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QUANTITATIVE CHARACTERISTICS OF SOLVENT  
INFLUENCE ON POSITION OF LONGWAVE ABSORPTION  
BONDS OF SOME ANTHRAQUINONE DERIVATIVES

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It has been established that the methods of Koppel-Palm and Kamlet-Taft prove useful when applied to characterize quantitatively the solvent influence on the position of longwave  $\pi\pi^*$  absorption bands of anthraquinone derivatives. Both methods lead to the close estimates of the contributions of specific interactions with solvents as well as complementary information about the role of non-specific interactions. Empirical equations are suggested for 1-methoxy-, 2-oxy- and 1-aminoanthraquinones which make it possible to calculate the  $\lambda_{\max}$  values of these compounds in a large number of solvents.

9,10-anthraquinone derivatives are widespread in nature and they are more and more used as synthetic dyes, pigments, luminescent solids, biologically active substances as well as catalysts of reduction-oxidation processes, etc.<sup>1</sup>. That is why research into the chromaticity of this class of compounds has not slowed down over many decades. There are over 1,300 publications which contain data on the electron absorption spectra of anthraquinones and although many of these spectra have been measured in different solvents (see, e.g. ref. 2), the general regularities showing solvent



influence on the position of longwave  $\pi_1, \pi^*$  bonds have not been found so far.

Attempts to relate the absorption bond shifts of individual anthraquinone derivatives to the values of refraction or dielectric constants have resulted only in establishing specific regularities<sup>2</sup>. Using the simplified formula of

McRae, Yoshida and Takabayashi the values which characterize the electrostatic and dispersion interactions of some anthraquinone monosubstitutes with solvents were calculated<sup>2</sup> and it was found that both types of interaction lead to the red shift of longwave absorption bonds. The latter could be explained by the enhanced polarity of the solute in the excited state in comparison with the ground one. The influence of specific interactions with the solvent is not considered by this formula.

Recently the use of multiparameter equations has extended notably. These equations are based on the conception of linearity of solvation energy. In order to characterize quantitatively solvent influence on the physico-chemical properties and reactivity of these compounds Koppel and Palm have suggested a four-parameter equation:

$$A = A_0 + Y \frac{\epsilon - 1}{2\epsilon + 1} + P \frac{n^2 - 1}{n^2 + 2} + eE + bB \quad (1)$$

where  $A$  and  $A_0$  are the characteristics of physicochemical properties or reactivity,  $\epsilon$  denotes the dielectric constant,  $n$  - refraction index,  $E$  and  $B$  are the general acidity and basicity parameters of solvent;  $p$ ,  $y$ ,  $e$  and  $b$  are the coefficients which characterize the given reaction series reflecting its sensitivity to the influence of the corresponding solvent properties. The members of eq. 1 describe the contribution of nonspecific solvation which is connected with the polarity and polarizability of solvents as well as specific solvation which is connected with their general acidity and basicity.

Makitra and Pirig added<sup>5</sup> the fifth member a  $\sigma^2$  to the equation of Koppel-Palm which reflects the influence of

cohesion energy density  $\delta^2$ , i.e. the energy when the solvent molecules interact with each other (self-association). They showed that the one- and two-parameter dependences found in literature can be observed in specific cases only.

In general the five-parameter equation has to be used but in concrete cases some of its members may appear to be negligible. It was shown that it is possible to mutually recalculate various basicity scales of solvents by way of linear multiparameter equations.

The scale of Koppel-Paju<sup>7</sup> is recommended for practical purposes. This scale is based on the measurement of phenol OH shifts in the infrared spectrum when the substances are in  $\text{CCl}_4$  solution, i.e. in the cases when the possibility of nonspecific solvation is almost out of the question. Reference 7 presents basicity values for almost 200 solvents. The parameters of electrophilicity E for 86 solvents are given in ref. 8, these values are based on the polarity parameters of Dimoth and Reichardt<sup>9</sup>. The equation of Koppel-Palm has not so far been applied to describe solvent influence on the characteristics of absorption spectra.

A similar approach has been developed by Kamlet and Taft who have proposed<sup>10-13</sup> a general solvatochromatic equation:

$$XYZ = XYZ_0 + s\pi^* + a\alpha + b\beta \quad (2)$$

where XYZ and  $XYZ_0$  are identical with A and  $A_0$  in eq. 1;  $\pi^*$ ,  $\alpha$  and  $\beta$  denote solvatochromic parameters:  $\pi^*$  characterizes solvent "dipolarity-polarizability" and is related to the value of its dipole moment,  $\alpha$ -characterizes the ability of the proton donor solvent to form the intermolecular hydrogen bond (IHB) with a proton acceptor solute,  $\beta$  denotes the ability of the proton acceptor solvent to form IHB with a proton acceptor solute; s, a and b are solvatochromic coefficients which characterize the reaction series and describe the sensitivity of XYZ to the respective solvatochromic parameters. The values of solvatochromic parameters have been inferred from the shifts of longwave absorption bands and



other physico-chemical properties of the compounds that were taken as indicators and these values are suggested for almost 100 solvents<sup>13</sup>.

Kamlet and Taft established that eq. 2 can be applied to describe quantitatively solvent influence on the position of absorption bands of a large number of various organic compounds and it was shown that nearly all the known solvent scales could be reduced to the combinations of solvatochromic parameters.

The term "dipolarity" according to Kamlet-Taft is identical with solvent "polarity" ("soft polarity") according to Koppel-Palm and is related<sup>14</sup> only to the nonspecific interaction of the solvent with the solute. It is different from Reichardt's term "effective" polarity under which the overall solvent influence on the value of this solute parameter is meant<sup>9</sup>.

As can be seen, the solvatochromic parameter of dipolarity-polarizability  $\pi^*$  is similar to the sum of polarity and polarizability factors according to Koppel-Palm. It has been pointed out that a drawback of the  $\pi^*$  scale is the fact that this unified parameter of nonspecific solvation does not differentiate between the discrete (and in the majority of cases) the different influence on the physico-chemical properties of medium polarity and polarizability.

Solvatochromic parameter  $\beta$  is analogous to the parameter of basicity  $B^{12}$ . On the whole the correlation between them is poor<sup>6,12,13</sup> but within each of the three groups of solvents it is good<sup>13</sup>. According to ref. 13 the division of solvents into groups is likely to be conditioned firstly by the influence of vibration energetics by the geometric-relationships between the vibration axes of H-X bonds of the proton donor substance as well as by the direction of the main dipole of the proton acceptor solvent. The second reason is the different hybridization of acceptor atoms that influences the mobility of the electron pair of the hydrogen bond. The absence of unified proportionality between parameters  $B$  and  $\beta$  is a fact that according to the authors of ref. 13 throws doubt upon the correctness of one of the



scales. According to ref. 6 parameter  $\rho$  correlates with the combination  $B, \delta^2, f(\delta), f(n)$  for nonassociated solvents and with  $E, \delta^2$  and  $f(\epsilon)$  for associated solvents (spirits).

The parameter of acidity  $E$  correlates with the combination of solvatochromic parameters  $\pi^*$  and  $\alpha^{12}$ . The existence of small but significant  $E$  values for such solvents as dimethylpermamide, dioxane, N-methylpyrrolidone which do not possess proton donor properties or Lewis' acidity is one of the drawbacks of scales  $E$ .

On the other hand,  $\pi^*, \alpha$  and  $B$  values depend to a certain extent on the indicators used for their derivation and have been repeatedly revised by Kamlet and Taft. It concerns particularly the  $\alpha$  parameter because several of its values retain elements of indefiniteness due to the various competing influences of amphiproton solvent self-association and for other reasons<sup>13</sup>. An advantage of the solvatochromic parameters of Kamlet-Taft is their equal normalization which facilitates the quantitative comparison of the contributions of various interactions to general solvent influence on the studied property of the given compound.

The objective of the current paper was to check whether equations 1 and 2 could be applied to describe quantitatively solvent influence on the position of longwave absorption peaks of anthraquinone derivatives and to compare the results thus obtained. The following compounds were selected for this purpose: 1-methoxy-anthraquinone forms IMB only with proton donor but not with proton acceptor solvents, 2-oxy- and 1-aminoanthraquinones form both forms of IBM and the latter differs from the former by the existence of the intramolecular hydrogen bond in its structure.

The values of  $\nu_{\max}$  have been taken from literature (the pertinent references are presented in Tables 1-3) or obtained by the authors themselves. The solvatochromic parameter values of Kamlet-Taft were taken from ref. 13. The compounds and solvents were purified by known methods, the absorption bands were measured on a spectrophotometer Specord UV-Vis, the calculations were done on a Mir-1 computer and with the system DASQ-2STM, the confidence level

being 0.95.

# 1 - Methoxyanthraquinone

Eq. (1) for this compound is as follows:

$$\begin{aligned} \gamma_{\max} &= (28.41 \pm 1.54)kK^{\pi} - (0.73 \pm 2.24)\frac{\xi-1}{2\xi+2} - (4.93 \pm 6.01) \\ &\frac{n^2-1}{n^2+2} - (0.047 \pm 0.051)E - (0.0007 \pm 0.0013)B \end{aligned} \quad (1a)$$

The number of solvents  $n=9$ , the multiple correlation coefficient  $R=0.975$ , the root-mean-square error  $SD=0.12$  kK. The addition of the fifth member to eq. 1a which indicates the contribution of the density of energy cohesion does not change the correlation coefficient, i.e. this term is statistically negligible. The alternate exclusion of parameters from the correlation leads to a decrease in the correlation coefficient: the exclusion of  $f(\xi)$  - up to 0.969,  $B$  up to 0.960,  $f(n)$  - up to 0.941,  $E$  - up to 0.931. The parameters of solvent polarity and general basicity are negligible, the exclusion of the former does not increase the root-mean-square error, the exclusion of the latter increases it insignificantly (up to 0.13 kK). Consequently, solvent influence on the  $\gamma_{\max}$  value of 1-methoxyanthraquinone can be satisfactorily described by the Koppel-Palm equation.

However, only two solvent parameters - general basicity  $E$  and polarizability  $f(n)$  can be used because this value is more sensitive to the influence of these.

Eq. 2a was obtained for 1-methoxyanthraquinone as follows:

$$\gamma_{\max} = (27.10 \pm 0.10)kK - (0.90 \pm 0.18)\pi^{\pi} - (0.49 \pm 0.14)\alpha \quad (2a)$$

$n=11$ ,  $R=0.982$ , the root-mean-square error  $SD=0.08$  kK almost coincides with the measuring error of the  $\gamma_{\max}$  value and is less than the error which is characteristic of the

$$\pi) \quad 1 \text{ kK (kilokaiser)} = 10^{-3} \text{ cm}^{-1}$$

Kamlet-Taft method (0.1 kK). This equation describes solvent influence on  $\nu_{\max}$  of 1-methoxyanthraquinone more precisely than eq. 1a. The value of the cross-section (27.10 kK) has a real physical sense: it comprises  $\nu_{\max}$  in cyclohexane for which the zero value of all solvatochromic parameters was postulated ( $\pi^* = 2 = 0$ ). The ratio of solvatochromic coefficients  $s/a=0.90:0.49=1.8$  evidences that the contribution of nonspecific interaction with solvents exceeds the contribution of IBM nearly twice.

In aprotic solvents a more simple dependence is well observed:

$$\nu_{\max} = (27.10 \pm 0.08) \text{ kK} - (0.92 \pm 0.14) \pi^* \quad (3a)$$

$n = 7, \quad R = 0.991, \quad SD = 0.05 \text{ kK}$

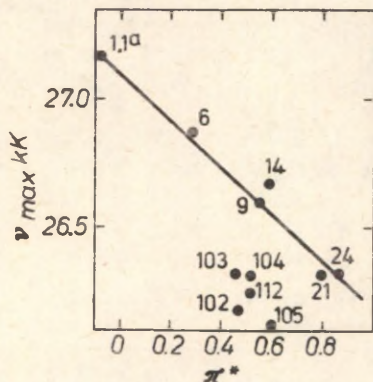


Fig. The  $\nu_{\max}$  correlation of 1-methoxyanthraquinone with solvatochromic parameters  $\pi^*$  (the constant solvent numbers according to Kamlet-Taft have been used, see Table 1).

The negative sign of all the coefficients in equations 1a, 2a and 3a gives evidence of the fact that any kind of interaction of 1-methoxyanthraquinone with solvents favors the bathochromic shift of the longwave absorption peak.



Table 1  
Comparison of the  $\nu_{\max}$  values of 1-methoxyanthraquinone  
obtained experimentally and those calculated according to  
equations 1a, 2a and 3a

Solvent number ac- cording to Kamlet-Taft	Solvent	$\nu_{\max}$ , $\text{cm}^{-1}$				Liter- ature
		Calculated according to equations			obtained experi- mentally	
		(1a)	(2a)	(3a)		
1	Hexane	27.15	27.18	27.18	27.17	2
1a	Heptane	27.11	27.18	27.18	27.17	2
6	Carbon tetrachlo- ride	26.90	26.84	26.85	26.88	15
9	Dioxane	26.63	26.61	26.61	26.60	2
14	Benzene	26.69	26.57	26.57	26.67	15
21	Methylene- chloride	-	26.38	26.32	26.32	2
2						
24	Pyridine	26.28	26.32	26.32	26.32	2
105	Methanol	26.20	26.08	-	26.11	2
104	Ethanol	26.26	26.20	-	26.32	2
112	1-Propanol	-	26.25	-	26.25	
103	Butanol	26.20	26.30	-	26.32	
102	2-Propanol	26.36	26.31	-	26.18	16

In Table 1 the experimentally obtained  $\nu_{\max}$  values of the 1-methoxyanthraquinone longwave absorption band have been compared with those calculated according to equations 1a, 2a and 3a.

Equations 1a and 2a lead to qualitatively equal results as to the relationship of specific and nonspecific interaction contributions of the studied substance with solvents, the quantitative estimation of this relationship is more conspicuous in eq. 2a. However, an essentially greater contribution of solvent polarizability in comparison with polarity can be established exclusively within the framework of the Koppel-Palm method.

## 2 - Oxyanthraquinone

The equation of Koppel-Palm describes satisfactorily solvent influence on the position of  $\pi_1$ ,  $\pi^*$  bond of 2-oxyanthraquinone:

$$\begin{aligned} \nu_{\max} = & (29.36 \pm 0.14)kK - (2.45 \pm 0.64) \frac{\xi - 1}{2\xi + 2} - (2.7 \pm 1.7) \frac{n^2 - 1}{n^2 + 2} - \\ & - (0.03 \pm 0.01)E - (0.0026 \pm 0.0005)B \quad (1b) \\ n = 13, \quad R = 0.967, \quad SD = 0.20 \text{ kK} \end{aligned}$$

The consideration of the density of energy cohesion is accompanied by an insignificant increase in the correlation coefficient ( $R=0.971$ ) and is statistically not justified. Alternate exclusion of other members of eq. 1b leads to a decrease in the multiple correlation coefficient:

$E$  - up to 0.955,  $f(\xi)$  - up to 0.946,  $B$  - up to 0.934,  $f(n)$  - up to 0.863. Consequently, the largest contribution to solvent influence is made by polarizability, the smallest - by general basicity.

The equation of Kamlet-Taft describes this dependence with a somewhat higher degree of precision:

$$\begin{aligned} \nu_{\max} = & (28.14 \pm 0.06)kK - (0.59 \pm 0.05)\pi^* - (0.11 \pm 0.05)\alpha - \\ & - (1.41 \pm 0.06)B \quad (2b) \end{aligned}$$

$$n = 18, \quad R = 0.980, \quad SD = 0.10 \text{ kK}$$

The largest contribution to the displacement of  $\nu_{\max}$  under the influence of solvents is made by IMB which forms in the place of the hydrogen atom of the oxy-group of 2-oxy-

anthraquinone, it exceeds more than twice the contribution of nonspecific interactions and more than 12 times the contribution of IMB which forms in the place of the hydrogen atom of proton donor solvents.

In neutral solvents which are not capable of IMB formation either proton donor or proton acceptor types a more simple dependence is observed:

$$\nu_{\max} = (28.14 \pm 0.06) kK - (0.64 \pm 0.18) \pi^{\pi} \quad (3b)$$

$$n = 9, \quad R = 0.955, \quad SD = 0.07 \text{ kK}$$

Table 2 illustrates the differences in  $\nu_{\max}$  values calculated according to equations from those obtained experimentally.

The comparison of solvatochromic coefficients obtained for 2-oxy- and 1-methoxyanthraquinones makes it possible to observe how the contribution of various interactions changes when the compound structure is changed. The total contribution of nonspecific interactions (see equations 2a and 2b) when passing over from a 1-methoxy- to 2-oxyderivative drops 0.90 : 0.59 = 1.5 times. At the same time it can be concluded from equations 1a and 1b that the contribution of solvent polarity at this increases 2.45 : 0.73 = 3.3 times. Both methods fix the decrease in the contribution of general basicity (proton donor activity) of solvents although quantitatively this decrease is estimated differently: according to Koppel-Palm it is 0.047 : 0.030 = 1.5 times and 0.49 : 0.11 = 3.4 times according to Kamlet-Taft.

#### 1 - Aminoanthraquinone

Equation 1 for this compound was obtained as follows:

$$\begin{aligned} \nu_{\max} = & (22.85 \pm 0.05) kK - (1.48 \pm 0.16) \frac{\epsilon - 1}{2\epsilon + 2} - \\ & - (2.65 \pm 0.47) \frac{n^2 - 1}{n^2 + 2} - (0.027 \pm 0.05) B - (0.0013 \pm 0.0001) B \quad (1c) \end{aligned}$$

$$n = 17, \quad R = 0.977, \quad SD = 0.09 \text{ kK}$$



Table 2

Comparison of the  $\sqrt{\text{max}}$  values of 2-oxyanthraquinone obtained experimentally and those calculated according to equations 1b ; 2b and 3b

Solvent	max KK			Obtained experimentally	Liter- ature
	Calculated according to equation				
	(1b)	(2b)	(3b)		
Hexane	28.29	28.18	28.19	28.17	15
Heptane	28.26	28.18	28.19	28.09	
Cyclohexane	28.17	28.14	28.14	28.25	15
Carbon tetrachloride	28.05	27.96	27.96	28.01	
p-Xylene	-	27.88	27.86	27.90	
Benzene	27.75	27.78	27.76	27.78	
Toluene	-	27.81	27.76	27.70	
Chlorobenzene	27.41	27.71	27.69	27.70	
Methylene- chloride	-	27.66	27.63	27.62	
Dioxane	27.41	27.29	-	27.40	
Ethyl acetate	27.23	27.18	-	27.40	18
Acetone	-	27.05	-	26.88	17
Dimethyl formamide	26.75	26.64	-	26.67	2
Ethanol	26.65	26.64	-	26.67	2
Methanol	26.69	26.80	-	26.88	2
Butanol	26.48	26.53	-	26.46	15
2-Propanol	26.67	26.43	-	26.38	

The parameter which takes into account the density of cohesion energy appears to be in this case statistically negligible as well since the multiple correlation coefficient does not practically undergo any changes ( $R=0.978$ ). The alternate exclusion of the members of eq.1c from the correlation decreases the multiple correlation coefficient:  $f(n)$ -up to 0.952,  $E$ -up to 0.951,  $f(\xi)$ -up to 0.922,  $B$ -up to 0.905. Consequently, the greatest contribution to solvent influence on the  $\sqrt{\text{max}}$  of 1-aminoanthraquinone is made by basicity, somewhat

less by polarity but the contribution of polarizability and general acidity is small.

The method of Kamlet-Taft gives a somewhat better approximation for 1-aminoanthraquinone:

$$\nu_{\max} = (21.96 \pm 0.06)kK - (0.64 \pm 0.09)\pi^* - (0.17 \pm 0.09)\alpha - (0.68 \pm 0.10)\beta \quad (2c)$$

$$n = 22, \quad R = 0.989, \quad SD = 0.06 \text{ kK}$$

The different values of solvatochromic parameters published in a number of communications do not lead to notably different solvatochromic coefficients. For example, if we applied the values of solvatochromic parameters in references 10, 11, 19 we would get similar results:

$$\nu_{\max} = (22.02 \pm 0.07)kK - 0.71 \pm 0.12 \pi^* - (0.18 \pm 0.12)\alpha - (0.67 \pm 0.13)\beta \quad (2d)$$

$$n = 19, \quad R = 0.988, \quad SD = 0.07 \text{ kK}$$

The comparison of solvatochromic coefficients enables us to draw the conclusion that the greatest contribution to the displacement of  $\nu_{\max}$  is made by nonspecific interactions, somewhat smaller by solvent proton acceptor activity, the contribution of solvent proton donor activity is estimated as the smallest  $0.71 : 0.17 \approx 4$  times.

For 10 neutral solvents a single-parameter dependence was obtained:

$$\nu_{\max} = (22.02 \pm 0.09)kK - (0.75 \pm 0.18)\pi^* \quad (3c)$$

$$n = 0.960, \quad R = 0.08 \text{ kK}$$

Table 3

The comparison of the  $\nu_{\max}$  values of 1-aminoanthraquinone obtained experimentally and those calculated according to equations 1c, 2c and 3c

Solvent	$\nu_{\max}, \text{KK}$			Liter- ature	
	Calculated according to equation		Obtained experi- mentally		
	1c	2c			3c
Hexane	22.00	22.07	22.08	22.03	
Heptane	21.98	22.07	22.08	22.08	2
Cyclohexane	21.90	22.01	22.02	21.88	2
Carbon tetrachloride	21.82	21.81	21.81	21.88	15
p-Xylene	-	21.71	21.70	21.55	15
Toluene	21.65	21.63	21.62	21.60	2
Benzene	21.65	21.59	21.58	21.55	15
Chlorobenzene	21.47	21.50	21.49	21.60	2
Chloroform	21.58	21.48	21.46	21.46	2
Methylene- chloride	-	21.45	21.44	21.50	2
Diethyl ether	21.45	-	-	21.51	
o-Dichlorobenzene	-	21.45	21.43	21.46	2
Dichloroethane	21.41	21.42	21.44	21.44	
Dioxane	21.45	21.37	-	21.37	2
Ethylacetate	-	21.31	-	21.37	2
Acetone	21.27	21.20	-	21.14	
Pyridine	20.83	20.95	-	20.94	
Dimethylformamide	20.99	20.91	-	20.92	15
Methanol	20.95	20.99	-	21.01	2
Ethanol	20.99	20.95	-	20.92	2
Butanol	20.99	20.94	-	20.92	15



As can be concluded from Table 3, for 13 solvents eq.2c gives more close values to the experimental ones than eq. 1c.

The change of structure when passing over from 2-oxy- to 1-aminoanthraquinone leads to the following changes in the interaction with solvents. The role of nonspecific interactions in general and solvent polarizability in particular do not change at this (the values of solvatochromic coefficients  $S$  in equations 2b and 2c as well as coefficients  $P$  in equations 1b and 1c are close) but the contribution of solvent polarity decreases  $2.45 : 1.48 \approx 1.5$  times. Both methods estimate the contribution of specific interactions similarly: the role of solvent proton donor activity (general acidity) increases slightly (0.027 and 0.03 according to Koppel-Palm, 0.11 and 0.18 according to Kamlet-Taft) but the role of solvent proton acceptor activity (general basicity) drops twice (from 0.0026 to 0.0013 according to Koppel-Palm and from 1.41 to 0.68 according to Kamlet-Taft).

Thus, the methods of Koppel-Palm and Kamlet-Taft can be used to characterize quantitatively solvent influence on the position of  $\pi^*1, \pi^*$  absorption bonds of anthraquinone derivatives. Both methods give evidence that any kind of interaction of the studied anthraquinone derivatives with solvents favors the bathochromic displacement of this bond. Both methods give a close qualitative and quantitative estimation as to the contributions of specific interactions with solvents and give complementary information about the role of nonspecific interactions. An advantage of the Koppel-Palm method is the possibility to differentiate between the contributions of solvent polarity and polarizability. The method of Kamlet-Taft can be applied to the longwave absorption peaks of anthraquinone substitutes and generally it gives somewhat more precise results. Both methods make it possible to calculate the  $\nu_{\max}$  values of the studied compounds in a large number of solvents.

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PHOTOELECTRON SPECTRA OF MOLECULES.

5. HALIDES

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The simplified method for the identification of the lone electron pair bands in the PES of halogensubstituted compounds has been suggested. The degeneration of the orbitals was taken into account while determining the weighted average IP-s of halide lone pairs. These IP do not depend on the halogen-halogen interactions and exercise the influence of the neighboring atoms and bonds in the molecule only.

The averaged IP could be linearly correlated with the bond energies of the inner shell electrons and with the shifts of the O-H stretching frequencies of phenol due to the hydrogen bond complex formation of the latter with halogen substituted molecules in  $\text{CCl}_4$  solution.

In the framework of the method of comparison the excellent linear inter-family relationships was established between the valence shell IP-s of compounds with the different (fixed) halogen atoms.

Alongside with the quantum chemical calculations various simplified empirical methods<sup>1</sup> have also been widely used for the interpretation of PES. As a rule, these schemes make use of the Koopmans' theorem.<sup>2</sup> It is assumed that the experimental spectral bands can be connected to the definite orbitals; the changes in the location, order and the shape of the bands with the molecular structure

are accounted for by the intramolecular orbital-orbital interactions and by the changes in the charge distribution in the molecule. The latter is usually characterized either by the formal atomic (Mulliken) charges, by the electronegativity of the substituent, Taft's (polar) substituent constants or by the other empirical parameters.

The concept about the orbitals (or the groups of orbitals) localized on the separate atoms or groups seems also rather useful. According to this scheme the influence of substituents could be visualized by the interaction of the localized orbitals. It is, e.g., assumed that the interaction of two localized orbitals of the close energy and of the same symmetry leads to the splitting of the PES lines. The energy spectrum of the orbitals and their symmetry is determined by the geometry of the molecule. As far as the initial AO-s are occupied the bonding as well as antibonding MO-s also will be occupied and this allows to characterize the overall effect also as nonbonding.

The orbital splitting can originate from the spin-orbital interaction<sup>\*</sup>, from interactions through the space and/or the bonds or due to the symmetry reasons<sup>3</sup>.

The interaction of orbitals is a rather general phenomenon and is not characteristic to a certain specific type of orbitals.

Throughout the present communication these simple model considerations will be used for the identification of IP-s, of halogen lone pairs from the PES of various halogen-containing molecules. It was shown<sup>4</sup> from the PES of methylhalides that the spin-orbital splitting amounts to 0.08 eV

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\* Spin-orbital interaction leads to the formation of several electronic states of the ions which result from the elimination of the electron from one MO. For example, two configurations  $2 \uparrow \pi_{3/2}$  and  $2 \uparrow \pi_{1/2}$  correspond in the PES to the abstraction of the electron from the HOMO of the halide molecules Hal<sub>2</sub>.

for chlorine, to 0.32 eV for bromine, and already to 0.63 eV for iodine. Its value changes somewhat with the structure of the compound. Sometimes, the PE spectrometers of the moderate resolution are not able to detect any splitting.

