЕ АДДИЦИОННОЕ СОЕДИНЕНИЕ ДИМЕТИЛФОРМАМИДА

М. Гальмош и Т. Могачи

Было изготовлено соляно-кислотное аддиционное соединение N_1N-диметилформамида оказавшееся моногидрохлоридом. Соединение можно перегонять без разложения, другие его свойства являются тождественными со свойствами подобных известных соединений.

THE SYNTHESIS OF PHENYL 2-PIPERIDINOETHYL SULPHIDE AND PHENYL 2-PIPERIDINOETHYL SULPHONE, AND THEIR QUATERNARY DERIVATIVES

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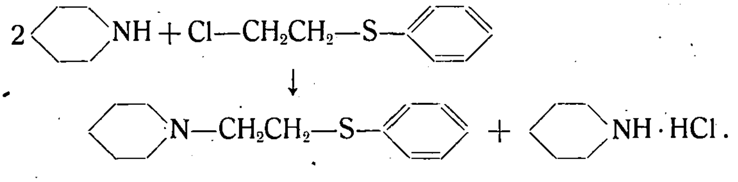
Phenyl 2-piperidinoethyl sulphide and sulphone, as well as their quaternary derivatives have been prepared with the purpose of investigating the physiological activity of the products. These compounds may be regarded as isosteres of phenyl 2-piperidinoethyl ether.

Aminoethyl phenyl ethers have been long since known as adrenaline-inhibiting agents. It is probable that the activity of this group of compounds should be explained by competetive mechanism [1]. By applying the principle of isosterism, we have synthesized phenyl 2-piperidinoethyl sulphide and the corresponding sulphone. The latter compound was made by oxidizing the sulphide with hydrogen peroxide.

These tertiary products were converted in absolute alcoholic medium to the corresponding quaternary derivatives.

The parent compounds were synthesized by condensing 2-chloroethyl phenyl sulphide or sulphone, respectively, with piperidine.



2 mols of piperidine were used for the reaction, since piperidine hydrochloride is formed as a by-product which may easily be filtered from the mixture after the condensation took place.

2-Chloroethyl phenyl sulphide was prepared from thiophenol and ethylene chlorohydrin in alkaline medium. 2-Hydroxyethyl phenyl sulphide, formed as a primary product, was converted to 2-chloroethyl phenyl sulphide by means of thionyl chloride [2] or phosphorus pentachloride [3]. Oxidation of the sulphide with hydrogen peroxide gave the corresponding sulphone [2]. This oxidation was tried before and after condensing the sulphide with piperidine; the same product was obtained in both cases.

Experimental

Thiophenol (benzenethiol) was most easily prepared by means of chlorosulphonic acid [4].

Phenyl 2-piperidinoethyl sulphide

2-Chloroethyl phenyl sulphide (15 g) was slowly added, under continuous stirring, to 15 g of piperidine, and the mixture was refluxed for half an hour at 120° C. The precipitate which separated after cooling was filtered, and 20 ml of distilled water was added to the solution to dissolve the remainder of hydrochloride. The aqueous solution was then extracted with ether. The ethereal layer was dried over anhydrous sodium sulphate, the solvent was evaporated and the residue fractionated. B. p. 138° C. Yield 13 g. Analysis: Calculated C: 70,60; H: 9,01%. Found C: 70,61; H: 9,12%.

From this material the *picrate* was prepared. M. p. 146° C. Analysis: Calculated N 12,44%. Found N 12,60%.

The *hydrochloride* was obtained by treating the ethereal solution of the material with a solution of hydrogen chloride in ether, and the product was recrystallized from ethanol. M. p. 191° C. Analysis: Calculated Cl 13,77%. Found: 13,67%.

The *methoiodide* was prepared in ethanol solution with the calculated amount of methyl iodide. M. p. 165° C. Analysis: Calculated I 34,95%. Found I 34,56%.

Phenyl 2-piperidinoethyl sulphone

2-Chloroethyl phenyl sulphone (13 g) was dissolved in 20 ml of anhydrous benzene and under continuous stirring a solution of 18,8 g piperidine in 20 ml of benzene was gradually added. The mixture was then heated on the steam bath for 20 minutes, filtered and washed with benzene. The benzene solution was then concentrated to one fourth of its original volume under reduced pressure (water pump), and the residue was allowed to stand overnight in a refrigerator. The crystalline precipitate was filtered and recrystallized from benzene. Yield: 10,5 g. M. p. 86—87° C. Analysis: Calculated C 61,70; H 7,50%. Found C 61,75; H 7,55%.

M. p. of *picrate:* 186° C. Analysis: Calculated N 11,60%. Found N 11,70%.

The *hydrochloride* was prepared in ether by means of an ethereal solution of hydrogen. M. p. 213—214° C. Analysis: Calculated Cl 12,25%. Found Cl 12,28%.

The *methoiodide* was prepared in ethanol with the theoretical amount of methyl iodide. M. p. 175° C. Analysis: Calculated I 33,40%. Found I 33,49%.

* * *

The authors express their thanks to the Analytical Department of this Institute for carrying out the analyses. Thanks are due also to Mr. B. KISZELY, undergraduate, for his help, and J. FÜLÖP for technical assistance.

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СИНТЕЗ ПИПЕРИДИНО β-ЭТИЛ-ТИОФЕНИЛЬНОГО ЭФИРА И ПРИПЕРИДИНО β-ЭТИЛЬНОГО СУЛЬФОНА И ЕГО ЧЕТВЕРТИЧНЫХ ПРОИЗВОДНЫХ

Ш. Фельдеак, Б. Маткович и *Й. Порсас*

Авторами были получены вышеупомянутые соединения а также их четвертичные производные, и они были подвергнуты фармакологическому исследованию. В упомянутых случаях — по сравнению с β-этил-фениловому эфиру пиперидина — был применен изостерный обмен.

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THE SYNTHESIS OF TERTIARY AMINOARYL-PROPENE AND -PROPANE DERIVATIVES

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(Received March 30, 1960)

Some secondary amino derivatives of cinnamyl chloride have been prepared as compounds of potential physiological activity. Attempts have been made to decide about the configuration of the obtained stereoisomers by examining the possibility of mixed crystal formation.

During the course of our pharmacological investigations involving several groups of materials [1], [2], we have prepared also some tertiary aminocynnamyl-(1-phenylpropene-2) derivatives. The relationship between physiological activity and structure has been studied also in this case.

A general formula of the compounds to be described in detail in the following, may be given as

$$R \cdot CH_2 \cdot CH = CH \cdot C_6H_5$$

where R = a secondary amine group. Our syntheses involved the preparation of the derivatives of piperidine, pirrolidine, morpholine and diethylamine. The general course of the synthesis may be illustrated by the following formulas:

$$2R_1R_2NH + Cl \cdot CH_2CH = CH \cdot C_6H_5 \rightarrow R_1R_2 \cdot$$
$$\cdot NCH_2CH = CH \cdot C_6H_5 + R_1R_2N \cdot HCl$$

where R_1R_2NH = piperidine, pyrrolidine, morpholine or diethylamine.

