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Errata

In the paper of V.A. Ignatov, R.A. Akchurina, and N.M. Romm, this journal, 11, 53 (1974):

		printid:	change for:
p. 57. Table 1,	Column 5	Hammet	Hammett
	Column 7	kcal/mol	1/mol.min
	Column 8	ccal/m	kcal/mol

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Kinetics of Reaction of Tetranitromethane with 1,1-Dianisylethylene

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Kinetics of the reaction of tetranitromethane with dianisylethylene was investigated in different solvents. First there were received the thermodynamical characteristics of the CTC, formed in the primary act of the reaction of TNM with dianizylethylene. Spectrophotometrical investigations of kinetics showed that CTC lies on the co-ordinate of the reaction. Obtained data on the thermodynamics of the limiting stage enabled us to specify the reaction mechanism. Study of the influence of the solvent on the reaction rate constant enabled us to estimate the dipole moments of the reaction complex in different solvents. According to thermodynamical data and dipole moments of the reaction complex structural models of the transition state were suggested.

The recent years special attention has been paid to the study of the mechanism of the reaction of TNM with alkanes.[1-8] But no detailed quantitative investigations of the kinetics of the reactions were undertaken.

The aim of this work is to investigate the properties of the CTC, which are, to everybody's opinion, pre-reactional ones, and to study the kinetics of this reaction using the idea of the influence of the solvent on the rate constant[9] for getting information about transition state. The well-studied reaction of TNM with dianizylethylene[10] yielding about 95% of nitroalkane was chosen for this purpose.

The investigations, taken earlier, showed that in this case, as well as in all other cases[11], the first stage of the reaction was the formation of the CTC.

The well-known half-life (τ) determination method was used to determine the reaction order. Experimental data obtained (Table 1) enabled us to state that the investigated reaction had the order close to 2 in all solvents.

Table 1. Data of the Half-life

Solvent	Heptane	CCl_4	$Cl_2C{=}CCl_2$	$Cl_2CH{-}CHCl_2$	CH_3NO_2
C_1/C_o	5	5	5	5	5
	4.83	4.91	4.87	4.81	4.79

Time-dependence of electron spectra was studied for proving the supposition about proceeding of the reaction through the CTC stage (Fig.1). Distinct isobestical point (IP) is seen in the spectra, but reduction of the optical hardness while $\lambda > \lambda_{I.P.}$ occurs due the decrease in the CTC concentration, and its growth ($\lambda < \lambda_{I.P.}$) due to the formation of the final product, viz. nitroalkane. Presence of IP in all solvents is the prove of proceeding of the reaction through the CTC stage.

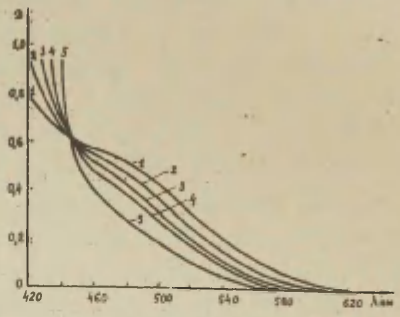

Fig. 1. Dependence of the electron absorption spectra on time.

Carried investigations enabled to suggest the following formal pattern of the proceeding of the reaction:

$$AC + DN \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} CTC \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \Pi^{\neq} \xrightarrow{k_3} NA + CD \qquad (1)$$

with AC as acceptor; DN as donor (alken), $\Pi^{\neq}$ as transitional stage; CD as nitroalkene, NA as nitrophorm, k_1; k_{-1}; k_2; k_{-2}; k_3 as proper rate constants of the elementary stages of the reactions.

The rate equation for the suggested pattern is as follows:

$$\frac{d\,(CD)}{dt} = \frac{k_1}{k_{-1}} \cdot \frac{k_2 \cdot k_3}{k_{-2}+k_3 \cdot \Pi^{\neq}} \cdot AC \cdot DN \cdot \Pi^{\neq} \qquad (2)$$

Having indicated $k \cdot k_2$ as k_c, with $k = k_1/k_{-1}$, and taking into account that k_1, $k_{-1} \gg k_2$ and $k_2 \ll k_3$, and DN << AC, we shall get finally:

$$\frac{d\,(CD)}{dt} = k_u^1 \cdot DN, \text{ where } k_u^1 = k_2 \cdot k \cdot AC \qquad (3)$$

Wit the help of Eq.(3) the processing of the experimental data on the kinetics of the reaction was carried out. The lgk_u and lgk values, and the values of the dielectric coefficient (ε) are given in Table 2.

Table 2. Logarythms of the Rate Constants and Thermodynamical Data of the TNM-DN Complex in Different Solvents

Solvent	$\frac{\varepsilon-1}{\varepsilon+2}$	$-lgk_u$		$-lgk$		$-\Delta H$	ΔF	$-\Delta S\ 10^5$.	Δk
		30°C	20°C	20°C	30°C				
heptane	0.235	3.11	3.63	0.76	0.79	0.8	1.0	6.1	0.92
CCl_4	0.292	3.10	3.32	0.82	0.85	1.2	1.1	7.8	1.1
$Cl_2C{=}CCl_2$	0.302	3.08	3.20	0.88	0.92	1.2	1.2	8.2	1.5
Cl_2CH-$CHCl_2$	0.702	2.66	2.95	1.21	1.23	1.1	1.6	9.2	4.2
$ClCH_2$-CH_2Cl	0.757	2.46	2.81	1.52	1.48[x]	1.1	2.2	11	5.6
CH_3NO_2	0.926	1.57	2.10	2.21	2.19[x]	0.8	3.0	13	29

Δk is the mean-square error (11-13 points) x t 10°C. Eq.(3) shows that the experimental constant k_u^1 is the product of the equilibrium constant k and true constant k_2 of the rate of transformation of the CTC into the reactionary complex. So, thermodynamical parameters of the complex in different solvents were determined by methods described earlier.[13] (Table 2). It should be noted that changes in the ln k_u and lnk values are close to each other in their absolute size. Really, vivid correlation is seen between these figures, R=0.98; S=0.20, with the slope being close to 1 (Fig. 2). Obtained correlation not only proves the conclusion about proceeding of the reaction through the CTC stage, made earlier, but enables us to predict practically alternation of the rate of the given reaction with the change of the solvent when knowing the corresponding values of the complex association constants. Data, given in Table 2, enable us to calculate both the rate constant k_2 and thermodynamical parameters of the limiting step. Data given in Table 3 show that the solvents, according to the type of their influence, may be conditionally divided into two groups: 1) heptane and nitromethane, 2) chlorine derivatives.

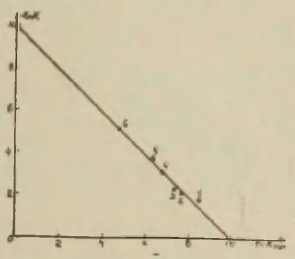

Fig. 2. Correlational relationship between the lg k_u and lg k. 1=C_7H_{16}; 2=CCl_4; 3=$Cl_2C{=}CCl_2$; 4=$Cl_2CHCHCl_2$;

5=$ClCH_2CH_2Cl$; 6=CH_3NO_2.

The first group is characterized by little positive alternation of entropy, in the second one considerably greater and positive in sign S is noted. So, the limiting step of the electrophilic substitution-addition cannot pass through spatially equal transitional states. S for chlorine derivatives can be explained by the specifical interaction of formed CTC and the molecule of the solvent. Little alternation of entropy in the transition state, characteristic of heptane and nitromethane, shows that given solvents do not interact specifically with the reaction complex.

Table 3. Thermodynamical Parameters of the Activation of the Reaction of TNM-DN and Electrical Characteristics of Transition State

Solvent	-ln k_2		$\Delta H^{\neq}$	$-T^{\neq}\Delta S$	$\Delta F^{\neq}$	lnA	μ_t' [δ]	Q_r
	20°C	30°C						
gepthane	6.58	5.35	21.4	-0.5	20.9	31.3	12	0.60
CCl_4	8.09	7.50	9.5	12.2	21.7	9.3	11	0.55
$Cl_2C{=}CCl_2$	7.62	6.84	5.8	15.6	21.4	3.4	11	0.55
$Cl_2CHCHCl_2$	6.19	5.57	10.0	10.6	20.6	12.0	12	0.60
$ClCH_2CH_2Cl$	5.53	6.41	13.9	6.4	20.3	16.7	12	0.60
CH_3NO_2	-0.27	1.07[a]	20.8	-3.8	17.0	37.0	15	0.80

a) t=10°C; b) in calculations according to Eq.(7) the ' value was taken equal to o.6; alternations of this parameter in the limits of 20% causes the alternation of in the limits of 10%.

Now we shall turn, to the examination of the connection between the activation parameters (relative error of their determination is 10-20%) and the macrocharacteristics of the solvents. Thus, definite correlation (R=0.95;S=0.097) is observed between the function of the dielectric coeffi-

cient and the rate constants. Fig. 3 shows that difference in the character of the influence of the two groups of the solvents on the thermodynamics of the limiting step, noted earlier, is distinctly held here. Really, the points are rallying about two independent lines; this proves different proceedings of the reaction in above-mentioned solvents. The fact of crossing of the lines in the point on the co-ordinate axis attracts attention to itself.

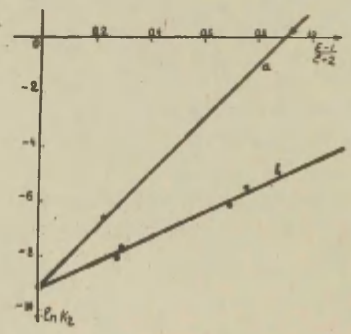

Fig. 3. Dependence of ln k_2 on $(\varepsilon-1)/(\varepsilon+2)$ at 20°C

a) heptane - nitromethane; b) chlorine derivatives - alkanes.

Interconnection given higher enables us, in principle, to get information on the dipole moment of the reaction complex, using the expression given in earlier papers.[9,14]

$$\ln k_x = \frac{1}{K \cdot T} \cdot \left(\frac{\mu_{\neq}^2}{a_{\neq}^3} - \frac{\mu_{CTC}^2}{a_{CTC}^3} \right) \cdot \frac{\varepsilon_x - 1}{\varepsilon_x + 2} + \text{const} \qquad (4)$$

where k_x is the rate constant in the solvent x; $\mu_{\neq}$, μ_{CTC}, $a_{\neq}$, a_{CTC} are the dipole moments and Onzager's radii of the reaction and pre-reaction complexes.

Correlation (4) is obtained for the case when the complex is in thermodynamical balance with the environment. Really, the process of reconstruction of the basic state into the transition one, accompanied by breaking off other connections, takes considerably more time than the orientations relaxation of the molecules of the solvent; so, the reaction may be regorded as that in the case of the balance.[9,14] The dipole moment of the transition state was estimated with the help of Eq.(4). The value of μ_{CTC}, necessary for the calculations and equal to 5.8 D, was determined with the help of the method used earlier.[13] For heptane-nitromethane (when molecule of the solvent does not interfere in the reaction complex) $a_{\neq} \approx a_{CTC}$. In this case the dipole moment of the transition state, calculated for the gas phase, will be ~ 11 D. Estimation of this figure for the reaction of chlorine derivatives needs taking into account the alteration of the Onzager's radius of the reaction complex. Having assumed that the latter interacts with one molecule of the solvent only, we estimated $a^3_{\neq}$ by the following

$$a^3_{\neq} = a^3_{CTC} + r^3_{sol} \qquad (5)$$

where r is the structural radius of the molecule of the solvent. The calculations showed that in this case the dipole moment of the reaction complex, $\mu_{\neq}$, is in the range of 9.1-9.3D. It was noted before that obtained values of the dipole moment were referred to the gas phase, still it is known[15] that the dipole moment in the liquid, μ', may differ greatly from μ. According to the ideas of the physics of dielectrics, these figures may be connected by the following relation:

$$\mu' = \mu + \alpha R, \text{ where } R = \frac{\mu 2\ (\varepsilon - 1)}{a^3 \cdot\ (\varepsilon + 2)} \qquad (6)$$

and α is polarization of the molecule, R is intensity of the reaction field. Whithin the limits of Onzager's ideas

for the given range of substances Eq.(6) may be transformed into:

$$\mu' = \mu \cdot \frac{2\varepsilon - 1}{(2 - 2\alpha/a^3)\cdot\varepsilon + 2\alpha/a^3 + 1} \qquad (7)$$

Now, with the help of Eq.(7) we can calculate the dipol moment of the transition state, $\mu'_{\neq}$, in every solvent (Table 3).

Obtained dipole moment values show that in the transition state further considerable polarization of the charges (compared with CTC) takes place. Let us estimate the transference rate of the charge Q in the reaction complex, having defined it as a ratio of $\mu'_{\neq}$ to the maximum value of the dipole moment of ion pair. Table 3 shows that Q alters from 0.55 to 0.8. the Q values show that the limiting step of the reaction takes an intermediate place between the CTC and the ion pair, but closer to the latter.

On the strength of the above-mentioned we can suggest the following transition state model and limiting stop mechanism.