The analysis of this particular situation has been made in several papers for halogen hydrides<sup>5</sup> and for the alkyl halides<sup>6,7</sup>. In such a cases PES has only one line for the single halogen atom despite the fact that it has two electron pairs.

In the general case, the "through space" and "through bond" interactions of the halogen lone pairs lead to the appearance of some additional spectral lines which are frequently degenerated.

The interaction of halogen atoms with two pairs of non-bonding orbitals and of the same symmetry should result in four MO-s of the different energy.

As a rule, while assigning the PES such an analysis is frequently performed. Nevertheless, this approach is rather seldom used for the determination of the averaged and weighted IP-s. As one from the few examples, the given procedure was used<sup>8</sup> for the interhalide compounds.

In the present work in the case of the splitting of the spectral lines the weighted average of the corresponding orbitals was considered as the IP of the given halogen. Simultaneously, the degeneracy of the orbitals is also taken into account while calculating these IP-s.

The present procedure accounts for the interactions between the orbitals of the halide lone pairs only.

While calculating the weighted averaged IP we, as a rule, used the data from Refs. 9 and 10 which list PES of the rather large number of compounds with the simultaneous assignment of the symmetry type and the level of degeneracy of the MO-s. For example, the first three bands in the PES of  $\text{CCl}_4$  are assigned to the halide lone pairs as follows (IP-s are given in eV units)<sup>9</sup>:  $t_1$  (11.69),  $t_2$  (12.44-12.65-12.78),  $e$  (13.37). The weighted and averaged IP of the lone pairs is in this case calculated as  $1/8 (3 \times 11.69 + 12.44 + 12.65 + 12.78 + 2 \times 13.37) = 12.46$  eV.



It should be mentioned that only in the case of interhalide molecules from two identical atoms such a procedure seems to be strict enough. It follows from the fact that only in the latter specific case the splitting of the orbitals is symmetrical relative to the energy of AO-s. The determination of the averaged IP for the diatomic interhalides consisting of two different elements is, often, rather complicated.

As a rule, the weighted and averaged IP values used in the present work (see Table 1) are calculated according to the interpretation of PES given in the original reference. In the case of alkyl halides and halogen hydrides it simply reduces to the correction for the spin-orbital interactions.

The interpretation of the derivatives of methane containing several halide substituents is also traditional and the calculation of the averaged IP-s could be performed in a rather unambiguous way<sup>\*</sup>.

The compilation of the averaged and weighted IP-s suggested and used throughout this paper is given in Table 1.

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
<sup>\*</sup> There are some problems in the case of  $CF_3I$  molecule. So, in the Ref. 8 the value of the averaged IP for the iodine lone pair was suggested as 11.09 eV whereas our calculations based on the assignment of the PES of this compound from the other literature source<sup>14</sup> lead to the somewhat lower (10.62 eV) value as an average from the excitation energies  $^2E_{3/2}$  and  $^2E_{1/2}$  of this species.

Table 1

The Averaged and Weighted IP-s of the Halogen Lone  
Pairs Corrected for the Orbital-Orbital and Spin-Orbital  
Interactions .  
A. Chlorides

No. Compound IP( $n_{Cl}$ )			No. Compound IP( $n_{Cl}$ )		
1	2	3	1	2	3
1.	Cl	13.07	28.	$Cl_2C=CCl_2$	12.34
2.	HCl	12.79	29.	$H_2C=CHCH_2Cl$	11.23
3.	MeCl	11.33	30.	$ClCH=CHCH_2Cl$	11.5
4.	BtCl	11.01	31.	$F_2C=CFCl$	12.97
5.	PrCl	10.88	32.	$HC=CCH_2Cl$	11.63
6.	BuCl	10.84	33.	$C_6H_5Cl$	11.51
7.	i-PrCl	10.78	34.	$C_6H_5CH_2Cl$	10.90
8.	i-BuCl	10.66	35.	p-MeC <sub>6</sub> H <sub>4</sub> Cl	11.2
9.	t-BuCl	10.61	36.	p-ClC <sub>6</sub> H <sub>4</sub> CHO	11.6
10.	Cy-C <sub>6</sub> H <sub>11</sub> Cl	10.67	37.	HOC1	12.09
11.	$CH_2Cl_2$	11.81	38.	$CCl_3CH_2OH$	12.5
12.	$CHCl_3$	12.19	39.	$CCl_3CMe_2OH$	12.41
13.	$CCl_4$	12.46	40.	$ClCH_2CH_2OH$	11.58
14.	$CH_2FC1$	11.90	41.	$Cl_2CO$	12.66
15.	$CHFCl_2$	12.45	42.	MeCOC1	12.00
16.	$CHF_2Cl$	12.6	43.	$ClCH_2CHO$	11.75
17.	$CF_3Cl$	13.00	44.	$CCl_3CHO$	12.42
18.	$CF_2Cl_2$	12.90	45.	$ClCH_2COCl$	11.81
19.	$CFCl_3$	12.65	46.	$CF_3COCCl_3$	12.70
20.	$ClCH_2CH_2Cl$	11.5	47.	$ClCH_2COOH$	11.5
21.	$CH_3CHCl_2$	11.58	48.	$ClCH_2\text{---}\overline{O}$	11.28
22.	$ClCF_2Cl$	12.89	49.	$ClCH_2CN$	12.05
23.	$BrCH_2CH_2Cl$	11.46	50.	$Cl_2CHCN$	12.40
24.	$H_2C=CHCl$	11.61	51.	$ClCH_2CH_2CN$	11.6
25.	$H_2C=CCl_2$	12.02	52.	$ClCH_2SCN$	11.77
26.	$ClCH=CHCl$	12.04	53.	$ClSCN$	13.05
27.	$ClCH=CCl_2$	12.21	54.	$ClNO$	11.5

continuation of Table 1


1	2	3	1	2	3
55.	$\text{ClNH}_2$	11.95	73.	$\text{Me}_3\text{SiCH}_2\text{Cl}$	11.0
56.	$\text{ClNHMe}$	11.47	74.	$\text{Me}_3\text{SiC}\equiv\text{CCl}$	13.6
57.	$\text{ClNMe}_2$	11.19	75.	$\text{GeH}_3\text{Cl}$	11.30
58.	$\text{SCl}_2$	12.46	76.	$\text{Me}_2\text{GeCl}_2$	10.93
59.	$\text{PCl}_3$	12.60	77.	$\text{SiCl}_4$	12.82
60.	$\text{S}_2\text{Cl}_2$	11.42	78.	$\text{GeCl}_4$	12.57
61.	$\text{PSCl}_3$	12.31	79.	$\text{SnCl}_4$	12.39
62.	$\text{BF}_2\text{Cl}$	12.8	80.	$\text{TiCl}_4$	12.06
63.	$1\text{-ClB}_5\text{H}_8$	10.03	81.	$\text{VCl}_4$	12.01
64.	$2\text{-ClB}_5\text{H}_8$	10.24	82.	$\text{Mn}(\text{CO})_5\text{Cl}$	8.94
65.	$\text{Cl}_2\text{SO}$	11.93	83.	$\text{Cr}(\text{CO})_5(4\text{-ClP}_y)$	12.18
66.	$\text{Cl}_2\text{SO}_2$	12.8	84.	$\text{MeHgCl}$	10.88
67.		11.24	85.	$\text{CaCl}$	8.54
68.	$\text{ClP}$	12.81	86.	$\text{KCl}$	8.7
69.	$\text{Cl}_2$	13.00	87.	$\text{InCl}$	9.75
70.	$\text{SiH}_3\text{Cl}$	11.65	88.	$\text{TlCl}$	10.14
71.	$\text{Me}_3\text{SiCl}$	10.58	89.	$\text{AgCl}$	10.11
72.	$\text{SiP}_3\text{Cl}$	13.44			

B. Bromides.

1.	Br	12.07	17.	$\text{ClCH}_2\text{CH}_2\text{Br}$	10.80
2.	HBr	11.83	18.	$\text{H}_2\text{C}=\text{CHBr}$	10.87
3.	MeBr	10.69	19.	$\text{F}_2\text{C}=\text{CFBr}$	11.94
4.	EtBr	10.44	20.	$\text{H}_2\text{C}=\text{CHCH}_2\text{Br}$	10.65
5.	PrBr	10.34	21.	$\text{C}_6\text{H}_5\text{Br}$	10.90
6.	BuBr	10.30	22.	$\text{C}_6\text{H}_5\text{CH}_2\text{Br}$	10.36
7.	i-PrBr	10.23	23.	p-MeC <sub>6</sub> H <sub>4</sub> Br	10.6
8.	i-BuBr	10.25	24.	$\text{BrCH}_2\text{CH}_2\text{OH}$	10.77
9.	t-BuBr	10.10	25.	$\text{MeCOBr}$	11.1
10.	t-BuCH <sub>2</sub> Br	10.19	26.	$\text{BrCH}_2\text{COOH}$	10.8
11.	Cy-C <sub>6</sub> H <sub>11</sub> Br	10.10	27.	$\text{BrCH}_2\text{C}\begin{smallmatrix} \diagup \\ \diagdown \end{smallmatrix}$	10.70
12.	$\text{CH}_2\text{Br}_2$	11.0	28.	$\text{BrSCN}$	12.14
13.	$\text{CHBr}_3$	10.89	29.	$\text{BrNO}$	10.9
14.	$\text{CBr}_4$	11.26	30.	$\text{BrNH}_2$	11.27
15.	$\text{CF}_3\text{Br}$	12.0	31.	$\text{BrNHMe}$	10.92
16.	$\text{BrCH}_2\text{CH}_2\text{Br}$	10.81	32.	$\text{BrNMe}_2$	10.56



continuation of Table I

1	2	3	1	2	3
33.	PF <sub>2</sub> Br	11.19	43.	Me <sub>3</sub> SiC≡CBr	12.6
34.	BF <sub>2</sub> Br	11.95	44.	GeH <sub>3</sub> Br	10.72
35.	1-BrB <sub>5</sub> H <sub>8</sub>	9.71	45.	Mn(CO) <sub>5</sub> Br	8.86
36.	2-BrB <sub>5</sub> H <sub>8</sub>	10.04	46.	Cr(CO) <sub>5</sub> (4-BrPy)	11.42
37.	 Te Br	10.7	47.	MeHgBr	10.30
38.	BrF	11.78	48.	CsBr	8.26
39.	Br <sub>2</sub>	11.83	49.	KBr	8.35
40.	SiH <sub>3</sub> Br	10.95	50.	InBr	9.41
41.	Me <sub>3</sub> SiBr	10.24	51.	TeBr	9.83
42.	SiF <sub>3</sub> Br	12.46	52.	AgBr	9.72

C. Iodides

1.	I	10.92	18.	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> I	9.63
2.	HI	10.71	19.	ICH <sub>2</sub> CH <sub>2</sub> OH	9.90
3.	MeI	9.85	20.	ICH <sub>2</sub> CH <sub>2</sub> OMe	9.72
4.	EtI	9.65	21.	ICH <sub>2</sub> COOH	10.0
5.	PrI	9.56	22.	ICN	11.18
6.	BuI	9.5	23.	SiH <sub>3</sub> I	10.06
7.	i-PrI	9.44	24.	GeH <sub>3</sub> I	9.84
8.	i-BuI	9.46	25.	PF <sub>2</sub> I	10.3
9.	t-BuI	9.4	26.	PI	10.5
10.	CH <sub>2</sub> I <sub>2</sub>	10.0	27.	Mn(CO) <sub>5</sub> I	8.59
11.	CF <sub>3</sub> I	10.62	28.	MeHgI	9.47
12.	CF <sub>3</sub> CH <sub>2</sub> I	10.25	29.	1-IB <sub>5</sub> H <sub>8</sub>	9.06
13.	ICH <sub>2</sub> CH <sub>2</sub> I	9.85	30.	2-IB <sub>5</sub> H <sub>8</sub>	9.30
14.	ICF <sub>2</sub> CF <sub>2</sub> I	10.59	31.	CsI	8.07
15.	H <sub>2</sub> C=CHI	10.10	32.	KI	7.9
16.	H <sub>2</sub> C=CHCH <sub>2</sub> I	9.80	33.	AgI	9.03
17.	C <sub>6</sub> H <sub>5</sub> I	10.05			

D. Fluorides

1.	F	17.45	5.	CH <sub>2</sub> F <sub>2</sub>	14.54
2.	HF	16.03	6.	CHF <sub>3</sub>	16.33
3.	MeF	13.1	7.	CF <sub>3</sub> Cl	17.35
4.	EtF	12.43	8.	CF <sub>3</sub> Br	17.24

continuation of Table 1

1	2	3	1	2	3
9.	$\text{SiF}_4$	17.27	13.	$\text{C}_6\text{H}_5\text{F}$	13.92
10.	$\text{GeF}_4$	16.49	14.	$\text{CF}_4$	17.26
11.	$\text{BF}_3$	16.98	15.	$\text{F}_2$	17.91
12.	$\text{CCl}_2\text{F}_2$	16.95			

Earlier<sup>11</sup> the existence of the excellent linearity between the  $\text{IP}(n_X)$  of the lone pairs of the electrons of the valence shell and the core level ionization energies  $E_B$  of ls electrons was demonstrated. The slopes of the corresponding straight lines for different classes of compounds were within their error limits indistinguishable from unity which evidences about the equal sensitivity of the IP-s of valence and inner shell electrons towards the substituent effects. On the example of the halogen-containing compounds one can see that the analogous linear relationships of the type

$$\text{IP}(n_X) = a + b E_B(x_X) \quad , \quad (1)$$

where a and b are constants and x denotes the energy level of the inner shell electrons (as different from Is ) of the halide atom X hold also for some higher level inner electron shells (ns, np, nd, where  $n > 1$  ).

Using the weighted average (with the degeneracy correction) IP values from Table 1 one can come to the rather satisfactory linear dependences of these quantities on the corresponding ionization energies of  $2p_{3/2}$  (Fig.1) and 2s (Fig.2) electrons of the chlorine atom. There are less data on the energies of the bromine  $3d_{5/2}$  electrons and the corresponding linearities in terms of Eqn.1 are statistically not so well determined.

The results of the regression analysis of the data by means of the least squares treatment in terms of this approach are given in Table 2.

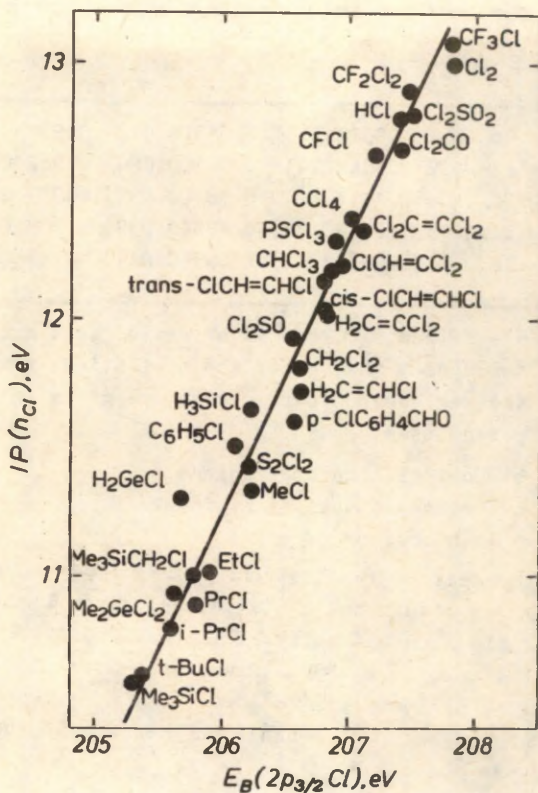


Fig. 1. The dependence of  $IP(n_{\text{Cl}})$  of the chlorine valence shell electrons on the corresponding  $E_B(2p_{3/2})$  energies of the same atom.



Table 2  
The Results of the Regression Analysis in Terms  
of Eqn. 1.<sup>a</sup>

No	The class of com- pounds	ESCA level	-a	b	r <sup>b</sup>	s <sup>c</sup>	n <sup>d</sup>
1.	XCl	2p <sub>3/2</sub>	205.83(4.81)	1.053(0.023)	0.993	0.11	30
2.	Xcl	2s	272.57(22.41)	1.024(0.080)	0.962	0.14	15
3.	XBr	3d <sub>5/2</sub>	64.49(6.82)	0.987(0.089)	0.973	0.24	9
4.	XI	3d <sub>5/2</sub>	537.24(20.36)	0.873(0.032)	0.993	0.08	12
5.	IF	1s	1132.81(33.14)	1.655(0.047)	0.991	0.22	26

Footnotes: a - IP and  $E_p^{13}$  are in eV units, here and throughout this paper the statistical error of the regression coefficients are given in the parentheses.

b - correlation coefficient

c - standard deviation, in eV

d - the number of points

As in the case of 1s electrons<sup>11</sup> the slopes of these linearities are within their statistical error limits indistinguishable from the unity. This result differs somewhat from the results of Ref. 12 where the correlation of 3d<sub>5/2</sub> energies of the alkyl iodides (HI was excluded) with their valence shell 5p<sub>1/2</sub> ionization energies is characterized by the slope b = 1.22.

Unfortunately, there is a relatively limited number of halogen substituted molecules with the fully and reliably interpreted PES. In the present study data for such a molecules were taken for the basis of the determination of the slope of the linear relationship in terms of Eqn. 1. The regularities obtained this way can be used for the assignment of the PES bands of the more complex halogen substituted compounds, especially with the several competitive ionization centers.

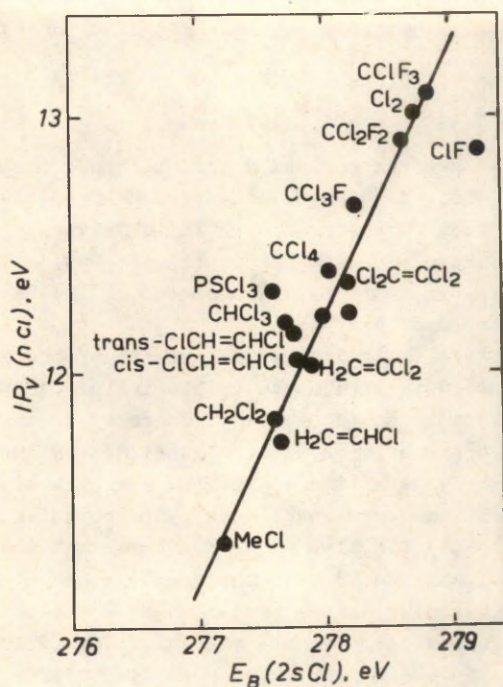


Fig. 2. The dependence of  $IP(n_{Cl})$  of the chlorine valence shell electrons on the corresponding 2s ionization energies of the same atom.

It is interesting to notify that even the data for some halide carbonyls of transition metals (e.g.,  $\text{Mn}(\text{CO})_5\text{Hal}$ ) which due the huge variation of the corresponding quantities are not shown on Figs. 1 and 2 fit the above mentioned linearities. On the other hand, diatomic interhalide compounds ( $\text{ClF}$ ,  $\text{ICl}$ , etc.) deviate noticeably from the major relation-

ship probably due to the fact that in this case it is hard to determine the correct IP-s of the lone electron pairs. The compounds of the general formula  $XCl_4$ , where  $X = Si, Ge, Sn, Ti, V$  also deviate from the relationship given in Table 2 (see also Fig. 1) and obey the more specific Eqn. 2:

$$IP(n_{Cl}) = 0.776(0.015)E_B(2p_{3/2}Cl) - 147.85(3.13) \quad (2)$$

$$r = 0.999, \quad s = 0.01 \text{ eV}, \quad n = 5.$$

As for as several germanium and silicon compounds ( $Me_3SiCl$ ,  $H_3SiCl$ ,  $Me_3SiCH_2Cl$ ,  $H_3GeCl$ , and  $Me_2GeCl_2$ ) fit Eqn. 1 from Table 2 the reason of the existence of the separate relationship (2) seems to be hard to explain reasonably. Unfortunately, the data on the energies of the 2s electrons for these compounds are absent.

On the basis of the relationships from Table 2 one can draw some conclusions relative to the influence of the structural factors on the ionization center in the halide substituted compounds. So it seems that the influence of substituent effects on the ionization energies of the valence, interim and core level ionization potentials is practically the same. One also might conclude that the presence of the additional electron shells in the atoms of the halides of higher periods does not change the mechanism of the substituent effects in the molecule. Therefore, one can expect that the mechanism of the substituent effects is basically the same for the different halide atoms as ionization centers. It seems even more so because the lone electron pair is rather definitely (with the exception of fluorine, vide infra) localized on the halogen atom.

On the basis of the abovesaid one might expect the existence of another type of linear relationships as expressed by Eqn. 3:

$$IP(n_X) = a' + b' IP(n_Y) \quad (3)$$

where  $a'$  and  $b'$  are constants and  $X$  and  $Y$  refer to the two different halide atoms as ionization centers.



Indeed, the statistical analysis of the data for a very wide range of substituents (alkyls, electronegative, aromatic, etc.) and even for the metalloorganic compounds shows that Eqn.(3) holds rather well. Table 3 lists the results of the statistical treatment of the corresponding data in terms of that equation.

Table 3  
The Results of the Regression Analysis in Terms  
of Eqn. 3<sup>a</sup>

No	X	Y	-a'	b'	r	s	n
1.	Cl	Br	1.821(0.179)	1.229(0.016)	0.996	0.11	49
2. <sup>b</sup>	Cl	Br	1.941(0.116)	1.238(0.010)	0.999	0.05	39
3.	Br	I	2.329(0.292)	1.323(0.030)	0.993	0.11	30
4. <sup>c</sup>	Br	I	1.312(0.156)	1.219(0.016)	0.998	0.05	23

a - See Footnotes to Table 2

b - The following compounds were excluded:

$\text{Me}_3\text{SiX}$ ,  $2\text{-XB}_5\text{H}_8$ ,  $\text{KX}$ ,  $\text{CsX}$ ,  $\text{PhCH}_2\text{X}$ ,  $\text{HOCH}_2\text{CH}_2\text{X}$ ,  $\text{H}_3\text{SiX}$ ,  
 $\text{MeCOX}$ ,  $\text{Me}_2\text{NX}$ ,  $\text{F}_2\text{C=CFX}$

c - The following compounds were excluded:

$\text{CF}_3\text{X}$ ,  $\text{FX}$ ,  $\text{Mn(CO)}_5\text{X}$ ,  $\text{InX}$ ,  $\text{CsX}$ ,  $\text{H}_2\text{C=CHX}$ ,  $\text{TiX}$ .

At the range of variation of IP-s for chlorides by 5eV, for bromides by 4 eV, and for iodides by 2.5 eV the standard deviations of the correlations are comparable to the generally accepted experimental uncertainties of determination of the vertical IP-s from PES. The data from Table 3 is visualized on Figs. 3 and 4 where the averaged and weighted IP-s are compared for chlorides and bromides and for bromides and iodides, respectively.<sup>x</sup>

<sup>x</sup> Note that for the sake of simplicity not all the points listed in Table 1 are not shown in Figs. 3 and 4. The IP values for the halogen atoms (shown as  $\text{X}_{\text{atom}}$  on Figs. 3 and 4) are determined taking into account the spin-orbital splitting in the PES<sup>15</sup>.

It is interesting to notify that all metalloorganic complexes and salts of monovalent metals with the known PES also fit Eqn. 3 satisfactorily. The compounds where halide atom is immediately attached to the silicon or germanium atom ( $H_3SiHal$ ,  $H_3GeHal$ ,  $F_3SiHal$ ) or contain the substituent with the  $\pi$ -electron system ( $Ph$ ,  $PhCH_2$ ,  $HC\equiv CCH_2$ , or  $CH_2=CHCH_2$ ) also do not deviate from the Eqn. 3.1 or 3.3 (see Table 3). The same is equally true for the compounds which have several lone pair atoms with not easily interpretable PES.  $HalNO^{16}$ ,  $MeCOHal^{10}$ ,  $HalCH_2COOH^{18}$ ,  $HalCH_2CH_2COOH^{17}$ ,  $HalNMe_2$ , and  $HalNH_2^{20}$  can serve as examples for this group of compounds. For the free radical  $PF_2$  inconsistent result emerge for  $Hal=Cl$ . So, in Ref. 22  $IP(n_{Cl})$  is identified as the second band (12.8 eV) in PES. Nevertheless, Eqn. 3.1 from Table 3 lead to another value of 11.9 eV. The discrepancy emerges probably from the significant mixing of  $n_{Cl}$  and P-P bands which is not taken into account in the present scheme. Rather complicated situation is characteristic for the assignment of halide lone pairs in PES of compounds  $HalSCN$ .<sup>23</sup> On the basis of Eqn. 3.1 one has to identify for  $ClSCN$   $IP(n_{Cl})=13.05$  eV whereas the band at 13.28 eV probably arises due to the vibrational excitation (the same idea is given in Ref. 23). Ab initio calculations on STO-3G basis support<sup>23</sup> the assignment of  $7a'$  (12.39) and  $2a''$  (12.65) bands in PES of  $BrSCN$  to the components of splitting of the bromine band. However, the doublet 11.89 and 12.39 eV which leads to the weighted and averaged value  $IP(n_{Br})$  as 12.14 eV better agrees with the Eqn. 3. The latter interpretation also corresponds better to the "sum rule."<sup>24</sup>

The interpretation<sup>25</sup> of PES of  $Me_3SiC\equiv CHal$  for  $Hal=Cl$  or  $Br$  agrees with ours but in the case of iodine those authors suggest  $IP(n_I)=11.8$  eV which corresponds to the 3rd band in PES and does not fit Eqn. 3. The value suggested by us (11.0 eV) probably refers to the vertical IP of the second band which belongs to e symmetry type (Ref. 25 lists only  $IP_g=10.4$  for this band).