The reactions are usually carried out in anhydrous solvents. The yield of the reaction is highly decreased by the formation of amine hydrochloride. This effect can often be eliminated by the use of pyridine as an acid binding agent.

Cinnamaldehyde, the first product of the synthesis leading to cinnamyl chloride, was prepared

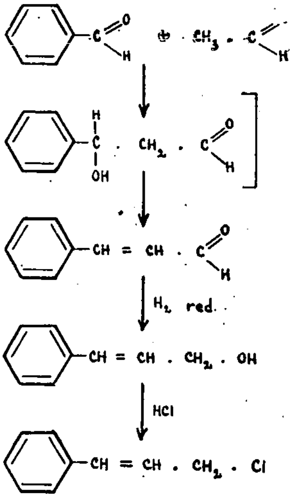

Fig. 1

by an aldol-type condensation of benzaldehyde and acetaldehyde [3]. Cinnamaldehyde was then converted to cinnamyl alcohol by means of aluminium isopropoxide [4], and the resulting alcohol was treated with hydrogen chloride to give cinnamyl chloride [5].

Since stereochemical relationships of the synthesis of cinnamyl chloride involving an aldol-type condensation are not clear, we tried to establish the cis or trans configuration, resp., of the derivatives obtained by the use of cinnamyl chloride.

First we attempted to apply BRUNI's rule, which was succesfully used by FODOR and KISS [6] for deciding about the cis-trans isomerism of sphingosine. 1-Phenyl-3-N-piperidino-propene-2 was hydrogenated, and the saturated and unsaturated derivatives were allowed to stand in a solvent in the molar ratios of 1:1. However, formation of mixed crystals did not take place, and only the unsaturated compound crystallized from the solvent. When these crystals were filtered, evaporation of the solution gave the saturated compound. In this case, of course, failure of the formation of mixed crystals affords no unequivocal proof for the cis configuration of the synthesized compound. BRUNI *et al.* [7] derived their rule from evidence obtained on model compounds having longer carbon chains.

Experimental

Materials

Piperidine: "Merck" piperidinium puriss. was used.

Acetaldehyde "pure for scientific use" was employed.

Benzaldehyde, puriss., was obtained from the Factory of Fine Chemicals "REANAL", Budapest.

Cinnamaldehyde prepared by the condensation of benzaldehyde and acetaldehyde [3] had b. p. 128—130°C/20 mm, m. p. 75°C.

Cinnamyl alcohol obtained by reduction with aluminium isopropoxide [4] had b. p. 100—102°C/15 mm.

Cinnamyl chloride was obtained by introducing hydrogen chloride into cinnamyl alcohol [5].

1-Phenyl-3-N-pirrolidinopropene-1

4 g of cynnamyl chloride dissolved in 5 ml of anhydrous benzene was slowly added to a solution of 4 g pirrolidine in 5 ml benzene. The mixture was allowed to stand half an hour, then the two layers were separated, the upper benzene layer dried over sodium sulphate, and the benzene distilled off under reduced pressure on the steam bath. The residue was fractionated to give 6,2 g product with b. p. 124—125°C/2 mm, $n_D^{25} = 1{,}5578$.

The *hydrochloride* of the compound was precipitated by means of hydrogen chloride dissolved in anhydrous ether. The finely dispersed precipitate was filtered and recrystallized from ethanol, m. p. 158°C. Analysis: Calculated C 69,77; H 8,11; Cl 15,86 %. Found C 69,51; H 7,96; Cl 15,62 %.

1-Phenyl-3-N-piperidinopropene-1

A solution of 20 g cinnamyl chloride in 30 ml anhydrous ether was slowly added to a stirred solution of 18 g piperidine in 30 ml anhydrous ether. When the addition was completed, the mixture was refluxed for 20 minutes, then it was allowed to stand for half an hour. The precipitate was filtered on a sintered glass filter, and the filtrate dried over sodium sulphate. After evaporating the ether, the oily residue was fractionated to give 21 g product, b. p. 130—132°C/2 mm, $n_D^{25} = 1{,}5572$. *The hydrochloride* of the compounds was precipitated by hydrogen-chloride dissolved in anhydrous ether. The finely dispersed precipitate was filtered and recrystallized from a mixture of ethanol acetone (1:6) m. p. 213°C. Analysis: Calculated C 70,70; H 8,48; Cl 14,93 %. Found C 70,70; H 8,68; Cl 15,10 %.

1-Phenyl-3-N-morpholinopropene-1

10 g of cinnamyl chloride was added under constant stirring to 8 g of morpholine. The mixture was allowed to stand one day, it was filtered from the precipitate, washed with anhydrous benzene, and the filtrate dried over sodium sulphate. The benzene was then evaporated, and the residue fractionated to give 10,5 g of the product, b. p. 133°/1 mm, $n_D^{25} = 1{,}5621$.

The *hydrochloride* of the compound was precipitated in the same way as described above, and recrystallized from a 1:10 mixture of ethanol and acetone. M. p. 215,5°C. Analysis: Calculated C 65,11; H 7,57; Cl 14,80 %. Found C 65,07; H 7,46; Cl 15,00 %.

1-Phenyl-3-N-diethylamino-propene-1

10 g of cinnamyl chloride was added to 7 g of diethylamine, the mixture was shaken vigorously and allowed to stand one day at room temperature. The precipitate was filtered and washed with anhydrous benzene, and the solution dried over sodium sulphate. The benzene was destilled off, and the residue fractionated to give 10,2 g of the product, b. p. 94°C/1 mm, $n_D^{25} = 1{,}5352$.

Its *hydrochlorid* was obtained as described above and recrystallized from anhydrous acetone. M. p. 149°C. Analysis: Calculated C 69,14; H 8,93; Cl 15,72 %. Found C 69,25; H 8,75; Cl 15,84 %.

1-Phenyl-3-N-piperidinopropane

4,5 g of 1-Phenyl-3-N-piperidinopropene-1 was dissolved in 20 ml of anhydrous ethanol, 2,5 ml of a 12 % hydrogen chloride solution in alcohol was added and the material was hydrogenated at atmospheric pressure and at room temperature in the presence of palladium charcoal catalyst. The theoretical amount of hydrogen (0,53 l) was taken up within half an hour. A calculated amount of alcoholic hydrogen chloride solution was added and the alcohol was evaporated at reduced pressure on the steam bath. The crystalline residue was recrystallized from a 1:6 mixture of ethanol and acetone.

M. p. 183°C. Analysis: Calculated C 70,11; H 9,25; Cl 14,80%. Found C 69,97; H 9,35; Cl 14,92%.

Experiment for mixed crystal formation

0,5 g of each of the saturated and unsaturated compounds (hydrochlorides) was dissolved in a 1:1 mixture of warm ethanol and acetone. The solution was allowed to stand in a refrigerator. A precipitation of crystal needles was obtained in 2 hours. After filtration and drying 0,55 g material was obtained, m. p. 212°C. Microhydrogenation showed the uptake of 1 mol of hydrogen. The formation of mixed crystals did not take place.