Case 1. (Molecule of the solvent does not take place in the transition state). During the formation of CTC one of the TNM nitrogroups interfere in π-electron cloud of the double-bond of the donor[13](Fig. 4a). As a result, alongside with relaxation of one of the C - N bonds loosening of the π-bonding takes place and C=C bond approaches simple σ-bonding. Inner rotation around this linkage may result in appearing of hydrogen atom near TNM remainder. In such a way conditions, favourable for nitrophorm and nitroalkene molecule formation, are created. But preceding state C will be the most energy-capacious and, therefore, transitional one, as in this case, on one hand, shielded configuration takes place, and on the other hand, relaxation of the π-bonding continues. Activation energy for the a-c transition may be regarded as the energy expended on overcoming the barrier of inner rotation. Thus, in the given example $H^- \approx$ 20 kcal is in the reasonable correspondence with the energy of rupture of

the π-bonding (~40 kcal)

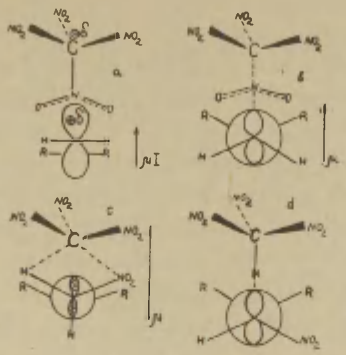

Fig. 4. Construction patterns of the reaction and pre-reaction complexes. a is starting CTC; b is prereaction complex; c is transition state; d is a state preceding to the reaction products.

Sharp decrease in the free energy, when passing from heptane to nitromethane, proceeds mainly on ac-count of additional stabilization of the transition state as a result of the orientation interaction of CH_3NO_2 with the reaction complex; in this case we mostly approach the ion pair state.

Case 2. The solvent molecule interacts specifically with the reaction complex. Above-mentioned pattern mechanism remains entirely in this case.

But its important difference from the first example lies in the fact that in this variant relaxation of the double-bond proceeds on account of specifical interaction of the solvent molecule with mobile non-divided pairs[12], with positively charged α-carbon atom. Really, the activation energy in the case of chlorine derivative alkanes is by 7-14 kcal/mol lower. But influence of reduction of the activation energy on the free energy of the reaction will be compensated by the entropy factor (Table 3), because definite orientation of the solvent molecules is needed for proceeding of the reaction.

On the strength of presented material on the reaction of TNM with 1.1-dianizylethylene we can draw a conclusion that suggested method of investigation as both pre-reaction complexes with charge transmission and reaction complexes, based on the pattern ideas of the physics of dielectrics with classical thermodynamical methods, enables not only to specify greatly mechanisms of the chemical reactions, but also to suggest new constructional patterns of activated complex on the strength of obtained figures of the dipole moments of the CTC and transition state. In conclusion the authors express their gratitude to Professor Nikolay Grigoryevich Bakhshiev for valuable notes, expressed in the process of discussion on the materials of the paper.

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AN ATTEMPT TO INTERPRET ACIDITY OF CARBON ACIDS USING φ-CONSTANTS OF SUBSTITUENTS

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A correlation analysis of the thermodynamical acidity of nitroalkanes, gem-dinitroalkanes, ethyl ethers of α-nitrocarboxylic and β-oxocarboxylic acids, and β-diketones is carried out. The possibility to correlate quantitatively the acidity of carbon acids of types cited using substituents inductive, steric, and φ-constants is demonstrated. The steric effect of the substituent is considered as a combination of two independent contributions. The effects of alkyl and electronegative substituents can be represented by a common equation for each type of carbon acids in question if the inductive constants for the formers are equalized to zero. When this approach is used the additional terms for electronegative substituents are always acid strengthening in their nature and they could be identified with resonance effects. A model is suggested according to which (i) the term proportional to the substituent φ-constant is related to the decrease in the relative free energy of the change $C_{sp3} \rightarrow C_{sp2}$ caused by an increase in the intensity of the φ-interaction, (ii) the contribution proportional to the substituent E_s'-constant reflects the increase in the relative free energy of anions caused by the steric inhibition of resonance, and (iii) the term proportional to the difference between the E_s^o-constants for a given and the reference substituent reflects the decrease in

the relative free energy of dissociation caused by an increase in the 1,7-interaction.

In an earlier report[1] it has been shown that the accepted views on the structure of nitroalkanes , $R_1R_2CHNO_2$, and nitronate anions , $R_1R_2CNO_2^-$, do not justify the interpretation of the observed effect of α-branching as caused by hyperconjugation. As the most likely explanation of this phenomenon it was proposed that the dependence of the R-C bond energy upon the hybridization state of the carbon atom was different for different R. In other words, it was suggested that there was a specific contribution to the relative changes in the dissociation energy of nitroalkanes (and other carbon acids) determined by the substituent ("environment") at the carbon atom whose hybridization state had been changed. It was shown that the substitution of the C-C bond for the C-H bond was likely to cause a change in the dissociation energy by about from 2 to 4 kcal/mol . On the other hand, Istomin and Palm have introduced a notion of "φ-interaction" connected, according to the model described already[3], with interactions between carbon atoms and the hydrogen strain. It appeared that between the bridging group C=C and adjacent hydrogen atoms a destabilizing contribution besides the φ-interaction is present being proportional (by coefficient 2.6 kcal/mol) to the number of such hydrogen atoms. This kind of interaction is absent in alkanes.[4]

The comparison of the results of an earlier investigation[4] with the conclusion that the "environment effect" [1] is significant in dissociation of carbon acids points out an analogy between the dissociation of carbon acids and the dehydration of alkanes. Therefore the study of the applicability of the φ-interaction to the dissociation of carbon acids and that of the possibility to model this reaction by dehydrogenation of alkanes are the main purpose of present investigation. The substituent constants used in respective calculations are listed in Table 1. For the numerical values see Refs. 3, 5 - 10.

Table 1

The Values of Substituent Constants

Substituent R	Substituent Constants for R				
	φ	φ_o	E_s' [a]	ΔE_s° [b]	σ^*
H	0.00	0.00	0.00	0.00	0.00
CH_3	3.94	3.94	-1.24	0.00	0.00
C_2H_5	3.38	3.38	-1.31	0.00	0.00
C_3H_7	3.19	3.19	-1.60	-0.29	0.00
C_4H_9	3.29	3.29	-1.63	-0.32	0.00
i-C_4H_9	3.38	3.00	-2.17	-0.86	0.00
nec-C_5H_{11}	3.47	2.83	-2.98	-1.67	0.00
i-C_3H_7	2.68	2.82	-1.71	0.00	0.00
sec-C_4H_9	2.87	2.63	-2.37	-0.68	0.00
t-C_4H_9	2.51	2.26	-2.78	0.00	0.00
$C_6H_5CH_2$	3.36	-	-1.62	-0.44	0.22
$CH_3O(CH_2)_2$	3.25	-	-2.01	-0.70	0.26
$HOCH_2$	2.46	-	-1.21	-0.12	0.56
CH_3OCH_2	2.64	-	-1.43	-0.25	0.67
$NCCH_2$	2.92	-	-2.38	-1.14	0.30
C_6H_5	(4.37)	-	-	-	0.62
I	3.74	-	-	-	0.22
Br	4.27	-	-	-	2.63
Cl	4.87	-	-	-	2.68
F	6.82	-	-	-	3.10
NC	(5.56)	-	-	-	3.25
O_2N	(6.96)	-	-	-	3.53

[a] $E_s' = E_s - 1.24$; [b] Difference between the E_s value for the given substituent which is able for 1.7-interaction and that for a substituent with a similar α-branching for which the 1,7-interaction is not possible.

Table 2

Date Used for the Analysis of the Structure-Dependence of the Acidity of Nitroalkanes $R_1R_2CHNO_2$

Serial number	R_1	R_2	pK_a'	$\Delta\Delta H$ (kcal/mol)	$\Delta\Delta G$ (kcal/mol)
1	H	H	10.69	32.7	24.2
2	"	CH_3	8.76	29.7	20.6
3	"	C_2H_5	9.28	30.1	21.1
4	"	C_3H_7	9.16	30.0	20.9
5	"	$i\text{-}C_4H_9$	8.86	31.1	22.7
6	"	$neo\text{-}C_5H_{11}$	8.54	30.1[a]	-
7	"	$i\text{-}C_3H_7$	9.51	30.0	21.4
8	"	$C_6H_5CH_2$	9.08	-	-
9	"	$CH_3O(CH_2)_2$	8.92	-	-
10	"	$HOCH_2$	9.67	-	-
11	"	CH_3OCH_2	9.56	-	-
12	"	$NCCH_2$	8.61	-	-
13	"	C_6H_5	7.18	28.1	19.9
14	"	Br	8.50	34.0	25.6
15	"	F	9.5	30.1[b]	-
16	"	CN	5.16	32.1	23.7
17	CH_3	CH_3	7.67	28.1	18.9
18	"	C_2H_5	8.38	28.2	19.2
19	Cl	H	7.50	34.6[c]	-
20	"	CH_3	6.97	-	-
21	"	C_2H_5	7.48	-	-
22	"	C_4H_9	7.15	-	-
23	"	$i\text{-}C_4H_9$	6.81	-	-
24	"	$t\text{-}C_4H_9$	10.26	-	-
25	"	Cl	5.99	31.4	23.3
26	F	F	12.40	35.5	27.4

[a] For 4,4-dimethyl-1-pentene ΔH_f^o = -19.2 kcal/mol;[14]

[b] For fluoroethylene ΔH_f^o = -32.4 kcal/mol;[15]

[c] For chloroethane ΔH_f^o = -26.2 kcal/mol [5].

N i t r o a l k a n e s

The data used in the analysis of the dependence of the acidity of nitroalkanes, $R_1R_2CHNO_2$, upon their structure are listed in Table 2. Values of $pK'_a = pK_a - \lg n_H$ are taken from recent papers [1,11,12], the values of

$$\Delta\Delta H = \Delta H^o_f(R_1R_2C{=}CH_2) - \Delta H^o_f(R_1R_2CHCH_3) \quad \text{and}$$

$$\Delta\Delta G = \Delta G^o_f(R_1R_2C{=}CH_2) - \Delta G^o_f(R_1R_2CHCH_3)$$

are calculated using the data at 298°K as listed in a review of Stull and coworkers.[13]

The relationships between pK'_a-values for nitroalkanes and $\Delta\Delta H$ (or $\Delta\Delta G$) for dehydrogenation of respective alkanes are represented in Fig. 1. For compounds lacking in β-branching alkyl, aromatic or heteroatomic substituents the pK'_a values are adequately (the SDs for regressions with $\Delta\Delta H$ and $\Delta\Delta G$ are 0.31 and 0.24 whereas the uncertainty level for those quantities is hardly lower than 0.3kcal/mol) correlated with these thermodynamical parameters for dehydrogenation process.

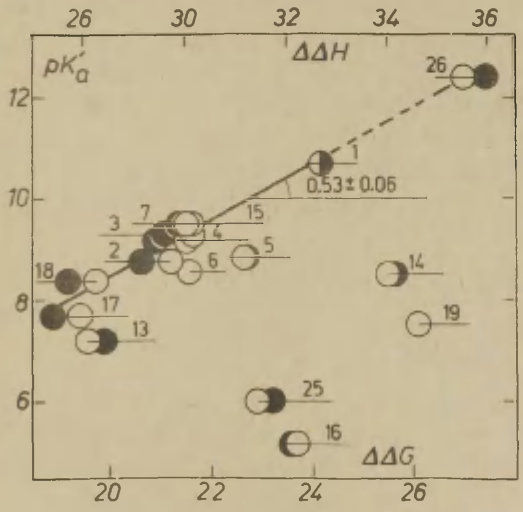


Fig. 1. The dependence between pK'_a-values for nitroalkanes, $R_1R_2CHNO_2$, and $\Delta\Delta H$ (○) or $\Delta\Delta G$ (●) for dehydration of respective alkanes (for compound numbers see Tables)

The deviations from the linearity could be attributed to the presence of more than a single interaction type between substituents and reaction centre. For compounds Nos 13 -15,24,25 the resonance and the effect of the bond change could be expected. Even the effects of alkyl substituents are not uniform. They can be subdivided into the interactions between carbon atoms and into terms reflecting the 1,6- and 1,7-interactions between unbound atoms (the H--strain[3]). Therefore the points for compounds with significant effect of bond change, resonance or H-strain are described by the relationship valid for simple alkyl substituents only if these additional effects appear in the dissociation of nitroalkanes and the dehydrogenation of respective alkanes in similar manner. Since these deviations for compounds (the serial numbers are given in paranthesis) under consideration actually equal 0.0 (26), 0.0 (15), 1.2 (5), 0.8 (6), 1.1 (13), 4.3 (19), 3.1 (14), 5.4 (16) and 4.3(25) log. units, such similarity can be observed only for fluorine (15, 26).

The effect of β-branching can be conveniently (there are quite a number of respective data) examined using the dependence of pK'_a on φ-values. One can realize that the common dependence $pK'_a = f(\varphi_i, \varphi_j, \ldots)$ can be expected only if either the insignificance of the triple interactions (nonadditive terms) is prooved or the respective terms are taken into account. Unfortunately only two series with one constant substituent can be considered: RCH_2NO_2(1-12) and $RCHClNO_2$ (19-24).