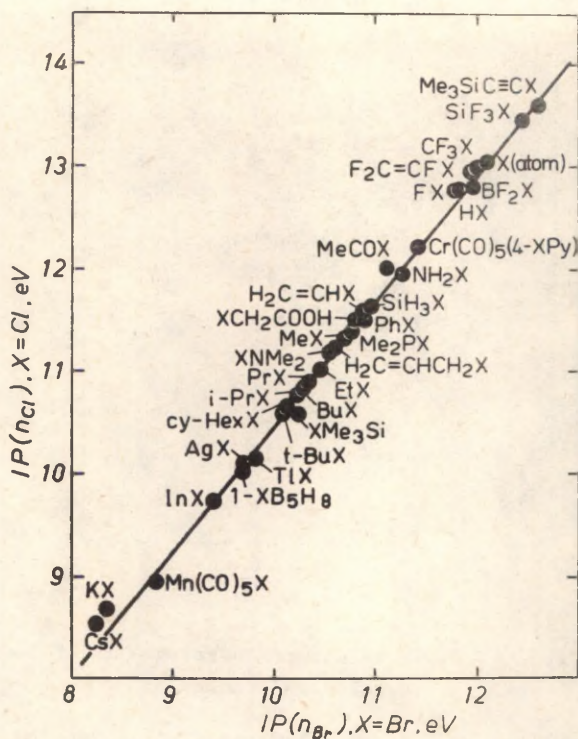


Fig. 3. The linear relationship between IP of lone pairs of chlorine and bromine



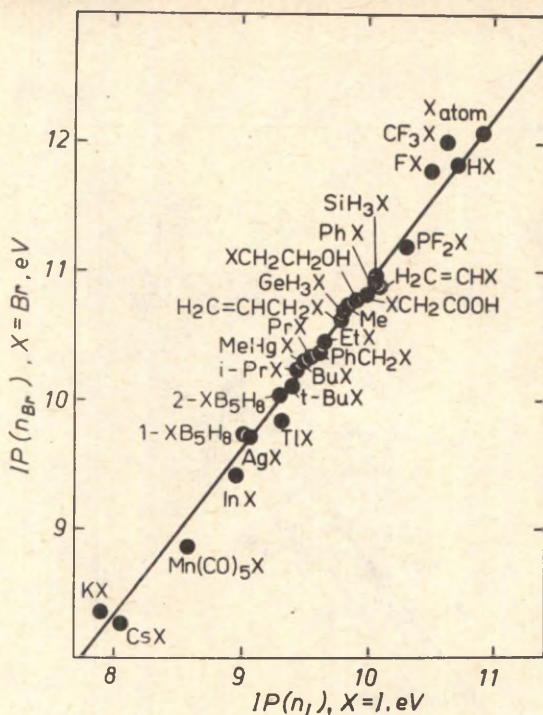


Fig. 4. The linear relationship between IP of lone pairs of bromine and iodine.

If the halide atom is attached immediately to the  $\pi$ -system of the triple bond when according to the MO-approach one cannot expect the appearance in the PES bands corresponding to the halide lone pairs.<sup>26</sup>  $\text{HC}\equiv\text{CHal}$ ,  $\text{HalC}\equiv\text{CHal}$  and  $\text{HalCN}$  are the typical representatives<sup>9</sup> of this group of compounds. In some sense the interhalide compounds can be included to this group. In these cases, on symmetry reasons, the halide lone pairs get mixed with the orbitals of the  $\pi$ -system and only one electron pair on the sp hybrid orbital of the axial symmetry can be considered localized on the halide atom. The analysis of PES of such a com-

pounds was published.<sup>26-28</sup> The calculations<sup>29</sup> with the approximate Hartree-Fock wave functions evidence about the anomalous strength of bonds adjacent to the triple bond. The significant transfer of  $\pi$ -electrons of the latter to the neighboring bond is believed to take place whereas the charge distribution in the region of the triple bond itself does not depend significantly on the variation of substituent. It seems that in these compounds the delocalization of orbitals (p- $\pi$  mixing) is so pronounced that the use of the concept of localized orbitals is unjustified. As a consequence of that it also seems impossible to identify the bands of the lone pairs in these systems.

On the other hand, in PES of compounds where halogen atom is attached to the  $\pi$ -system of double bonds (alkenes) or to the aromatic ring (halide substituted benzenes) there appear bands which IP-s obey Eqn.3. The probable explanation of this seems to be that halogen atoms in these systems still have in their disposal the lone pairs which due to the symmetry reasons are not able to interact with the adjacent  $\pi$ -electron system<sup>x</sup>.

The linearities from Table 3 can be (with a certain probability) used for the further determination of the averaged IP-s of the other halide atoms if one has in his disposal the information on the IP of the reference compound with the similar structure. As a matter of fact these regularities alone do not allow to identify the PES. However, taking into account their huge range and relatively satisfactory statistical characteristics they might occur useful for the check of the various possible interpretations of the PES of halide containing molecules. Of course, there are situations which cannot be resolved by the use of the method comparison. One of such examples is characteristic to the PES of halogen substituted adamantanes. So, for their 1-Cl and -Br deriva-

<sup>x</sup> The conjugated n-orbital of the halide atom gives in PES of these compounds the band with the rather evident vibrational structure. The fact that the same is not true for the nonconjugated n-orbital could be used for its identification.



tives Worley<sup>30</sup> suggests  $IP(n_{Cl})=11.0$  eV and  $IP(n_{Br})=10.45$  eV, respectively. These quantities do fit Eqn.3.1 from Table 3, but the same is also true for the corresponding 1st IP-s of these compounds (9.89 eV and 9.68 eV). It seems that the correct interpretation of PES is in this case complicated because not all the spectral bands for these compounds are determined.

The ionization of the fluorine lone pairs is reflected in PES of its derivatives by the wide bands in the spectral region which usually corresponds to the ionization of the electrons of chemical bonds. Mainly because of that reason the assignment of these lines is performed seldom whereas the interpretations by various authors are at variance with each other.

So, from one hand, on the grounds of the certain similarity of the electronic structure of fluorine to the other halides one might expect that the above-described procedure of determining of the averaged and weighted IP-s would be applicable also for the case of the derivatives of this element. On his basis by the analogy with Cl, Br and I the observance of the linearity (1) should be expected for the fluorides. The check of this hypothesis is complicated by the fact that there is only a relatively limited number of fluorine compounds with the fully and reliably identified PES bands which, in its turn, should result in the low reliability of the determination of the slope of the linearity (1). The problems arise even with alkyl fluorides. Assuming the observance of Eqn.(1) for these compounds one has to assume against the most widespread concept<sup>10</sup> (the energy of the  $n_F$  band is usually identified in the region of 17 eV) that the 1st PES bands in MeF and EtF belong to the ionization of fluorine atom. The latter is equivalent to the assumption that in the alkyl fluorides C-H and C-F bands are being ionized at higher energies than fluorine lone pairs.\*

\* This postulate was used in Ref.31 for the analysis of PES of fluoroform. The "usual" order of ionization fluorine lone pairs and CH and CF bands was assumed e.g. in Ref. 32.



In its turn, even according to this scheme C-Cl and C-Br bands ionize easier than fluorine atom.

Using this "unconventional" approach one really comes up to the satisfactory linear relationship between  $IP(n_p)$  values and  $1s$  energies of the fluorine atom. At the same time the facts that the slope of this relationship differs significantly from unity (see Table 2) and the serious deviations of the points for  $F_2$  and  $CF_4$  molecules (with the reliably identified PES) from the relationship 1.4 towards the decreasing of the slope of the straight line closer to its unity value call for the serious precautions. However, as one can see from Table 2 and Fig. 5 the clear majority of points at least formally fits the relationship (1). \*

According to the above described ("unconventional") approach it is reasonable to check the observance of the corresponding data for the F-compounds to the Eqn.3 (see also Table 3). It turns out that this interpretation of PES of these compounds indeed leads to the linear dependence of the  $IP(n_p)$  on  $IP(n_{Cl})$  values for a rather wide range of compounds.

The fluorine and chlorine atoms <sup>15</sup> fit the correlation while  $H_3GeF$ ,  $H_3SiF$  and  $SiF_4$  deviate significantly from that relationship.

According to the alternative and the most wide-spread "traditional" approach the behavior of fluorides is considered exceptional amongst the other halogen derivatives assuming simultaneously the impossibility to identify in PES of fluorides the bands which correspond to the lone pairs of fluorine.

It is evident, that in terms of this approach neither Eqn.(1) nor Eqn.(3) should lead to any reasonable linear correlation between  $IP$ -s of fluorine and other halides.

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\* The reported <sup>9</sup> interpretation of PES of  $NF_3$  and  $PF_3$  leads to somewhat increased values of the averaged  $IP(n_p)$  (17.33 eV and 17.0 eV, respectively).

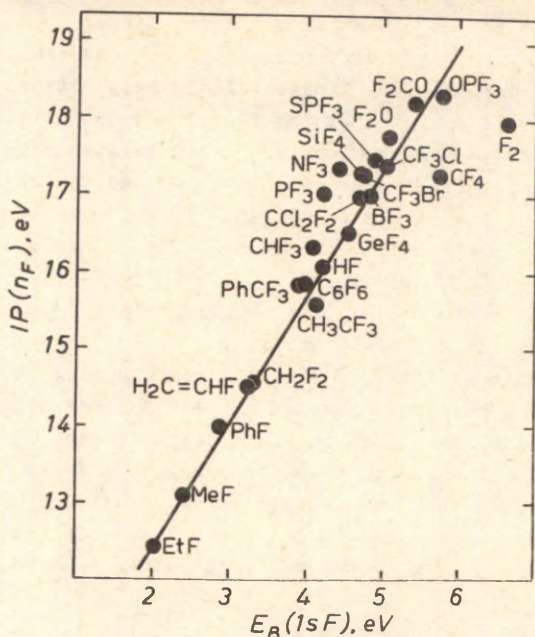


Fig. 5. The dependence of  $IP(n_F)$  of the fluorine valence shell lone pairs on the energy of its  $1s$  electrons.

The line shapes of fluorine bands in PES and the results of the quantum chemical calculations evidence mostly in favor of the latter ("traditional") approach.

It seems that due to the rather scarce data on the fluorine  $1s$  electron energies as well as because of the limited number of PES of fluorides with the fully interpreted and assigned bands the decision making between these two alternative approaches should be postponed at least at the present time.

For the check of the assignment of  $IP(n_X)$  of the lone pairs in the PES the empirical relationship (4)

$$IP(n_X) = a'' + b'' \Delta \nu_{PhOH} \quad (4)$$

where  $a''$  and  $b''$  are constants

between the IP of lone electron pair of the base and the complex formation shifts induced by the latter on of the stretching frequencies of the phenol OH-band in  $\text{CCl}_4$  solution. The relationship (4) was earlier used for the correlation of data for alcohols<sup>33</sup>, ethers<sup>34</sup> and nitriles.<sup>35</sup>

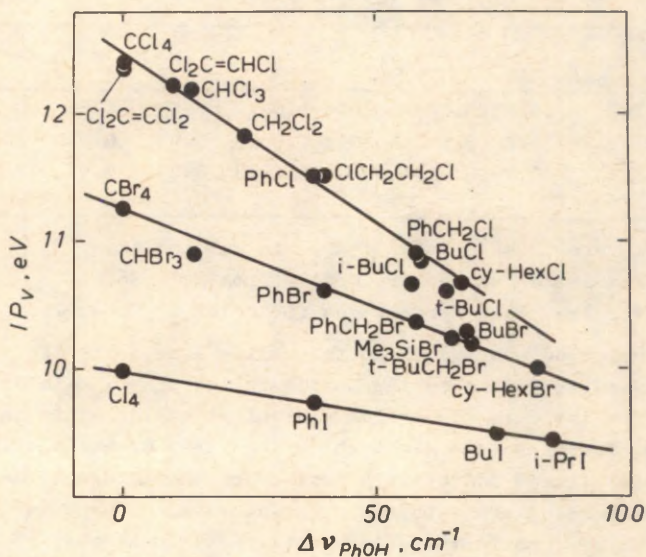


Fig. 6. The dependence of the averaged IP of the halide lone pair on the complex formation shifts of the stretching frequencies of phenols OH-group  $\Delta \nu_{\text{PhOH}}$  in  $\text{CCl}_4$  solution.

It should be mentioned that the absolute values of the phenol OH frequency shifts induced by the halide containing bases are relatively small and their uncertainty is rather high. Despite these complications the statistical least squares analysis reveals the presence of the fully definite correlation in terms of Eqn.(4) for chlorides, bromides and



iodides. The results of the regression analysis are given in Table 4 and visualised in Fig. 6. It is evident that the sensitivity of the IP values towards the  $\Delta V_{\text{PhOH}}$  parameters is highest for the chlorides and lowest for iodides.

Table 4  
The Results of the Regression Analysis of IP Values  
in Terms of Eqn. 4<sup>a</sup>

No	Class of Compounds	a''	b''	r	s	n
1.	ICl	12.45(0.04)	0.026(0.001)	0.993	0.09	10
2.	XBr	11.18(0.04)	0.014(0.001)	0.991	0.06	8
3.	XI	9.99(0.01)	0.006(0.001)	0.999	0.01	4

a - IP are in eV units,  $\Delta V_{\text{PhOH}}$  in  $\text{cm}^{-1}$  units.

The latter values are mostly from Ref. 36.

For the other symbols see footnotes to Table 2.

The weighted average IP of the halide lone pairs are not believed to depend on the halide-halide  $p_{\pi} - p_{\pi}$ -interactions for the case of several equivalent halide atoms in molecule. Therefore one might think that they depend mostly on the substituent inductive effect or on the interactions with some bonding orbitals. As a consequence, the dependence of such an IP-s on Taft's polar substituent constants  $\sigma^{\pi}$  is expected. As a matter of fact this relationship really exists. The results of the statistical treatment are given in Table 5 (see also Ref. 37).

Table 5  
The Dependence of the Weighted Average IP of the Halide  
Lone Pairs on the Taft's  $\sigma^{\pi}$  Constants According to the  
Equation  $\text{IP} = a''' + b''' \sigma^{\pi}$

No	The Class of Compounds	a'''	b'''	r	s	n
1.	ICl	11.31(0.03)	0.48(0.02)	0.974	0.13	40
2.	XBr	10.58(0.05)	0.42(0.03)	0.969	0.16	19
3.	XI	9.75(0.04)	0.35(0.03)	0.953	0.15	14

Alkyl and hydrogen substituent (HX) were not included into the correlations from Table 5 because in these cases the other structural factors start to dominate (polarizability, the effect of attached hydrogen atoms, etc.).<sup>37</sup> As one can see from Table, the inductive effect is the major factor which determines the IP values for halides with electro-negative substituents.

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DISSOCIATION OF 2-, 3-, and 4-SUBSTITUTED  
ADAMANTANE-1-CARBOXYLIC ACIDS IN DIMETHYLSULFOXIDE

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$pK_a$  values of the dissociation of several 2-, 3-, and 4-substituted adamantane-1-carboxylic acids and some aliphatic acids  $XC(O)OH$  were determined in dimethylsulfoxide by titration with  $Bu_4NOH$ .

It was shown that the structural effect on the acidity of these compounds is satisfactorily correlated by Taft's inductive substituent constants.

The problem of the attenuation of polar substituent effects through some alicyclic systems is also discussed.

The problem of the attenuation of substituent inductive effect through different alicyclic systems is still far from its satisfactory solution<sup>1</sup>. At that time, the problem of the mechanism of transmission via such cyclic fragments was most widely and thoroughly discussed. Various arguments for the mechanism assuming only the through-space attenuation as well as for the alternative, through-bond transmission mechanism were used (see Ref. 1 for the review of the problem as well as for the further references on the

topic).

Naturally, the compromise mechanism - simultaneous attenuation of the inductive effect through the chemical bonds and via the space inside the cavity or around the latter - are also represented.

Recently some additional theoretical considerations<sup>2</sup> which favor the through-space attenuation mechanism were suggested.

Unresolved is also a very important from the practical and theoretical viewpoints problem of the dependence of the inductive attenuation factor of the given cycle

$$Z_{\text{cycle}}^* = \rho_{\text{cycle } Y}^* / \rho_Y^* \quad , \quad (1)$$

where  $\rho_{\text{cycle } Y}^*$  and  $\rho_Y^*$  refer respectively to the systems X-cycle-Y and X-Y and represent the sensitivity of the property ( $pK_a$ ,  $\log k$ ) of the corresponding system (with the alicyclic attenuating fragment and without the latter)

upon the variation of the substituent X on the nature of the reaction series and medium<sup>1</sup>. Despite the unquestioned fact that the quantities  $Z_{\text{cycle}}^*$  do depend<sup>1</sup> on these two factors, up to now even the major regularities which govern the basic trends of the variation of the empirically determined attenuation factors of the different cycles on the nature of the chemical reaction and/or on the nature and composition of the solvent could not be considered firmly established.

On the other hand, it is found that the  $Z_{\text{cycle}}^*$  values calculated on the basis of the experimental data from Eq. (1) are for all reaction series higher (or equal to)<sup>1</sup> than those which are calculated from the simple model

$$Z_{\text{cycle}}^* = \sum_i (Z_c^*)^{n_i} = Z_{\text{bonds}}^* \quad (2)$$

where  $Z_c^*$  is the attenuation factor of the  $\text{CH}_2$  fragment for the series  $\text{X}(\text{CH}_2)_n\text{Y}$ , where n is the number of carbon atoms between the substituent X and reaction center Y.



based on the concept of the purely through-bond attenuation of the inductive effect.

Unfortunately, the analysis of the available experimental material does not indicate unambiguously what is the reason of that difference between the values of  $Z_{\text{cycle}}^{\pi}$  calculated from experimental data (Eqn.(1)) and by Eqn.2. On the one hand, one might think that this inconsistency is due to the simultaneous operation of the two above-mentioned different mechanisms of attenuation of the inductive effect which could be represented formally by Eqn. (3):

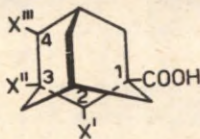
$$Z_{\text{cycle}}^{\pi}(\text{Eqn.1}) = Z_{\text{cycle}}^{\pi}(\text{Eqn.2}) + Z_{\text{cycle}}^{\pi}(\text{through-space}) \quad (3)$$

On the other hand, however, the difference between the "experimental" and predicted on the basis of Eqn.(2)  $Z_{\text{cycle}}^{\pi}$  values might be ascribed to a certain (not very significant) variation<sup>1</sup> of the attenuation factor of the carbon fragment (e.g.,  $-\text{CH}_2-$ )  $Z_{\text{C}}^{\pi}$  depending on the reaction series or the nature of the solvent. Naturally, the condition

$Z_{\text{cycle}}^{\pi}(\text{Eqn.1}) \gg Z_{\text{cycle}}^{\pi}(\text{Eqn.2})$  could be connected to the simultaneous action of these two reasons.

A somewhat limited number and type of the chemical reactions to (dissociation of carboxylic acids, hydrolysis of their esters and the interaction of the former with the diphenyldiazomethane) and media (water and aqueous alcohols) studied makes it difficult<sup>1</sup> to resolve these problems unambiguously.

The present study was designed in order to investigate the influence of the nonaqueous dipolar aprotic solvent - dimethylsulfoxide - on the transmittivity of the inductive effect through the adamantane cycle on the basis of reaction of the acidic dissociation of 2-, 3-, and 4-substituted -adamantane-1-carboxylic acids in that solvent.



Earlier this reaction was thoroughly studied in the aqueous ethanol by one of us<sup>3-5</sup> as well as by two other<sup>6,7</sup> groups.

### Experimental

Reagents. DMSO was purified as described by Ritchie<sup>8</sup> and Faleyev<sup>9</sup>. It was dried using 4Å molecular sieves and BaO and distilled from CaH<sub>2</sub> under the flow of argon. The middle fraction was distilled from NaCH<sub>2</sub>SOCH<sub>3</sub> which was prepared by the reaction of sodium amide with DMSO. The purity of DMSO was determined by the potentiometric titration with the solution of Bu<sub>4</sub>NOH in the mixture of benzene and i-PrOH. The amount of the acidic impurities does not exceed  $6 \times 10^4$  mole/l, the specific conductivity  $\kappa$  is lower than  $1 \cdot 10^{-7} \Omega^{-1} \text{cm}^{-1}$ .

Benzene was kept on CaCl<sub>2</sub> and distilled from sodium wire.

i-PrOH (Chemically pure grade) was dried with CaCl<sub>2</sub>, BaO and thereupon distilled twice.

The solution of Bu<sub>4</sub>NOH was prepared according to Denesh<sup>10</sup> from Bu<sub>4</sub>NI and silver oxide in anhydrous i-PrOH. It was flown through the column filled up with anionite Amberlite IRA-400(Serva). The concentration of the Bu<sub>4</sub>NOH in the mixture (1:4) of i-PrOH and benzene was continuously (every day) monitored by the potentiometric titration of benzoic acid in DMSO solution. The stock solution of the titrant was kept in refrigerator.

2,6-(NO<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>OH had m.p. 62.5°, phenol 41.5°C.

Tetraethylammonium Perchlorate was prepared according to Ref. 11.

The synthesis and purification of all 2-, 3-, and 4-substituted adamantane-1-carboxylic acids used in this work were already thoroughly described by one of us.<sup>3-5</sup> Samples of the previously shown quality were used.

Benzoic acid ("chemically pure") was purified by sublimation.

For the sake determination of the  $\rho^{\star}_{Z^{\star} \text{XCOOH}}$  value which was necessary for the calculation of  $Z^{\star}_{\text{cycle}}$  from Eqn.(1),



the  $pK_a$  values of the following aliphatic carboxylic acids  $XCOOH$  were also determined in DMSO solution ( $X=H, CH_3, t-Bu, CH_2=CHCH_2, CH_3OCH_2, CHF_2, HC\equiv C, CF_3, AdCH_2$ ). For the determination of the dependence of these values on the structure the joint statistical analysis of the literature and our present data was performed. As a rule these  $pK_a$  values are compatible with the available literature data on this reaction series.<sup>9,12-14</sup> The complete description of the latter experiments together with the  $pK_a$  values gotten will be published separately.

The technique for the potentiometric measurement of  $pK_a$  values of acidic substances in DMSO solution was already used by us for the determination of  $pK_a$  of the strongly acidic alcohols.<sup>15</sup>

In the following the more detailed description of this technique will be given. (see also Ref. 11). A pH-meter (pH-262) rebuilt into millivoltmeter (scale range from -800 to 1000 mV) was used. Radiometer A 2222B or HCT electrodes filled up with mercury<sup>8</sup> were used. The latter procedure speeds up the time of reaching the electrode equilibrium and shifts its potential (due to the change of its inner resistance) into the more convenient range. After the measurements the electrode was washed with distilled water and with anhydrous ethanol. It was kept in pure DMSO.  $Ag/0.01M AgNO_3$  in DMSO/ electrode attached to the test solution through the U-shaped bridge filled with 0.1 M solution of  $Et_4NClO_4$  was used as a reference electrode. Through the thermostated ( $25.0 \pm 0.05$ ) cell the prepurified and dried argon gas was blown. Titrant was added from a microburette or from an automatic titrator by small amounts (0.02-0.05 ml). The upper part of the burette was closed with the teflon stopcock which via the tube led to the closed system to protect the titrant from the  $CO_2$  and moisture. The solution was stirred by the argon flow. Constant equilibrium electrode potentials were usually reached within 1-2 minutes, and nearly the equivalence point within 5 minutes time.



The concentrations of the solution of the acids studied were in the ranges from 0.001 - 0.008 mole/l, whereas the concentration of the titrant was  $(2-5) \times 10^{-2}$  moles/l.

The calibration of glass electrode was made using  $pK_a$  values of benzoic acid (11.0)<sup>16</sup>, 2,6-dinitrophenol (4.9)<sup>16</sup> and phenol (16.9)<sup>16</sup> as references.

The calibration straight line was drawn as a plot in coordinates  $E(mV)$  vs.  $p_aH$ , where

$$p_aH = -\log a_{H^+} \quad \text{and} \quad a_{H^+} = \frac{[A^-] f_{A^-}}{[AH] f_{AH} K_A},$$

$[A^-]$  and  $[AH]$  are the concentrations of the anionic and neutral forms of the acid  $AH$ ,  $f_{A^-}$  and  $f_{AH}$  are their activity coefficients.

Within the experimental errors the slope of the calibration plot does not differ from the theoretical value (59.1). However, some relatively small (10-20 mV) parallel shift of the calibration line along the  $E$  axis was observed. Such a shift also occurs with the samples of DMSO from different stock solutions.

To minimize errors of that origin the every day check of the proper functioning of the electrode system was undertaken by the repeated titration of the standard substance-benzoic acid.

On the basis of the titration curves and results of the calibration of a glass electrode  $pK_a$  values of carboxylic acids studied were calculated ( $pK_a$  value 11.0 was used as a reference for the absolute calibration of the acidity scale):

$$pK_a = p_aH + \log [AH]/[A^-] + \log f_{A^-}$$

Values of  $\log f_{A^-}$  were formally calculated on the grounds of the ionic strength  $I$  of the solution using the Debye-Hückel equation for the DMSO in form:  $-\log f_{A^-} = 1.1\sqrt{I}$ .

The contribution of the correction terms from  $-\log f_{A^-}$  does not exceed in any case 0.04 - 0.09  $pK_a$  units. Activity coefficient for the neutral acid was assumed to be equal

a unit ( $\log f_{AH} = 0$ ).

As a rule, the calculated for the different ionization ratios  $[AH]/[A^-]$   $pK_a$  values coincide within the limits of experimental errors. For each acid the titration was repeated 2-5 times. From the mean values of the individual runs the arithmetic mean  $pK_a$  values were calculated. The latter are listed in Table 1.

Table 1.

$pK_a$  for Some 2-, 3- and 4-Substituted-Adamantane-1-Carboxylic Acids in DMSO.

Substituent		$pK_a$	Substituent		$pK_a$
1.	H	$13.09 \pm 0.11$	9.	3 - $CH_3$	$13.16 \pm 0.07$
2.	2 - $NO_2$	$11.20 \pm 0.13$	10.	3 - $CH_2Br$	$12.65 \pm 0.03$
3.	2 - Br	$11.88 \pm 0.08$	11.	3 - $CH_3CO$	$12.33 \pm 0.06$
4.	2 - O=	$12.79 \pm 0.09$	12.	3 - $CH_3O_2C$	$12.52 \pm 0.04$
5.	3 - Br	$12.11 \pm 0.05$	13.	4 - Br	$12.42 \pm 0.03$
6.	3 - $NO_2$	$11.77 \pm 0.05$	14.	4 - O=	$12.38 \pm 0.01$
7.	3 - OH	$12.66 \pm 0.07$	15.	4 - $NO_2$	$12.17 \pm 0.09$
8.	3 - $ONO_2$	$11.84 \pm 0.04$			

The statistical least-squares treatment of the experimental data in order to get necessary for the calculation of the cycle attenuation factors  $Z_{cycle}^*$  values of  $\rho_{cycle Y}^*$  and  $\rho_Y^*$  was performed, as a rule, in terms of the single parameter Taft equation

$$pK_a(X) = pK_a^O(X) + \rho_{cycle Y}^* \sigma_X^* \quad (X-AdCOOH) \quad (3)$$

or

$$pK_a(X) = pK_a^O(X) + \rho_Y^* \sigma_X^* \quad (\text{aliphatic acids } XCOOH), (4)$$

where  $pK_a^O(X)$  refer to methyl substituent. For the series of 3-substituted-adamantane-1-carboxylic acids and aliphatic carboxylic acids  $XCOOH$  in DMSO also a parallel statistical treatment was made adding to Eqns.(3) and (4) also the so

called polarizational term<sup>17,18</sup> which is significant for gas phase ion-molecule processes in the following form:

$$pK_a(X) = pK_a^0(X) + \rho^*_{\text{cycleY}} \sigma_X^* + a \Delta R \quad (3a)$$

and

$$pK_a(X) = pK_a^0(X) + \rho^*_Y \sigma_X^* + a^1 \Delta R, \quad (4a)$$

where  $a$  and  $a^1$  are constants and

$\Delta R = MR_D(X) - MR_D(CH_3)$ ,  $MR_D$  is the molecular refractivity of the substituent  $X$ .