* * *

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СИНТЕЗ ТРЕТИЧНОГО-АМИНО-АРИЛ-ПРОПАНА И ПРОИЗВОДНЫХ ПРОПАНА

Ш. Фельдеак, Б. Маткович и *Й. Порсас*

Исходя из хлористого арил-пропена были изготовлены несколько секундерно-аминовых производных, ввиду их фармакологического значения. Кроме того авторы стремились установить пространственную структуру путем образования простого кристалла-смеси

NEUE NITRO-CHALKONE IV[1]

Von GY. SIPOS, T. SZÉLL und I. VÁRNAI
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(Eingegangen am 24. März 1960)

Verschiedene Nitro-hydroxy-acetophenone wurden mit Benzaldehyd und substituierten Benzaldehyden in Gegenwart von $AlCl_3$ bzw. wässerigem NaOH kondensiert. Als Ergebnis der Kondensation wurden unbekannte Chalkone erhalten. Betreffs der die Kondensation beeinflussenden Rolle der Hydroxylsubstituenten des Benzaldehydteils und der Nitro-hydroxysubstituenten des Acetophenonteils kamen wir zu dem erwartungsgemäßen Ergebnis.

Vorliegende Arbeit ist ein weiterer Beweis für die frühere Beobachtung, daß die Darstellung der Nitro-hydroxy-chalkone nicht nur mit basischen (NaOH), sondern auch mit sauren Katalysatoren ($AlCl_3$) zu verwirklichen ist [1]; sie liefert auch neuere Daten hinsichtlich des von den Substituenten des Benzaldehydteiles auf die Chalkonbildung ausgeübten Einflusses, da unsere experimentellen Untersuchungen zu der Feststellung führten, daß die Hydroxysubstituenten des Benzaldehydteiles: 3-OH>2-OH und 4-OH, die Chalkonbildung in der theoretisch zu erwartenden Reihenfolge fördern. Diese Reihenfolge wird bewiesen durch die Tatsache, daß unter den Umständen der mit 3-Hydroxybenzaldehyd durchgeführten Kondensation der 4-Nitro-2-hydroxy- und 5-Nitro-2-hydroxy-acetophenone weder das 2-Hydroxy-, noch das 4-Hydroxybenzaldehyd mit den erwähnten Ketonen kondensierte; diese wurden unverändert zurückerhalten.

Weiter stellten wir fest, daß die Nitro-hydroxy-substituenten des Acetophenonteils die Chalkonbildung in dieser Reihenfolge begünstigen: $2\text{-}NO_2\text{-}5\text{-}OH > 4\text{-}NO_2\text{-}2\text{-}OH > 5\text{-}NO_2\text{-}2\text{-}OH > 3\text{-}NO_2\text{-}4\text{-}OH$. Eine frühere Arbeit [2] machte bereits die Reihenfolge $4\text{-}NO_2\text{-}2\text{-}OH > 5\text{-}NO_2\text{-}2\text{-}OH > 3\text{-}NO_2\text{-}4\text{-}OH$ wahrscheinlich, doch war der minimale Unterschied in der Ausbeute der aus 4- und aus 5-Nitro-2-hydroxy-acetophenonen gebildeten Chalkone nicht ganz überzeugend. Wir fanden jetzt, daß die Chalkonbildung von 3-Hydroxy-benzaldehyd mit 4-Nitro-2-hydroxy-acetophenon unter milderen Bedingungen eintritt als mit dem 5-Nitro-2-hydroxy-acetophenon. Ferner zeigte sich, daß das 2-Nitro-5-hydroxy-acetophenon der beste Chalkonbildner unter den vier Ketonen ist, da es unter den [2] beschriebenen Bedingungen schon nach 15 Min. das Chalkon in 80 proz. Ausbeute liefert, obwohl das Chalkon-Natriumsalz im Gegensatz zu den sich ausscheidenden Natriumsalz der anderen drei Nitro-hydroxy-

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[1] III. Mitteilung: Acta Phys. et Chem. Szeged 5, 70 (1959).

chalkone in Lösung bleibt, d. h. das Gleichgewicht sich nicht so schnell erschieben kann.

Die dargestellten Chalkone sind tabellarisch zusammengestellt.

Beschreibung der Versuche[2]

Die Chalkone Nr. 6, 8, 10 und 12 der Tabelle wurden durch alkalischen Kondensation, die Chalkone 5 und 7 durch säure Kondensation erhalten. Die Kondensationen wurden nach [3] ausgeführt.

Abweichend von den Verhältnissen [3] verlief die alkalische Kondensation im Falle der Chalkone 1, 2, 3, 4, 9, 11 und 13.

2'-Nitro-5'-hydroxy-chalkon (Nr. 1 der Tab.). Das 2-Nitro-5-hydroxy-acetophenon wurde nach A. R. OSBORN und K. SCHOFFIELD [4] dargestellt. Schmp. 167° C.

Analyse: $C_8H_7O_4N$ (181,1)

Berechnet: C 53,1 H 3,9 N 7,7

Gefunden: C 52,7 H 3,8 N 7,7

0,18 g 2-Nitro-5-hydroxy-acetophenon (1 mMol) wurde unter Erwärmen in 15 ccm 1 n NaOH (15 mMol) gelöst und nach Abkühlen auf 20°C 0,106 g Benzaldehyd (1 mMol) zugegeben. Unter dauerndem Schütteln wandelte sich die Emulsion nach 5 Min. plötzlich scharf in eine klare Lösung um. Nach weiteren 5 Min. wurde mit 3,2 ccm 5 n HCl angesäuert, die ausgeschiedene blaßgelbe Substanz filtriert, mit Wasser gewaschen und getrocknet. Ausb. 0,22 g (80 % d. Th). Mit Ausnahme von Benzol und Aether löst sich die Substanz in den üblichen organischen Lösungsmitteln schon in der Kälte; läßt man das Reaktionsgemisch einen Tag stehen, so ist das ausgefällte und umkristallisierte Chalkon nicht farblos, sondern braun.

2', 4-Dinitro-5'-hydroxy-chalkon (Nr. 2). 0,18 g 2-Nitro-5-hydroxy-acetophenon (1 mMol) und 0,15 g 4-Nitro-benzaldehyd (1 mMol) wurde durch Erwärmen bis zum Siedepunkt in einem Gemisch von 6 ccm 2,5 % NaOH (2.2 mMol) und 4 ccm Äthanol gelöst und 5 Min. bei dieser Temperatur gehalten. Die noch warme, klare Lösung wurde mit Wasser verdünnt, das Chalkon mit 1 ccm 5 n HCl ausgefällt, mit Wasser säurefrei gewaschen und getrocknet. Ausb. 0,21 g (63,6 % d. Th).