For series RCH_2NO_2 with R = alkyl substituent, only two possible ways of the separation of the gross substituent effect were tested: $pK'_a = f(\varphi_o, \varphi - \varphi_o)$ and $pK'_a = f(\varphi, \Delta E_s^o)$. The first of them is based on the model described previously[3], the second one on the linearity between free energies of dissociation of nitroalkanes and dehydrogenation of respective alkanes observed in this study for substituents without β-branching (1,7-interactions). The term corresponding to 1,7-interactions has been consid-

ered to be proportional to the difference between the E_s^o--value for the given substituent and that for the substituent with similar α-branching but not being able for 1,7-interactions (for primary alkyls such a reference substituent should be CH_3OH_2, for secondary alkyls $(CH_3)_2CH$, and for tertiary alkyls $(CH_3)_3C$). Introduction of this scale of corrections for 1,7-interactions is consistent with the conclusion[3] that E_s^o-values reflect mainly the 1,6- and 1,7-interactions. As a result the following equations were obtained:

$$pK_a' = (10.70\pm0.10) - (0.47\pm0.03)\,\varphi_o - (1.24\pm0.15)(\varphi-\varphi_o) \quad (1)$$

$$R = 0.993, \quad s = 0.10$$

and

$$pK_a' = (10.72\pm0.09) - (0.46\pm0.03)\,\varphi + (0.34\pm0.06)\,\Delta E_s^o \quad (2)$$

$$R = 0.994, \quad s = 0.10$$

From the statistical wiewpoint both of them are equivalent.

When the second principle of data processing was applied to the whole series (compounds 1-12) the following equation proved to be valid:

$$pK_a' = (10.77\pm0.13) - (0.46\pm0.04)\,\varphi + (0.43\pm0.08)\,\Delta E_s^o + - (0.13\pm0.11)\,\sigma^* \quad (3)$$

$$R = 0.999, \quad s = 0.14$$

From Eq. (3) the insignificance of the inductive term can be noticed. All equations listed also contain no term reflecting the steric hindrance of resonance. The possibility to neglect this term is probably connected with the limited set of data used. At least the pK_a' value (11.5) expected for $(CH_3)_3CCH_2NO_2$ from the dependence of pK_a' on $\Delta\Delta H$ considerably deviates from those predicted by using Eqs. (1)-(3).

For series $RCHClNO_2$ no good correlations according to equations of type (1) or (2) are observed. Although, assuming the significance of the steric inhibition of resonance and the proportionality of the respective term to the

E'_s-value of substituent (see below) the data for this series are correlated by equation:

$$pK'_s = (7.50\pm0.08) - (1.56\pm0.05)E'_s - (0.62\pm0.03)\varphi + (2.31-0.11)\Delta E^o_s \quad (4)$$

$$R = 0.999, \quad s = 0.09$$

Constants E'_s, φ_o and $\varphi - \varphi_o$ result in the more rough correlation (s = 0.50).

Geminal Dinitroalkanes

The data used for the analysis of the acidity of geminal dinitroalkanes $RCH(NO_2)_2$ are listed in Table 3. For the values of $pK'_a = pK_a - lgn_H$ see Refs. 1, 16, for those of E^* (the excitation energies of respective nitronate anions) Refs. 16 through 20.
$\Delta\Delta H = \Delta H^o_f(RCH_3C{=}CH_2) - \Delta H^o_f(RCH_3CHCH_3)$ and $\Delta\Delta G =$

$= \Delta G^o_f(RCH_3C{=}CH_2) - \Delta G^o_f(RCH_3CHCH_3)$ are calculated using data for 298° K (See Ref. 13).

In distinction from nitroalkanes the dependence between pK'_a-values for gem.-dinitroalkanes and $\Delta\Delta H$ or $\Delta\Delta G$ of the dehydrogenation of respective alkanes appears to be non-linear (see Fig. 2). From this fact one can conclude that in this series (by the analogy with the series $RCHClNO_2$) the stability of anions shall considerably depend on some other factor not reflected by φ-values. This additional influence can be taken into account using E'_s-constants. There is an analogy between the excitation of dinitrocarbanions[21] and the reaching of activated state in ester hydrolysis[22]. Indeed, when 1,7-interactions are absent the influence of α-branching on the excitation energies of dinitrocarbaniones is correlated with E'_s-constants of respective substituents (see Fig. 3). In more precise approximation the term proportional to the φ-constants is to be taken into account. Whole series (27-29, 31, 33-38) is correlated by equation:

$$\Delta E^* = (2.33\pm0.19)E_s' - (0.21\pm0.08)\varphi - (1.89\pm0.13)\Delta E_s^o + (4.43\pm0.11)\sigma^* \quad (5)$$
$$R = 0.999,\ s = 0.12$$

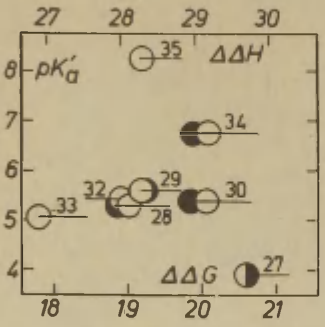
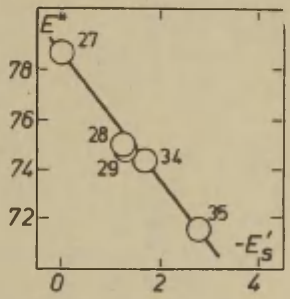


Fig. 3. Dependence of excitation energies of nitronates $RC(NO_2)_2^-$ upon substituent constants E_s'

Fig. 2. Dependence between pK_a'-values of gem.-dinitroalkanes $RCH(NO_2)_2$ and $\Delta\Delta H$ (o) or $\Delta\Delta G$ (●) of dehydrogenation of respective alkanes.



For dissociation of compounds (27-35) with alkyl substituent only the relationships $pK_a' = f(E_s', \varphi, \Delta E_s^o)$ and $pK_a' = f(E_s', \varphi_o, \varphi - \varphi_o)$ were tested. It appeared that the former, represented by Eq. (6), is considerably more

$$pK_a' = (3.96\pm0.17) - (1.78\pm0.10)E_s' - (0.21\pm0.07)\varphi + (2.09\pm0.14)\Delta E_s^o \quad (6)$$
$$R = 0.999,\ s = 0.18$$

reliable than the latter (R = 0.996, s = 0.61).

As the susceptibility factors for E_s' and E_s are nearly equal within the limits of their uncertainty Eq. (6) can be reduced to the practically equivalent relationship (7):

$$pK_a' = (3.97\pm0.24) - (0.29\pm0.08)\varphi - (1.85\pm0.14)\Delta E_s' \quad (7)$$
$$R = 0.985,\ s = 0.24$$

where $\Delta E_s'$ represents the steric term caused by α-braching only (equals -1.31 for primary, -1.71 for secondary and -2.78 for tertiary alkyls).

The whole series (27-39) is correlated by equation:

$$pK_s' = -(1.78\pm0.10)E_s' - (0.21\pm0.08)\varphi + (2.06\pm0.15)\Delta E_s' + (2.29\pm0.15)\sigma^* \quad (8)$$

$R = 0.999, \quad s = 0.20$

Table 3

Data Used for the Analysis of Structure-dependence of the Acidity of Dinitroalkanes $RCH(NO_2)$

Serial number	Substituent R	pK_a'	E^* kcal/mol	$\Delta\Delta H$ kcal/mol	$\Delta\Delta G$ kcal/mol
27	H	3.93	78.7	29.7	20.6
28	CH_3	5.30	75.0	28.1	18.9
29	C_2H_5	5.61	74.8	28.2	19.2
30	C_3H_7	5.39	-	29.2	19.8
31	C_4H_9	5.45	74.8	-	-
32	$i\text{-}C_4H_9$	5.40	-	28.0[a]	-
33	$neo\text{-}C_5H_9$	5.05	74.2	26.9[b]	-
34	$i\text{-}C_3H_7$	6.77	74.4	29.2	19.9
35	$t\text{-}C_4H_9$	8.24	71.6	28.3[c]	-
36	$C_6H_5CH_2$	4.54	75.8	-	-
37	$HOCH_2$	4.24	78.1	-	-
38	CH_3OCH_2	3.56	78.3	-	-
39	$NCCH_2$	2.34	78.7	-	-
40	C_6H_5	3.89	76.5	-	-
41	I	3.19	73.2	-	-
42	Br	3.58	74.3	-	-
43	Cl	3.53	74.1	-	-
44	F	7.70	74.3	-	-
45	CN	-6.22	82.9	-	-
46	O_2N	0.14	81.8	-	-

[a] For 2,4-dimethyl-1-pentene $\Delta H_f^\circ = -20.27$ (Ref. 14)
[b] For 2,4,4-trimethyl-1-pentene $\Delta H_f^\circ = -26.68$ (Ref. 14)
[c] For 2,3,3-trimethyl-1-butene $\Delta H_f^\circ = -20.67$ (Ref. 14)

Using Eq. (5) the effects of nonalkyl substituents adjacent to reaction centre on the $C_{sp^3} \rightarrow C_{sp^2}$ transition could be estimated and the respective effective E'_s-values calculated. Although these E'_s-constants (see Table 4) reflect not only the steric effect of substituent as it is the case for alkyl substituents they represent the quantitative measure of the gross effect of these substituents on the transition $C_{sp^3} \rightarrow C_{sp^2}$.

Table 4

Effective Values of E'_s-constants for Some Substituents Estimated Using Eq. (5)

Substituent	C_6H_5	I	Br	Cl	F	NC	NO_2
$-E_s$	1.7	6.3	6.5	6.6	7.2	3.9	4.8

Acidities of gem-dinitroalkanes with these substituents should now equal the values calculated by Eq. (8) and these E'_s-constants if no additional interaction type is present. In fact the following deviations ($R_{d.n.} = pK'_{a,exp} - pK'_{a,calc}$) are observed: -0.7 ($C_6H_5$), -6.0 (I), -5.0 (Br), -5.0 (Cl), -0.5 (F), -8.4 (CN), and -2.7 (NO_2).

Consequently, for all gem-dinitroalkanes containing these substituents (excluding possibly C_6H_5 and F) the additional interaction type causing the increase of acidity is present. These additional terms are satisfactorily proportional (see Fig. 4) to the deviations of respective points from the linearity of pK'_a on $\Delta\Delta H$ for mononitroalkanes (see Fig. 1).

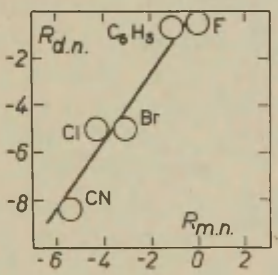


Fig. 4.

The dependence between differences of experimental and calculated pK'_a-values for mononitroalkanes ($R_{m.n.}$) and gem-dinitroalkanes ($R_{d.n.}$).

Other Carbon Acids

Acidity data of ethyl α-nitrocarboxylates and β-oxocarboxylates, as well as of β-diketones suitable to proove the applicability of correlations considered are represented in Table 5.

Table 5

Data Used for Analysis of the Structure Effects on Acidity of Ethyl α-Nitrocarboxylates, Ethyl β-Oxocarboxylates and β-Diketones

Substituent	pK_a		
	$RCH(NO_2)CO_2C_2H_5$	$RCH(CH_3CO)CO_2C_2H_5$	$RCH(CH_3CO)COCH_3$
H	6.12	10.94	9.30
CH_3	6.57	12.42	10.87
C_2H_5	7.20	12.87	11.34
C_3H_7	6.83	-	-
C_4H_9	6.86	13.2[a]	-
i-C_4H_9	6.53	-	-
i-C_3H_7	8.08	15	12.85
sec-C_4H_9	7.25	-	-

[a] Not considered in correlation

The test of the relationship $pK_a' = f(\varphi, \Delta E_s^o, E_s')$ leads us to following results: (i) for ethyl α-nitrocarboxylates

$$pK_a' = (6.13\pm0.17) - (1.65\pm0.20)E_s' - (0.30\pm0.08)\varphi + (2.44\pm0.32)\Delta E_s^o \quad (9)$$

$R = 0.999$, $s = 0.17$

(ii) for ethyl β-oxocarboxylates

$$pK_a' = (10.93\pm0.17) - (3.55\pm0.24)E_s' - (0.76\pm0.10)\varphi \quad (10)$$

$R = 0.998$, $s = 0.17$

and (iii) for β-diketones

$$pK_s' = (9.30\pm0.01) - (287\pm0.01)E_s' - (0.51\pm0.01)\varphi \qquad (11)$$

$$R = 0.999, \quad s = 0.01$$

In series of ethyl β-oxocarboxylates the point for $R = C_4H_9$ deviates by a unity making possible the estimation of the susceptibility factor for ΔE_s° to be equal 3.

D i s c u s s i o n

The results obtained confirm that the dissociation of nitroalkanes in water medium can be modelled by the dehydrogenation of respective alkanes in gas phase facilitaded by an increase of short-range interactions. For gem.-dinitroalkanes such a straightforvard modellation is impossible. The reason is that, probably, the interaction between R and CH_3, on the one hand, and between R and NO_2, on the other hand, are not of the same nature because the steric hindrance to the resonancs is involved in the latter case. This hindrance can quantitatively be taken into account using the E_s' substituent constant. Consequently, the most important substituent effects affecting the acidity of carbon acids cannot be related to any solvation effects being specific for the reaction studied.