Alongside with the experimental data for the DMSO the additional recalculation of the earlier data<sup>3-5</sup> for the dissociation of 2,-3- and 4-substituted-adamantane carboxylic acids in aqueous ethanol (50 per cent by volume).

The results of the statistical data processing in terms of Eqns. (3,4,3a, and 4a) are given in Table 2. and partially shown on Fig. 1.

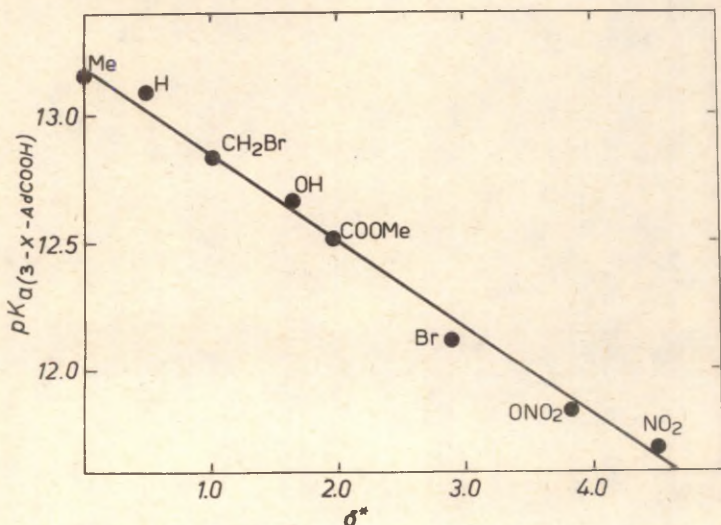


Fig.1. The dependence of  $pK_a$  values of 3-substituted-adamantane-1-carboxylic acids on  $\sigma^*$  substituent constants in DMSO.



Table 2

Results of Statistical Treatment of  $pK_a$  Values for 2,-3- and 4-Adamantane-1-Carboxylic Acids and Aliphatic Acids  $XCOOH$  in Terms of Eqns. (3),(4), (3a) and (4a). Along With Regression Coefficients of These Equations Experimental ( $Z_{cycle}^*$ (Eqn.(1) and Predicted from Eqn. (2) Through-Bond ( $Z_{cycle}^*$  Eqn.(2),  $Z_c^*=0.36$ ) Attenuation Factors of Cycles, Formal Contribution of Through-Space Attenuation  $\Delta$ , and Calculated On Basis of Through-Bond Model (Assuming the Equality of  $Z_{cycle(1)}^* = Z_{bonds}^*$ (Eqn.2)) Effective Attenuation Factors For Carbon Atom  $Z_c^*$ .

Reaction Series	$pK_a^O(X)$	$-\rho^*$	$-a(a')$	r	s	$Z_{cycle(1)}^*$ Eqn.(1)	$Z_{bonds(2)}^*$ Eqn.(2), $Z_c^*=0.36$	$\Delta=Z_{cycle(1)}^*-Z_{bonds}^*$	$Z_c^*(effective)$	
1	2	3	4	5	6	7	8	9	10	11
1. 2-X-AdCOOH, Et5O X=H, Ph, MeO, I, Br, Cl, NO <sub>3</sub>	7.04 (0.07)	0.294 (0.051)	-	0.976	0.09	0.172	0.134	0.038		0.41
2. 2-X-AdCOOH, DMSO X=H, Br, NO <sub>2</sub>	13.30 (0.07)	0.473 (0.072)	-	0.999	0.07	0.152	0.134	0.018		0.38
3. 3-X-AdCOOH, Et5O <sup>a)</sup> X=H, Br, OH, NO <sub>3</sub> NO <sub>2</sub> , I, Ph, CH <sub>2</sub> Br, <sup>b)</sup> MeCO, MeCONH, MeO, COOMe	6.87 (0.05)	0.206 (0.022) 0.205 (0.023)	- (0.0005)	0.947	0.09	0.121	0.058	0.063		0.442

Table 2 continued

1	2	3	4	5	6	7	8	9	10	11	
4.	3-X-AdCOOH, DMSO	a)	13.15	0.339		0.988	0.09	0.109	0.058	0.051	0.43
	X=H, Me, Br, NO <sub>2</sub> ,		(0.05)	(0.021)							
	NO <sub>3</sub> , OH, CH <sub>2</sub> Br,	b)	13.16	0.328	0.016	0.997	0.05				
	COOMe		(0.03)	(0.013)	(0.005)						
5.	4-X-AdCOOH, Et50		6.95	0.100	-	0.998	0.02	0.059	0.034	0.025	0.40
	X=H, Br, Cl,		(0.01)	(0.006)							
6.	4-X-AdCOOH, DMSO		13.17	0.220	-	0.977	0.10	0.071	0.034	0.047	0.417
	X=H, Br, NO <sub>2</sub> , O=		(0.11)	(0.033)							
7.	XCOOH, Et50			1.70 <sup>21</sup>							
				(0.07)							
8.	XCOOH, DMSO	a)	12.26	3.11	-	0.992	0.37				
	X=Me, Et, t-Bu,		(0.15)	(0.12)							
	ClCH <sub>2</sub> , H, Cl <sub>2</sub> CH,										
	PhCH <sub>2</sub> , CNCH <sub>2</sub> ,										
	CH <sub>2</sub> COOEt, COOEt,	b)	12.28	3.12	0.003	0.992	0.38				
	CH <sub>2</sub> OMe, CH <sub>2</sub> CH=		(0.20)	(0.12)	(0.015)						
	=CH <sub>2</sub> , CHF <sub>2</sub> , CF <sub>3</sub>										

Footnote: The following notations have been used:  $r$  - correlation coefficient,  $s$  - standard deviation. In the parenthesis under the regression coefficients their error range is shown.  $Z_{\text{bonds}(2)}^*$  is calculated according to Eqn.2 accepting the original Taft's value  $Z_c^* = 0.36$  (see also Ref. 19). The  $Z_c^*$ (effective) is calculated from Eqn.2 assuming that the experimental attenuation factor calculated from Eqn.(1) could be fully accounted for by Eqn.(2). For the latter calculations  $Z_{\text{bonds}(2)}^*$  for the 2-X-AdCOOH was taken as  $Z_c^{*2} + 2 Z_c^{*6}$ , for 3-X-AdCOOH  $Z_{\text{bonds}(2)}^* = Z_c^{*3} + 2 Z_c^{*5}$  and for 4-X-AdCOOH  $Z_{\text{bonds}(2)}^* = 2(Z_c^{*4} + Z_c^{*6})$ . For the 4-substituted bicyclo-[2,2,2] -octane-carboxylic acids  $Z_{\text{bonds}(2)}^* = 3 Z_c^{*4}$ , for 4-substituted-cubane-1-carboxylic acids  $Z_{\text{bonds}(2)}^* = 6 Z_c^{*4}$ . For the correlations via Eqns.(3), (3a), (4), (4a) were made using  $\sigma^*$ -constants from Ref. 20.



It should be mentioned that (within the error limits of determining the  $pK_a$  values) for 3-X-AdCOOH as well as for XCOOH the contribution of the polarizability term in Eqn. (3a) or (4a) is practically negligible for DMSO and Et50 media.

### Discussion

Rather low accuracy of correlations reported in Table 2 for alicyclic systems, significantly more poor choice of substituents in 2- and 4- positions as compared with 3-position, relatively narrow maximum range of variation of  $pK_a$  values for alicyclic acids (about 1 log units for X-AdCOOH in aqueous ethanol and no more than 1.7 log units in DMSO solution), and even somewhat uncertain  $\rho^*_{\text{cycle Y}}$  value for XCOOH in Et50(v/v) does allow to make only a few conclusions about the influence of the nature of the solvent on the inductive transmittivity of the adamantane cycle.

One can see from Table 2 that analogously to the aliphatic series the change of the hydroxylic aqueous-organic media for the dipolar aprotic solvent increases significantly (1.5-2 times) the sensitivity ( $\rho^*_{\text{cycle Y}}$ ) of the corresponding alicyclic (adamantane) system towards the substituent effects. However, Table 2 also shows that the transfer of the aliphatic series into DMSO results, in turn, in comparable if not even larger increase of the  $\rho^*_{\text{Y}}$  value. As a result of that, the experimental attenuation factor of the inductive effect for DMSO calculated from Eqn.(1) as a ratio of these two quantities is comparable if not even lower than  $Z^*_{\text{cycle Y}}$  value for aqueous ethanol solution. For both media the order of decrease of  $Z^*_{\text{cycle Y}}$  values with the position of the substituent in the adamantane ring remains also the same:

$$Z^*_{\text{cycle Y}}(2) > Z^*_{\text{cycle Y}}(3) > Z^*_{\text{cycle Y}}(4)$$

---

\* Only very moderate accuracy of the correlations of  $pK_a$  values with  $\sigma^*$  or  $\sigma_I$  constants is characteristic to the most series of alicyclic reaction series.<sup>1,3-6</sup>

The  $\Delta$  values (see Table 2, column 10), however, decrease in the reversed order. This parameter was formally calculated as the difference between the "experimental" conductivity of the cycle  $Z_{\text{cycle Y}}^{\pi}$  and the through-bond attenuation factor calculated from Eqn.(2) assuming  $Z_C^{\pi} = 0.36$  as originally suggested by R.W. Taft<sup>+</sup>:

$$\Delta = Z_{\text{cycle Y}(1)}^{\pi} - Z_{\text{cycle Y,Eqn.(2)}}^{\pi}, Z_C^{\pi} = 0.36 \quad (4)$$

In the framework of the "dualistic" hypothesis about the simultaneous and independent attenuation of the inductive effect of the substituents through the space as well as via the bonds the quantity  $\Delta$  can be identified as the contribution of the inductive field effect.

However, one can see from Table 2 that it is impossible to draw any well-founded conclusions in favor of the unambiguous presence of the latter interaction mechanism. On the contrary, column 11 of Table 2 shows that all observed deviations  $\Delta$  of the experimental attenuation factors  $Z_{\text{cycle Y}(1)}^{\pi}$  from that calculated on the basis of Eqn. (2) can be easily explained accepting only a rather modest change of the attenuation factor of the carbon atom  $Z_C^{\pi}$  ( $0.38 \leq Z_C^{\pi} \leq 0.44$ ) with the variation of its position in the conducting fragment.

For the further investigation of the influence of solvent effects on the transmittance of inductive effect via alicyclic systems the studies of the behavior of these systems in the absence of the solvent molecules - i.e. in the gas phase - are highly welcome. In that connection we would limit ourselves only with the reference<sup>22</sup> on the results of the recent ICR study of some series of acidic dissociation of alicyclic carboxylic acids in the gas phase which show that "experimental"  $Z_{\text{cycle Y}}^{\pi}$  values frequently increase with the transfer from solution into the gas phase more

<sup>+</sup> Later on (see Ref. 1) several other values of  $Z_C^{\pi}$  (0.35 - 0.5) were calculated by various authors on the basis of experimental data for different reaction series.

than twice (e.g.  $Z_{\text{cycle Y}}^*(3\text{-X-AdCOOH})=0.30$ ;  $Z_{\text{cycle Y}}^*(4\text{-X-} \text{---} \text{COOH})=0.39$ ,  $Z_{\text{cycle Y}}^*(4\text{-X-cubane-1-carboxylic acids}) = 0.30$ , etc.). In the framework of the still unproved hypothesis of the constancy of  $Z_{\text{C}}^*$  values (e.g. 0.36-0.40) these quantities, of course, evidence about the dominant role of the inductive field effect. On the other hand, based on the through-bond attenuation model these largely increased  $Z_{\text{cycle Y}}^*$  values would assume already very significant changes in the inductive effect conductivity of the carbon atom (for these three systems  $Z_{\text{C}}^*$  will be respectively 0.55, 0.60 and 0.47).

However, the Wepster's <sup>23</sup> idea about the necessity to include the special electrostatic correction term even in the absence in the molecule of ionic substituents into the correlation equations qualifies the above-mentioned interpretation of the gas-phase results also as preliminary.

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$E_T$  PARAMETERS OF BINARY MIXTURES OF ALCOHOLS  
WITH DMSO AND MeCN. SYNERGETIC SOLVENT EFFECT  
OF HIGH INTENSITY

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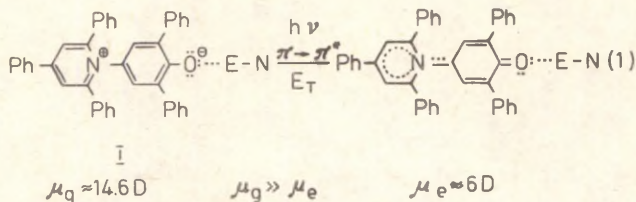
The  $E_T$  parameters of the gross polarity of the binary mixtures of alcohols with DMSO and acetonitrile were determined. It was found that in some of these systems (for DMSO-ROH (R= i-Pr and t-Bu), and for MeCN-ROH (R=Et, i-Pr, t-Bu)) the dependence of the solvatochromic transition energies of the long wavelength  $\pi \rightarrow \pi^*$  absorption maxima of the pyridinium-N-phenoxide betaine dye on the composition of the binary mixture goes through the extremum (maximum). Due to the peculiar synergetic solvent effect the corresponding to this maximum  $E_T$ -values are higher than those for the two pure components.

In the rest of cases considered in this work the similar special solvent effect was not detected.

The analysis of these data reveals a close analogy between the influence of binary mixtures of aliphatic alcohols with MeCN and DMSO on the energies of  $\pi \rightarrow \pi^*$  optical transition of pyridinium-N-phenoxide dye from one hand, and on the  $\log k$  values of the monomolecular  $S_N1$  heterolysis of tertiary alkyl and aralkyl halides, from the other.

The possible interpretations of the appearance of the above-mentioned maxima on the  $E_T$ -composition plots were discussed.

The empirical  $E_T$ -scale of the solvating power of the solvents<sup>1-3</sup> is based on the measurements of the solvatochromic shifts of excitation energies which correspond to the long-wavelength absorption maximum ( $\pi \rightarrow \pi^*$  transition) of the pyridinium-N-phenoxide betaine dye (I)



where EN is in this case electrophilically solvating moiety.

Up to now  $E_T$ -parameters have been determined for almost 250 individual solvents.<sup>4</sup> Not very different by their results estimates of this parameter for the gas phase ( $26^{+2}$  kcal/mol) have been made also.<sup>4-6</sup>

In the framework of the multiparameter approach<sup>5</sup> to the quantitative correlation of the solvent effects  $E_T$  parameters were used as a basis for the derivation of the electrophilicity scale  $E^6$  which is freed from the contribution of the nonspecific solvent-solute interactions present in the gross  $E_T$ -values. It seems essential that the availability of a rather large number of the experimental  $E_T$ -values makes it desirable, and necessary to revise, redefine and significantly complement the set of E-values. It is not excluded that it is reasonable to split the presently existing set of E-parameters into two separate "electrophilicity" scales - one for proton donating solvents ( $\text{H}_2\text{O}$ , alcohols, carboxylic acids, etc.) and the other for the dipolar aprotic solvents (DMSO,  $\text{MeNO}_2$ , MeCN, etc.).



Much less attention <sup>1,3,7-11</sup> has been focused on the determination of  $E_T$ -values<sup>+</sup> for solvent mixtures. It was found in the latter cases that, as a rule, the dependence of  $E_T$  values of binary mixtures on the ratio of their components is characterized by the monotonous change, without the presence of extremums on the plots of  $E_T$  vs. composition.

However, in a very few occasions<sup>8,11</sup> (mixtures of the chloroform with acetone and trialkylphosphates, and the system  $\text{CH}_2\text{Cl}_2$  - acetone ) it was noticed that at the some ratios of the components the energy of the solvatochromic  $\pi \rightarrow \pi^*$  transition of dye (I) is higher than for the corresponding pure components, i.e. there is the evidence about the presence of a certain synergistic solvent effect of a binary mixture.

Some facts about the solvation effects of the same nature on the logk values of the heterolytic  $S_N1$  solvolysis of tertiary alkyl and arylalkyl halides in the binary mixtures of dipolar aprotic solvents with hydrogen bond donors are known already for a long time. So, the extremum (maximum) was noticed<sup>13</sup> on the logk - composition plot for the solvolysis of t-BuCl in the mixtures of t-BuOH with acetonitrile, DMF and nitrobenzene and in the mixtures of DMSO with i-PrOH.<sup>14</sup>

Later on, similar and even more pronounced maxima were observed<sup>15</sup> also for the  $S_N1$  solvolysis of tertiary cumyl chloride in the binary systems MeCN-alcohol (t-BuOH, i-PrOH, EtOH). Even more complicated picture was found by the latter workers for the mixtures of DMSO with alcohols.

Some other cases of the observance of the maxima on the curves of logk vs. molar fraction of one of the components of the binary mixture are also known.<sup>16-17</sup>

As a rule, in most cases the increase of the logk values above the corresponding quantities for the pure individ-

\* E-parameters of some aqueous-organic mixtures were calculated by us<sup>12</sup> a few years ago.

ual components does not exceed 0.2 - 0.3 log units. The above-cited work<sup>15</sup> could be considered as a positive exception because the logk value for the solvolysis of PhCMe<sub>2</sub>Cl in the mixtures of MeCN with t-BuOH exceeds the logk value for the pure alcohol almost by 0.7 log units (0.95 kcal/mol). Sometimes, however, the positive deviations from the quantities which characterize the pure components are only slightly above their error limits (see Refs.13,14,18).

Keeping in mind much higher (even as compared with the S<sub>N</sub>1 heterolysis) sensitivity of the spectral  $\pi \rightarrow \pi^*$  transition (1) towards solvent effects, an attempt was made in the present work to check the behavior of the E<sub>T</sub> - parameters for the presence of the above-mentioned synergetic solvent effects in those systems (DMSO-alcohols and MeCN-alcohols) where this phenomenon was observed in the case of the solvolysis of t-BuCl and PhCMe<sub>2</sub>Cl. The dependence of E<sub>T</sub> - values on the composition of the aqueous acetonitrile was recently studied by Eastel.<sup>11</sup> For the comparison, E<sub>T</sub> parameters for the mixture of the aqueous dimethylsulfoxide were also determined.

#### Experimental.

All individual solvents were carefully purified and dried according to the earlier used techniques.<sup>13,19,20</sup> Binary mixtures of the necessary composition were prepared by weighing. The concentration of the pyridinium-N-phenoxide betaine (I) was 10<sup>-4</sup>-10<sup>-5</sup> mole/l.

The spectra were recorded using Hitachi EPS-3T recording spectrophotometer in the thermostated (25.0°C) cells relative to the blank solutions identical in composition to each sample except for the absence of the solute dye(I).

The accuracy of the assignment of the wavelengths of the maximum absorption was in the range of  $\pm 1$ -2 nm.

Reproducibility of the different experiments is in the same range and depends significantly on the quality of the purification and drying of the solvents.

Pyridinium-N-phenoxide betaine(I) was kindly delivered by Prof. C. Reichardt (University of Marburg, FRG) and by

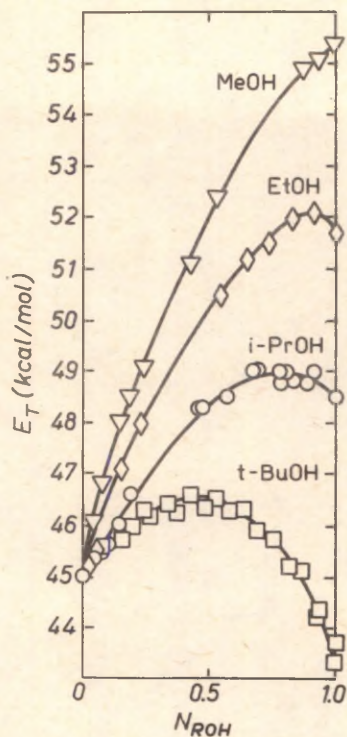


Fig. 1. The dependence of  $E_T$  parameters of binary mixtures of DMSO-ROH on the mole fraction of the latter.

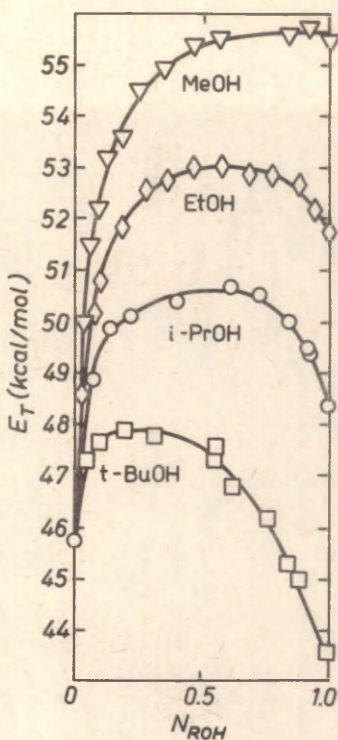


Fig. 2. The dependence of  $E_T$ -parameters of binary mixtures of MeCN-ROH on the mole fraction of the latter.



Table 1

Solvatochromic Shifts of the Maximum of the Long Wavelength Absorption Band of  
Pyridinium-N-Phenoxide Betaine Dye(I) in Binary Mixtures of DMSO with Alcohols ROH and H<sub>2</sub>O

N <sub>ROH</sub>	MeOH		N <sub>ROH</sub>	EtOH		N <sub>ROH</sub>	i-PrOH		N <sub>ROH</sub>	t-BuOH		HOH		
	$\lambda_{\max}$	E <sub>T</sub>		$\lambda_{\max}$	E <sub>T</sub>		$\lambda_{\max}$	E <sub>T</sub>		$\lambda_{\max}$	E <sub>T</sub>	N <sub>HOH</sub>	$\lambda_{\max}$	E <sub>T</sub>
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
0	636	45.0	0	638	44.8	0	637	44.9	0	635	45.0	0	632	45.2
0.044	621	46.0	0.032	632	45.2	0.050	631	45.3	0.020	632	45.2	0.079	629	45.5
0.083	611	46.8	0.061	628	45.5	0.071	629	45.5	0.056	630	45.4	0.149	620	46.1
0.156	593	48.2	0.147	618	46.3	0.097	624	45.6	0.086	627	45.6	0.279	602	47.5
0.179	590	48.5	0.163	607	47.1	0.152	621	46.0	0.097	627	45.6	0.508	571.5	50.0
0.239	583	49.0	0.233	595	48.0	0.195	614	46.6	0.138	624	45.8	0.630	550.5	51.9
0.433	560	51.1	0.548	566	50.5	0.474	592	48.3	0.166	625	45.7	0.730	530	53.9
0.526	546	52.4	0.646	558	51.2	0.480	592	48.3	0.197	623	45.9	0.793	515	55.5
0.877	521	54.9	0.741	555	51.5	0.574	590	48.5	0.249	618	46.3	0.862	498	57.4
0.941	519	55.1	0.833	550	52.0	0.678	584	49.0	0.273	619	46.2	0.903	486	58.8
1.00	516	55.4	0.920	549	52.1	0.686	584	49.0	0.332	616	46.4	0.942	474	60.3
			1.00	553	51.7	0.785	580	49.3	0.374	619	46.2	0.971	465	61.5
						0.789	586	48.8	0.432	614	46.6	0.984	460	62.2
						0.807	584	49.0	0.476	617	46.3	0.988	457	62.6

Table 1 continued

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
						0.841	586	48.8	0.538	615	46.5	1.00	453 <sup>1</sup>	63.1 <sup>1</sup>
						0.890	586	48.8	0.578	617	46.3			
						0.920	584	49.0	0.637	617	46.3			
						1.00	592	48.3	0.685	622.5	45.9			
									0.758	625	45.7			
									0.802	633	45.2			
									0.869	634	45.1			
									0.937	647	44.2			
									1.00	655	43.7			

<sup>1</sup> -  $\lambda_{\text{max}}$  values are given in nanometer units,  $E_T$ - parameters are in kcal/mol.

Table 2

Solvatochromic Shifts of the Maximum of the Long Wavelength Absorption Band of Pyridinium-N-Phenoxide Betaine Dye(I) in Binary Mixtures of Acetonitrile with Alcohols ROH.

$N_{ROH}$	MeOH		$N_{ROH}$	EtOH		$N_{ROH}$	i-PrOH		$N_{ROH}$	t-BuOH	
	$\lambda_{max}$	$E_T$		$\lambda_{max}$	$E_T$		$\lambda_{max}$	$E_T$		$\lambda_{max}$	$E_T$
0	626	45.7	0	626	45.7	0	626	45.7	0	626	45.7
0.029	574	49.8	0.021	592	48.3	0.07	585	48.9	0.043	605	47.3
0.062	555	51.5	0.044	578	49.5	0.140	573	49.9	0.094	599	47.7
0.093	548	52.2	0.066	570	50.2	0.220	571	50.1	0.194	597	47.9
0.127	537	53.2	0.090	563	50.8	0.400	567	50.4	0.309	598	47.8
0.185	533	53.6	0.182	551	51.9	0.610	564	50.7	0.551	605	47.3
0.248	525	54.5	0.274	544	52.6	0.725	568	50.3	0.553	601	47.6
0.355	521	54.9	0.361	541	52.8	0.843	571.5	50.0	0.607	623	45.9
0.465	516.5	55.4	0.462	539	53.0	0.909	578	49.5	0.624	611	46.8
0.569	515	55.5	0.571	538	53.1	0.916	578.5	49.4	0.756	619	46.2
0.838	514	55.6	0.680	540	52.9	1.00	590.5	48.4	0.840	631	45.3
0.922	512.5	55.8	0.774	540	52.9				0.885	636	45.0
1.00	515	55.5	0.879	542	52.7				1.00	656	43.6
			0.944	548	52.2						
			1.00	552	51.8						

a - see a footnote to Table 1.



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The results of the determination of  $E_T$ -values for the binary mixtures studied are reported in Tables 1 and 2. Their dependence on the composition of the solvent mixture is visualized in Fig. 1 and 2.

#### Discussion

One can see from Tables 1 and 2 and from Figs. 1 and 2 that for both binary systems consisting of dipolar aprotic solvent and alcohol there are clearly expressed extremums (maximums) on the plots of the dependence of the energies of the solvatochromic  $\pi \rightarrow \pi^*$  transition (1) of betaine (I) on the composition of the binary mixture.