2'-Nitro-5'-hydroxy-4-chlor-chalkon (Nr. 3). 0,18 g 2-Nitro-5-hydroxy-acetophenon (1 mMol) und 0,14 g 4-Chlor-benzaldehyd (1 mMol) wurde unter Erwärmen in einem Gemisch aus 8 ccm 1 n NaOH und 4 ccm Äthanol gelöst, 5 Min. auf dem Wasserbad erhitzt, dann mit Wasser verdünnt, das Chalkon mit 2 ccm 5 n HCl ausgefällt, bis zur Säurefreiheit gewaschen und getrocknet. Ausb. 0,18 g (56,2 % d. Th).

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[2] Die Schmelzpunkte sind unkorrigiert.

Übersicht über die dargestellten Chalkone

Nr.	—chalkon	Umkristallisierbar	Aussehen	Schmp. °C (unkorr.)	Summenformel	Mol.Gew.	N-Gehalt in %	
							Ber.	Gef.
1	2′-Nitro-5′-hydroxy	Benzol	farblose Nadeln	185—186	$C_{15}H_{11}NO_4$	269,2	5,20	5,31
2	2′,4-Dinitro-5′-hydroxy	Methanol	blaßgelbe „	200—201	$C_{15}H_{10}N_2O_6$	314,2	8,91	9,12
3	2′-Nitro-5′-hydroxy-4-chlor	Benzol	„ „	174—175	$C_{15}H_{10}NO_4Cl$	303,7	4,61	5,06
4	2′-Nitro-5′, 3-dihydroxy	Benzol/Methanol 10 : 1	„ „	178—179	$C_{15}H_{11}NO_5$	285,2	4,91	5,11
5*	3′-Nitro-4′-hydroxy-4-chlor	Äthanol/Essigester 1 : 1	hellgelbe „	183—184	$C_{15}H_{10}NO_4Cl$	303,7	4,61	4,80
6*	4′-Nitro-2′-hydroxy-4-chlor	Äthanol/Essigester 1 : 1	gelbe „	192—193	$C_{15}H_{10}NO_4Cl$	303,7	4,61	4,91
7*	5′-Nitro-2′-hydroxy-4-chlor	Äthanol/Essigester 1 : 1	gelbe „	216 - 217	$C_{15}H_{10}NO_4Cl$	303,7	4,61	4,80
8	3′-Nitro-4′, 2-dihydroxy	Äthanol/Essigester 1 : 1	gelbe „	194—195	$C_{15}H_{11}NO_5$	285,2	4,91	4,58
9	3′-Nitro-4′, 3-dihydroxy	Äthanol/Essigester 1 : 1	gelbe „	212—214	$C_{15}H_{11}NO_5$	285,2	4,91	4,72
10*	3′-Nitro-4′, 4-dihydroxy	Äthanol/Essigester 1 : 1	bräunlichgelbe „	214—216	$C_{15}H_{11}NO_5$	285,2	4,91	5,22
11	4′-Nitro-2′, 3-dihydroxy	Äthanol/Essigester 1 : 1	gelbe „	197—198	$C_{15}H_{11}NO_5$	285,2	4,91	4,82
12	5′-Nitro-2′, 2-dihydroxy	Äthanol/Essigester 1 : 1	gelbe „	182—183	$C_{15}H_{11}NO_5$	285,2	4,91	4,61
13	5′-Nitro-2′, 3-dihydroxy	Äthanol/Essigester 1 . 1	zitronengelbe „	186—187	$C_{15}H_{11}NO_5$	285,2	4,91	5,25

* Bekannte Verbindungen; Nr 5 und 7 wurden mit Hilfe von $AlCl_3$ dargestellt. [3]

2'-Nitro-5', 3-Dihydroxy-chalkon (Nr. 4). 0,18 g 2-Nitro-5-hydroxyacetophenon (1 mMol) wurden durch Kochen in 8 ccm 1 n NaOH (8 mMol) gelöst und mit 0,12 g 3-Hydroxy-benzaldehyd (1 mMol) versetzt. Nach 10 Min. langem Erwärmen der klaren Lösung wie bei [3] wurde wie dort aufgearbeitet. Ausb. 0,12 g (40 %. d. Th). Beim umkristallisieren aus Benzol/Methanol (10:1) schied sich eine schwarzbraune Substanz an der Wand des Kolbens ab, nochmals aus Benzol/Methanol und dann nur aus Benzol umkristallisiert wurde. Es handelt sich offensichtlich um zwei Substanzen. In reichlich Benzol wird eine weiße Substanz heraus gelöst und es bleiben blaßgelbe Nadelkristalle zurück.

3'-Nitro-4', 3-dihydroxy-Chalkon (Nr. 9). Die Lösung von 0,36 g 3-Nitro-4-hydroxy-acetophenon (2 mMol) in 30 ccm 1 n NaOH (30 mMol) wurde mit 0,244 g 3-Hydroxybenzaldehyd (2 mMol, Schmp. 104°) 2,5 Stunden auf dem Wasserbad erhitzt und dann mit 2 ccm Eisessig angesäuert. Es schied eine gelbe Substanz aus.

4'-Nitro-2', 3-dihydroxy-chalkon (Nr. 11). Die Lösung von 0,37 g 4-Nitro-2-hydroxy-acetophenon (2 mMol) und 0,25 g 3-Hydroxy-benzaldehyd (2 mMol) in 5 ccm Äthanol und 8 ml 1 n NaOH wurde 15 Min. bei Zimmertemperatur und weitere 15 Min. auf dem Wasserbad gehalten, dann in 20 ccm Wasser gegossen, mit 3 ccm Eisessig angesäuert, worauf sich 0,37 g gelbe Substanz ausschieden.

Bei längerem Erhitzen (45 Min.) erhält man kein Chalkon mehr, sondern einen klebrigen undefinierbaren Stoff. Bei dem gleichen Ansatz mit 2- oder 4-Hydroxy-benzaldehyd erhält man das Keton, nach dem Ansäuern, quantitativ zurück. Führt man die Umsetzung wie unter 13 beschriebene durch, so entsteht eine klebrige, undefinierbare Verbindung.

5'-Nitro-2', 3-dihydroxy-Chalkon (Nr. 13). Die Lösung von 0,37 g 5-Nitro-2-hydroxy-acetophenon (2 mMol) in 7 ccm 1 n NaOH (7 mMol) wurde, mit 0,25 g in 3 ccm Äthanol gelöstem 3-Hydroxy-benzaldehyd versetzt, 1 Stunde bei 40°C stehen gelassen, mit 1,5 ccm Eisessig angesäuert, filtriert und das ausgeschiedene bräunlichgelbe rohe Chalkon mit 5 ccm Wasser gewaschen. (Ausb. 0,48 g.)

Unter den obigen Bedingungen kondensierte weder 2-, noch 4-Hydroxybenzaldehyd mit dem Keton, letzteres konnte zurückgewonnen werden. Führt man die Reaktion mit 4-Hydroxy-benzaldehyd ebenso aus wie die Darstellung von 5'-Nitro-2', 2-dihydroxy-chalkon [3], so erhält man gelbe Nadeln vom Schmp. 163—164°C (Gef. N 6,3), die nicht weiter untersucht wurden. Die Substanz ist kein Chalkon.