In a first approximation the effects of alkyl and substituted alkyl substituents (of type XCH_2) related to the short-range interactions are in the case of dissociation characterized by φ - and σ^*-constants, and by $E_s'(E_s)^-$ and σ^*-constants if the stability of anions is considered. The "anomaly" (for which see Refs. 1,23) of substituents of type XCH_2 appears to be a simple consequence of the low values of φ.

The extrapolation of these regularities to electronegative substituents leads us to the conclusion that an additional acid strenghtening interaction mechanism is introduced by these substituents. It is noteworthy that according to another interpretation[23] of pK_a- values for nitrocompounds and spectral characteristics of their carbanions the effect which in present work is presented by

the term proportional to E_s'-constant (in minor part also in term proportional to φ-constants) is involved in wether inductive contribution or in deviation from the linearity of pK_a' vs. σ^*-constants defined for a subseries with selected substituents. These deviations being acid weakening are interpreted as the "α-effect" caused by the interaction of reaction centre with p-electrons of substituents leading to the destabilization of anions. The interpretation suggested in present work results in the reversed sign of the additional effect for these substituents and excludes for them any repulsive interaction in carbanions not identified with the usual steric effect wich is taken into account in Eqs. (4) and (8). Proportional contributions in series of mono- and dinitroalkanes for substituents F, Cl, Br, C_6H_5 and CN makes reasonable to interpret this effect as the manifestation of acceptor polar resonance effect of these substituents. This effect is common for all substituents listed (Cl and Br possess vacant p-orbitales) but F. Indeed, the deviations for F equal practically zero both for mono- and dinitroalkanes. This is also the case for C_6H_5 in the series of dinitroalkanes, as one might expect since the phenyl cycle in respective anion is not in coplanar position[23] (steric hindrance of resonance).

Among the long-range interactions the 1,7- ones are most important. As acid strenghtening effect it can be taken into account using the differences $(\varphi - \varphi_o)$ or $\Delta E_s^\circ = E_s^\circ - E_{s(model)}^\circ$ ($E_{s(model)}^\circ$ is the E_s°-value for simplest alkyl representing the α-branching present in the substituent considered), the latter being of a wider applicability.

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Influence of Specific Solvation on the Rate of the Reaction between Trans-phenyl-β-chlorovinyl Ketone and Amines

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The influence of various solvents on the rate of the reaction of trans-phenyl-β-chlorovinyl ketone with benzylamine, diethylamine and triethylamine has been studied. The effect of the specific solvation of a number of solvents (dioxane, benzene, acetone, methanol, isopropyl alcohol, dimethyl acetamide) has been evaluated quantitatively, and the mechanism of the influence of these solvents on the reaction rate of the processes has been discussed. The data obtained are in agreement with the previous assumption concerning the possibility of intramolecular hydrogen bond formation in the transition state for a reaction with primary and secondary amines.

Earlier[I], in investigating the influence of the medium effects on the rate of the reaction between trans-aryl-β-chlorovinyl ketones and amines proceeding in accordance with equations*/ (I) and (2) it was found out that the influence of solvents interacting with reagents by the mechanism of non-

$$ArCOCH{=}CHCl + 2HNR_1R_2 \longrightarrow ArCOCH{=}CHNR_1R_2 + R_1R_2\overset{+}{N}H_2 \cdot Cl^- \quad (I)$$

$$ArCOCH{=}CHCl + R_1R_2R_3N \longrightarrow ArCOCH{=}\overset{+}{C}HNR_1R_2R_3Cl^- \quad (2)$$

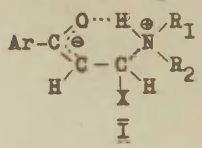
specific solvation was described well by the Kirckwood equation:

*/ Equation (I) is valid for the reactions with primary and secondary amines, and equation (2) for tertiary ones.[1]

$$\lg k = \lg k_0 + \beta \frac{\varepsilon - 1}{2\varepsilon + 1} \qquad (3)$$

Here k and k_0 — are the reaction rate constants in a medium with the dielectric permittivity ε and in the gas phase ($\varepsilon = 1$), respectively, and β is a coefficient characterizing the reaction sensitivity to the nature of solvent. The value of the coefficient is determined by the difference between the polarities of the initial substances and those of the transition state.[2]

In this case the influence of the dielectric constant of the solvent on the reaction rate of the process with tertiary amines turned out to substantially differ from that for a reaction with primary and secondary amines. On the basis of these data and other data[3], a conclusion[I] was drawn about the possibility of stabilizing the transition state in the latter case by the intramolecular hydrogen bond of the type:



I

With a view of further particularizing the mechanism of the processes in point, it is undoubtedly interesting to study the influence of solvents acting by specific solvation mechanism on their rates. The present work deals with studying the influence of the solvents mentioned above on reactions of trans-phenyl-β-chlorovinyl ketone with representatives of primary (benzylamine), secondary (diethylamine) and tertiary (triethylamine) amines.

The rate of the reactions investigated in all the solvents is described well by second-order equations in the form of Eq.(4) for the case of primary and secondary amines and in that of Eq.(5) for tertiary ones.

$$\frac{dx}{dt} = k(a-x)(b-2x) \qquad (4)$$

$$\frac{dx}{dt} = k(a-x)(b-x) \qquad (5)$$

The rate constants calculated from the integrated forms of these equations are listed in Table I.The data previously obtained for the same reactions in some non-specific solvents (tetrachloroethylene and nitrobenzene) are given therin for comparison.The comparison of the results obtained shows that the processes under investigation are sensitive to the effect of specific solvation. The latter phenomenon shows itself, for example, in the fact that the reaction rate in benzene or dioxane is markedly different from the rate of tetrachloroethylene (cf. Nos.I,2 and 8 in Table I) which is close to them in polarity. These differences are especially considerable for the process with triethylamine. The comparison of the data for the reactions in solvents such as dimethyl formamide (No 4), methanol (No 7) and nitrobenzene (No 9) whose polarities are the same also shows a prononced influence of specific solvation on the rate of the processes in question. In this case, its influence turnes out to be different for reactions with various amines. The latter fact is especially clearly seen when passing from nitrobenzene (No 9) to acetone (No 3) where for the case of benzylamine nearly a two-fold accelaration of the process occurs, and for the reaction with triethylamine a marked decrease in the rate takes place (almost three times as slow).

In quantitatively considering the influence of the specific solvation of the solvents investigated it is necessary to take into account that they interact with the participants of the reaction simultaneously and by the mechanism of non-specific solvation. The influence of the latter effect can be evaluated by equation (3) on the basis of the previously obtained[1,5] values of $\lg k_o$ and b and also of the ε-values (Table I). The differences between the rate constant values calculated in such a way and the experimental ones $(\Delta \lg k)_{sp}$, are numerically equal to the deviations of the corresponding points in Figure I characterize the effect of specific solvation only. Their values are collected in Table 2. The observed exhibition of specific solvation is due in every

Table I

Rate Constants for the Reactions of trans-Phenyl-β-chlorovinyl Ketone with Amines in Various Solvents at 25°

Nos	Solvents	$\varepsilon_{25°}$	Benzylamine		Diethylamine		Triethylamine	
			$k \cdot 10^4$ l/mol·sec.	N[a]	$k \cdot 10^4$ l/mol·sec.	N[a]	$k \cdot 10^4$ l/mol·sec.	N[a]
I.	Benzene	2.284[b]	200 [5]	-	5950±20	28	II.0±0.I	7
2.	Dioxane	2.209	838±5	53	6840±60	4I	20.9±I.2	8
3.	Acetone	20.74	804±8	I7	6080±40	I2	98.6±I.2	8
4.	Dimethyl formamide	36.7[b]	-	-	I7400±200	20	287±4	I0
5.	Dimethyl acetamide	37.78	-	-	-	-	I35±2	5
6.	Isopropyl alcohol	I8.30	3550 [3]	-	I6300 [6]	-	340± 6	I2
7.	Methanol	32.65	I850±20	24	7390±I20	32	360±5	7
8.	Tetrachloroethylene	2.300	-	-	3070 [I]	-	0.303	-
9.	Nitrobenzene	34.82[b]	462 [5]	-	-	-	274 [I]	-

a) Number of experimental points from which the mean constant value was calculated.
b) At 20°.

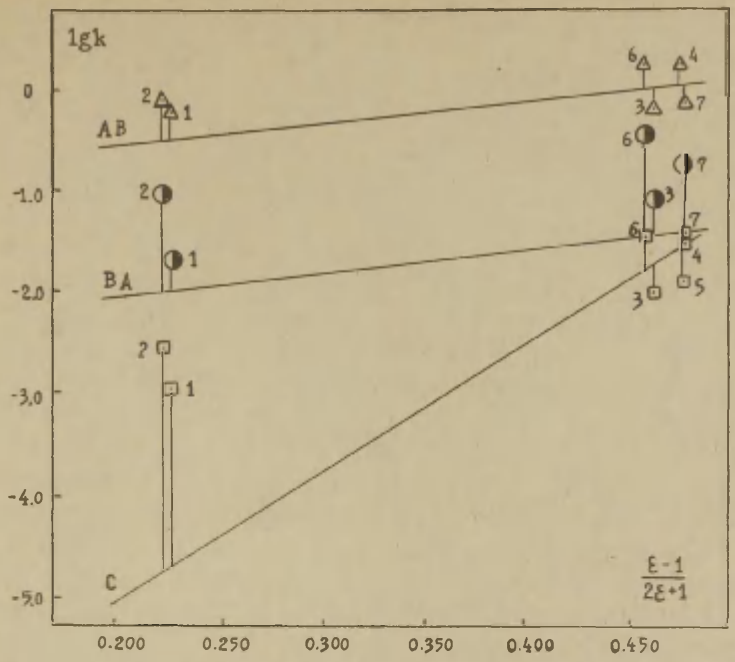
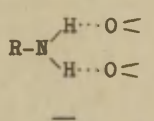


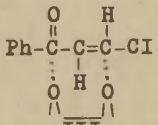
Figure I. Correlation between the values of lg k of the reaction of the trans-phenyl-β-chlorovinyl ketone with benzeneamine (A), diethylamine (B) and triethylamine (C) and the values of $\frac{\varepsilon-1}{2\varepsilon+1}$ of some solvents. The straight lines are drawn with regard to the influence of non-specific solvation.[1] The numbering of points corresponds to Table I.

case to forming various complexes between the molecules of the solvent and the participants of the reaction.

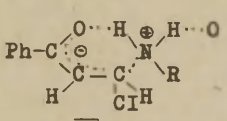
The following interactions are possible for solvents usually being, in such cases, electron-donors (the reaction with primary amine is under discussion):



II



III



IV

Table 2

Values of $(\Delta \lg k)_{sp}$ for the Reactions of trans-Phenyl-β-chlorovinyl Ketone with Amines in Various Solvents

Nos	Solvent	Benzyl Amine	Diethyl Amine	Triethyl Amine
I.	Benzene	+0.30	+0.27	+I.70
2.	Dioxane	+0.94	+0.39	+2.06
3.	Acetone	+0.30	-0.24	-0.36
4.	Dimethyl formamide	-	+0.I7	-0.I0
5.	Dimethyl acetamide	-	-	-0.42
6.	Isopropyl alcohol	+0.96	+0.I9	+0.24
7.	Methanol	+0.63	-0.20	+0.0I

The formation of an associate of type II, then converting into IV, at the cost of increasing the electron density on the nitrogen atom in amine is to result in a rise in the process rate. At the same time the solvation of the electron centres of the trans-phenyl-β-chlorovinyl ketone by type III contributes to the deceleration of the process due to the blocking of these centres with respect to the attack on them by the nucleophile.

In the case of a reaction with secondary amine which has only one hydrogen atom the formation of type II structure is, on the one hand, to increase the process rate and, on the other hand, it is to decrease the rate owing to the hindrance to forming the intramolecular hydrogen bond of type I.

The interaction between the solvent and amine of type II does not occur in a reaction with tertiary amines, and the influence of the solvation on the process rate will be determined only by the formation of structure III.

Let us consider the corresponding influence of acetone in terms of the above concepts of the specific effect of electron-donating solvents on the kinetics of the reaction under investigation. Here, as it follows from Table 2 and Figure I, a pronounced inhibition of the process with tri-

ethylamine occurs due to the above-mentioned solvation of the electrophile. The reaction with diethylamine is also retarded to approximately the same extent, where the accelerating and retarding actions of the solvation of amine after type II seems to be balanced out, and the observed effect, as well as in the reaction of tertiary amine, is due only to the formation of structure III. An increase in the process rate occurs only for the reaction of benzylamine where the accelerating action of solvation after type II and especially after type IV exceeds the retarding action which is due to complex formation after type III and to breaking one of the hydrogen bonds of type II in forming the intramolecular bond (see structure IV).