In the case of the systems DMSO-alcohol these maximums are observed for the mixtures of the aprotic compound with the t-BuOH, i-PrOH and probably also with ethanol. For the mixtures of acetonitrile with alcohols maximums with all the above-mentioned hydroxylic solvents are more clearly pronounced. The presence of the extremum for the mixture of MeCN with methanol can't be considered unambiguously proved.

Fig. 1 shows that for the binary mixtures of DMSO with alcohol the maximum deviation (increase) from the corresponding value for the pure DMSO (system DMSO-t-BuOH) amounts up to 1.7 kcal/mol while the maximum synergetic effect in the mixture of acetonitrile with t-BuOH (relative to MeCN) is by 0.4 kcal/mol higher (see Fig. 2).

The deviations  $\Delta E_T$  of the experimental  $E_T$ -values from those predicted on the basis of their mole fractional additivity are even more pronounced (see Fig. 3 and 4).

One can see that the non-additivity for both of these systems reaches rather significant values. So for the mixtures of DMSO with alcohols the maximum  $\Delta E_T$ -values are about  $2 \pm 0.5$  kcal/mol whereas for another system (MeCN-ROH) they are even higher (from 3 kcal/mol (t-BuOH) up to 6 kcal/mol (MeOH)).

For the mixtures of DMSO with ROH the maximum deviations of  $E_T$ -values from additivity occur, as a rule, at  $N_{ROH} \geq 0.5$  (the system DMSO-MeOH seems to be exceptional) while the

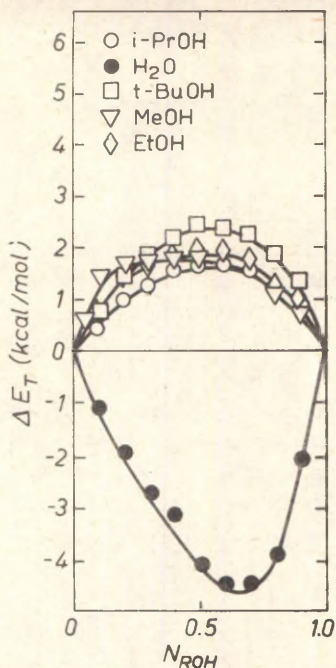


Fig. 3. The deviations  $\Delta E_T$  of the  $E_T$ -parameters from the values predicted on the basis of their mole fractional additivity

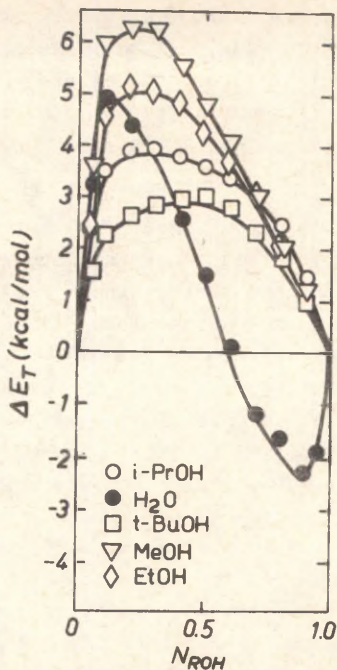


Fig. 4. The deviations  $\Delta E_T$ -parameters for the binary mixtures MeCN-ROH and MeCN-H<sub>2</sub>O from the values predicted on the basis of their mole fractional additivity.

maximum  $\Delta E_T$ -values for the binary mixtures of MeCN-ROH are observed at the excess of the dipolar aprotic component.

The aqueous DMSO and aqueous acetonitrile differ sharply and qualitatively from the behavior which is characteristic to the systems dipolar aprotic solvent-alcohol. So, throughout the all range of compositions in aqueous DMSO the deviations of  $E_T$ -values from their additive values are nega-

tive ( $\Delta E_T \leq 0$ ) and the maximum value reaches  $-4.5$  kcal/mol. Much more complicated pattern of the dependence of  $\Delta E_T$  values on composition is characteristic for the aqueous acetonitrile<sup>11</sup> (see Fig. 4). In this case at  $N_{H_2O} \leq 0.6$   $\Delta E_T$  values are positive and at the excess of water ( $N_{H_2O} \geq 0.6$ ) they invert their sign and reach another extremum ( $\Delta E_T = -2.4$  kcal/mol) at  $N_{H_2O} \approx 0.9$ .

The formal picture of the above-described solvent effects in binary mixtures characterized by the observance of the extrema (maximums) on the dependencies of the spectral transition energy or logk of the heterolytic  $S_N1$  solvolysis on the composition of the solvent mixture is identical for both processes. This is evidenced by the far-reaching parallelism in the behavior of  $E_T$ -parameters from one hand, and logk values for the solvolysis of  $PhCMe_2Cl$  in the mixtures of alcohols with DMSO and MeCN, from the other.

The closeness of the parameters of the correlation equations for these systems

MeCN - ROH

$$\log k = (0.229 \pm 0.013)E_T - (15.48 \pm 0.64) \quad (2)$$

$$r = 0.951; \quad s = 0.24; \quad s\% = 8; \quad n = 37$$

and

DMSO - ROH

$$\log k = (0.197 \pm 0.010)E_T - (13.56 \pm 0.49) \quad (3)$$

$$r = 0.944; \quad s = 0.21; \quad s\% = 7.8; \quad n = 48$$

where  $r$  - is correlation coefficient,  $s$  - standard deviation,  $s\% = (s / \Delta \log k_{\max})100$ ,  $n$  - the number of points,  $\Delta \log k_{\max}$  - the maximum range of variation of logk.

allows one to combine these two linearities into a single, approximate equation:

$$\log k = (0.196 \pm 0.009)E_T - (13.67 \pm 0.44) \quad (4)$$

$$r = 0.925; \quad s = 0.27; \quad s\% = 9; \quad n = 85$$



In the case of the transfer (1) from the highly polar and basic ground state into the relatively less polar and less basic excited state the first additions of the hydrogen bond donors (e.g., alcohols) to the dipolar aprotic solvent will result in the increase of the  $\pi \rightarrow \pi^*$  transition energy. For the  $S_N1$  heterolysis of tertiary alkyl or arylalkyl halides the situation is exactly inverted: the transfer from the low basic and low polar initial state into highly polar (ionic) and significantly basic transition state is facilitated by the additions of the electrophilic component which leads to the increase of  $\log k$  values.

Naturally, in both cases in the same direction with the addition of the electrophilic component should act also the increase of polarity<sup>5</sup> and polarizability<sup>5</sup> of the binary solvent as well as its ability to form solvation complexes due to association of dipolar molecules of the dye(I) (or  $S_N1$  transition state) with the solvent molecules of the same quality. As regards the polarity and polarizability of the DMSO-alcohol mixtures then according to Ref.21 both the dielectric constants and refractive indexes usually change (decrease) monotonously by the decrease of the alcohol's mole fraction in the binary mixture. The analogous situation could probably be true also for the mixtures of MeCN with alcohols.

However, the dependence of the viscosity<sup>22</sup> of the mixtures of DMSO with EtOH and n-PROH on their composition has an extremum. These systems display the minimums of the activation energies of the viscous flow in the region when  $0.1 \leq N_{ROH} \leq 0.5$  which is interpreted<sup>22</sup> as the increase of the inner mobility of the structure of these binary mixtures as compared with the same property of the pure compounds. In that concentration range the latter behavior could be ascribed to the simultaneous realization of several counter-acting processes: destruction (depolymerization) of the pure polymeric (chain-like) DMSO, complex formation between the monomeric or polymeric DMSO with alcohol molecules or with their polymeric aggregates, and destruction (depolymeriza-

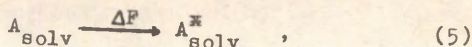
tion) of the aggregated alcohol clusters due to the interaction with the molecules of the dipolar aprotic component.

The studies of the dielectric losses<sup>21</sup> and deviations of the heats of mixing<sup>23</sup> of these binary systems lead to the same conclusions.

It is proper to underline that similar to their specific behavior on the plot of  $\Delta E_T$  vs. composition ( see Fig. 3) for the aqueous DMSO, the deviations of the heats of mixing<sup>23</sup> as well as viscosity<sup>22</sup> of the same system have the opposite direction (sign) as compared to the behavior of mixtures of DMSO with the alcohols .

On the other hand, the NMR studies<sup>24,25</sup> of the chemical shifts of the hydroxylic proton  $\delta_{\text{H}_2\text{O}}$  in binary mixtures of DMSO with alcohols (R= Me, Et, i-Pr, t-Bu) show that there is no extremum on the dependence of this quantity on the composition of these binary systems. At the relatively high concentration of the aprotic component ( $N_{\text{ROH}} \approx 0.3 - 0.5$ ) where all alcohol molecules are complexed with DMSO molecules or clusters  $\delta_{\text{H}_2\text{O}}$  remains practically constant. Further increase of the alcohol content shifts  $\delta_{\text{H}_2\text{O}}$  value significantly towards the lower field. The inspection of the deviations of the measured characteristic from its additive value displays very similar to Fig. 3 picture. With the exception of DMSO-methanol system the positions of the maximum values of the deviations  $\Delta \delta_{\text{H}_2\text{O}}$  are at the same ratio of the components of the binary mixture.

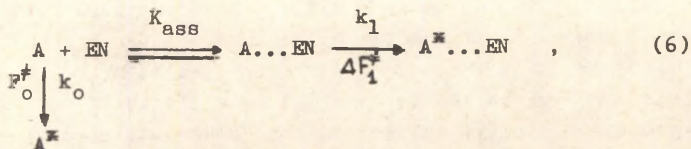
It seems that the main features of the behavior of  $E_T$ -values and logk values for the  $S_N1$  heterolysis of tertiary alkyl- and arylalkyl halides in the above-mentioned binary mixtures can be formally qualitatively accounted for on the basis of the earlier suggested<sup>13-15,20,26,27</sup> scheme. Let us consider the following generalized monomolecular process (chemical reaction, spectral transition):



where A and  $A^{\ddagger}$  refer to the ground (initial) and excited (transition) states of molecule A.

In the absence of the specific solvent-solute interactions the gross solvent effect reduces only to the influence of the nonspecific stabilization of the initial and final states of the transition (5). The intensity of these interactions should be determined by the polarity and polarizability of the solvent<sup>5</sup>.

The influence of the specific solvation<sup>5</sup> of A and  $A^{\ddagger}$  by the generalized addition EN (E and N represent the electrophilic and nucleophilic fragments of the molecule; if E and N are ionized then EN might represent either the ion pair or free ions) could be in the simplest case accounted for by the following scheme, which includes the fast pre-limiting stage complex formation equilibrium between the solute A and solvent molecules (e.g. EN):



where in the case of the solvolysis of alkyl halides the rate constants  $k_0$  and  $k_1$  refer to the monomolecular limiting heterolysis of specifically nonsolvated (A) and complexed with the solvent molecules ( $A \dots EN$ )



moieties,  $K_{\text{ass}}$  - is the association constant between the solute and active molecules of the solvent EN.

Let us denote the stoichiometric concentrations of substrate A and active solvent component EN as  $a_0$  and  $b_0$ , and the current concentration of the solvation complexes as  $c$ . Then  $K_{\text{ass}} = c/(a_0 - c) \cdot (b_0/c)$  and at the excess of EN over A ( $b_0 \gg a_0$ )  $c = K_{\text{ass}} a_0 b_0 / (K_{\text{ass}} b_0 + 1)$  and the current concentration of A equals  $a = (a_0 / K_{\text{ass}} \cdot b_0)$ .

In the case if the transfer (5) represents the chemical reaction then the total observed rate constant  $k_{\text{obs}}$  for the conversion of A and A...EN into products could be written as follows:

$$k_{\text{obs}} = (k_0 + k_1 K_{\text{ass}} b_0) / (1 + K_{\text{ass}} b_0) \quad (7)$$

It could be easily seen that in the framework of scheme (6) the electrophilic catalysis of the monomolecular  $S_N1$  heterolysis of tertiary alkyl- and arylalkyl halides in the mixtures of nonpolar aprotic and dipolar aprotic solvents with electrophiles (alcohols, phenols, carboxylic acids, etc.) reduces to the shift of the solvation equilibrium (7) towards the formation of complexes A...EN (e.g.  $R'Cl \dots HOR$ ) which have higher conversion rates into the reaction products than specifically non-solvated molecules A.

Simple model calculations show that the nature of the dependence of the calculated by Eqn. (7) values of  $k_{\text{obs}}$  on the concentration of EN is determined by the ratio of the rate constants  $k_0$  and  $k_1$  and by the value of the association constant  $K_{\text{ass}}$  of the substrate with molecules of EN. One can see that the sharp catalytic effect with the consecutive plateau-formation is characteristic to high values of  $K_{\text{ass}}$ .

It is evident that in the initial stage of the variation of the concentration of EN in the binary mixture (at moderate or low values of  $K_{\text{ass}}$ ) the solvent effect on  $k_{\text{obs}}$  is characterized by the complex picture of simultaneous action of electrophilic catalysis, shifts of the solvation equilibrium and accompanying variation of the nonspecific sol-

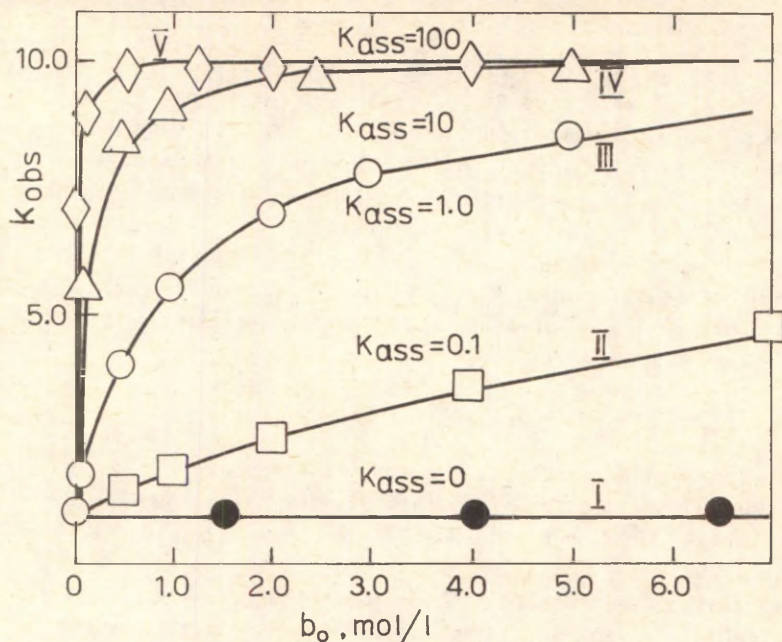


Fig. 5. Model calculations (scheme (6), Eqn.(7)) of the values of  $k_{obs}$  on the variation of the concentration of the "active" component of the solvent EN. Curves I-V refer to the different values of association constants  $K_{ass}$  between A and EN at the fixed values of  $k_o = 1.0$  and  $k_1 = 10$ ;  $a_o \ll b_o$ ;  $a_o = \text{const.}$

vating power (polarity and polarizability of the binary solvent).

In the case of binary mixtures of two similar specifically solvating (with the different intensity) components (e.g. EN and  $EN_1$ ) the above-mentioned situation is further complicated by the resolution of the solute A with the molecules of the more active component of the mixture.

Further, at the fully established positions of the solvation equilibria (high "enough" concentrations of EN or

high values of  $K_{ass}$ ) the observed rate constant  $k_{obs}$  depends mainly\* on the variation of the nonspecific solvent-solute interactions (polarity, polarizability), and on the variation of the intensity of the hydrogen bond in solvation complexes A...BN.

In the case of solvolytic  $S_N1$  reactions in the mixtures of nonpolar aprotic solvent ( $C_6H_6, C_7H_{16}$ , etc.)<sup>13,15,20</sup> with the electrophilic (alcohols) or dipolar aprotic (DMSO,  $PhNO_2$ , MeCN, etc.) component the latter is always characterized with the higher polarity than the former. Because of that, even after the establishment of the solvation equilibrium (7),  $k_{obs}$  values continue to increase somewhat due to the gradual increase of the more polar component of the binary system.

Qualitatively another, more complicated situation is expected for the systems consisting of the more polar (higher dielectric constant) but simultaneously less active specifically solvating component (e.g. DMSO, MeCN, etc.) and of the less polar but highly specifically active (electrophilic) component (e.g. alcohols). In this case after the resolution and establishment of the solvation equilibrium (6) the gradual increase of the concentration of the less polar component (alcohol) starts sometimes to depress to some extent the  $k_{obs}$  value with the increase of the mole fraction of the (more electrophilic and) less polar component of the binary mixture. The additions of the most electrophilic alcohol - methanol which is also the closest by the polarity to the dipolar aprotic solvents do not usually cause the further damping of the  $k_{obs}$  values at  $N_{ROH} \rightarrow 1$ .

For the solvolysis of t-BuCl in the mixtures of nitrobenzene-alcohols the maximum on the plot  $\log k$  vs.  $N_{ROH}$  is observed only for t-BuOH<sup>13</sup> whereas for the system DMSO-ROH<sup>14</sup> the extremum is present for i-PrOH (additions of t-BuOH to DMSO decrease the  $\log k$  at all ratios of the concentration of DMSO and alcohol). The study of the solvolysis of  $PhCMe_2Cl$  in the mixtures of MeCN with ROH<sup>15</sup>, however, shows that the extremums on the  $\log k - N_{ROH}$  plots are observed for all

\* see, however, lower.



alcohols except MeOH.

By analogy with the explaining of some features of the dependence of the rate constants of some heterolytic reactions on the composition and nature of the binary solvent, the primitive scheme (6) could be also used for the analysis of the main trends of the dependence of the spectral transition energies  $E_T$  of the pyridinium-N-phenoxide betaine (1) on the composition and nature of the binary mixture.

In the case if A and E...EN are the molecule which absorbs the quantum of light and its solvation or coordination complex then it follows<sup>27</sup> from scheme (6) that at the frequency  $\nu_i$  the optical density  $D_i(\nu_i)$  of their solution (at the optical path of the light-1 cm) is given by the following expression:

$$D_i(\nu_i) = (\epsilon_A + \epsilon_C K_{ass} b_o) a_o / (1 + K_{ass} \cdot b_o) \quad , \quad (8)$$

where  $\epsilon_A$  and  $\epsilon_C$  are the molar extinction coefficients of A and A...EN and  $a_o \ll b_o$ .

Formulae of that type are widely used<sup>28</sup> for the determination of dissociation constants of the donor-acceptor complexes.

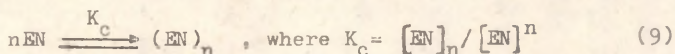
The energy of the transition of the betaine dye (I) and its complexes A...EN into their excited states depend, in the principle, on the solute-solvent interactions which are analogous to those already considered while discussing the dependence of  $\log k$  values of some  $S_N1$  type reactions on the nature and composition of the binary mixture. Therefore, all the above-given considerations should be also valid in this case\*. However, due to the significantly higher sensi-

\* One, naturally, has to keep in mind that the spectral  $\pi \rightarrow \pi^*$  transition (1) is as a mirror image (transfer of the very polar and relatively highly basic ground state into much less polar and definitely less basic excited state) of the solvolysis mechanism of tertiary alkyl- and arylalkyl halides. Therefore, all the major trends in the influence of nonspecific and specific solvent-solute interactions for the spectral transition (1) should be inverted as compared with the situation for the heterolytic  $S_N1$  reactions of tertiary alkyl halides

tivity of the transition (1) towards the solvent effects<sup>5</sup> the range of the observance of solvatochromic solvent effects is much wider than for the solvolytic reactions.

It, however, seems to us that due to the following shortcomings the simplified scheme (6) and derived on that basis equations (7) and (8) are not fit for the quantitative calculation of the influence of the significant variations of the composition and nature of the mixed solvents on the solvolytic processes and spectral transitions discussed in this paper.

So, scheme (6) does not take into account the possibility of the autoassociation of the component EN at the variation of its concentration in the binary system in a wide range:



On the other hand, it is very hard if not impossible task to predict a priori which of the forming autoassociates has the highest catalytic or solvating ability in the solvolytic reactions on spectral transfer of type (1).

At the significant variation of the composition of the binary mixture it also seems necessary somehow to take into account the dependence of the constants  $k_0$ ,  $k_1$ , and  $K_{\text{ass}}$  on the change of the nonspecific solvating power (e.g. polarity and polarizability) of the solvent with its composition.

In the simplest case probably the assumption about the logarithmic dependence of these quantities on the property of the solvent (e.g.,  $1/\epsilon$ ) could be used:

$$\log k_0 = \log k_0^0 + \alpha/\epsilon \quad (10)$$

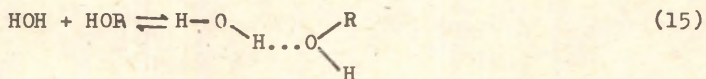
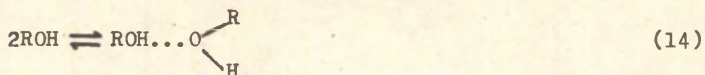
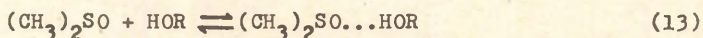
$$\log k_1 = \log k_1^0 + \alpha'/\epsilon \quad (11)$$

$$\log K_{\text{ass}} = \log K_{\text{ass}}^0 + \alpha''/\epsilon, \quad (12)$$

where  $\log k_0^0$ ,  $\log k_1^0$ ,  $\log K_{\text{ass}}^0$ ,  $\alpha$ ,  $\alpha'$ , and  $\alpha''$  are constants, and  $\epsilon$  - the dielectric constant of the mixture.

The scheme (6) used in this work does not take explicitly into account also the possibility of the competitive complex formation (heteroassociation) between the components of the

binary mixture. It is believed that the interactions of the latter type might play a significant<sup>14,15</sup> or even decisive<sup>8</sup> role in the mixtures of electrophilic components (water, alcohols,  $\text{CHCl}_3$  etc.) with the dipolar aprotic solvents in the systems alcohol-alcohol, DMSO-alcohol, alcohol-water, etc.:



It seems reasonable to assume that the heteroassociation equilibria of the latter type (specific solvent - solvent interactions) can significantly change the chemical composition as well as the specific and nonspecific solvating power of the components of the binary mixture.

Our nonempirical quantum-chemical calculations (STO-3G basis) of free molecules and their solvation complexes show that the latter are frequently characterized by the enhanced polarity whereas the dipole moments of these complexes are sometimes higher than the sum of the dipole moments of their separate components. So, one might guess that the stronger interaction between DMSO and alcohols (as compared with the systems MeCN - ROH) is responsible<sup>14,15</sup> for the shifts of the values  $\Delta E_T$  and  $\Delta \log k$  of the maximum deviations from the additivity towards higher mole fractions of the alcohol due to the damping by DMSO of the specific interactions of the alcohol molecules with the solute at the low values of  $N_{\text{ROH}}$ .

One can also see from Fig. 3 and 4 that the maximum absolute values of the deviations from the additivity are for the systems DMSO-ROH also lower than the corresponding values for MeCN-ROH mixtures. The intensity of the interaction of the alcohol molecules with the much less basic<sup>5</sup> molecules of MeCN is significantly lower and therefore the solute-



solvent interactions between betaine dye(I) and alcohol reach their maximum intensity already at relatively low concentrations of the hydroxylic component.

The dependence of logk values of the  $S_N1$  solvolysis of t-BuCl on the composition of mixtures of  $(CF_3)_2CHOH$  with water<sup>29</sup> (logk has a minimum at  $N_{H_2O} \approx 0.7$ ) and variation of logk values of the decomposition of the  $\sigma$ -complexes of 3,5-dinitrobenzene with potassium acetate in aqueous acetone<sup>17</sup> (at  $0.2 \leq N_{H_2O} \leq 0.8$  the shallow maximum of logk was observed) are even not in a qualitative accord with scheme (6). In both cases the ideas about the complex-formation between the components of the binary aqueous solvents, as well as the hypothesis about the destruction of the structure of these binary mixtures by the former processes were used for accounting for the behavior of the experimental data.

For some practical calculations of the solvent effects via multiparameter approach<sup>5</sup> it is of some interest to calculate also the electrophilicity parameter E of the above-mentioned binary systems.

By analogy of Ref. 12 the following equation can be used for this purpose:

$$E = E_T - 25.10 - 14.84(\xi - 1)/(\xi + 2) - 9.59(n_D^2 - 1)/(n_D^2 + 2) \quad (16)$$

Due to the lack of the data on the dielectric constants and refractive indexes of the systems MeCN-ROH we have to limit ourselves only with calculations of four mixtures of hydroxylic components ( $H_2O$ , MeOH, EtOH and t-BuOH) with DMSO ( $\xi$  and  $n_D$  values are taken from Refs. 21, 31, 32; and  $n_D$  values of the system DMSO-n-PrOH were used for i-PrOH-DMSO).

The calculated E-values are displayed in Table 3.

Table 3

Electrophilicity Parameters E of Some Mixtures of  
DMSO with Hydroxylic Solvents

No	E (kcal/mol					
	$N_{ROH}$	H <sub>2</sub> O	MeOH	EtOH	i-PrOH	t-BuOH
1.	0	3.3	3.3	3.3	3.3	3.3
2.	0.1	4.0	5.3	4.7	4.2	4.0
3.	0.2	4.9	7.1	5.9	5.0	4.6
4.	0.3	5.7	8.2	7.0	5.8	5.1
5.	0.4	6.7	9.5	8.1	6.5	5.4
6.	0.5	7.9	10.6	9.1	7.2	5.6
7.	0.6	9.5	11.7	9.8	7.9	5.8
8.	0.7	11.2	12.5	10.6	8.3	5.7
9.	0.8	13.7	13.4	11.1	8.5	5.6
10.	0.9	16.9	14.1	11.6	8.6	5.2
11.	1.0	21.7	14.8	11.3	8.1	4.5

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$E_T$ -PARAMETERS OF SOME BINARY  
MIXTURES OF HYDROXYLIC AND APROTIC  
SOLVENTS

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Dimroth's and Reichardt's  $E_T$  parameters were determined for the following mixtures of two assumedly similar solvents: alcohol-alcohol (MeOH-EtOH and EtOH-t-BuOH), dipolar aprotic solvent-dipolar aprotic solvent (DMSO-MeCN) and apolar aprotic solvent - aprotic solvent ( $C_2H_6$ -pyridine). The dependence of  $E_T$  values in these systems on the mole fraction of one of the components is monotonous (no extremums!), however not always linear. For the comparison, the behavior of the betaine-like dye was also studied in the mixtures of apolar aprotic solvent (benzene) with the protic (methanol) or dipolar aprotic (DMSO, MeCN) solvents.

In the previous work<sup>1</sup> the  $E_T$  parameters of binary mixtures of alcohols with acetonitrile and DMSO were determined. It was found that the dependence of the energy of the long wavelength  $\pi \rightarrow \pi^*$  transition of the pyridinium-N-phenoxide betaine dye on the composition of the solvent mixture is often characterized by the extremums (maximums) on plots  $E_T$  vs.  $N_{ROH}$ .