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НОВЫЕ НИТРО-КАЛКОНЫ (IV.)

Дь. Шипош, Т. Селл и И. Варнаи

Нитро-гидрокси-ацетофеноны были конденсированы с различными ароматическими альдегидами в присутствии $AlCl_3$ и водянистого NaOH. В результате конденсации получились неизвестные калконы. При образовании калконов, насчет роли влияющей конденсацию нитро-гидрокси заместителей ацетофеноновой части и заместителя бензальдегидовой части получились ожидаемые результаты.

FRIES REARRANGEMENT OF MONONITROPHENYL BENZOATES

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(*Received June 15, 1960*)

Mononitrophenyl benzoates have been subjected to FRIES rearrangement in nitrobenzene using anhydrous aluminium chloride as catalyst. In the case of 2- and 4-nitrophenolic esters the products of the isomerisation were the para and ortho isomers, respectively, while 3-nitrophenyl benzoate gave no nitrohydroxy ketone.

It has been reported [1] that our attempst to subject mononitrophenyl benzoates to FRIES rearrangement had been unsuccesful. Further experiments showed, however, that under proper conditions FRIES rearrangement takes place in the presence of 1—1,25 moles of aluminium chloride using nitrobenzene as solvent. In the case of 2-nitrophenyl benzoate 3-nitro-4-hydroxy-benzophenone, in that of 4-nitrophenyl benzoate 5-nitro-2-hydroxy-benzophenone could be isolated in a yield of 3,5 % and 4 %, respectively. The 3-nitro-4-hydroxy-benzophenone was identified by its known 2,4-dinitrophenylhydrazone [2]. The 5-nitro-2-hydroxy-benzophenone which proved to be identical with an authentic preparate [3], was characterized by its so far unknown phenylhydrazone and 2,4-dinitrophenylhydrazone. The expected corresponding ketone, however, could not be so far isolated on rearrangement of 3-nitrophenyl benzoate under the conditions deschribed above. Attemps to realize this rearrangement are still in progress.

*Experimental**

Rearrangement of 2-nitrophenyl benzoate

5,5 g of anhydrous aluminium chloride (41,2 millimoles) was dissolved in 20 ml of nitrobenzene. 10 g of 2-nitrophenyl benzoate (41,2 millimoles, prepared from 2-nitro-phenol and benzoyl chloride, m. p.: 54° C) was added, and kept at 165—175° C for an hour. A vivid evolution of hidrogen chloride was observed. The solution was decomposed with 10 ml of concentrated hydrochloric acid, and nitrobenzene removed by steam distillation. The residue was cooled and filtered. The solid mixture, remained on the filter, was dissolved in 20 ml of hot ethanol which was previously used to extract the

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* Melting points are not corrected.

material stuck at the wall of the flask. The filtrate was extracted with 4 × 40 ml of tetrachloro-methane. The combined extract was heated and added to the hot ethanol solution, then it was diluted with 20 ml of water, and filtered. The resinous products separated, remained on the filter. The tetrachloro-methane solution was extracted with 5 × 20 ml of sodium hydroxide (6 g pro 100 ml of water). The combined extract was heated and acidified with concentrated hydrochloric acid. The upper aqueous layer was decanted from the brown oil separated. In order to dry the oil, it was dissolved in 10 ml of ethanol, and the solvent evaporated. The residue was extracted with three portions of 20 ml of hot ligroin. Having removed the ligroin the yellowish-brown residue was recrystallized from ethanol, giving 0,35 g of brownisch-yellow crystals melting at 76—81° C. Recrystallization twice from methanol and twice from ligroin gave yellow 3-nitro-4-hydroxy-benzophenone m. p. 91—92° C (R. A. ABRAMOVICH *et al* found 90° C [2]). (Found: N 5,94 %, $C_{13}H_9O_4N = 243,2$ requires: N 5,76 %). The 2,4-dinitrophenylhydrazone was prepared from a 50 % aquous ethanol solution of 3-nitro-4-hydroxy-benzophenone by adding a solution of 2,4-dinitrophenylhydrazin (1 g dissolved in 100 ml of concentrated sulphuric acid) to it. On heating orange-yellow crystals precipicated, m. p.: 261° C (R. A. ABRAMOVICH *et al* found 261° C [2]). (Found: N 16,2 %, $C_{19}H_{13}O_7N_5 = 423,3$ requires: N 16,5 %).

Rearrangement of 4-nitrophenyl benzoate

3,5 g of anhydrous aluminium chloride (26,2 millimoles) was dissolved in 20 ml of nitrobenzene. 5 g of 4-nitrophenyl benzoate (20,6 millimoles, prepared from 4-nitro-phenol and benzoyl chloride, m. p.: 142° C) was added and kept at 170° C for an hour. Hydrogen chloride evolved vigorously during the reaction. The cooled solution was poured into the mixture of 100 g of water and 10 ml of concentrated hydrochloric acid and stirred for an hour. The nitrobenzene layer was added to a mixture of 20 ml of 10 N sodium hydroxide and 20 ml of sodium fluoride solution (35 g per litre) and subjected to steam distillation until free from nitrobenzene. The residue was filtered, acidified with concentrated hydrochloric acid.

The aqueous layer was decanted from the resinous product separated, and extracted with 4 × 40 ml of tetrachloro-methane. The resinous residue was dissolved in 10 ml of ethanol and mixed with the combined and heated tetrachloro-methane extract. Having filtered, it was dried with anhydrous sodium sulphate and the solvent removed. The residue was dissolved in ethanol and allowed to stand overnight in refrigerator. 5-Nitro-2-hydroxy-benzophenone (0,2 g) crystallized, m. p.: 108—115° C. Having recrystallized from ethanol it had a m. p. of 122—124° C (ULLMANN, MALLET found 124—124,5° C [3]). (Found: N 5,65 %, $C_{13}H_9O_4N = 243,2$ requires: N 5,76 %). The phenylhydrazone was prepared from a 60 % ethanol solution by giving a calculated amount of phenyhydrazine to it. The separated brick-red needles melted at 190—191° C, (Found: N 12,9 %, $C_{19}H_{15}O_3N_3 = 333,3$ requires: N 12,9 %). The 2,4-dinitrophenylhydrazone was prepared as in the case of 3-nitro-4-hydroxy-benzophenone-2,4-dinitrophenylhydrazone. Yellow crystals, m. p.: 283—285° C. (Found: N 15,7 %, $C_{19}H_{13}O_7N_5 = 423,3$ requires: N 16,5 %).

The attempted rearrangement of 3-nitrophenyl benzoate

6,6 g of anhydrous aluminium chloride (49,5 millimoles) was dissolved in 40 ml of nitrobenzene, 10 g of 3-nitrophenyl benzoate (41,2 millimoles, prepared from 3-nitro-phenol and benzoyl chloride, m. p.: 93—95° C) was added and kept at 175° C for an hour. Hydrogen chloride evolved during the heating. Working up the mixture was the same as used in the case of 4-nitrophenyl benzoate. Only 3-nitro-phenol and benzoic acid could be isolated.