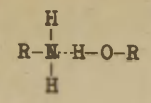
Similarly, one might interprete the observed specific influence of such solvents, too, as dimethyl formamide and dimethyl acetamide which can act as strong electron donors[4] when various associates are formed. As to the influence of dioxane, which is also an electron-donor solvent, the results obtained here (Table 2, No 4) point to its more complex interaction with the participants of the reaction than it is described by structures II-IV. For instance, a considerable (more than 100 times as fast) acceleration is detected for the reaction of tertiary amine instead of the relative deceleration predicted above. This acceleration exceeds considerably that for the reaction with primary and secondary amines. Here, in addition to the electron-donor properties of dioxane its conformational polarizability[8] appears to show themselves as well as in other analogous reactions.[7] The essence of this effect consists in that dioxane changes from the less polar conformation("chair") to more polar one ("boat") in the field of a strong dipole. Thus the specific influence of dioxane is due to two components: electron donation and polarizability. Their complete separation has presented certain difficulties so far. However, on the basis of an approximate equality of logarithms of acetone and dioxane association constants with phenol (1.03+1.06 and 0.63+1.21,[9] respectively) and B-values characterizing their

nucleophilic ability (116 and 129 [4]) one can assume, in order to take semiquantitative comparisons, that electron-donor properties of these solvents are approximately equal.[10] It follows that the difference in their values, $(\Delta \lg k)_{sp}$ in Table 2, will characterize only the influence of dioxane polarizability.

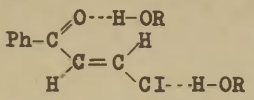
Since the polarizability of a solvent is to increase with the growing dipole moment of the particles being solvated[8], the deviation caused by this effect from Kirckwoods straight line, $(\Delta \lg k)_{sp.}$, will be due to the difference in the polaritis of the transition and initial states. This same difference also determines the slope of the Kirckwood straight line.[2] Therefore the accelerating effect of dioxane which is due to its conformational polarizability must be linear with the δ-value in equation (3), and the corresponding line must pass through the origin of coordinates. Indeed, as it follows from Fig.2A, the indicated relationship between the difference between $(\Delta \lg k)_{sp.}$ for dioxane and acetone on the one hand and the δ-values on the other holds true. Whith allowance made for the approximate nature of the above assumptions and possible errors in calculating numerical values for the corresponding quantities it should be acknowledged that all the points satisfactorily lie in the common line.

An analogous relation (Fig.2B) is obtained when the δ-values are compared with the $(\Delta \lg k)_{sp}$ -values for benzene whose specific influence is mainly due to the polarizability of its molecules.[7]

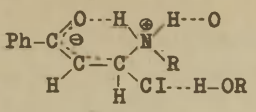
When considering the influence of the specific solvation of alcohols it is necessary to take into account that they can act both as electron acceptors and as electron donors when hydrogen bonds are formed. In the latter case their complexes with the reaction participants discussed in the present work will have a structure of type II-IV. But if a molecule of alcohol is an electron acceptor when the hydrogen bond is formed then the corresponding complexes will take the form:



V



VI



VII

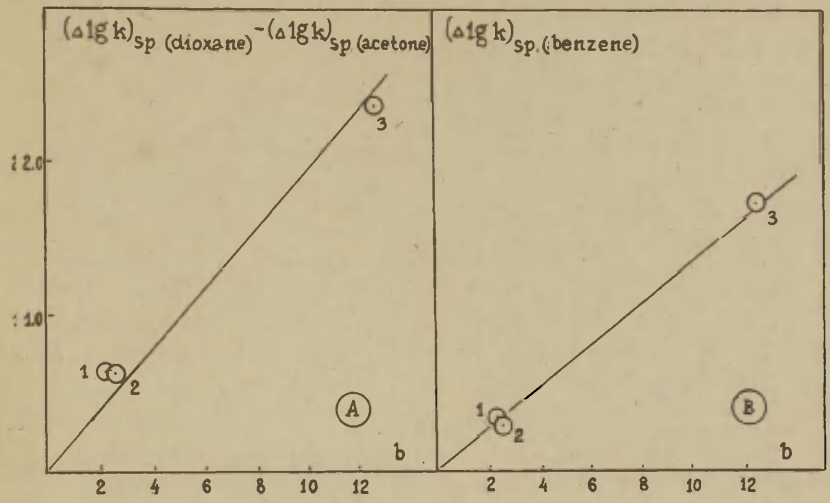


Figure 2. Dependence of $(\Delta \lg k)_{sp\ (dioxane)}-(\Delta \lg k)_{ap\ (acetone)}$ (A) and $(\Delta \lg k)_{ep\ (benzene)}$ (B) on the senaitivity of reactions to the variation of medium polarity, δ, for the reaction of trans-phenyl-β-chlorovinyl ketone with benzylamine (I), diethylamine (2) and triethylamine (3).

The formation of the indicated bonds will influence process rates in different ways. The association after type II which then changes to IV will, as was mentioned above, contribute to a reaction with primary amines and will not affect the reactions of secondary and tertiary amines,

The interaction between alcohols and amines after type V will decelerate the rate of the process with all the amines both by decreasing the electron density at the nitrogen atom and also because of ateric hindrance to it. The interaction of the solvents in question with the electrophilic reagent

after type III is also to hinder the reaction. The formation of hydrogen bond of the type CI···H-O-R in VI which also remains in VII must promote a slight increase in the process rate for the reactions of all the amines at the expense of an increase in the shortage of electrons on the β-carbon atom. But the C=O···H-OR-bond in VI which contributes to the withdrawal of the electron density from the remaining fragments of the molecule must not perhaps influence the rate of reactions with primary and secondary amines since it will then hinder the formation of complex I (see structure VIII). In the case of tertiary amines this bond must probably promote the reaction through the stabilization of the negative charge on the oxyden atom in the transition state.

Thus the influence of the alcohols on the reactions under discussion has been proved to be very complicated. The observed acceleration for the reaction of primary amine (see Nos.6 and 7 in Table 2 and in Fig.I) seems to be due to the fact that the accelerating influence of solvation after types II, VI, VII exceeds the inhibiting effect due to the formation of structures III and V. In the case of the reaction of secondary amine the formation of structure II does not influence the process rate, and it is not formed at all for tertiary amine, and therefore the observed increase in the reaction rate has turned out to be considerably less. In this case the slightly larger acceleration of the reaction of tertiary amine as compared with secondary one might be associated with a positive influence of the solvation of the type C=O···H-O-R in VI.

It is interesting to note that the accelerating action of the specific solvation of isopropyl alcohol has proved to be more effective than that of methyl alcohol in all the cases. This fact agrees well with the previously obtained data on the specific influence of alcohols on the rate of the interaction between phenacyl bromide and aliphatic amines where the inhibiting influence of methyl alcohol was larger than that of isopropyl alcohol.[10,11] The observed difference in

influence of both the alcohols is difficult to explain so far, although one may assume that the inhibition of reactions with all the amines turnes out to be more significant in methanol as in a more acidic alcohol[12] at the cost of the solvation of type V.

Experimental

trans-Phenyl-β-chlorovinyl ketone[13], benzenamine[3] and diethylamine[6] were prepared for the kinetic measurements according to the methods described previously. Triethylamine[4] was distilled over a small amount of p-toluene sulphochloride (I g per 100 ml of triethylamine), twice distilled over metallic sodium taking the mean fraction. B.p. 89.0-89.5, Ref.14.p.213, Benzene[13], isopropyl alcohol[13], acetone[15], dioxane[16], dimethyl formamide[17] were purified in the usual manner. Purification of dimethyl acetamide was carried out similary to that of dimethyl formamide.

The method of the kinetic measurements and the mathematical treatment of the results have been described in a previous paper.[13]

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Reactivity of Polycyclic Aromatic Hydrocarbons in Light-Initiated Degradation

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Rate constants of light-initiated destruction for 27 polycyclic aromatic hydrocarbons (PAH) dissolved in benzene were determined in presence of oxygen or under argon. The correlations of the rate constants with various MO-indexes, and Streitwieser's σ_r constants were established. The reaction rate is weakly sensitive to the changes in electron density at the reaction center. It was shown that the more reactive is a PAH, the more cancerigenic it is.

A number of polycyclic aromatic hydrocarbons (PAH) show strict canderigenity which has initiated a vivid researche for the relationships between the structure of PAH and their physiological activity or reactivity in various chemical processes. At present various MO-indexes of reactivity have been most freaquently used as quantitative characteristics of the structure of PAH.

Besides of the MO-indexes, the Streitwieser's[4] scale of empiric polar constants, σ_r, is being used. The latter expresses the relationship between the structure and the reactivity of PAH in a mode of Hammett equation

$$\lg k/k_o = \sigma_r \rho' ,$$

where k is the rate constant of the reaction at the position

r of the substance and k_o is that at the α - position of naphtalene, the latter taken as reference substance. The sensitivity constant of the reaction, ϱ', is taken as a unit for the protonation equilibrium. Hence, the σ_r constants represent a measure of relative basicity of the position r in any PAH.

The validity of linear free energy relationships in reactions of PAH has been investigated insufficiently. The model processes investigated are the protonation reactions in anhydrous hydrofluoric acid[1], deuterodeprotonation[2], nitration[3], and chlorination [4-5] reactions. The reactions of radical substitution have been investigated in the cases of interaction of PAH with methyl-[6] and trichloromethyl[7-8] radicals. The examples concern mainly the reactions of alternant hydrocarbons. In conclusion we refer to an interesting attempt (Zahradnik and Koutecky[9]) to make use of correlation analysis for the interpretation of available data for the reactivity of various alternant PAH.

In this paper we present the results of our attempt to compare quantitatively the reactivity of some PAH in transformations initiated by UV-radiation with their MO-indexes and σ_r-constants. Lightinitiated degradation was chosen for the investigation on the bases of some considerations, known from the literature,[10-11] about certain similarity between the mechanisms or, at least, general trends of the reactions of photodecomposition and methabolic oxydation of these substances.

Experimental

A set of 27 PAH (listed in Table 1) were subjected to an experimental investigation in 2×10^{-4} M benzene solution. The merqury-quartz valves SVD-120A (intensity 10^{16} quant/cm^3 sec) were used as the irradiation source. The experiments were carried out at $25 \pm 1^{\circ}$C in solutions saturated with oxygen, and under argon gas. The experimental techniques is described elsewhere.[12] The variation of the concentration of initial substances during the reaction was followed by

Table 1

List of investigated PAH

1. PHENANTHRENE [a]
2. TRIPHENYLENE [a]
3. PYRENE [a]
4. CHRYSENE [b]
5. 1,2-BENZANTHRACENE [c]
6. 2,3-BENZANTHRACENE [d]
7. PERYLENE [a]
8. 3,4-BENZOPYRENE [e]
9. 1,2-BENZOPYRENE [g]
10. 1,2,3,4-DIBENZANTHRACENE [g]
11. 1,2,5,6-DIBENZANTHRACENE [g]
12. 1,2,7,8-DIBENZANTHRACENE [g]
13. 1,12-BENZOPERYLENE [a]
14. 1,2,3,4-DIBENZOPYRENE [h]
15. CORONENE [a]
16. FLUORENE [a]
17. 3-METHYLCHOLANTHRENE [e]
18. 9-METHYL-1,2-BENZANTHRACENE [h]
19. 10-METHYL-1,2-BENZANTHRACENE [h]
20. 3'-METHYL-1,2-BENZANTHRACENE [h]
21. 9,10-DIMETHYL-1,2-BENZANTHRACENE [g]
22. 1-METHYL-BENZOPYRENE [h]
23. 6-METHYL-BENZOPYRENE [h]
24. 1,6-DIBENZO-PYRENE [h]
25. 5,8-DIMETHYLBENZOPYRENE [h]
26. 5,10-DIMETHYLBENZOPYRENE [h]
27. DIMETHYL-ANTHANTHRENE [h]

[a] Soyuzkhimreaktiv [b] Austrowaren [c] British Drug Houses Ltd.
[d] Schuchardt [e] Fluka AG Buchs SG [g] Gee Lawson Chemicals
[h] from Institut de Chimie des Substances Naturelles CNRS, France

spectrophotometric analysis of samples worked up by thin layer chromatography on aluminum oxyde of second grade activity (eluation by mixed solvent white spirit - chloroform 9:1, chromatograms developed in UV-light or by sulphuric acid).

The rate constants of photodecomposition of PAH were calculated from the decrease of the concentration according to the law of a pseudo-zeroeth-order reaction. The reproducibility was about $\pm$ 5%. The rate constants are listed in Table 2.

Discussion

In search for the quantitative relationships between the structure of PAH and their reactivity in photodegradation from numerous MO-parameters the indexes of free valency, F^{max}, and localization energies for radical reactions, L_r^{min}, ^{r} were used. The former are related to isolated molecules; the calculation of the latter bases on certain ideas about the structure of the transition state. Nevertheless, a good correlation[4] between the values of F_r^{max} and L_r^{min} could be observed. In addition to the MO indexes Streitwieser's empiric σ_r constants, which also correlate with MO-indexes, were used in the correlation analyses. The values of F_r^{max}, L_r^{min}, and σ_r, taken from the literature, are listed in Table 2.

The literature values of σ_r for substances 3 and 5 (pyrene and 1,2-benzanthracene) deviate from the linear correlations with indexes of free valency and localization energies. Therefore the values of corresponding σ_r for the substances were corrected on the bases of the correlation equations VII-VIII in Table 3. In a similar way, from the correlation between L_r^{min} and F_r^{max} (Eq.IX in Table 3), the value of L_r^{min} for substance 9 was estimated to be equal to 2.26. The new values of the constants (see Table 2) were used in the correlation analyses of our experimental data.