For some special cases (e.g. the mixtures of t-BuOH with MeCN and DMSO) it was found that the deviations of the

measured quantities from the mole fractional additivity are rather significant. It was suggested that the complex, non-monotonous behavior of these systems is due to the simultaneous influence of the counteracting solvent-solute interactions on the solute.

The solvent effects of two similar solvents (the pairs of aprotic solvents, the pairs of hydroxylic components, etc) on the rates of the various chemical reactions were studied in several works (see, e.g., Refs. 2-4, 6-9 and the book<sup>10</sup> for the additional references).

It was established that most frequently<sup>9</sup> in these cases the linearity between the  $\log k$  value and the mole fraction of one of the components holds (the solvolysis of *t*-BuCl, decomposition of the  $\sigma$ -complex of 3,5-dinitrobenzene with  $\text{KCH}_2\text{COCH}_3$ , the interaction of pyridine with *t*-butyl ester of the hydroperoxide of the formic acid, etc.) .

The influence of the composition and chemical nature of the binary mixtures of this type on the optical characteristics of the solute has been studied much less thoroughly.

So, most probably, the linear dependence of  $\lambda_{\max}$  on the composition of the binary mixture (acetone-DMSO) is present for the decomposition of the above-mentioned  $\sigma$ -complexes of 3,5-dinitromethane (however,  $\lambda_{\max}$  changes only by 4 nm). More clearly expressed linearities were found for the dependencies of  $E_T$  parameters on the composition of the mixtures of trimethylphosphate with tributylphosphate<sup>11</sup> and of 1,2-dibromoethane with 1,2-dibromopropane<sup>12</sup>.

However, in the binary mixtures of two dipolar aprotic components of more different chemical nature (e.g., acetone and trimethylphosphate) such a mole fractional additivity no longer holds.<sup>11</sup>

In the present work the solvent effects of the following binary mixtures of the assumedly similar solvents on the energies of the solvatochromic  $\pi \rightarrow \pi^*$  long-wavelength absorption maximum of pyridinium-*N*-phenoxide betaine were measured: methanol-ethanol, ethanol-*t*-BuOH, DMSO-MeCN and benzene-pyridine. Also the  $E_T$  parameters of the mixtures of apolar aprotic solvent benzene with methanol, DMSO and



acetonitrile were determined for comparison.

The experimental technique and procedures of the purification of solvents were the same as described in our previous papers<sup>1,4,5</sup>. It seems necessary once more to underline the urgent need to exercise the utmost care for the purification of aprotic solvents and handling of them in the atmosphere of dry inert gas (argon, nitrogen). These precautions can be of the decisive importance in the case if both components have the close values of  $E_T$ -s (e.g., DMSO and MeCN). They are even more important in those cases when one deals with the mixtures of the moderately polar but potentially hygroscopic solvent (e.g., pyridine) with an aprotic apolar component (e.g., benzene). In the latter situation even the slightest traces of moisture in the former component can uncontrollably influence even the qualitative picture of the dependence of  $E_T$ -values of the composition of the mixture.

The results of the determinations of  $E_T$ -values<sup>\*</sup> for the binary solvents studied are reported in Tables 1 and 2 and displayed on Figs. 1-3.

### Discussion

In the framework of the earlier suggested<sup>1,4,9,10,14-16</sup> scheme the linear dependence of some characteristic (logk,  $E_T$ , etc.) of the solute  $A_i$  on the mole fraction of one of the components of the binary mixture should be observed primarily in the case of the influence of some single factor (polarity, polarizability, electrophilicity, basicity)<sup>17</sup> which is responsible for the solvent-solute interaction of the medium with  $A_i$ . On the other hand, for the constant mechanism of solvation (the influence of the nonspecific

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\*  $E_T$  values for DMSO and MeCN are slightly lower than those given in our previous paper<sup>1</sup> and in the literature.<sup>12,13</sup>

This can be ascribed to the full-scale use of precautions for the handling of the solvents outlined in the text.

Table 1  
Solvatochromic Shifts of the Maximum of Long-Wavelength Absorption Band of  
Pyridinium-N-Phenoxide Betaine in Binary Mixtures of Alcohol-Alcohol and  
DMSO-MeCN<sup>a</sup>

$N_{MeOH}$	EtOH - MeOH		$N_{EtOH}$	EtOH-t-BuOH		$N_{MeCN}$	DMSO - MeCN	
	$\lambda_{max}$	$E_T$		$\lambda_{max}$	$E_T$		$\lambda_{max}$	$E_T$
0	552	51.8	0	651	43.9	0	638	44.8
0.070	551	51.9	0.079	628	45.5	0.078	636	45.0
0.203	545	52.5	0.154	619	46.2	0.096	636	45.0
0.335	540	52.9	0.289	603	47.4	0.181	635	45.0
0.435	539	53.0	0.420	589	48.5	0.285	633	45.2
0.536	533	53.6	0.470	581	49.2	0.440	634	45.1
0.637	529	54.1	0.613	576	49.6	0.541	632	45.2
0.728	526	54.4	0.870	557	51.3	0.614	631	45.3
0.810	525	54.5	0.937	554	51.6	0.722	632	45.2
0.871	520	54.9	0.968	551	51.9	0.798	632	45.2
0.891	520	55.0	1.00	551	51.9	0.875	632	45.2
0.965	521	54.9				0.965	630	45.4
1.00	516	55.4				0.983	632	45.2
						1.00	630	45.4

a -  $\lambda_{max}$  is given in nanometers,  $E_T$  - in kcal/mol

Table 2  
Solvatochromic Shifts of the Maximum of Long-Wavelength Absorption Band of  
Pyridinium-N-Phenoxide Betaine in Binary Mixtures of Benzene with Pyridine,  
MeCN, DMSO, and MeOH.<sup>a</sup>

C <sub>5</sub> H <sub>5</sub> N			CH <sub>3</sub> CN			DMSO			MeOH		
N C <sub>6</sub> H <sub>6</sub>	$\lambda_{\max}$	$\epsilon_T$	N C <sub>6</sub> H <sub>6</sub>	$\lambda_{\max}$	$\epsilon_T$	N C <sub>6</sub> H <sub>6</sub>	$\lambda_{\max}$	$\epsilon_T$	N C <sub>6</sub> H <sub>6</sub>	$\lambda_{\max}$	$\epsilon_T$
1	2	3	4	5	6	7	8	9	10	11	12
0	707	40.4	0	627	45.6	0	637	44.9	0	517	55.3
0.062	710	40.3	0.037	628	45.5	0.040	636	45.0	0.023	519	55.1
0.071	708	40.4	0.046	628	45.5	0.083	642	44.5	0.048	522	54.8
0.166	712	40.2	0.062	629	45.5	0.091	640	44.7	0.075	527	54.3
0.237	718	39.8	0.127	638	44.8	0.146	642	44.5	0.102	528	54.2
0.347	730	39.2	0.197	643	44.5	0.168	648	44.1	0.133	533	53.6
0.421	735	38.9	0.276	650	44.0	0.201	649	44.1	0.163	536	53.4
0.481	738	38.7	0.371	651	43.9	0.239	649	44.1	0.198	538	53.1
0.530	748	38.2	0.468	660	43.3	0.285	652	43.7	0.225	542	52.8
0.644	760	37.6	0.570	682	41.9	0.351	654	43.7	0.313	550	52.0
0.748	775	36.9	0.692	700	40.8	0.424	661	43.3	0.357	555	51.5
0.849	790	36.2	0.831	732	39.1	0.449	659	43.4	0.459	560	51.1
0.933	810	35.4	1.00	825	34.7	0.553	669	42.7	0.576	569	50.3
1.00	829	34.5				0.655	675	42.4	0.722	582	49.1
						0.784	688	41.6	0.897	612	46.7



Table 2 continued

1	2	3	4	5	6	7	8	9	10	11	12
						0.788	698	41.0	0.947	636	44.9
						0.824	703	40.7	1.00	825	34.7
						0.878	716	39.9			
						0.880	725	39.4			
						0.911	738	38.7			
						0.936	742	38.5			
						0.942	755	37.9			
						0.968	780	36.7			
						1.0	825	34.7			

a - See the footnote to Table 1.

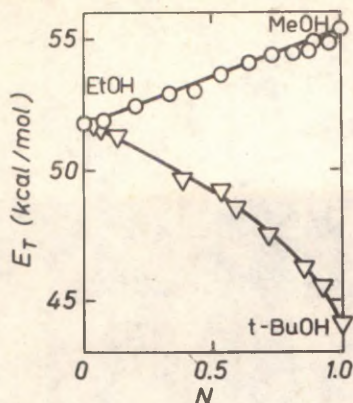


Fig. 1. The dependence of  $E_T$ -values of binary mixtures of ethanol with methanol and t-BuOH on the mole fraction of the one component.

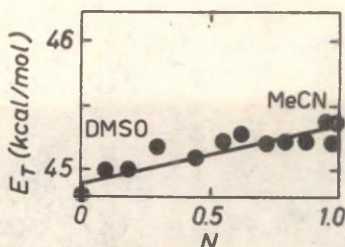


Fig. 2. The dependence of  $E_T$ -values of the binary mixture DMSO-MeCN on  $N_{\text{MeCN}}$ .

solvation only, the parallel simultaneous action of non-specific and specific solvation at the fully established solvation equilibrium between solute  $A_i$  and specifically solvating component of the binary solvent mixture) this situation could be realized<sup>9,10</sup> also for the additive non-homogenous solvent-solute interactions.

One can see from Figs. 1 and 2 that from four binary mixtures consisting of the components of similar nature only in the case of the MeOH-EtOH and DMSO-MeCN systems the linearity of  $E_T$  values on the mole fraction  $N$  holds over the full variation range of the components ratio.

Most probably, for the former system the solvent effect reduces to the additive and parallel influence of the non-specific solvent-solute interactions and over-solvation of the solute by the similar but more electrophilic hydro-

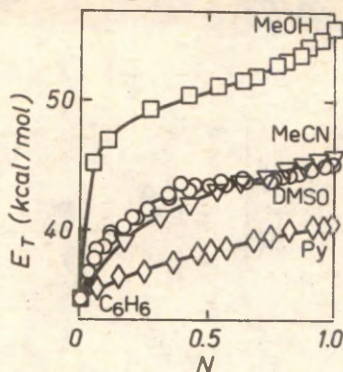
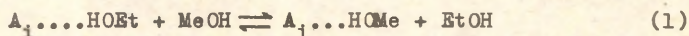


Fig. 3. The dependence of  $E_T$ -values of the binary mixtures of benzene with pyridine ( $\diamond$ ), methanol ( $\square$ ), DMSO ( $\circ$ ), and acetonitrile ( $\nabla$ ).

xylic solvent according to the following scheme:



It is possible that the linear relationship between  $E_T$ -values and the composition ( $N_{\text{MeCN}}$ ) of the mixture of DMSO and MeCN also evidences about the analogous over-solvation of the betaine dye and its complexes with DMSO molecules with the molecules of MeCN while the concentration of the latter increases. At the same time it is somewhat surprising to acknowledge that this preferential over-solvation can be achieved despite the lower dipole moment of the more "active" component ( $\mu_{\text{MeCN}} = 3.45 \text{ D}$ ;  $\mu_{\text{DMSO}} = 3.9 \text{ D}$ ). One has also to keep in mind that the dielectric constant of acetonitrile (37.5)<sup>17</sup> is also lower than that for DMSO (46.4).<sup>17</sup> It could be suggested that the better solvation of the dye by the less polar and lower polarity component acetonitrile is due to the steric characteristics of the solvent molecules which make less bulky MeCN more accessible to the



betaine <sup>\*</sup>.

For the system consisting of somewhat more different hydroxylic compounds - ethanol and t-BuOH - the linearity between  $E_T$ - parameters and  $N_{ROH}$  no longer holds for all ratios of the components. One can see from Fig. 4 that in this case there are already rather modest but statistically reliable deviations  $\Delta E_T$  of  $E_T$  from its additive values (compare with systems DMSO - alcohol<sup>1</sup>) whereas the maximum value of  $\Delta E_T$  (1.3 kcal/mol) corresponds to the excess of the less polar component ( $N_{EtOH} \approx 0.3-0.4$ ).

The deviations from the additivity are even less for the system consisting of benzene and pyridine.

It should be mentioned that unlike the behavior of  $E_T$ -parameters in the latter systems ( t-BuOH-EtOH and  $C_6H_6$ - $-C_5H_5N$ ), the solvent effects of these binary mixtures on the logk of the solvolysis of t-BuCl<sup>2-4,9</sup> are described by the mole fractional additivity.

The observance in the present case of some inhomogeneity of their influence on the  $E_T$  values might be connected either to the significantly higher sensitivity of the  $\pi-\pi^*$  transition of the betaine dye to the excited state towards the solvent properties<sup>17</sup> or caused by some peculiarities of the specific solvation of the betaine dye by the components of the binary mixture (e.g., the steric hindrances to the specific solvation).<sup>+</sup>

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<sup>\*</sup> It is not excluded that the solvation of the highly polar, relatively highly basic and highly polarizable N-phenoxide ion is exercised by two separate channels - via the dipole-dipole association of the type  $N^+ - O^-$  or through  $O^- - S^+$

the direct interaction of dye's basicity center (oxygen atom) with the electrophilicity center (sulfur atom) of the solvent molecule<sup>18</sup>.

<sup>+</sup> Strictly speaking, despite all precautions to eliminate the possible effects of the moisture there is no absolute guarantee that for the mixture of benzene with Py the deviations from the additivity are not partially due to the microtraces of water which could be introduced by the more hygroscopic pyridine solvent (the difference between  $E_T$  values of  $C_6H_6$  and  $H_2O$  amounts to 29 kcal/mol (1)).

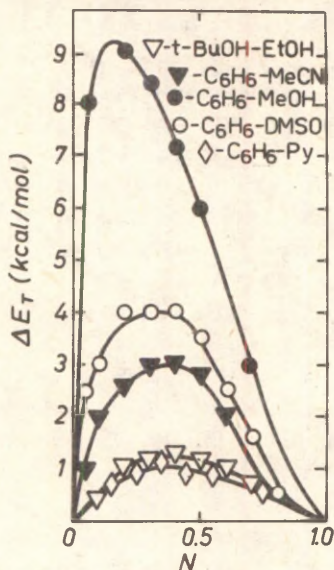


Fig.4. The deviations  $\Delta E_T$  of the  $E_T$ -solvent polarity parameters of some binary mixtures from the values predicted on the basis of their mole fractional additivity.

The behavior of  $E_T$  parameters in the mixtures of methanol, acetonitrile and DMSO with the apolar aprotic solvent benzene is characterized (see Fig. 3) by the nonadditive (nonlinear) dependence of  $E_T$  on the mole fraction of the more "polar" component. Fig. 4 reveals that the deviations from the additivity are more pronounced ( $\Delta E_T = 3-11$  kcal/mol) than for the above-mentioned mixtures of the assumedly similar solvents.

The general pattern and the main trends of the solvent effects of the binary solvents of that type agree qualitatively with the ideas used earlier<sup>4,9,14,16</sup> for the accounting for the dependence of the  $\log k$  values of the heterolytic  $S_N1$  reactions on the composition of the binary solvent. Fig. 5 also demonstrates the rather similar influence of the solvent effects of benzene mixtures with MeOH, MeCN, and DMSO on the  $E_T$  parameters, on one hand, and on  $\log k$  values of the solvolysis of tertiary cumyl chloride, on the other,

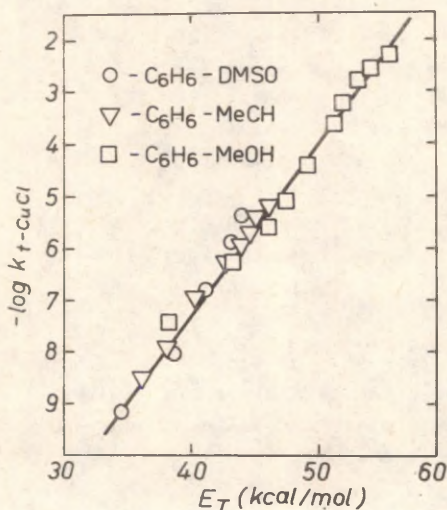


Fig. 5. The relationship between  $\log k$  of the solvolysis of  $\text{PhCMe}_2\text{Cl}$  and  $E_T$ -values for the mixtures of benzene with MeOH, MeCN and DMSO.

The behavior of the three latter systems also fits the scheme used in our previous paper<sup>1</sup> in order to explain the data for the mixtures of alcohols with DMSO and acetonitrile.

The dependence of  $E_T$  values on the composition of the mixture of benzene with dipolar aprotic solvent DMSO deserves an additional comment. So, Fig. 6 shows that the



change of  $E_T$  values in this system is reasonably well characterized by the function of the dielectric constant of the mixture  $(\epsilon - 1)/(\epsilon + 2)$ .

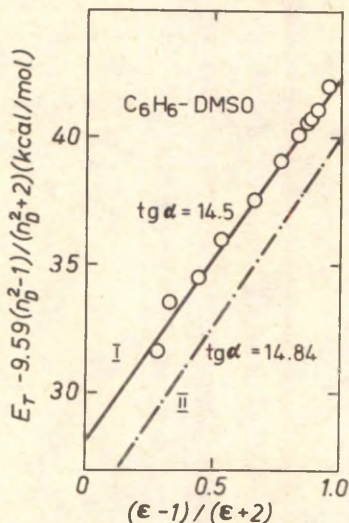


Fig.6. The dependence of the corrected for the polarizability term  $E_T$ -values for the binary mixture of  $C_6H_6$ -DMSO on the dielectric function  $(\epsilon - 1)/(\epsilon + 2)$  (I). The line (II) characterizes the analogous relationship (see Eqn.(2) from the text) for the individual reference solvents.<sup>17,19</sup>

The corresponding straight line has the slope  $(14.5 \pm 0.5)$  which practically coincides with the analogous value suggested<sup>9</sup> earlier for the description of the dependence of  $E_T$  parameters on the polarity and polarizability (see Eqn.(2) of the individual solvents:

$$E_T = 25.1 + 14.84(\epsilon - 1)/(\epsilon + 2) + 9.59(n_D^2 - 1)/(n_D^2 + 2) \quad (2)$$

Taking into account the practically constant contribution of polarizability term  $(9.59 \times (n_D^2 - 1)/(n_D^2 + 2) \approx 2.8$  kcal/mol) into the gross  $E_T$ -values, the intercept of the straight line plot of  $E_T - 2.8$  vs.  $(\epsilon - 1)/(\epsilon + 2)$  becomes equal to 28 kcal/mol. In other words, due to some sort of specific solvent solute interactions (not described by Eqn.

(2)) of approximately the same intensity but different nature the straight line which describes the dependence of  $E_T$  values on the polarity of the present binary system is shifted upwards parallel to the line for the individual media selected for the reference solvents for defining the electrophilicity parameters of solvents.<sup>17, 19</sup>

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A STUDY OF THE KINETICS OF NITROCOMPOUND  
COMPLEXES WITH ACETONE

VIII. Relative Stability of Yanowski Complexes  
of Polynitrodiphenylsulfides

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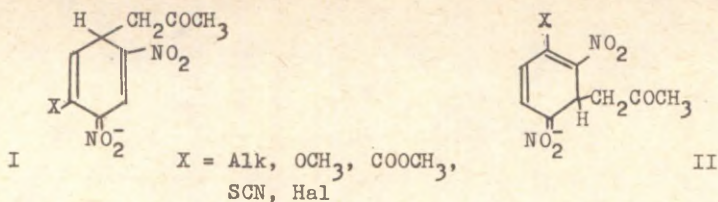
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The decomposition kinetics of polynitro-diphenylsulfide  $\sigma$ -complexes with acetone has been studied in acetone and its mixture with methanol. The rate constants for pseudofirst and first order reactions were determined. The introduction of nitro groups into the thiophenyl substituent increases the stability of  $\sigma$ -complexes(III) more than isomers of type(IV). It was established spectrophotometrically that complex(III<sub>d</sub>) isomerizes into adduct (IV<sub>d</sub>) which is thermodynamically more stable.

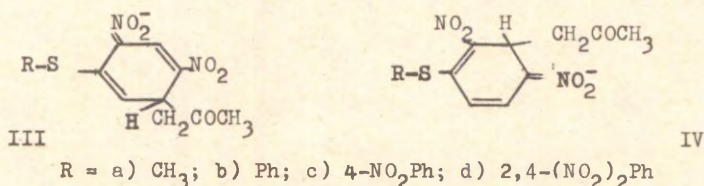
The elaboration of synthesis and separation methods of free form isomeric  $\sigma$ -complexes of Yanowski types (I) and (II) for *m*-dinitrobenzene and its derivatives which contain various substituents makes it possible to study comprehensively their structure and properties.

As a result of the study of the decomposition kinetics of these  $\sigma$ -complexes<sup>1-3</sup> under various conditions it was established that the adducts of type (1) appear to be more stable than those of type (II). The latter are difficult to separate in small quantities in the mixture with a more stable isomer (1). Recently<sup>4</sup> it was shown that 1-X-2,4-di-



nitrobenzenes (X=Salk, SAR) form mostly  $\delta$ -complexes of type (II), their decomposition proceeds more quickly than that of adducts of type (I).

The task of the current work was to study the decomposition kinetics of the Yanowski series of polynitrodiphenylsulfides (III b-d), (IV b-d) and 2,4-dinitrothioanisole (IIIa), (IVa).



The decomposition rate was determined by varying in time optical density in the absorption peaks of the solutions of complexes (III a-d) or (IV a-d) in acetone and acetone-methanol mixtures. The presence of the isosbestic point at 576 nm in the absorption spectrum of the acetone solution of tetranitrodiphenylsulfide  $\delta$ -complexes gives evidence of the isomerization of the less stable adduct (IVd) in the thermodynamically less stable complex (IIIId) (Fig.1). Therefore, the study of the decomposition kinetics of adducts of type (III) was carried out after isomers of type (IV) had been preliminarily fully decomposed.

Earlier it was shown<sup>5,6</sup> that the addition of proton donor solvents (alcohols, water) to acetone considerably quickens the decomposition reaction of Yanowski's  $\delta$ -complexes. At this the value of pseudofirst order rate constant is linearly related to the concentration of ethanol (water) only in a certain interval which is the smaller the higher is the de-

composition rate of the complex. In accordance with this the decomposition of isomers (III) and (IV) was carried out in acetone the content of methanol being from 2 to 15 per cent.

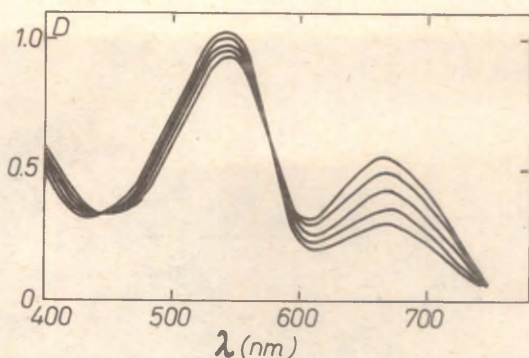


Fig. 1. The time-dependence of electron absorption spectra of the acetone solution of  $\delta$ -complexes of tetranitrodiphenylsulfide.

The arrangement of dependences in the coordinates of the logarithm of the optical density - time indicates that all the experimental points fit the straight lines well. With an increase in methanol concentration the decomposition rates of  $\delta$ -complexes increase linearly (Fig. 2) which enabled us on the basis of the slope angle of straight lines to calculate the second order rate constants for both isomers. For the more stable ones - adducts (IIIc) and (IIId), the experimental determination of decomposition constants appeared to be more complicated in acetone. They were obtained by the extrapolation of linear dependences given in Fig. 2 into the zero value of methanol in acetone (Table). Extrapolation is justified because for all the isomer  $\delta$ -complexes of polynitrodiphenylsulfides a rather good coincidence is observed between the experimentally determined pseudofirst order rate constants in acetone which contains up to 0.2% water and the values obtained from the dependence  $\lg k - C_{CH_3OH}$  (Fig. 2). Besides, such a convergence gives evidence of



the fact that at the low content of proton agents in acetone solution their influence on the decomposition rate of anionic  $\sigma$ -complexes is additive.

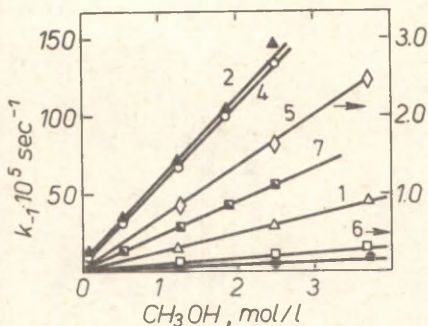


Fig. 2. Dependence of decomposition rate constants of  $\sigma$ -complexes of sulfides: 1-IIIa, 2-IVa, 3-IIId, 4-IVb, 5-Vc, 6-IIId, 7-IVd on methanol concentration in acetone.

As can be seen from the obtained data (Table), with the introduction of the nitro group into the thiophenyl substituent (PhS) the stability of the complexes of types (III) and (IV) enhances. However, if the influence of the electron acceptor substituent R on the stability of adducts of type (IV) is negligible ( $k_{-1}^{\text{IVa}}/k_{-2}^{\text{IVd}} = 4$ ) then for isomers (III) considerable stabilization is observed when passing over from the thioanisole substituent to the dinitrothiophenyl one ( $k_{-1}^{\text{IIIa}}/k_{-1}^{\text{IIId}} = 170$ ). Similar regularities are observed when one compares second order constants. Despite the fact that isomers of type (IVa-c) are formed in the synthesis in rather large quantities (up to 80%), their decomposition proceeds at a higher rate.

The comparison of the values obtained (Table) with the decomposition constant values of the  $\sigma$ -complexes of I-X-2,4-dinitrobenzene<sup>4</sup> testifies to the high decomposition rate of both complexes -(IIIa,b) as well as of type (IVa,b) but for isomers of type (III) this difference is more distinct. On

Table

Decomposition Rate Constants of Isomeric Yanowski's  $\sigma$ -Complexes  
of Types (III) and (IV) in Acetone and its Mixture with Methanol

Substituent R	Struc- ture	$\lambda_{\max}$ nm	$k \cdot 10^5, \text{sec}^{-1}$							$k \cdot 10^5$ l/mol·sec in ace- tone
			in acetone		mixture of methanol (%) with acetone					
			exp	calc	2	5	7,5	10	15	
CH <sub>3</sub>	IIIfa	570	1.37	1.25	—	14.80	—	30.06	48.06	12.50
	IVa	654	10.29	9.95	34.32	71.0	102.8	148.1	—	55.0
Ph	IIIfb	562	0.43	0.47	—	3.45	—	6.27	9.47	3.94
	IVb	660	7.09	7.38	33.01	68.3	98.2	134.2	—	53.33
4 · NO <sub>2</sub> Ph	IIIfc	556	—	0.08	—	0.87	—	1.61	2.48	0.667
	IVc	667	3.99	4.24	20.26	44.89	66.0	85.8	—	35.08
2,4 (NO <sub>2</sub> ) <sub>2</sub> Ph	IIIfd	546	—	0.008	—	0.09	—	0.20	0.32	0.081
	IVd	670	2.54	2.68	15.15	28.42	43.9	55.9	—	23.04

The relative standard deviation according to the data of parallel kinetic experiments is 0.6 - 4.7%.

the other hand, the  $\pi$ -nitrothiophenyl substituent is as to its stabilizing influence in the adducts of type (IIIc) close to the acceptor group  $\text{COOCH}_3$  but the stability of a similar isomer of tetranitrodiphenylsulfide (IIId) is close to the Yanowski complex of symm-trinitrobenzene<sup>1</sup>. At the same time the decomposition of the corresponding addition compounds of acetone-potassium between the nitrogroups (IVc,d) proceeds with rates that are two or three orders higher than those of complexes (IIIc,d).