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ПЕРЕРАСПРЕДЕЛЕНИЕ ФРИЗА МОНОНИТРОФЕНИЛЬНЫХ ЭФИРОВ

А. Фурка и Т. Селл

Было осуществлено перераспределение фриза катализовано хлористым алюминием мононитрофенильных бензоатов в нитробензольном растворе. При перераспределении 2- и 4-нитрофенильных эфиров, соответствующие пара- и ортоизомеры были получены и 3-нитро-фенильный бензоат не перераспределился.

DECOMPOSITION OF MONONITROPHENOLIC ESTERS IN THE PRESENCE OF ALUMINIUM CHLORIDE

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(Received May 15, 1960)

In the presence of anhydrous aluminium chloride thermal decomposition of mononitrophenols, mononitrophenolic esters and nitro-hydroxy-acetophenones has been observed. The temperature of decomposition depends mainly on the position of the nitro group and on the nitro compound aluminium chloride ratio, respectively.

It has been observed by several workers that some nitrophenolic esters subjected to FRIES rearrangement in the absence of a solvent, decompose on heating instead of yielding the expected corresponding nitro-hydroxy-ketones. The slight explosion produced charred, tarry materials and bad smelling gases [1]—[3]. Other authors reported similar phenomena using phenolic esters of nitrobenzoic acids [4]. It seemed therefore to be of interest to investigate factors influencing the decomposition of nitrophenols and of their derivatives. To compare this property of the different compounds, the temperature was measured at which decomposition took place under given and reproducible conditions.

Results

Table I shows that the decomposition of nitrophenolic esters is due to the nitro group introduced in the phenolic nucleus, as phenyl acetate, phenyl benzoate and thyml acetate do not decompose while nitrophenolic esters do. Nitro group having *ortho-* or *para*-position results in reducing the temperature of decomposition compared with that observed in the case of *meta*-nitrophenolic esters. This effect due to the position of the nitro group could be observed on the decomposition of mononitrophenols as well (Table II). The data summarized in table III show that the temperature of the decomposition also depends on the nature of the acyl part of nitrophenolic esters, though this effect is slighter than that caused by the change of the position of the nitro group. Further, the decomposition takes place generally at somewhat lower temperature in the case of 0-acylated phenols than in that of nitrophenols. On the other hand, when introducing an acyl group into the nucleus of nitrophenols the decomposition takes place at higher temperature. In the case of nitrophenols acylated in nucleus the temperature of decomposition is higher than in that of the corresponding nitrophenolic esters, wherefrom the former are formed by FRIES reaction. (Tables I, II, III). The aluminium chloride-ester ratio has a prominent effect on the decomposition. 4-Nitrophenyl acetate did not decompose as long as only equimolar quantities of aluminium chloride were used, but in the presence

Table I

Effect of nitro group on the decomposition of phenolic esters

	$AlCl_3$-ester ratio	Ester (g)	$AlCl_3$ (g)	Temperature of decomp. (°C)
2-Nitrophenyl acetate	2 : 1	0,90	1,30	104
3-Nitrophenyl acetate	2 : 1	0,90	1,30	187
4-Nitrophenyl acetate	2 : 1	0,90	1,30	134
2-Nitrophenyl benzoate	2 : 1	0,90	0,98	129
3-Nitrophenyl benzoate	2 : 1	0,90	0,98	193
4-Nitrophenyl benzoate	2 : 1	0,90	0,98	132
Phenyl acetate	2 : 1	0,90	1,80	—
Phenyl benzoate	2 : 1	0,90	1,20	—
Thymyl acetate	2 : 1	0,90	1,20	—

Table II

Decomposition of mononitrophenols

	$AlCl_3$-nitrophenol ratio	Nitrophenol (g)	$AlCl_3$ (g)	Temperature of decomp. (°C)
2-Nitro-phenol	2 : 1	0,90	1,70	163
3-Nitro-phenol	2 : 1	0,90	1,70	198
4-Nitro-phenol	2 : 1	0,90	1,70	165

Table III

Effect of acyl group on the decomposition of esters

	$AlCl_3$-ester ratio	Ester (g)	$AlCl_3$ (g)	Temperature of decomp. (°C)
3-Nitrophenyl acetate	2 : 1	0,90	1,30	187
3-Nitrophenyl propionate	2 : 1	0,90	1,23	183
3-Nitrophenyl kloroacetate	2 : 1	0,90	1,10	173
3-Nitrophenyl phenylacetate	2 : 1	0,90	0,93	162
3-Nitrophenyl benzoate	2 : 1	0,90	0,98	193
3-Nitrophenyl-4-nitro-benzoate	2 : 1	0,90	0,83	195
4-Nitrophenyl acetate	2 : 1	0,90	1,30	134
4-Nitrophenyl propionate	2 : 1	0,90	1,23	135
4-Nitrophenyl benzoate	2 : 1	0,90	0,98	132

Table IV

Decomposition of nitro-hydroxy ketones

	$AlCl_3$-ketone ratio	Ketone (g)	$AlCl_3$ (g)	Temperature of decomp. (°C)
5-Nitro-2-hydroxy-acetophenone	2 : 1	0,90	1,30	207
5-Nitro-2-hydroxy-acetophenone	3 : 1	0,90	1,90	202
4-Nitro-3-hydroxy-acetophenone	2 : 1	0,90	1,30	174
4-Nitro-2-hydroxy-acetophenone	2 : 1	0,90	1,30	—

Table V

Effect of aluminium chloride — ester ratio on decomposition

	$AlCl_3$-ester ratio	Ester (g)	$AlCl_3$ (g)	Temperature of decomp. (°C)
4-Nitrophenyl acetate	0,5 : 1	0,90	0,32	—
4-Nitrophenyl acetate	1,0 : 1	0,90	0,64	—
4-Nitrophenyl acetate	1,5 : 1	0,90	0,96	144
4-Nitrophenyl acetate	2,0 : 1	0,90	1,30	134
4-Nitrophenyl acetate	2,5 : 1	0,90	1,60	131
3-Nitrophenyl acetate	1,0 : 1	0,90	0,65	—
3-Nitrophenyl acetate	2,0 : 1	0,90	1,30	187
3-Nitrophenyl phenylacetate	1,0 : 1	0,90	0,47	166
3-Nitrophenyl phenylacetate	2,0 : 1	0,90	0,93	162

Table VI

Effect of the experimental conditions on decomposition

	$AlCl_3$-ester ratio	Ester (g)	$AlCl_3$ (g)	Starting temp. (°C)	Temperature of decomp. (°C)
4-Nitrophenyl acetate	1 : 1	0,90	0,64	65	—
4-Nitrophenyl acetate	1 : 1	0,90	0,64	105	—
4-Nitrophenyl acetate	1 : 1	0,90	0,64	145	153
3-Nitrophenyl kloroacetate	2 : 1	0,90	1,10	65	173
3-Nitrophenyl kloroacetate	2 : 1	0,90	1,10	130	174
3-Nitrophenyl kloroacetate	2 : 1	0,90	1,10	150	175
3-Nitrophenyl propionate	2 : 1	0,90	1,23	65	183
3-Nitrophenyl propionate	2 : 1	0,90	1,23	140	185
4-Nitrophenyl acetate	2 : 1	0,10	0,15	65	137
4-Nitrophenyl acetate	2 : 1	0,40	0,58	65	138
4-Nitrophenyl acetate	2 : 1	0,90	1,30	65*	134

* Working at constant temperature, at 105 °C, no decomposition was observed, while at 116 °C decomposition took place after one and a quarter of a minute.