Table 2

Rate Constants of Lightinitiated Decomposition of PAH (k_1 in oxygen, k_2 in argon), the Values of Indexes of Free Valency, Iocalization Energies, and σ_r

Substance	Rate constant mol.l^{-1}. hour^{-1} $k_1 \cdot 10^5$	$k_2 \cdot 10^5$	F_r^{max} [a]	L_r^{min} [b]	σ_r [c]	r
I	0.56	0.24	0.452	2.30	0.5	1
2	0.44	0.29	0.439	2.374	-0.8	1
3	0.60	0.3	0.469	2.19	2.9 e	1
4	0.592	0.203	0.457	2.24	2.6	6
5	1.42	1.84	0.514	2.04	8.2 e	7,12
6	100	99	0.530	1.93	9.8	5
7	1.15	0.60	0.473	2.139	8.4	3
8	1.74	1.25	0.529	1.94	11.1	6
9	0.5	0.5	0.46 d	...	1.8 e	6
10	1.08	1.35	0.499	2.12	6.4 e	5
11	1.08	1.68	0.498	2.13	6.5	7
12	1.44	2.52	0.510	2.08	7.7 e	7
13	1.05	0.84	...	...	...	...
14	4.63	2.21	...	...	...	...
15	0.53	0.33	0.449	2.307	1.7	1
16	26.5	12.0	...	...	...	...
17	12.3	8.2	...	...	...	...
18	1.87	1.09	...	...	...	...
19	8.9	6.41	...	...	...	...
20	1.28	2.47	...	...	...	...
21	6.1	...	...	...	...	...
22	2.9	1.5	...	...	...	...
23	4.0	2.3	...	...	...	...
24	3.8	1.07	...	...	...	...
25	6.07	3.39	...	...	...	...
26	5.10	2.76	...	...	...	...
27	9.87	3.95	...	...	...	...

[a] Ref.13 [b] Refs.13,14 [c] Ref.4 [d] Ref.15 [e] estimated in this work

The obtained correlation equations are given in Table 3 (see also Figs.1 and 2). The first three of them express the relationships in the reaction of initiated decomposition in oxygen, the next three equations (IV-VI) refer to photodegradation of PAH in argon. It follows, first of all, that reactivity of PAH is determined by both the value of the free valency of the most active carbon atom and the localization energy of its bonds. Relative reactivity of the substance decreases with increasing localization energy and decreasing value of the index of free valency. The best correlation was obtained with the values of free valency F_r^{max} (see Table 3).

It is noteworthy that the data for the degradation of benzanthracenes unsubstituted in meso-positions (substances 5,6,10,11,12,20), in argon, could be involved in the correlations only when a statistical factor as high as two was introduced. Substitution of hydrogen by methyl group in meso-position cancels the need for such a correction (substances 18 and 19). Such a phenomenon still remains without explanation. It is clear, at least, that the correction has no direct physical meaning of a statistical factor, because the use of the latter is warranted only in the case of substances 5, 12, and 20 due to equal reactivity of unsymmetric meso-positions. At the same time the data for the reaction in oxygen correlate without any correction even in the case of the same substances, that is not less unexpected.

The rate constants of both reaction series for all the investigated substances, including benzanthracenes with corresponding correction, can be well compared with each other (the correlation coefficient, r=0.978, see Fig. 3).

Most of the investigated substances react slower under argon than in solution saturated with oxygen. The sensitivity to the structure of the initial substance seems to be higher in the former case, although, to be more exact, the sensitivity constants cannot be statistically distinguished because of considerable scattering of the data from the experiment under argon. The latter fact is probably caused by oxygen traces in solution. Thus, one can assume the participa-

Fig. 1

Dependence of the rate of degradation of PAH in oxygen upon the index of free valency and localisation energy. For the point number see Table 1.

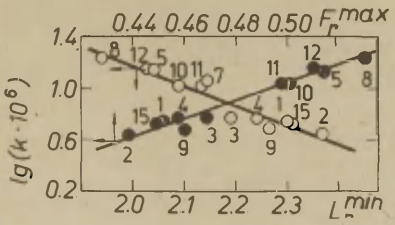

Fig. 2

Dependence of the rate of degradation of PAH in argon upon the values of Streitwieser σ_r constants. For the point number see Table 1.

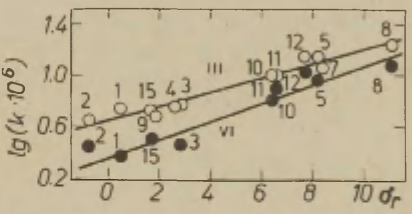

Fig. 3

Comparision of decomposition rate constants of PAH in oxygen (k_1) with those in argon (k_2). For the point number see Table 1. An arrow indicates the shift due to the statistical factor.

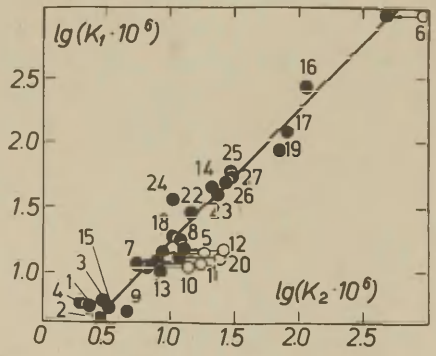

Table 3

Correlation Equations for the Reactivity of PAH (Substances 1-12,15) in Photodecomposition and Those Used for Calculation of New Constants

No.	Number of points	Correlation equation	r	s
I	11	$\lg k_1 = -8.40 \pm 0,19 + (6,90 \pm 0,39) F_r^{max}$	0.986	0.038
II	12	$\lg k_1 = -1,71 \pm 0,31 - (1,56 \pm 0.14) L_r^{min}$	0.962	0.061
III	12	$\lg k_1 = -5.40 \pm 0.04 + (0.058 \pm 0.006) \sigma_r$	0.950	0.074
IV	12	$\lg k_2 = -9.18 \pm 0.66 + (8.15 \pm 1.38) F_r^{max}$	0.881	0.138
V	9	$\lg k_2 = -1,23 \pm 0.70 - (1.87 \pm 0.32) L_r^{min}$	0.877	0.128
VI	12	$\lg k_2 = -5.68 \pm 0.08 + (0.07 \pm 0.01) \sigma_r$	0.879	0.139
VII	11	$\sigma_r = -52.3 \pm 3.3 + (117.8 \pm 6,8) F_r^{max}$	0.985	0.843
VIII	9	$\sigma_r = 59.9 \pm 3.4 - (25.5 \pm 1.5) L_r^{min}$	0.975	0.792
IX	12	$L_r^{min} = 4.31 \pm 0.09 - (4.46 \pm 0.19) F_r^{max}$	0.991	0.023
X	8	$\lg k_1 = 13.8 \pm 1.8 - (4.18 \pm 0.55) \bar{K}$	0.953	0.105

tion of oxygen in the rate limiting step of photodegradation of PAH. On the other hand, it is known[4] that ϱ' values for electrophilic reactions of PAH vary in the range of 0.3-0.6. Regarding the low sensitivity in this case (ϱ'=0.06) one can suppose that the reaction proceeds via a radical mechanism. However, despite of plausibility of such a conclusion, very low value of constant ϱ' may also be connected with that that under these conditions total rate of the process is only partly determined by the step in which PAH participates.

In conclusion let us consider some possible relationships between reactivity of PAH and their physiological activity. It should be pointed out an attempt of Franke[16] to connect the influence of PAH to methabolic transformations of benzopyrene and dimethylbenzanthracene with some calculated and experimental values. Some of his correlations cannot lead to unambiguous conclusion because of the lack of experimental data. However he could show that activity of PAH was connected with their solubility in water, molecular refraction, and some MO-indexes, e.g., with the indexes for K-region after Pullman.[17] The latter had been suggested as the measure of cancerigenity of PAH[17].

It appeared that the rate constants of light - initiated decomposition of PAH satisfactorily correlate with values of Pullman K-indexes (Eq. X in Table 3), and that the more reactiv is a PAH the more cancerigenic it is.

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INVESTIGATION OF BENZOIC ESTERS PROTON-ACCEPTOR ABILITY BY IR-SPECTROSCOPIC METHOD

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By IR-spectroscopic method the association constants (K_{ass}) of the series of esters C_6H_5COOR with phenol were determined. lg K_{ass} and $\Delta\nu_{OH}$ were linearly correlated with σ^* for R and thus they are a satisfactory measure for esters proton-acceptor ability. In contrast the intensity of hydrogen-bonded hydroxyl band A_{ass} and enthalpy ΔH_{ass} in this series retain almost constant.

In course of our investigations of the influence of substituents in the alcoholic part of esters on their properties [1,2] it was of interest to study the dependence between the proton-acceptor ability of esters C_6H_5COOR and nature of R. One of the most widely used and convenient methods of studying this ability is the IR-spectral determination of characteristics of hydrogen bond formed between these substances and some standart donors. Recently this method was used for determination of basicities for many compounds [3-5] but the esters in this respect have been studied quite fragmentally. This paper reports some IR characteristics for hydrogen bond between phenol and esters C_6H_5COOR (I-X).

Experimental

The synthesis and properties of esters C_6H_5COOR (I-X) are reported already.[1] Their purity was controlled by GLC (LChM-7A with catharometer, on the 1 m x 6 mm with 7% Carbowax/Celite column, velocity of He is 80-100 ml/min, temperature is 170-190°); impurity content no more than 0.4%.

Phenol was washed with cyclohexane and was kept in a dropper. Phenol-esters mixtures IR-speotra were recorded on an UR-20 spectrophotometer with LiF prism in 0.04-0.1 cm cells in CCl_4 solution. The spectral slit width was 4 cm^{-1} over investigated region 3100-3800 cm^{-1}. The examples of speotra are given in Fig. 1.

For the association constants determination the area of unbonded hydroxyl band in ternary mixtures of CCl_4, phenol (0.04-0.13M) and ester (0.1-0.3M) was measured by the Bourgen-Ramsay method [6]. The unassociated molecules concentration X is calculated by Eq.(1):

$$X = \frac{1.55 \cdot D \cdot \Delta\nu_{1/2}}{l \cdot A^{o}_{OH}} \qquad (1)$$

where A^{o}_{OH} is the intensity of OH-absorption in the free phenol spectra (= $1.1 \cdot 10^4$ l/mol cm^2), D is the peak intensity of unbonded OH band, $\Delta\nu_{1/2}$ is their halfwidth, and l is the pathlength in cm. K_{ass} is calculated by Eq.(2):

$$K_{ass} = \frac{C^{o}_{PhOH} - X}{X\,(C^{o}_{est} - C^{o}_{PhOH} + X)} \qquad (2)$$

The average of 3-5 K_{ass} values with their mean errors are given in Table 1.

In carrying the measurements of the hydrogen-bonded hydroxyl band integral intensity the ester concentration was 3M, phenol concentration being varied from 0.004 to 0,02M. From low frequency side a band was slightly distorted because of an appearance C = O stretching first

overtone of the range 3400 cm^{-1}. For this reason for A_{oo} determination the area of high frequency half-band by numerical integration methods were measured and then the obtained value was doubled. The A_{co} values were obtained at the different C^{o}_{PhOH} and l values and were extrapolated to $C \cdot l = 0$[x]. The accuracy of A_{co} values is ~ 10%. ΔH_{ass}

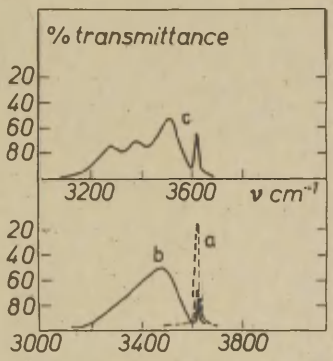

Fig. 1

IR-spectra in CCl_4 solutions: a) free phenol, b) phenol + methyl benzoate(IV), c) phenol + cyanmethyl benzoate (X).

x) It is noteworthy that slope of A vs C·l plot is positive for the esters with electron-donating substituents (II-IV), negative for the esters with electron-withdrawing substituents (VI-IX) and approaches to zero for (V).

Table 1

Characteristics of Phenol-esters, C_6H_5COOR, Hydrogen Bond (in CCl_4 solutions, 25°)

№	R	ν^{ass}_{OH} cm^{-1}	$\Delta\nu_{OH}$ *) cm^{-1}	K_{ass} l/mol	$\Delta\nu_{1/2}$ cm^{-1}	$A_{ass}\cdot10^{-4}$ $l\cdot cm^{-2}\,mol^{-1}$	$-\Delta H$ kcal/mol
I	cyclo-C_6H_{11}	3441	170	7.2±0.4	195	~11	-
II	C_3H_7	3440	171	7.1±0.4	119	7.50	4.9
III	C_2H_5	3445	166	7.6±0.6	132	7.79	5.1
IV	CH_3	3450	161	6.0±0.7	140	8.30	5.3
V	$CH_2CH_2C_6H_5$	3465	146	-	130	9.0	5.6
VI	$CH_2C_6H_5$	3451	160	5.3±0.7	136	9.4	5.9
VII	CH_2CH_2Cl	3465	146	3.7±0.4	147	10.4	6.3
VIII	$CH_2C{\equiv}CH$	3480 xx)	131	9.6±1.2	-	-	-
IX	CH_2Cl	3505	106	1.9±0.3	123	7.7	5.0
X	$CH_2C{\equiv}N$	3495 xxx)	116	6.4±0.2	-	-	-

x) For the free phenol ν^{o}_{OH} = 3611 cm^{-1}.
xx) Maximum is observed also at 3310 cm^{-1}.
xxx) Maximums are observed also at 3375 and 3270 cm^{-1}.

values were calculated by Eq.(3) proposed by Iogansen [3]. The accuracy of these values is ~ 0.5 kcal/mol.

$$-\Delta H_{ass} = 2.9\left[A_{ass}^{1/2} - A_{o}^{1/2}\right] \qquad (3)$$

Discussion

The data listed in Table 1 show that all the obtained characteristics may be divided into two groups. To the first group the association constants K_{ass} and the OH adsorption frequency shift $\Delta\nu_{OH}$ are related. One can see that K_{ass} for PhOH-C_6H_5COOR system decreases systematically with increasing electron-withdrawing properties of R. Fig.2 shows that a good correlation between lg K_{ass} and Taft constants σ^* is observed (the correlation parameters are given in Table 2).