Since the  $\sigma$ -values for 4- $\text{NO}_2\text{PhS}$  and 2,4- $(\text{NO}_2)_2\text{PhS}$  groups have not been published we checked the interdependence of the logarithms of decomposition rate constants with the  $\sigma$ -constants of nitrogroups of the thioaryl substituent. The analysis carried out showed that higher correlation coefficients ( $r_{\text{III}} = 0.9945$ ,  $r_{\text{IV}} = 0.9978$ ) are observed in the case of the  $\sigma$ -values which characterize the direct polar conjugation of acceptor  $\text{NO}_2$  groups with the electron donor cyclohexadiene ring. As can be seen from the graphs (Fig. 3) the sensitivity coefficient for isomers of type (III) ( $\rho = 0.68$ ) is 3.7 times higher than the one for the complexes of structure (IV,  $\rho = 0.18$ ).

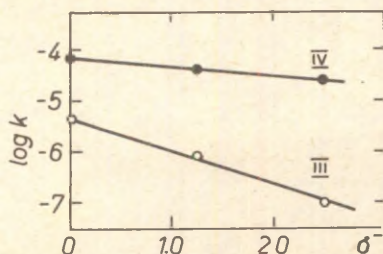


Fig. 3. Dependence of  $\log k$  on the  $\sigma$ -values of the nitrogroups of the substituent.

Thus, in addition to the electron nature of the substituent the stability of the studied products is essentially influenced by the complex structure and how the electron influence on the reaction centre is transmitted.

#### Experimental

$\sigma$ -complexes of polynitrodiphenylsulfides have been obtained in accordance with the methods described in ref. 4.



The structure of the separated products was determined by the methods of NMR, infra-red rays, electron spectroscopy and componential analysis<sup>4</sup>.

Solvents were purified and dried according to the known methods<sup>7</sup>. Their mixtures were prepared by way of mixing the corresponding aliquot amounts.

The study of decomposition kinetics of 6 complexes was carried out in accordance with the methods described earlier<sup>5</sup>. The decomposition rate of adducts of type (III) was measured after the isomers of type (IV) had been preliminarily decomposed. For this purpose the acetone solution of the mixture of complexes was kept for 7-12 hours at room temperature. The electron absorption spectra were recorded on a spectrometer SF-14 in a thermostatically controlled cell at 25<sup>0</sup><sub>±</sub> 0.1<sup>0</sup>C. The kinetic data were processed according to the equation for a first order reaction:  $k\tau = 2.303(\log D_0 - \log D)$ .

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UV - SPECTRA AND ACID - BASE PROPERTIES OF 5-SUBSTITUTED  
2-PYRIMIDINECARBOXYLIC ACIDS HYDRAZIDES

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The method of UV-spectroscopy has been used in order to study the acid-base properties of 5-R-2-pyrimidinecarboxylic acid hydrazides, where  $R = \text{NH}_2$ ,  $\text{CH}_3$ , H, Cl, Br. It was found that in the acid solutions of hydrazides protonation takes place firstly on  $-\text{NH}_2$  group of the hydrazide grouping and then on the heterocyclic nitrogen atom of pyrimidine ring; in the basic solutions - the dissociation of  $-\text{NH}-$  group of the hydrazide grouping occurs. The ionization constants of  $-\text{NH}-$  and  $-\text{NH}_2$  groups of the hydrazide grouping were correlated with substituent constants and the data obtained in the pyrimidine series were compared with those for the analogous series of hydrazides of p-substituted benzoic acids.

Previously<sup>1</sup> we have studied the substituent effect on the proton chemical shifts of aminogroups of 5-substituted 2-pyrimidinecarboxylic acids hydrazides in their <sup>1</sup>H-NMR spectra. In the present work the method of UV-spectroscopy has been used in order to investigate both the acid-base properties of the titled compounds and the influence of substituents on their ionization constants.

The UV-spectra of hydrazides of 5-substituted 2-pyrimidinecarboxylic acids (I) in the neutral aqueous solutions consist of two absorption peaks (Table 1). When the acidity of the solutions of hydrazides is increased in the region of pH=7.0 to 1.0 the shorter wave length absorption band

Table 1

Characteristics of UV-Spectra of 5-Substituted  
2-Pyrimidinecarboxylic Acids Hydrazides (I) and  
their Acid-Base Forms (in Water)

R	I, pH=7.0	I·H <sup>+</sup>	I·2H <sup>+</sup>	I, 1N NaOH
	$\lambda_{\max, \text{nm}}(\lg \epsilon)$	$\lambda_{\max, \text{nm}}(\lg \epsilon)$	$\lambda_{\max, \text{nm}}(\lg \epsilon)$	$\lambda_{\max, \text{nm}}(\lg \epsilon)$
NH <sub>2</sub>	280 (4.20)	288 (4.23)	300 (4.21) 340 (3.97)	280 (4.12)
OH <sub>3</sub> O	248 (4.11) 270 (4.01) <sup>ss</sup>	255 (4.16)	263 (4.13) 295 (4.02)	280 (3.96)
CH <sub>3</sub>	225 (4.04) 250 (3.86) <sup>ss</sup>	230 (4.10)	230 (4.00) 263 (3.91)	285 (3.79)
H	211 (3.84) 245 (3.64)	218 (3.95)	218 (3.93) 253 (3.83)	290 (3.68)
Cl	230 (4.08) 258 (3.84) <sup>ss</sup>	235 (4.12)	245 (4.08) 273 (3.94)	300 (3.83)
Br	240 (4.08) 263 (3.89) <sup>ss</sup>	245 (4.14)	255 (4.05) 285 (3.93)	302 (3.81)

<sup>ss</sup> shoulder;

<sup>ssss</sup> Characteristics of the long wave length absorption band.

undergoes a bathochromic shift and shows hyperchromic effect while the absorption curves form an isosbestic point (Fig. 1a, curves 1,2,3). The analogous changes in these conditions were observed in UV-spectra of hydrazides of para-substituted benzoic acids (II), too <sup>2</sup>.

If the acidity of the aqueous solutions of hydrazides I is further increased a new absorption peak appears in the long wave length region of spectrum (Fig. 1b), which depending on the substituent finally forms at  $H_0 = -2.5 - -6.5$ . The absorption curves of hydrazides of benzoic acids (II) in the analogous conditions undergo an insignificant bathochromic shift



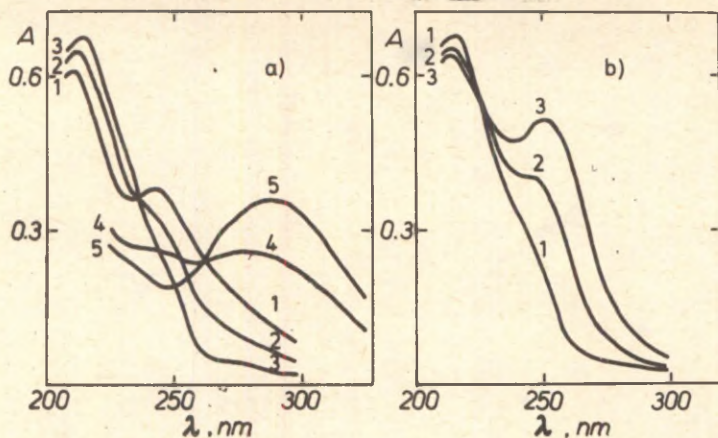


Fig. 1. Absorption spectra of hydrazide of 2-pyrimidine-carboxylic acid in solutions of different acidity,  $c = 7.9 \cdot 10^{-5}$  mol/l. a) pH: 1 - 7.0; 2 - 2.24; 3 - 1.07; 4 - 11.65; 5 - 1N NaOH. b) pH: 1 - 1.07;  $H_0$ : 2 - -1.60; 3 - -4.05.

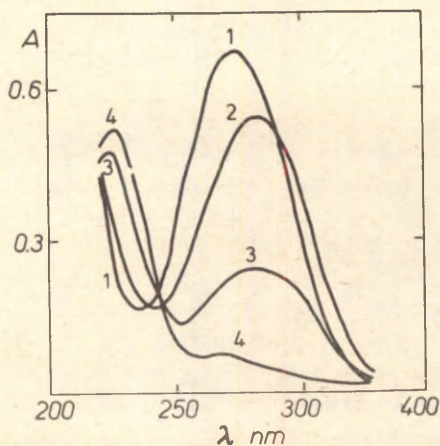
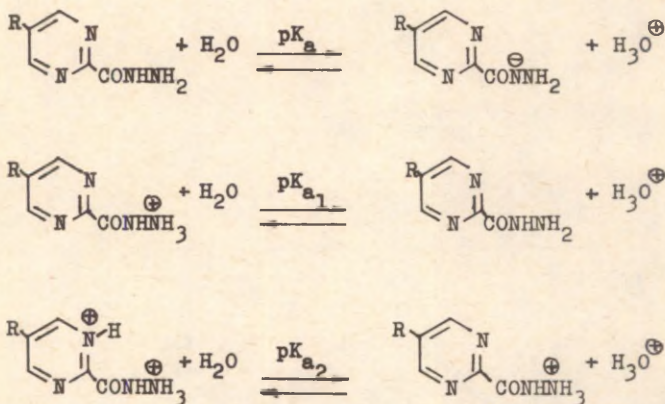


Fig. 2. Absorption spectra of hydrazide of para-aminobenzoic acid,  $c = 5 \cdot 10^{-5}$  mol/l. pH: 1 - 7.0; 2 - 3.05; 3 - 2.11; 4 - 1.07.

caused by changes in the polarity of the solutions.

In the alkaline medium the UV-spectra of hydrazides I show the same changes as those of aromatic hydrazides<sup>2,3</sup> (Fig. 1a, curves 1,4,5).

It can be concluded on the basis of the above results that the changes in the UV-spectra of 2-pyrimidinecarboxylic acid hydrazides are caused by the following acid-base equilibria:



It is necessary to note that the increasing acidity of the solutions of hydrazide of 5-amino-2-pyrimidinecarboxylic acid causes the same changes in its UV-spectra as those of the other hydrazides of this series, i.e. the basicity of the aminogroup in the 5th position of pyrimidine ring is less expressed than that of the primary aminogroup of the hydrazide grouping. The UV-spectra of para-aminobenzoic acid, -hydrazide, presented in Fig. 2, show that the increasing acidity of solutions causes a hypsochromic shift of absorption bands. Obviously it is due to the fact that the proton reacts with the lone pair of electrons of the aminogroup in the para-position of the benzene ring.

It should also be pointed out that the first protonation in the hydrazides of 5-substituted 2-pyrimidinecarboxylic acids (I) takes place on the primary aminogroup of

the hydrazide grouping while in the hydrazides of pyridine-carboxylic acids it occurs on the heterocyclic nitrogen atom of the pyridine ring<sup>4</sup>.

In order to evaluate quantitatively the reactivity of 5-substituted 2-pyrimidinecarboxylic acids hydrazides (I) we have determined their acid ( $pK_a$ ) and basic ( $pK_{a_1}, pK_{a_2}$ ) ionization constants, the values of which are presented in Table 2. Table 2 also presents the values of  $pK_a$  and  $pK_{a_1}$  for the analogous hydrazides of para-substituted benzoic acids.

Table 2

Ionization Constants of Hydrazides of 5-Substituted 2-Pyrimidinecarboxylic (I) and para-Substituted Benzoic Acids (II)

R	$pK_a^P$	$\lambda_{an}^{P}$	$pK_{a_1}^P$	$\lambda_{an}$	$pK_{a_2}^P$	$\lambda_{an}$	$pK_a^B$	$pK_{a_1}^B$
NH <sub>2</sub>	12.60 $\pm$ $\pm 0.05$	245	2.97 $\pm$ $\pm 0.05$	235	-0.03 $\pm$ $\pm 0.06$	340	-	-
CH <sub>3</sub> O	12.08 $\pm$ $\pm 0.04$	247	2.57 $\pm$ $\pm 0.04$	231	-1.75 $\pm$ $\pm 0.06$	295	12.83 $\pm$ $\pm 0.03$	3.25 $\pm$ $\pm 0.03$
CH <sub>3</sub>	11.96 $\pm$ $\pm 0.04$	285	2.56 $\pm$ $\pm 0.03$	270	-0.86 $\pm$ $\pm 0.05$	263	12.75 $\pm$ $\pm 0.03$	3.15 $\pm$ $\pm 0.03$
H	11.65 $\pm$ $\pm 0.02$	290	2.52 $\pm$ $\pm 0.02$	265	-1.41 $\pm$ $\pm 0.06$	253	12.52 $\pm$ $\pm 0.03$	3.05 $\pm$ $\pm 0.03$
Cl	11.40 $\pm$ $\pm 0.03$	300	2.46 $\pm$ $\pm 0.04$	273	-3.57 $\pm$ $\pm 0.06$	273	12.09 $\pm$ $\pm 0.03$	3.02 $\pm$ $\pm 0.03$
Br	11.40 $\pm$ $\pm 0.05$	302	2.39 $\pm$ $\pm 0.04$	280	-3.72 $\pm$ $\pm 0.07$	285	12.15 $\pm$ $\pm 0.05$	3.00 $\pm$ $\pm 0.03$

<sup>P</sup> P - pyrimidine series, B - benzene series;

<sup>P</sup> $\lambda_{an}$  - analytical wave-length, nm;

<sup>3</sup> Refs. 2, 3.

Comparison of the values of  $pK_a$ ,  $pK_{a_1}$  of hydrazides I with the corresponding ionization constants of hydrazides II



shows that the basicity of the primary aminogroup of hydrazides of benzoic acids is greater than that of 2-pyrimidine-carboxylic acid hydrazides, but the acidity of the secondary aminogroup in the benzene series is less expressed than in the pyrimidine series. It might reasonably be expected since the 2-pyrimidinyl group exhibits more expressed electron-attracting properties than the phenyl group<sup>5</sup>.

From the data, presented in Table 2, one can see that the ionization constants of the hydrazides depend on the nature of substituents. For the evaluating the influence of the substituents electronic effects on the  $pK_a$ ,  $pK_{a1}$  values of compounds I and II by the least square method we have calculated parameters of correlation equations (Table 3).

Table 3  
Data of Correlations between  $pK_a$ ,  $pK_{a1}$  of Hydrazides  
I, II and Substituent Constants

Eq.No.	y	$y_o^{\pi}$	$\rho$	$\rho_R^+$	s	r	n	Subst. Const.
1	2	3	4	5	6	7	8	9
1	$pK_a^P$	$11.7 \pm 0.006$	$-1.37 \pm 0.019$	-	0.015	0.998	6	$\sigma^-$
2	$pK_a^P$	$11.84 \pm 0.026$	$-1.77 \pm 0.112$	-	0.063	0.966	6	$\sigma^0$
3	$pK_a^P$	$11.57 \pm 0.025$	$-0.78 \pm 0.04$	-	0.051	0.978	6	$\sigma^+$
4	$pK_a^{P, \pi, \pi}$	$11.698 \pm 0.04$	$-1.22 \pm 0.13$	$-0.31 \pm 0.12$	0.053	0.972	5	$\sigma^0, \sigma_R^+$
5	$pK_{a1}^P$	$2.52 \pm 0.016$	$-0.565 \pm 0.048$	-	0.037	0.940	6	$\sigma^-$
6	$pK_{a1}^P$	$2.576 \pm 0.021$	$-0.705 \pm 0.092$	-	0.052	0.876	6	$\sigma^0$
7	$pK_{a1}^P$	$2.46 \pm 0.021$	$-0.32 \pm 0.033$	-	0.043	0.916	6	$\sigma^+$
8	$pK_{a1}^{P, \pi, \pi}$	$2.56 \pm 0.03$	$-0.69 \pm 0.09$	$-0.39 \pm 0.08$	0.051	0.974	5	$\sigma^0, \sigma_R^+$

1	2	3	4	5	6	7	8	9
9	$pK_a^B$	$12.47 \pm 0.012$	$-1.48 \pm 0.058$	-	0.027	0.992	5	$\sigma^-$
10	$pK_a^B$	$12.58 \pm 0.016$	$-1.63 \pm 0.084$	-	0.034	0.987	5	$\sigma^0$
11	$pK_a^B$	$12.34 \pm 0.051$	$-0.765 \pm 0.132$	-	0.103	0.877	5	$\sigma^+$
12	$pK_a^B$	$12.53 \pm 0.03$	$-1.49 \pm 0.12$	$-0.108 \pm 0.098$	0.045	0.983	5	$\sigma^0, \sigma_R^+$
13	$pK_{a1}^B$	$3.1 \pm 0.009$	$-0.44 \pm 0.05$	-	0.021	0.948	5	$\sigma^-$
14	$pK_{a1}^B$	$3.12 \pm 0.017$	$-0.43 \pm 0.087$	-	0.036	0.842	5	$\sigma^0$
15	$pK_{a1}^B$	$3.05 \pm 0.003$	$-0.268 \pm 0.009$	-	0.007	0.995	5	$\sigma^+$
16	$pK_{a1}^B$	$3.06 \pm 0.01$	$-0.299 \pm 0.03$	$-0.218 \pm 0.03$	0.013	0.985	5	$\sigma^0, \sigma_R^+$

\*  $y_0, \rho, \rho_R^+$  - Coefficients in equations  $y = y_0 + \rho x$  ( $x = \sigma^-$ ,  $\sigma^0$  or  $\sigma^+$ ),  $y = y_0 + \rho \sigma^0 + \rho_R^+ \sigma_R^+$ ;

\*\* Without hydrazide I ( $R = NH_2$ ).

The values of the correlation coefficients  $r$  of equations (1-3, 5-7, 9-11, 13-15) show that  $pK_a^P$ ,  $pK_{a1}^P$  and  $pK_a^B$  correlate better with Hammett  $\sigma^-$  constants than with  $\sigma^0$  or  $\sigma^+$  while  $pK_{a1}^B$  correlate precisely with Brown  $\sigma_R^+$  constants. Thus, it is possible to suppose that in hydrazides I and II between the substituents R and reactionary centers in the hydrazide grouping there exists resonance interaction<sup>6</sup>. In order to evaluate its contribution, we have performed the correlations of ionization constants with  $\sigma^0$ ,  $\sigma_R^+$  substituent constants according to the equation  $y = y_0 + \rho \sigma^0 + \rho_R^+ \sigma_R^+$ . A choice of  $\sigma^0$ ,  $\sigma_R^+$  constants was based on the data<sup>7</sup>.

Comparison of the values  $\rho$  and  $\rho_R^+$  in equations (4,8) and (12,16) indicates that the contribution of polar reso-

nance effect of substituents on the values  $pK_{a1}$  in the hydrazides I, II is larger than that on  $pK_a$ . Besides, the influence of polar resonance effect on  $pK_a^B$  is practically insignificant comparing with the influence of inductive effect ( $\rho_R^+/\rho=0.07$ ). These facts can be explained taking into account the interaction between substituents and reactionary centers in the transition states of the protolytic reactions.

The different importance of polar resonance effect to the values of  $pK_{a1}^P$  and  $pK_{a1}^B$  ( $\rho_R^+/\rho=0.57$  and  $0.73$  for the series I and II, respectively, see eq. 8, 16), is likely to be caused by the different geometry of the hydrazide grouping in compounds I and II, since in the hydrazides of 2-pyrimidinecarboxylic acids (I) the intramolecular hydrogen bond between the hydrogen of  $-NH-$  group of the hydrazide grouping and nitrogen atom of pyrimidine ring can be formed<sup>1</sup>.

## Experimental

Synthesis of hydrazides I was described previously<sup>1</sup>. Parameters of correlation equations were calculated on a computer "Minsk-22" using the programs elaborated by V. Balevicius. The substituent constants were taken:  $\sigma, \sigma^+$  - from<sup>6</sup>;  $\sigma^0, \sigma_R^+$  - from<sup>7</sup>.

Determination of ionization constants. The ionization constants were determined by spectrophotometric ally at a temperature  $25 \pm 0.2^\circ\text{C}$  according to the standard procedure<sup>8</sup>. A spectrophotometer SF-4A and the cells of 1 cm were used. Concentrations of the solutions of hydrazides were approximately  $6 \cdot 10^{-5}$  mol/l. The measurements were carried out at such a wave length ( $\lambda_{an}$ ) where the differences in the absorption of the ionized and nonionized forms of compounds investigated were highest possible.

For the determination of  $pK_a$  the solutions of NaOH, free of carbonates<sup>8</sup>, were used. Concentration of  $\text{OH}^-$  ions was determined by titrating the solutions prepared with the standard solution of hydrochloric acid. The activity coef-



ficients were calculated according to the equation

$\lg f_2 = \frac{0.505 \sqrt{\mu}}{1 + 1.6 \sqrt{\mu}}$ , where  $\mu = 0.5 \sum_{i=1}^n c_i z_i^2$  ( $c$  - concentration of  $\text{Na}^+$  and  $\text{OH}^-$  ions in mol/l,  $z$  - charge of the ions). Concentration of  $\text{H}^+$  ions was calculated according to the formula  $[\text{H}^+] = \frac{K_w}{[\text{OH}^-]}$ , where  $K_w = 1.0 \cdot 10^{-14}$ .

Determination of  $\text{pK}_{a_1}$  was carried out in the buffer solutions of glycine-hydrochloric acid with the constant ionic strength equal to 0.01 maintained with sodium chloride. pH of the solutions was measured with a pH-meter pH-340.

The  $\text{pK}_{a_2}$  determination was carried out using the sulphuric acid solutions of various concentrations, the  $\text{H}_0$  values of which were obtained by interpolation from the values in refs.<sup>9</sup>

The values of ionization constants were calculated from the following equation<sup>8</sup>  $\text{pK}_a = \text{pH} \pm \lg I \pm \lg f_2$ , where  $I$  is the indicator ratio. In the case of  $\text{pK}_{a_2}$  calculations the equation  $\text{pK}_{a_2} = \text{H}_0 + \lg I$  was used. The errors of ionization constants were calculated using Student's criterion 0.95.

Since the tangents of angles of the linear relationships between the  $\lg I$  and pH (or  $\text{H}_0$ ) were equal to a unit or differed from a unit insignificantly (in interval 0.02-0.08 from unit) the corrections of the ionization constants were not made.

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TRANSESTERIFICATION OF ESTERS OF CARBOXYLIC  
ACIDS BY TITANIUM ALKOXIDES

IV. Solvent Effects upon Transesterification  
Kinetics of Butyl Chloroacetate by sec-Butyl  
Orthotitanate

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Transesterification kinetics of butyl chloroacetate by sec-butyl orthotitanate has been examined in 11 solvents as well as in some binary mixtures of these solvents. Activation parameters of the reaction have been determined in carbon tetrachloride, benzene and 2-butanol. A three-parameter equation  $\log k_{II} = \log k_o + s\pi^* + h\sigma_H + eE$  has been found to describe medium effects upon transesterification rate with a satisfactory adequacy.

In the preceding papers of this series<sup>1-3</sup> we have published the results of an examination of substituent and temperature effects upon the transesterification reactivity of esters towards sec-butyl orthotitanate  $Ti(OBu^s)_4$  in heptane. In the present work the transesterification kinetics of butyl chloroacetate by sec-butyl orthotitanate in carbon disulfide, triethylamine, carbon tetrachloride, diethyl ether, tetrahydrofuran, benzene, nitrobenzene, fluorobenzene, 1,2-dichloroethane, chloroform, 2-butanol, and in some binary solvent mixtures, heptane-chloroform and heptane - 2-butanol has been studied as a continuation of a complex examination of transesterification by orthotitanates. Kinetic runs in carbon tetrachloride, benzene and 2-butanol have been carried out in a wide temperature



range and activation parameters of the reaction in these solvents have been determined.

### EXPERIMENTAL

Reagents. The methods of preparation and purification of sec-butyl orthotitanate and determination of its concentration have been reported earlier<sup>1</sup>. Butyl chloroacetate was distilled before the use, its purity being not less than 99% (GLC). The purification and drying of solvents were carried out according to standard procedures<sup>4</sup>. Solvents were stored over 4Å molecular sieves<sup>5</sup>.

Kinetic Runs. The methods of performing kinetic runs, analysis of samples by GLC as well as calculating rate constants have been published elsewhere<sup>1</sup>. A glass column 0.3 x 300 cm (7% fluoro-silicone elastomer SKTFT-100 on a chromaton-N Super) was employed for GLC analysis. Tridecane was used as internal standard.

### RESULTS AND DISCUSSION

We studied the transesterification kinetics of butyl chloroacetate by sec-butyl orthotitanate in 11 solvents and in some their mixtures. The pseudo-first-order conditions were granted by the use of a large (not less than 20-fold) excess of orthotitanate over the ester. The first order rate constants were calculated from the relationship  $\ln \Psi - t$  ( $\Psi$  is the ratio of peak heights of the initial ester and the internal standard;  $t$  is reaction time) by the method of least squares. The first-order rate constants  $k_I$  depend proportionally on the alkoxide concentration in a wide range of its variation. Therefore the kinetic measurements were carried out at 2-3 concentrations of ortho titanate and the second-order rate constants  $k_{II}$  were calculated as follows:

$$k_{II} = k_I / c_{Ti}.$$

The average values of the rate constants for duplicate runs obtained so and their standard deviations are listed in Tables 1 and 4.

Table 1

Rate Constants  $k_{II}$  for the Transesterification  
of Butyl Chloroacetate by sec-Butyl Orthotitanate.