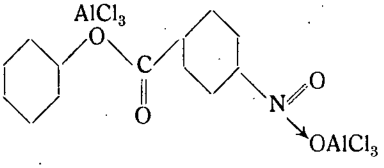
Tabele VII

Temperature (°C)	Time (min)	Temperature (°C)	Time (min)
65	0,0	150	10,0
75	1,5	160	11,3
90	3,5	170	12,8
100	4,5	180	14,5
110	5,5	190	16,3
120	6,6	200	18,7
130	7,7	210	21,8
140	8,8		

of 1,5 or more moles, heating resulted in decomposition. It seems, howewer, increasing the aluminium chloride-ester ratio over two, there is no considerable influence on the temperature of charring (Table V). It is to be noted that the temperature of the decomposition also depends more or less on the experimental conditions applied (Table VI).

Discussion

The authors' observation, that a mixture of a phenolic ester and aluminium chloride melts twice while being heated (see experimental part), is in accordance whit the well known assumption that aluminium chloride forms complex with phenolic esters. At first the ester melted, then the complex formed. G. S. SAHARIA explained the decomposition observed with phenolic esters of *p*-nitro-benzoic acid in the presence of two moles of aluminium chloride as a consequence of a complex formation type I. The aluminium chloride in this complex tends



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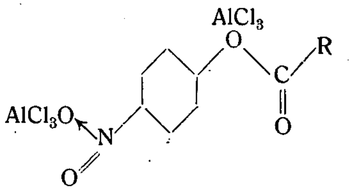

II.

to pull away the electrons from the nitro group which affects the electron density of the oxygen atom of the ester group where another aluminium chloride molecule is attached; resulting in an abnormal electron demand and, consequently in decomposition [4]. On the basis of our results this explanation may be extended to nitrophenolic esters, nitrophenols and nitro-hydroxy ketones, as well (*e. g.* from 4-nitrophenolic esters the formation of complex II may be assumed). The stability of the complex greatly depends on the position of the nitro group. *Orto-* and *para-* position of nitro group (concerning the phenolic oxygen atom) results in formation of complexes less stable than those formed from *meta* isomers. Only the relatively high temperature of the decomposition of 5-nitro-2-hydroxy-acetophenone (Table IV) appears to be inconsistent with this statement. There is reason, however, to suppose that this may be due to a stable ring complex which is formed from such type of ketones and from aluminium chloride [5].

*Experimental**

Materials

Aluminium chloride anhydrous (B. D. H. preparate).

Nitrophenols. Commercial grade.

Phenolic esters. Phenyl acetate [6], b. p.: 194—197° C; phenyl benzoate [7], m. p.: 69—70° C; thymyl acetate [8], b. p.: 243—246° C; 2-nitrophenyl acetate [9], m. p.: 39—40° C; 3-nitrophenyl acetate [10], m. p.: 54—55° C; 4-nitrophenyl acetate [6], m. p.: 79—80° C; 3-nitrophenyl propionate [11], m. p.: 49° C; 4-nitrophenyl propionate [3], m. p.: 63—64° C; 3-nitrophenyl chloroacetate [3], m. p.: 78—79° C; 3-nitrophenyl phenylacetate [3], m. p.: 61—63° C; 2-nitrophenyl benzoate [12], m. p.: 54° C; 3-nitrophenyl benzoate [12], m. p.: 93—95° C; 4-nitrophenyl benzoate [12]. m. p.: 142° C; 3-nitrophenyl-4-nitro benzoate prepared from sodium-3-nitrophenolate by treating il with 4-nitrobenzoyl chloride in benzene, m. p.: 173—174° C.

Ketones. 5-nitro-2-hydroxy-acetophenone [13], m. p.: 102—103° C; 4-nitro-3-hydroxy-acetophenone [9], m. p.: 131—132° C; 4-nitro-2-hydroxy-acetophenone [3], m. p.: 67—68° C.

Determination of temperature of decomposition

The powdered samples of nitrophenols, esters or ketones were intimately mixed with powdered anhydrous aluminium chloride in a round-bottomed flask (25 ml) connected with a flask (5 l) fitted with a guard tube. Paraffin wax was molten and allowed to stand till the temperature dropped to 60° C. The bath was then heated. When the temperature reached 65° C again the flask containing the samples was dipped into the bath and the heating continued till max. 210° C with a rate illustrated in Table VII.

On heating the molten substances subsequently solidified owing to complex formation, melted again at a higher temperature and a gas evolution was observed, then decomposed (if at all) with a slight explosion.

In the case of 3-nitrophenyl phenylacetate the black residue was boiled with dil. hydrochloric acid, twice with ethanol and finally with tetrachloromethane. 0,7 g remained insoluble consisting of 5,6 % N, 67,2 % C, 3,3 % H and 0,4 % inorganic material.

Carrying out a number of repeated measurements it was concluded that the average error of determination is less than 3° C.

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* Melting points are uncorrected.

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РАЗЛОЖЕНИЕ МОНОНИТРОФЕНОЛЬНЫХ ЭФИРОВ В ПРИСУТСТВИИ ХЛОРИСТОГО АЛЮМИНИЯ

А. Фурка и *Т. Селл*

Авторы наблюдали что в присутствии хлористого алюминия мононитрофенолы, мононитрофенольные эфиры и нитрогидрокси-ацетофеноны, в результате нагревания, распадали. Температура распада зависит главным образом от положения нитро-группы и от соотношения молей нитро-соединения и хлористого алюминия.

FRIES REARRANGEMENT OF SOME NITROPHENOLIC ESTERS IN THE ABSENCE OF SOLVENT

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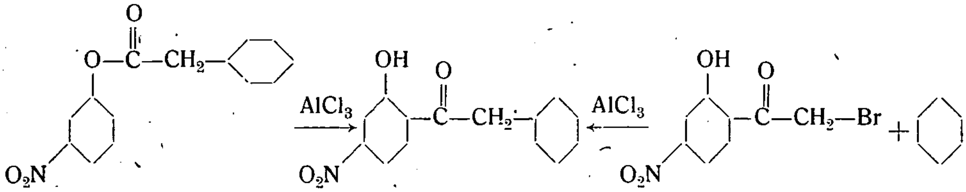
(Received May 15, 1960)

The aluminium chloride catalysed FRIES isomerisation of 4-nitrophenyl acetate, 3- and 4-nitrophenyl phenylacetate was carried out in the absence of a solvent. The products formed were the corresponding ortho hydroxy ketones.