From this it can be concluded that the electron density at the ester group acting as proton-acceptor center is a dominant factor in the ester-phenol association. This density is changed by the inductive effect of R; steric effect of R in this series appears to be unessential. Propargyl and cyanmethyl benzoate (VIII,X) are deflected from this correlation to larger K_{ass} This may be due to the presence of, besides the ester group, other proton acceptor centers in the molecule as the triple bonds C≡C and C≡N, and the nitrogen atom of the C≡N group. It leads to a variety of possible associates which is confirmed by a complicated nature of spectra (Fig.1c). As a result the apparent K_{ass} value is increased.

One can see from Fig.2 that the $\Delta\nu_{OH}$ values, too, are well correlated with σ^*. Consequently they are satisfactory measures of the hydrogen bond strength which is measured by the free energy of association ΔF_{ass} (and K_{ass}). The point for ester (IV)(R = $CH_2CH_2C_6H_5$) shows some deviation from this correlation but it may be seen from Table 2 that this does not change significantly the correlation parameters.

The second group of properties includes the OH band integral intensity A_{ass} and the hydrogen bond enthalpy ΔH_{ass} which are connected with each other according to Eq.(3). It has been found that in the investigated series these properties change slightly fairly irregularly. It may be seen from Table 2 and Fig.3 that $-\Delta H_{ass}$ increases slightly with increasing σ^* in esters (II-VII). However the whole range of the ΔH_{ass} value is less than 1.5 kcal/mol whereas the accuracy of its determination is ~0.5 Kcal/mol. Paying attention to the ΔH_{ass} value for IX we believe as more well-grounded to take ΔH_{ass} = const = - 5.5±0.4 kcal/mol.

This value is near to 4.7 kcal/mol given by Iogansen [3] for the system of phenol and ethyl acetate. Thus it appears that the equilibrium of phenol-esters association is a series close to isoenthalpic and a change in K_{assis} mainly governed by the change in the association entropy. Recently an essential change in ΔS_{ass} depending on the proton acceptor has

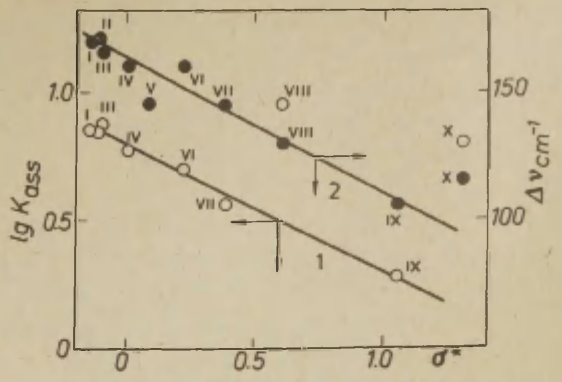

Fig. 2

Relationship between the characteristics of phenol-esters, C_6H_5COOR, hydrogen bond and σ^* - constants for R, 1 = lg K_{ass}, 2 = $\Delta\nu_{OH}$.

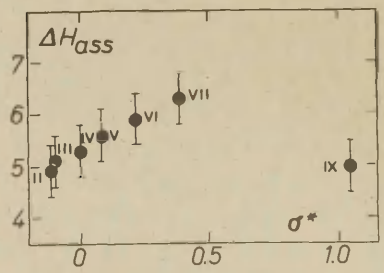

Fig. 3

Relationship between ΔH_{ass} values calculated according to Eq.(3) and σ^*.

also been reported.[7]

Then, the results obtained confirm that no direct connection between $\Delta\nu_{OH}$ and ΔH_{ass} can be observed even for compounds of related structures [5,8,9]. From the other hand, they show that not in all cases proton-acceptor ability of compounds is characterized by hydrogen bond enthalpy.[9] Probably a more general measure of this is the ΔF_{ass} value or K_{ass}, respectively.

Table 2

Correlation of Phenol-esters, C_6H_5COOR, Hydrogen Bond Parameters (by the equation $Y = Y_0 + \rho^* \sigma^*$)

Parameter Y	Compounds involved in correlation	ρ^*	r	s	Y_0
lg K_{ass}	I-IV,VI,VII IX	-0.50±0.03	0.995	0.027	0.80±0.01
$\Delta\nu_{OH}$	I-IV,VI,VII, IX	-53±4	0.985	4.4	164±2
$\Delta\nu_{OH}$	I - IX	-52±6	0.955	6.9	162±3
$-\Delta H_{ass}$	II - VII	2.65±0.17	0.991	0.075	5.3±0.1
$-\Delta H_{ass}$	II-VII,IX	0.06±0.56	-	-	5.5±4[x)]

x) Mean deviation; in all other cases mean square deviations are pointed out.

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STUDY OF KINETICS OF tert-BUTYL HALIDE IONIZATION IN ACETONITRILE USING TRIPHENYI VERDAZYL RADICALS

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A spectroscopic method is suggested for the study of ionization kinetics of tert-butyl halides in aprotic organic solvents. The reaction is carried out in the presence of triphenyl verdazyl radicals (λ_{max}= 720 nm) reacting rapidly and quantitatively with splitting out halogen hydride. The ionization kinetics of Me_3CX (X=Cl, Br, I) in acetonitrile, v= k(Me_3CX), is studied. The values of k for Me_3CCl, Me_3CBr, and Me_3CJ at 25°C relate as 1:545:23013. The increase in the reaction rate is caused by decreasing activation energy.

tert-Butyl halide solvolysis and isobutylene elimination, whose rates are determined by alkyl halide ionization stage[1], have great theoretical value and are the subjects of extensive studies.[2]

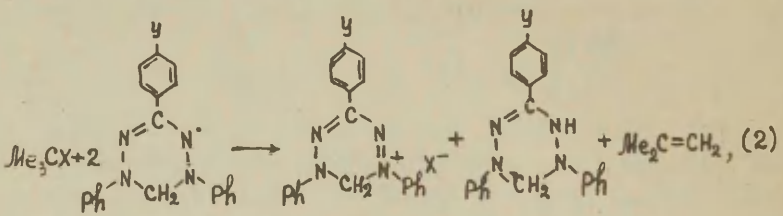
$$Me_3CX \rightleftharpoons Me_3C^+X^- \rightleftharpoons Me_2C=CH_2+HX \qquad (1)$$

The data on medium effect upon the rate of the above reactions were used for quantitative account of the solvent effect.[3] Solvent effect on Me_3CCl ionization rate has received the most study.[4,5] Hydrogen chloride evolving in Me_3CCl decomposition is sufficiently stable and readily detectable, though reversibility of the reaction and hydrogen chloride catalytic effect may cause considerable errors in ionization constant determination.[6] Moreover, the rate of this reaction in non-polar solvents is very low[4] which makes its determination more difficult and affects the precision.

Little attention has paid to the medium effect on ionization rates[5] of Me_3CBr and especially to that of Me_3CBr.[7] In this case an additional source of errors may appear in halogen hydride oxidation. Literature findings suggest that in low polarity solvents the ionization rates of Me_3CBr and Me_3CI should be higher than that of Me_3CCl by 3-4 and 5-6 orders of magnitude, respectively. With an effective method for halogen hydride evolution control Me_3CBr and Me_3CI may appear useful for medium effetc investigation.

Me_3CX ionization in aprotic and low polarity solvents is usually studied in the presence of various quantities of tertiary amines; liberating acid concentration is determined by titration; rate constants are found by extrapolation the base concentration to zero.[6,8]

We found that the rate of acid liberation from Me_3CX in organic solvents could be easily controlled spectroscopically if the reaction was carried out in the presence of small concentrations ($\sim 10^{-4}$ mol/l) of triphenyl verdazyl radicals which rapidly and practically quantitatively react with halogen hydride.[9] In an aprotic solvent the whole process may be represented as follows:



where Y = H, NO_2, CH_3O, Cl.

The reaction rate may be measured both by Y-RN$^{\bullet}$ radical (in CH_3CN for H-RN$^{\bullet}$ λ_{max}= 720 nm, lg ε = 3.61) and by Y-RN^{+}X^{-} salt cation (in CH_3CN for H-RN^{+} λ_{max}= 550 nm, lgε= 4.06). Verdazyl leuco base, Y-RNH, has no absorption in the visible range (in benzene for H-RNH λ_{max}= 300 nm, lgε=4.41, Ref.10).

In the present paper we submit some data on the rate

of halogen hydride liberation from Me_3CI, Me_3CBr and Me_3CCl in acetonitrile. Alkyl halides were purified by distillation under nitrogen. The reaction was carried out in a temperature controlled cell of a СФ-4 spectrophotometer. Y-RNH formation was proved spectroscopically, that of isobutylene by gas chromatography.

Fig. 1 and 2 show kinetic curves typical for the reactions between Me_3CBr and Cl-RN$^{\bullet}$ and for those of Me_3CI with H-RN$^{\bullet}$. Descending curves illustrate the radical concentration change in the experiment, ascending ones show the changes in salt concentration. A sharp jump on the initial part of the kinetic curve is due to a rapid reaction of Y-RN$^{\bullet}$ with haloid acid (3) and/or halogen (4)[10], formed during Me_3CX decomposition prior to determination.

$$2Y\text{-}RN^{\bullet} + HX \longrightarrow Y\text{-}RN^{+}X^{-} + Y\text{-}RNH \qquad (3)$$

$$2Y\text{-}RN^{\bullet} + X_2 \longrightarrow 2Y\text{-}RN^{+}X^{-} \qquad (4)$$

For Me_3CBr the jump in Y-RN$^{\bullet}$ curve is twice higher than that in Y-RN^{+} curve (Fig. 1, exp. 2 and 3), which conforms to the stoichiometry of reaction (3). In some experiments the difference is smaller (Fig. 1, exp. 1). This points to partial oxidation of HBr into Br_2. For Me_3CI the Y-RN$^{\bullet}$ concentration change in the initial period is somewhat greater or the same as that of Y-RN^{+} (Fig. 2) which is indicative of considerable or complete oxidation of HI to I_2. Initial changes in Y-RN$^{\bullet}$ and Y-RN^{+} concentrations due to Me_3CCl decomposition are small and relate as 2:1. In the course of kinetic experiment the concentration change of Y-RN$^{\bullet}$ and Y-RN^{+} complies with Eg. (3) in all cases. Therefore, halogen hydride that forms during Me_3CX decomposition does not oxidize in the presence of Y-RN$^{\bullet}$. The Y-RNH oxidation does not occur in the experiment either.

In all cases studied, alkyl halide decomposition rate is described by $v=k(Me_3CX)$ being unaffected by the concentration and nature of triphenyl verdazyl (Table 1, exp. 1 to 5). The values of k calculated from concentration chan-

ges of Y-RN$^{\cdot}$ and Y-RN^{+} are sufficiently coincident (Table 1); the reaction rate is the same in the air and under nitrogen (exp. 6 and 7). Additions of N-butyl quinoline iodide (QI) do not affect Me_3CI ionization rate (as evidenced by the radical, exp. 10 and 11). The calculations of k values based on Y-RN^{+} concentration changes in the presence of QI give underrated values resulting from inhibited dissociation of triphenyl verdazyl salt in the presence of a like ion. Indeed, the authors have found that the absorbance of H-RN^{+}I^{-} solution in acetonitrile at 540 nm (λ_{max} H-RN^{+}) is decreasing with the QI concentration increase.