Solvent	t, °C	$10^3(k_{II} \pm s)^+$
1. heptane	25.0	$(8.59 \pm 0.29)^{++}$
2. carbon disulfide	25.0	$3.70 \pm 0.22$
3. triethylamine	25.0	$3.66 \pm 0.36$
4. carbon-tetrachloride	25.0	$3.00 \pm 0.11$
5. diethyl ether	25.0	$2.27 \pm 0.06$
6. tetrahydrofuran	25.0	$1.74 \pm 0.05$
7. benzene	25.0	$1.48 \pm 0.13$
8. nitrobenzene	25.0	$1.30 \pm 0.03$
9. fluorobenzene	25.0	$1.20 \pm 0.07$
10. 1,2-dichloroethane	25.0	$0.767 \pm 0.063$
11. chloroform	25.0	$0.522 \pm 0.019$
12. 2-butanol	25.0	$3.00 \pm 0.31$
13. heptane	0.0	$(2.32 \pm 0.12)^{++}$
14. heptane	55.0	$(30.85 \pm 1.31)^{++}$
15. carbon tetrachloride	0.0	$0.569 \pm 0.020$
16. carbon tetrachloride	55.0	$14.27 \pm 1.60$
17. benzene	14.0	$0.796 \pm 0.012$
18. benzene	40.0	$3.10 \pm 0.37$
19. benzene	55.0	$6.26 \pm 0.11$
20. 2-butanol	0.0	$0.723 \pm 0.061$
21. 2-butanol	55.0	$10.62 \pm 0.91$

<sup>+</sup> Average value  $\pm$  standard deviation; units of  $k_{II}$  are  
l . mole<sup>-1</sup>. s<sup>-1</sup>

<sup>++</sup> Data from our paper<sup>1</sup>

Table 2

Activation Parameters of Transesterification  
of Butyl Chloroacetate by sec-Butyl Orthotitanate<sup>+</sup>

Solvent	log A	E, $\frac{\text{kcal}}{\text{mole}}$	$\Delta H^\ddagger, \frac{\text{kcal}}{\text{mole}}$	$\Delta S^\ddagger, \text{e.u.}$	$\Delta G^\ddagger, \frac{\text{kcal}}{\text{mole}}$
Heptane <sup>++</sup>	4.08 $\pm$ 0.07	8.39 $\pm$ 0.09	7.80	-41.87	20.28
Carbon tetra- chloride	5.08 $\pm$ 0.13	10.40 $\pm$ 0.17	9.81	-37.22	20.91
Benzene	4.00 $\pm$ 0.22	9.33 $\pm$ 0.30	8.74	-42.21	21.32
2-Butanol	3.84 $\pm$ 0.18	8.71 $\pm$ 0.23	8.12	-42.98	20.93

+ The values of log A and E are determined from the Arrhenius relationship by the method of least squares (including all log  $k_{II}$  values for duplicate runs);  $\Delta H^\ddagger$ ,  $\Delta S^\ddagger$  and  $\Delta G^\ddagger$  are calculated from the values of log A and E (at 25°C)

++ Data for the reaction in heptane are from our earlier paper<sup>1</sup>.



In the case of some solvents the kinetic runs were carried out at 3-4 temperatures and on the basis of the obtained constants activation parameters of the reaction were determined. Values of these parameters are available in Table 2.

Statistical treatment of the kinetic data was carried out using a program<sup>2</sup> of multilinear regression analysis written by Prof. V. Palm for the computer Nairi-3. The values of solvent constants for the data treatment are presented in Table 3.

The rate constants of the reaction under discussion are only slightly influenced by solvent (see Table 1): the rate constants for the reaction in heptane and chloroform differ only by 16.5 times. Low sensitivity to the medium effects is also characteristic to some other acyl transfer reactions.<sup>6</sup> It has been established<sup>6</sup>, that the influence of solvent polarity (characterized by the function of the dielectric constant  $\epsilon$ ) on the rates of acyl transfer reactions may be opposite in direction, in spite of the similarity of the mechanisms supposed for these reactions.

A great number of single- and multiple-parameter correlation equations has been suggested for describing the solvent effect on the rates of chemical reactions.<sup>21,22</sup> As the total solvent effect is the result of diverse and complex interactions between reagents and solvent molecules, any single-parametric attitude using only one empirical solvent parameter cannot be universal.<sup>7</sup> Yet in the case of the present reaction a good linearity was obtained in the coordinates  $\log k_{II} - (\nu_o - \nu_s)/\nu_o$ , where  $\nu_o$  is the carbonyl IR frequency of ethyl trifluoroacetate in gas phase and  $\nu_s$  is the corresponding frequency in the solvent (see Fig. 1).  $\Delta \nu / \nu_o$  values have been reported<sup>8</sup> for only 8 solvents which were used in our experiments.  $\log k_{II}$  vs.  $\Delta \nu / \nu_o$  plot of the results is shown in Fig. 1, where it may be seen that only the point for polarizable  $CS_2$  deviates from the relationship.

For several solvents a linearity is also found in the dependence of  $\log k_{II}$  upon G-parameter of Allerhand and

Values of Solvent Constants Used for the Data Treatment

Table 3

Solvent	$\gamma^{(a)}$	$\rho^{(a)}$	$E^{(a)}$	$B^{(a)}$	$A_S^{(b)}$	$B_S^{(b)}$	$\eta^{\star(e)}$	$\sigma_H^{(f)}$	$10^3 \Delta V/\nu_o^{(h)}$	$G^{(j)}$
Heptane	0.1906	0.3164	0	0	0	0	-0.081	7.42	5.4	44
Carbon disulfide	0.2612	0.4520	0	15	0.10	0.38	0.514	10.0	8.2	74
Triethylamine	0.2432	0.3250	0	650	0.08	0.19	0.140	7.45 <sup>(g)</sup>	-	62
Carbon tetrachloride	0.2261	0.3615	0	0	0.09	0.34	0.294	8.58	7.4	69
Diethyl ether	0.3449	0.2932	0	280	0.12	0.34	0.273	7.50 <sup>(g)</sup>	7.2	64
Tetrahydrofuran	0.4049	0.3292	0	287	0.17	0.67	0.576	9.30 <sup>(g)</sup>	-	-
Benzene	0.2306	0.3852	2.1	48	0.15	0.59	0.588	9.15	8.3	80
Nitrobenzene	0.4788	0.4147	0	67	0.29	0.86	1.010	10.4	-	-
Fluorobenzene	0.3733	0.3647	0	38	0.20 <sup>(c)</sup>	0.65 <sup>(c)</sup>	0.622	9.00	-	-
1,2-Dichloroethane	0.4309	0.3524	3.0	40	0.30	0.82	0.807	9.91	9.6 <sup>(i)</sup>	95
Chloroform	0.3587	0.3357	3.28	14	0.42	0.73	0.760	9.24	10.3	106
2-Butanol	0.4540	0.3229	7.4	240	0.59 <sup>(d)</sup>	0.44 <sup>(d)</sup>	0.505	10.8	7.0	-

(a) Ref. 18. (b) - Ref. 11. (c) -  $A_S$  and  $B_S$  values for chlorobenzene<sup>11</sup>. (d) -  $A_S$  and  $B_S$  values for 2-propanol<sup>21</sup>. (e) - Ref. 12. (f) - Hildebrand solubility parameters from Ref. 17. (g) - Ref. 16. (h) - Ref. 8. (i)  $\Delta V/\nu_o$  value for dichloromethane<sup>8</sup>. (j) - Ref. 9.

Schleyer.<sup>9</sup> When including in data treatment these  $\log k_{II}$  values for which the  $G$  values are known (see Table 3), the following equation is obtained (after excluding at the 0.97 confidence level the points for  $CS_2$  and  $Et_2O$ ):

$$\log k_{II} = - (1.18 \pm 0.07) - (0.0201 \pm 0.0007)G$$

$$s = 0.036; s_o = 0.088; R = 0.996.$$

On the basis of separation of specific and nonspecific solute - solvent interactions Koppel and Palm suggested<sup>10</sup> a four-parameter equation:

$$\log k = \log k_o + yY + pP + eE + bB.$$

Here  $k_o$  is the rate constant in the gas phase ;  $Y = (\epsilon - 1)/(2\epsilon + 1)$  and  $P = (n^2 - 1)/(n^2 + 2)$  are used as polarity and polarizability parameters;  $E$  and  $B$  are parameters of general acidity (electrophilicity) and general basicity (nucleophilicity), respectively. Coefficients  $y$ ,  $p$ ,  $e$  and  $b$  describe the susceptibility of  $\log k$  to the respective solute-solvent interaction type.

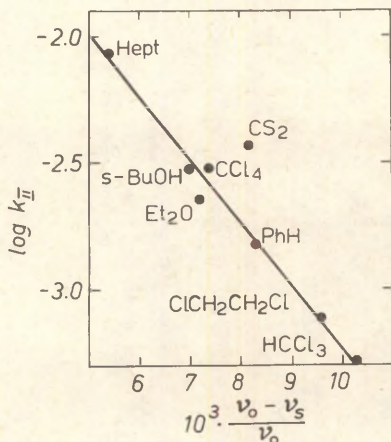


Figure 1. Plot of  $\log k_{II}$  vs.  $(v_o - v_s) / v_o$  for the transesterification of butyl chloroacetate by sec-butyl orthotitanate at 25°C (for the key see text and Table 3).



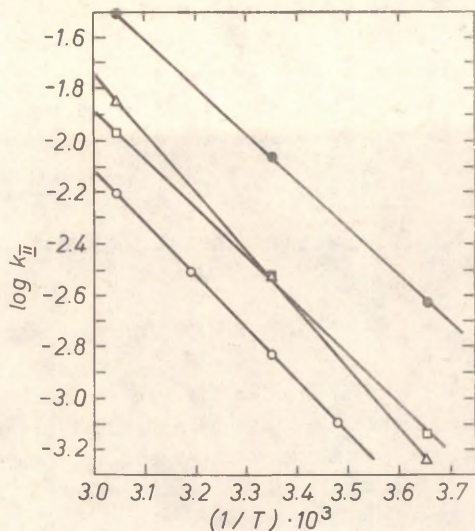


Figure 2. Plots of  $\log k_{II}$  vs.  $1/T$  for the transesterification of butyl chloroacetate by sec-butyl orthotitanate in heptane ●, carbon tetrachloride Δ, benzene ○, and 2-butanol □.

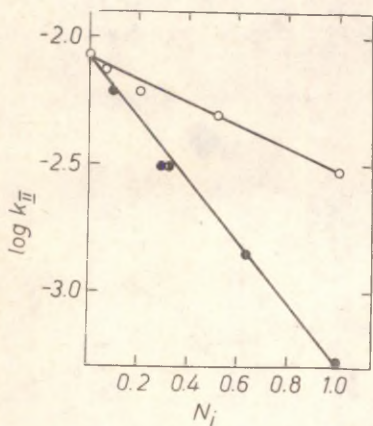


Figure 3. Plots of  $\log k_{II}$  vs. mole fraction  $N_i$  of chloroform ● and 2-butanol ○ in binary mixtures with heptane for the reaction of butyl chloroacetate with sec-butyl orthotitanate at 25°C.

The Koppel-Palm equation has been used for the correlation analysis of medium effects on the rates of acyl-transfer reactions in a few cases only, and usually poor correlations were obtained. E.g., for the reaction of aniline with benzoyl chloride in 12 aprotic solvents the data treatment according to the Koppel-Palm equation leads<sup>10</sup> to the following result:

$$\log k_{II} = -(3.27 \pm 0.49) + (3.70 \pm 1.58)Y + (0.174 \pm 0.086)E + \\ + (0.0164 \pm 0.0046)B$$

The statistical indices  $s\% = 16.3$ ;  $R = 0.903$  represent a rather poor correlation.

In the case of the reaction under discussion, transesterification of butyl chloroacetate by sec-butyl orthotitanate at 25°C, in the course of data treatment according to the Koppel-Palm equation all terms, except polarity, turned out to be statistically insignificant:

$$\log k_{II} = -(2.05 \pm 0.40) - (1.96 \pm 0.86)Y \\ s = 0.28; s_o = 0.89; R = 0.456$$

Low values of statistical indices show that the equation obtained (actually the Kirkwood equation) does not describe the experimental data with the required adequacy and that the addition of P, E and B parameters does not improve the correlation essentially.

The data treatment according to a two-parameter equation proposed recently by Swain et al<sup>11</sup>:

$$\log k = \log k_o + a A_S + b B_S$$

where  $A_S$  and  $B_S$  are parameters, characterizing the solvent ability to solvate anions and cations, respectively, gave also a rather poor correlation. In the course of data treatment the  $aA$  term proved to be statistically insignificant and the significantly deviating point for chloroform was excluded (at the confidence level of 0.95). The obtained equation has bad statistical indices:

$$\log k_{II} = -(2.16 \pm 0.13) - (1.03 \pm 0.13) B_S$$

$$s = 0.112; s_0 = 0.40; R = 0.91$$

Kamlet and Taft proposed<sup>12</sup> a multiple-parameter equation (1) to describe medium effects upon many free energy proportional physico-chemical properties and reactivity of organic compounds:

$$XYZ = XYZ_0 + s(\pi^* + d\sigma) + a\alpha + b\beta \quad (1)$$

In this equation a  $\pi^*$  scale of polarity/polarizability describes the solvent's ability to stabilize a charge or a dipole by virtue of its dielectric effect;  $\sigma$ , a polarizability correction term, is 0.0 for nonchlorinated aliphatic solvents, 0.5 for polychlorinated aliphatics, and 1.0 for aromatic solvents;  $\alpha$  and  $\beta$  are the solvent HBD (hydrogen bond donor) acidity and HBA (hydrogen bond acceptor) basicity parameters, respectively. Since the values of  $\sigma$  are not universal<sup>13</sup> and  $\alpha$  and  $\beta$  values for some solvents used in our study are not yet determined or are known with great statistical uncertainty (e.g.,  $\alpha$  values 0.0<sup>14</sup> and 0.22<sup>15</sup> are reported for chloroform), we could not use equation (1) for data treatment.

Recently Kamlet and Taft proposed<sup>16</sup> a modification of equation (1) to describe solvent effects on free energies of solution:

$$\Delta G_S^0 = (\Delta G_S^0)_0 + s\pi^* + h\sigma_H, \quad (2)$$

where  $\sigma_H$  is the Hildebrand solubility parameter. The employment of equation (2) for data treatment gave the following result (after excluding on the confidence level of 0.99 a significantly deviating point for nitrobenzene):

$$\log k_{II} = -(3.61 \pm 0.36) - (1.72 \pm 0.16)\pi^* + (1.91 \pm 0.38)\sigma_H$$

$$s = 0.088; s_0 = 0.27; R = 0.964$$

As it was suggested by the authors<sup>16</sup> of equation (2), in some cases where solute-solvent hydrogen bonding effects are also applied, the involvement of acidity and basicity



terms in equation (2) may be necessary. For the reasons cited above we could not use the  $\alpha$  and  $\beta$  scales in such an equation. Instead of these scales we used the parameters of general acidity and general basicity of Koppel and Palm (E and B, respectively). During the data treatment the basicity term turned out to be statistically insignificant and the following equation was obtained (after excluding the point for nitrobenzene):

$$\log k_{II} = -(4.14 \pm 0.25) - (1.79 \pm 0.09) \pi^* + (0.26 \pm 0.03) \sigma_H - (0.039 \pm 0.009) E \quad (3)$$

$$s = 0.050; s_0 = 0.129; R = 0.988$$

In the light of the uncertainties in the experimental determinations of the  $\sigma_H$  values which are evidenced by the spread of published values<sup>16</sup>, the obtained equation (3) must be regarded as having quite satisfactory adequacy. The deviation of the nitrobenzene point from the hyperplane described by equation (3) ( $\log k_{\text{exp}} - \log k_{\text{calc.}} = -0.36$ ) may be just caused by the improper  $\sigma_H$  value for nitrobenzene. E.g., the use of the  $\sigma_H$  value for this solvent from the publication of Dack<sup>19</sup> ( $\sigma_H = 12.6$ , recalculated from the value  $\sigma_H^2 = 159$ ) leads to the deviation of the nitrobenzene point to the opposite direction from the hyperplane (3) ( $\log k_{\text{exp.}} - \log k_{\text{calc.}} = +0.21$ ).

When all the 21 values of  $\log k_{II}$  at various temperatures listed in Table 1 were included in the data treatment, the additive model was used (cross terms, represented by the products of solvent constants with  $1000/T$  were not included), which presumes isoenthalpicity by every solvent parameter:

$$\log k_{II} = \log k_0 + s \pi^* + h \sigma_H + eE + bB + t.1000/T$$

After excluding at the confidence level of 0.99 significantly deviating points for nitrobenzene and carbon tetrachloride at 0°C, the following correlation was obtained:

$$\log k_{II} = (2.49 \pm 0.32) - (1.71 \pm 0.07) \pi^* + (0.243 \pm 0.025) \sigma_H - (0.039 \pm 0.008) E - (1.94 \pm 0.07) 1000/T$$

$$s = 0.050; s_0 = 0.108; R = 0.994$$

Although the obtained equation has good statistical indices, the isoenthalpicity by all parameters is uncertain. As it may be seen from the values of activation parameters listed in Table 2 (see also Fig. 2), the reaction under discussion has no equal activation energies in these four solvents where they were determined.

The  $\log k_{II}$  values in some binary solvent mixtures heptane-chloroform and heptane-2-butanol are given in Table 4. Fig. 3 visualizes the approximate linearity in the relationship between  $\log k_{II}$  and  $N_1$  ( $N_1$  is the mole fraction of the solvent added to heptane in binary mixtures). Koppel and Palm have established<sup>23</sup> that the linear dependence of  $\log k$  on the composition of solvent mixture indicates that no shifts in solvent-solute interaction equilibria takes place. In the case of the process under discussion the obtained result is somewhat unexpected. It is known from the data on IR spectra<sup>8</sup> that esters (ethyl acetate, ethyl trichloroacetate, ethyl trifluoroacetate) form hydrogen-bonded complexes with chloroform as well as with 2-butanol. The published<sup>24</sup> value of association constant  $K$  between ethyl acetate and chloroform in cyclohexane is :

$$K_{28^\circ\text{C}} = \frac{[\text{EtOAc} \dots \text{HCCl}_3]}{[\text{EtOAc}] \cdot [\text{HCCl}_3]} = 0.674 \pm 0.025$$

In chloroform to such a value of  $K$  corresponds the following ratio of concentrations of free and associated with chloroform ethyl acetate (presuming that  $K$  in chloroform does not differ from its value in cyclohexane):

$$[\text{EtOAc}] / [\text{EtOAc} \dots \text{HCCl}_3] = 1/(12.5 \cdot 0.67) = 0.12$$

Taking into consideration the smaller basicity of butyl chloroacetate if compared to ethyl acetate, the fraction of free butyl chloroacetate in chloroform must be even greater. It means that in the solvent mixture heptane-chloroform a shift of the solvation equilibria takes place and the linearity of the coordinates  $\log k_{II} - N_1$  is not expected.

Table 4

Rate Constants  $k_{II}$  for the Transesterification of  
Butyl Chloroacetate in Binary Solvent Mixtures  
Chloroform-Heptane and 2-Butanol-Heptane at 25°C.

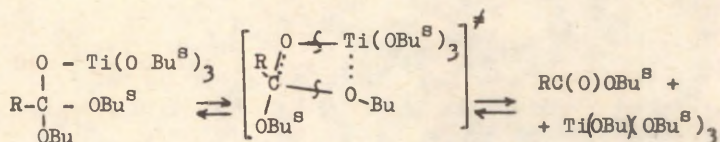
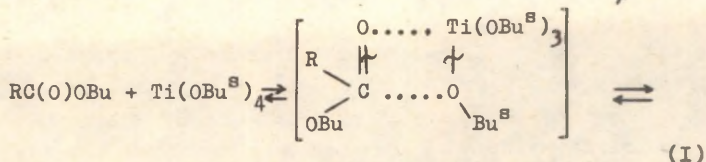
Medium <sup>+</sup>		$10^3(k_{II} \pm s)^{++}$	Medium <sup>+</sup>		$10^3(k_{II} \pm s)^{++}$
0.0901	(1)	$6.06 \pm 0.38$	0.0666	(2)	$7.39 \pm 0.30$
0.288	(1)	$3.14 \pm 0.09$	0.199	(2)	$6.14 \pm 0.20$
0.313	(1)	$3.13 \pm 0.13$	0.510	(2)	$4.96 \pm 0.34$
0.633	(1)	$1.39 \pm 0.06$			

<sup>+</sup> Mole fraction of : (1) - chloroform, (2) - 2-butanol  
in the binary mixture with heptane.

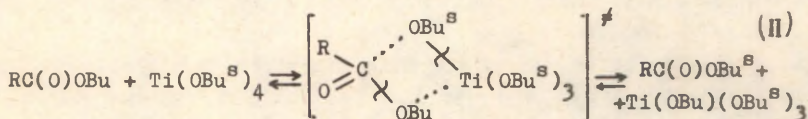
<sup>++</sup> Average value  $\pm$  standard deviation; units of  $k_{II}$  are  
l . mole . s<sup>-1</sup>



In an earlier paper of this series<sup>3</sup> the mechanism of the reaction was discussed. Of the two alternative schemes the first includes the coordination of carbonyl oxygen by titanium and leads to the tetrahedral intermediate<sup>+</sup>:



On the other hand, a concerted mechanism without a formation of the tetrahedral intermediate is also likely:



Although the first scheme requires the direct participation of the carbon oxygen in the formation of the transition state, the direction of the influence of electrophilic solvation is difficult to foresee. The electrophilic solvation on the one hand reduces the electron density on the carbonyl carbon, so increasing the electrophilicity of the ester. On the other hand, the solvation acts against forming of the bond between carbonyl oxygen and titanium, so decreasing the reaction rate.

\* In this scheme the dotted lines stand for the forming bonds and the crossed out lines for the breaking bonds (when proceeding from reagents towards products).

If we presume that the reaction proceeds according to the second scheme (II), only the first of these phenomena, i.e. the increase of electron deficiency on carbonyl carbon, is expected (in the case of both schemes the electrophilic solvation of the other reagent, sec-butyl orthotitanate probably leads the fall of reaction rate).

A comparison of  $k_{II}$  values listed in Table 1 shows that electrophilic solvation does not have a strong influence on rate constants. The negative sign before  $eE$  term in equation (3) indicates that such a solvation restrains the reaction<sup>+</sup>.

In spite of the growing interest in the examination of nucleophilic displacement reactions of esters in aprotic solvents, their mechanism has not been univocally established yet. Majority of the limited kinetic data on these reactions published in literature concerns the aminolysis reaction.<sup>25-26</sup> The reaction of acetate ion (potassium acetate + 18-crown-6) with esters in apolar and dipolar aprotic solvents has also been under examination.<sup>29-31</sup> The results obtained show that the employment of aprotic solvents instead of aqueous ones leads to drastic changes not only in reaction rates but even in their mechanisms.

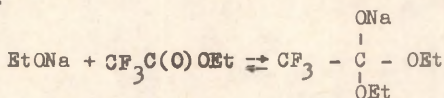
Transesterification by titanium alkoxides is differing from these two types of reactions. The nucleophilic reagent in transesterification reaction, sec-butyl orthotitanate, is electroneutral in contrast to the charged acetate ion. The drastic differences in the values of activation entropies for the reaction of acetate ion with 2,4-dinitrophenyl acetate<sup>29</sup> in acetonitrile ( $\Delta S^\ddagger = +9.32$  entr.un.) and benzene ( $\Delta S^\ddagger = +19.4$  entr.un.) on the other hand, and for transesterification of butyl chloroacetate by sec-butyl orthotitanate on the other hand indicate that these reactions probably have different mechanisms.

Titanium alkoxides are also substantially different from the primary and secondary amines, the nucleophilic reagents

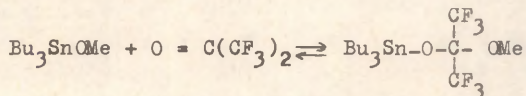
\* As the other parameters in equation (3) have a complex character (e.g.<sup>10</sup>,  $\sigma_H = (0.68 \pm 1.04) + (5.92 \pm 2.25)Y + (21.91 \pm 4.40)P + (0.507 \pm 0.052)E$ ;  $s\% = 5.3$ ;  $R = 0.946$ ), we cannot declare it with a full firmness.

in aminolysis reactions, as the former<sup>8</sup> contain no hydrogen atom connected with nucleophilic center. But it is just the proton transfer that determines the energetics in aminolysis reactions.<sup>26,32</sup>

A well-known feature of carbonyl and carboxyl compounds is their ability to form tetrahedrol addition compounds with nucleophilic reagents. Such compounds are also known for metal alkoxides. E.g., in the case of sodium ethoxide the following equilibrium is shifted far to the right<sup>33</sup> in di-  
butyl ether:



It has also been established that tin alkoxides (the polarity of the tin-oxygen bond is slightly different from the polarity of the corresponding bond in titanium alkoxide) readily add to aldehydes and ketones<sup>34</sup>:



In the case of this reaction, in all probability, simultaneously with the nucleophilic attack of the oxygen atom of alkoxide on carbonyl carbon goes the electrophilic attack of tin on carbonyl oxygen<sup>34</sup>. Such kind of mechanism reminds the mechanisms of addition reactions of magnesium<sup>35</sup> and aluminiumorganic<sup>36</sup> compounds with ketones. From this aspect the first scheme (I) for transesterification by titanium alkoxides seems quite reasonable: in connection with the symmetrical character of the reaction, the formation of an instable tetrahedral intermediate in the result of the nucleophilic addition of alkoxide to an ester certainly, with some velocity, leads to the products of the reaction. The first scheme (I) is also in accordance with the restraining effect of electrophilic solvation of carbonyl oxygen, as it hinders bond making between titanium and carbonyl



oxygen<sup>+</sup>.

Although according to the Hammond postulate<sup>37</sup>, that requires the similarity of the structures of activated complex and not stable tetrahedral intermediate, such a mechanism(I) is in disaccord with the small difference in the energies of resonance stabilization between the initial and activated states obtained for the transesterification of butyl benzoate in heptane ( $E^\ddagger = 3.0$  kcal/mole) if compared with the resonance energy between phenyl and carbonyl groups (7-11 kcal/mole<sup>38</sup>); the low value of the resonance stabilization is in good keeping with a low degree of the carbonyl double bond alternation in the transition state in the case of some acyl transfer reactions. It is worth mentioning that such contradictions with the Hammond postulate are quite typical<sup>39</sup> of concerted reaction mechanisms where a simultaneous change in the degree of several bonds takes place.

On the other hand, the data on transesterification reaction obtained in our works (values of  $\rho^\ddagger$  and  $\delta$  in the case of the variation of the acyl portion of an ester<sup>3</sup>, activation parameters,  $\Delta E^\ddagger_\psi$ , solvent effects) are also in accordance with the second scheme of the reaction. There certainly, is a possibility that the alternative schemes (I) and (II) are parallel to one another and their relative importance depends on the character of reagents and reaction conditions (solvent, temperature)<sup>40</sup>.

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+

The low value of this effect can be explained by the fact, that even in the case of a substantial decrease in ester's reactivity due to its electrophilic solvation, it cannot lead to a greater fall in the reaction rate than is the decrease in the fraction of free ester. But the calculations cited above show that the fraction of free ester in the solvents used in our experiments is quite substantial.

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