In a previous work [1] it has been found that nitrophenolic esters decompose on heating in the presence of aluminium chloride and the factors having an effect on decomposition determined. These results made possible to choose proper experimental conditions under which, instead of decomposition FRIES rearrangement may take place (if at all). A. S. U. CHOUGHULAY *et al* [2] reported that 4-nitrophenyl acetate, using 2,2 moles of aluminium chloride and no solvent, decomposed instead of rearranging. Our attempt [3] to rearrange 3-nitrophenyl phenylacetate in the presence of 2 moles of aluminium chloride also failed. Using, however, 0,8—0,85 moles of the catalyst the realisation of the FRIES reaction of 4-nitrophenyl acetate, 3-nitrophenyl phenylacetate and that of so far unknown 4-nitrophenyl phenylacetate in the absence of a solvent was successful. Products of these reactions were the known 5-nitro-2-hydroxy-acetophenone [4] (yield*: 28 %), the so far unknown 4-nitro-2-hydroxy-ω-phenyl-acetophenone (yield: 3,5 %), and 5-nitro-2-hydroxy-ω-phenyl-acetophenone (yield: 6 %), respectively. The structure of 4-nitro-2-hydroxy-ω-phenyl-acetophenone was proved by the Friedel-Crafts reaction of 4-nitro-2-hydroxy-ω-bromo-acetophenone [8] with benzene, which gave identical product with that obtained by the FRIES reaction of 3-nitrophenyl phenyl acetate.



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* The rearrangement carried out in nitrobenzene gave yields of 24,7 %, [5], 25,1 %, [6], 25 % [2] and 35 %, [7].

It may be concluded that in order to avoid decomposition it is not advisable to use more than one mole of aluminium chloride when rearranging nitrophenolic esters. This is also supported by the fact that we could isomerize 2-nitrophenyl acetate [3] in the presence of one mole of aluminium chloride, while LINDEMAN and ROMANOFF [4] could not, using probably more than one mole of the catalyst.

*Experimental**

Fries reaction of 4-nitrophenyl acetate

Ester prepared according to the method of F. D. CHATTAWAY [9] (10 g, 55,3 millimoles) was thoroughly mixed with anhydrous aluminium chloride (6,2 g, 46,6 millimoles), introduced into a flask provided with a guard tube and kept for 25 minutes at 140—150°C on a sand bath. On heating the ester melted, gas evolved, then it solidified again. The cooled mixture was dissolved in 30 ml of ethanol, made acid by adding 10 ml of concentrated hydrochloric acid and 300 ml of water and allowed to stand in a refrigerator for 2 hours. The black precipitate was filttered off and dissolved in 10 ml of hot ethanol. The filtrate was extracted with 4×40 ml of tetrachloro-methane which was then combined, heated and added to the hot ethanolic solution. Next the solution was cooled, filtered through cotton and shaken with 5×40 ml of 1,5 N sodium hydroxyde solution. On acidifying the alcalic extract a black material separated (6,5 g) which was dissolved in 150 ml of hot ligroin (resins remained undissolved) and allowed to stand in a refrigerator for 3 hours. The separated orange yellow crystals (3,6 g) were recrystallized from ethanol, then from ligroin. The colourless product (2,8 g) melted at 101—102°C and was found to be identical with 5-nitro-2-hydroxy-acetophenone obtained by a different method [5] (Found: N 7,42 %, $C_8H_7O_4N = 181,1$ requires: 7,73 %). Phenylhydrazone melted at 224—225°C, 2,4-dinitrophenylhydrazone at 255—258°C.

Fries reaction of 3-nitrophenyl phenylacetate

The ester prepared as described previously [3] (13 g, 50 millimoles) was intimately mixed with aluminium chloride (5,3 g, 40 millimoles) and warmed on a paraffin wax bath for 25 minutes at 140°C (gas evolved). Having decomposed the mixture as described above a black oil and an aqueous layer were obtained. The method of the isolation of the ketone was the same as that of 5-nitro-2-hydroxy-acetophenone, but before extracting the tetrachloromethane solution with aqueous sodium hydroxide, it was shaken with 50 ml of water, filtered through cotton and the organic layer removed.

Yellowish crystals were obtained (0,45 g), m. p.: 152—153°C. (Found: N 5,8 %, $C_{14}H_{11}O_4N = 257,24$ requires: 5,44 %). Phenylhydrazone was prepared from the ketone by boiling it with phenylhydrazine in 60 % ethanol for a

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* Melting points are uncorrected.

few minutes. Red needles, m. p.: 198—199°C. (Found: N 12,4 %, $C_{20}H_{17}O_3N_3 = 347,36$ requires: 12,1 %). The ketone was found to be identical with the product obtained by boiling 4-nitro-2-hydroxy-ω-bromo-acetophenone in benzene in the presence of 2 moles of aluminium chloride for an hour.

Preparation of 4-nitrophenyl phenylacetate

Sodium-4-nitrophenolate (8,1 g, 50 millimoles) (prepared from 4-nitrophenol dissolved in benzene by giving ethanolic sodium ethylate to it) was treated with phenylacetyl chloride (7,7 g, 50 millimoles) in benzene (50 ml), the mixture refluxed for 30 minutes and filtered to remove sodium chloride. The solvent from the filtrate was evaporated and the residual oil poured into water (100 ml) while being stirred. The separated oil was then treated with ethanol (5 ml) and petroleum ether (25 ml), and allowed to stand in a refrigerator for 3 days when white platelets of the ester were obtained (9 g), m. p.: 64—65°C. On recrystallizing from ethanol it had a m. p.: 65—66°C. (Found: N 5,80 %, $C_{14}H_{11}O_4N = 257,24$ requires: 5,44 %).

Fries reaction of 4-nitrophenyl phenylacetate

The mixture of ester (3,7 g, 13,6 millimoles) and aluminium chloride (1,5 g, 11,4 millimoles) was placed into a paraffin wax bath of 105°C, and the temperature raised to 140°C in 12 minutes. On heating a slight explosion was observed at 134°C, dark gases evolved. The ketone (0,22 g) was isolated as desribed in the case of the rearrangement of 3-nitrophenyl phenylacetate. Colourless needles, m. p.: 115—116°C. (Found: N 5,78 %, $C_{14}H_{11}O_4N = 257,24$ requires: 5,44 %). The yellow phenylhydrazone melted at 185—186°C (Found: N 12,5 %, $C_{20}H_{17}O_3N_3 = 347,36$ requires: 12,1 %).

* * *

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ПЕРЕРАСПРЕДЕЛЕНИЕ ФРИЗА НЕСКОЛЬКИХ ЭФИРОВ НИТРОФЕНОЛА В ОТСУТСТВИИ РАСТВОРИТЕЛЯ

А. Фурка и *Т. Селл*

Перераспределение Фриза 4-нитро-фенильного ацетата, 3- и 4-нитро-фенильного-фенильацетата, катализовано хлористым алюминием было исполнено без растворителя. Продукты были соответствующие орто-гидрокси-кетоны.

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