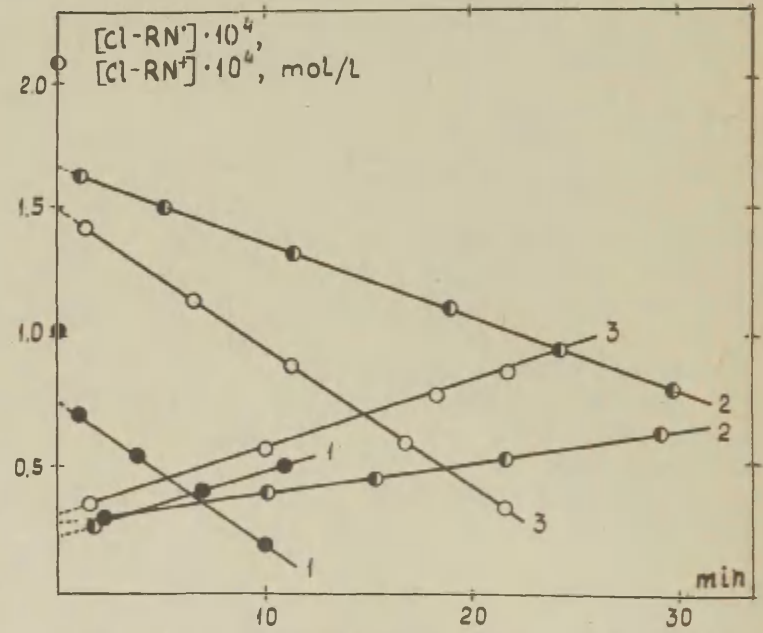


Fig. 1. The kinetics of HBr liberation from Me_3CBr in the presence of Cl-RN$^{\cdot}$ at 25.7°C.
The concentrations of Cl-RN$^{\cdot}$ and Me_3CBr are
1. $1.03.10^{-4}$, 0,0352
2. $2.06.10^{-4}$, 0.0176
3. $2.06.10^{-4}$, 0.0352 mol/l, accordingly

Table 1

The Kinetics of Me_3CX Ionization in Acetonitrile

Exp. No.	Reaction	$(Me_3CX)\cdot 10^2$, mol/l	$(Y\text{-}RN^{\cdot})\cdot 10^4$, mol/l	°C	$10^7 \cdot k$, $sec.^{-1}$ by $Y\text{-}RN^{\cdot}$	$10^7 \cdot k$, $sec.^{-1}$ by $Y\text{-}RN^{+}$
1	$Me_3CBr+CH_3O\text{-}RN^{\cdot}$	4,50	2.70	25	11,7	11.5
2		3.30	2.90	25	12.0	11.0
3		4.40	1.93	25	11.8	11.3
4	$Me_3CBr+NO_2\text{-}RN^{\cdot}$	3.10	3.20	25	12.0	12.5
5	$Me_3CBr+H\text{-}RN^{\cdot}$	6.05	3.60	25	12.5	12.5
6		0.320	4.70	13.5	4.31	4.30
7[x]		0.320	4.70	13.5	4.37	4.53
8	$Me_3CCl+Cl\text{-}RN^{\cdot}$	155.5	1.95	44.9	0.275	0.273
9		155.5	1.95	44.9	0.273	0.283
10	$Me_3CI+H\text{-}RN^{\cdot}$	0.0442	3.54	40	2280	2300
11[xx]		0.0442	3.50	40	2250	-

[x] Under nitrogen

[xx] In the presence of $3.07\ 10^{-3}$ mol/l N-butyl quinoline iodide

In our experiments the degree of conversion was app. 50 %, 1 %, and 0.01 %, and the errors of ionization constant determination were 3–4 %, 1–2 % and less than 1 % for Me_3CI, Me_3CBr and Me_3CCl, respectively. With Me_3CJ concentrations close to that of Y-RN°, errors reach as much as 10 % in some experiments.

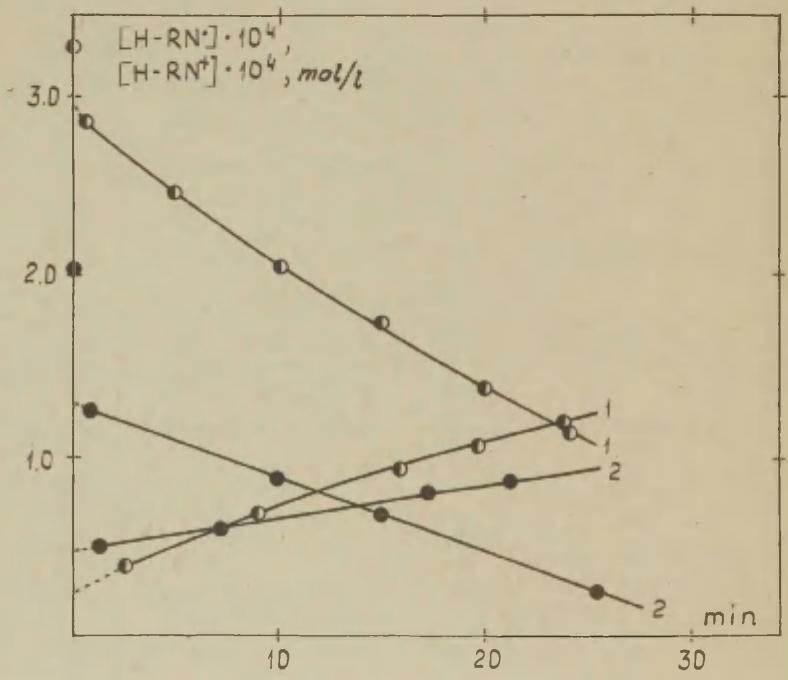


Fig. 2. The kinetics of HI liberation from Me_3CI in the presence of H-RN°.
The concentrations of H-RN° and Me_3CI are
1. $3.27.10^{-4}$, $3.20.10^{-4}$ (42°C)
2. $2.05.10^{-4}$, $6.30.10^{-4}$ mol/l (25°C),
respectively.

The ratio of Me_3CCl (at 25°C k= $2.29.10^{-9}$ sec^{-1}), Me_3CBr and Me_3CI ionization constants at 25°C is 1:545:23013.

Table 2

Kinetic Parameters of Me_3CX Ionization in Acetonitrile*)

Reaction	°C	$k \cdot 10^7$, sec^{-1}	E kcal/mol	$-\Delta S^{\neq}$ e.u.
$Me_3CCl+Cl-RN^{\cdot}$	25.1	0.0231±0.0002		
	34.7	0.0800±0.0006	24,5±0.4	18±1
	42.8	0.2080±0.0006		
	44.9	0.2780±0.0005	r = 0.999	
$Me_3CBr+H-RN^{\cdot}$	13.5	4.37±0.06		
	25.0	12.5±0.2		
$Me_3CBr+NO_2-RN^{\cdot}$	25.0	12.6±0.2		
$Me_3CBr+CH_3O-RN^{\cdot}$	25.0	12.3±0.2	20.1±0.5	15±2
$Me_3CBr+Cl-RN^{\cdot}$	25.8	13.5±0.2		
	27.0	16.0±0.3	r = 0.996	
	29.0	24.1±0.3		
	38.8	50.1±0.2		
$Me_3CI+Cl-RN^{\cdot}$	21.0	350±20		
	37.7	2060±60		
	43.0	2660±80	17.07±0.7	21±2
$Me_3CI+H-RN^{\cdot}$	25.0	527±20		
	31.7	1080±100	r = 0.991	
	40.0	2280±30		

*) E and $\Delta S^{\neq}$ calculated by the least-squares method.

This ratio is 1:26:53 in water and 1:40:143 in methanol.[7] The reaction rate increase in CH_3CN is connected with the activation energy decrease (Table 2).

Earlier, the ionization rate of Me_3CBr in CH_3CN was determined in the presence of tributyl amine[11] (at 24.5°C $k = 12 \cdot 10^{-7}$ sec^{-1}, $E = 23$ kcal/mol, $\Delta S^{\neq} = -10$ e.u.). Rate constant value at 24.5°C is in sufficient agreement with our findings; activation energy value obtained by us is lower by 3 kcal/mol. It should be noted that in the work of Hoffman[11] the base concentration effect on reaction rates was not taken into account. In the study of Me_3CBr ionization in nitromethane in the presence of pyridine it has been shown, however, that the reaction rate depends upon the base concentration.[12] The activation energy of Me_3CBr ionization in nitromethane, found from the constants after extrapolation base concentration to zero is 20.6 kcal/mol, which value is close to that obtained in the present work for acetonitrile. Ionization constant for Me_3CCl in CH_3CN at 45°C [$(2.57 \pm 0.1)\ 10^{-8}$, sec^{-1}] has been given by Kevill and Dorsey[13], and that at 120°C [$(6.96 \pm 0.42) 10^{-5}$ sec^{-1}] reported by Koppel.[14] In both cases pyridine concentration has been shown not to affect the reaction rate. The constant value at 45°C is in good agrement with our data. The value at 120°C calculated from our data is also sufficiently coincident: $k^{120} = (4.6 \pm 1.9) 10^{-5}$ sec^{-1}. No published data on Me_3CI ionization in CH_3CN are available.

The use of triphenyl-verdazyl radicals[3] opens up new possibilities to the investigators of tert-alkyl halide ionization kinetics. It helps to avoid errors caused by haloid acid liberation. The method is simple and convenient. It may be used to study other reactions that procede with the liberation of haloid or any other strong acid.

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INFLUENCE OF IONIC STRENGTH ON HYDROLYSIS OF SOME BENZOATES WITH CHARGED SUBSTITUENTS

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The alkaline hydrolysis of some benzoic esters in water is investigated. It is shown that the hydrolysis rate of uncharged esters does not depend on the KCl concentration in solution. For the ammonium group containing esters this dependence has a complex character - for a small μ values a linear dependence between lg k and $\sqrt{\mu}$ with the following bend is observed; for high μ values lg k does not depend on μ. The slope of the straight line, φ, and the $\Delta \lg k = \lg k_{\mu=0} - \lg k_{\mu\to\infty}$ value decreases with increasing distance between ammonium and ester groups. The results obtained are explained from the point of view of the hypothesis about the ion pair participation in process. An attempt is made to calculate the constants for these ion pairs formation.

The influence of the ionic media on the alkaline hydrolysis of esters which contain a charged ammonium group in alcohol part has been studied for a long time [1] but at present the data only for few compounds are available. In the recent papers [2,3] it was shown that the ionic strength influence on the hydrolysis rate constants of esters $C_6H_5COO\text{-}Z\text{-}N(CH_3)_3^+ X^-$ did not agree with the Brønsted-Hükkel ideas but depended on the distance between an charged substituents and a reaction center. Analogous results of the investigation of phosphonic esters alkaline

hydrolysis were obtained [4]. It was interesting to extend the series of carboxylic esters with a view to verify and develop the relevant hypothesis.[2-4] Present article describes the investigations results of salt concentrations influence on alkaline hydrolysis of charged benzoates, $C_6H_5COO(CH_2)_3N(CH_3)_3^+ I^-$(I), $C_6H_5COOCH_2C{\equiv}CCH_2N(CH_3)_3^+ I^-$(II), and C_6H_5COO  $N(CH_3)_2^+I^-$ (III), as well as neutral benzoates, $C_6H_5COOCH_2C{\equiv}N$ (IV) and $C_6H_5COOCH_2C{\equiv}CH$ (V). These substances may be considered as a sequel of a studied series.[2,3] The substances II and III are of special interest since a problem of reaction conformation determination, which is significant for I and benzoylcholine [2], is not significant for II and III owing to the rigidity of their structure.

Experimental [x)]

Iodomethylates (I-III) were prepared from appropriate bases and methyl iodide as described in Refs.5 and 6, and were purified by cristallisation from alcohol. Cyanmethyl benzoate (IV) was prepared after Freedman [7], propargyl benzoate as described by Kruglikova et al.[6].

Hydrolysis was performed in water at 25° and 50°C in thermostatic cell. A constant pH (10.5-11.5 at 25° and 8-10.3 at 50°) was supported by means of LPM-60-pH-stat with an autotitration block BAT-12M3. Ionic strength in the range of 0.03-1.0 was set up by KCl, $\mu < 0.03$ calculated as a sum of alkali and ester concentrations. In case of IV, low dissoluble in water, the experiments were done in presence of 2% methanol.

The pH-stat [9] and spectrophotometric (λ = 261 and 274 nm) methods [8] were used for the reaction rate measurements. Spectral characteristics of esters are listed in Table 1; for benzoate-ion $\varepsilon_{261} = 670$, $\varepsilon_{274} = 490$. The rate constants determined by both methods coincided well with each other (see Table 2). The measurements were done

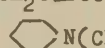
x) With the participation of the student E.Bezuglova.

at several alkali concentrations and the results were an evidence of the first order by each of components (see Tables 2-6). In some cases the measurements were performed in 0.05M boric buffer with necessary addition of KCl, and the alkali concentration was calculated by means of the experimental plot pH_{obs} vs. lg C_{OH}. As seen from Table 2 the buffer catalysis is absent. The second-order rate constants at different values of ionic strength are listed in Tables 2-6. The extrapolation to $\mu = 0$ is performed by least-squares method. The extrapolation range, the slope ψ, the calculated $k_{\mu=0}$ values, $k_{\mu\to\infty}$ values, and the E_{act} values determined by using Arrhenius equation are presented in Table 7.

Discussion

The dependences between lg k (at 25 and 50°) and μ for esters I-V are shown in Fig.1 as well as the data for benzoylcholine (VI) taken from Ref.2. It is seen that the alkaline hydrolysis rate of uncharged esters (IV,V) does not depend on the ionic strength. For the charged esters (I-III, VI) a linear dependence of lg k on μ for the low μ values is observed; then it is bended and for a high μ values the rate constant does not depend on the ionic strength. This value may be designated as $k_{\mu\to\infty}$. It is remarkable that both the slope ψ of linear dependence of lg k on μ and $\Delta \lg k = \lg k_{\mu=0} - \lg k_{\mu\to\infty}$ are not constant within this series but diminish when the distance between the ammonium and ester group increases (see Tables 7,8). These results are in accordance with the data in Refs.2,3 and with the hypothesis discussed ibidem. According to that idea the influence of a charged substituents is a sum of both inductive and electrostatic effects and the latter effect decreases with increasing ionic strength due to the ion pair formation, in which the charge is neutralised and the electrostatic effect is absent. In terms of those ideas the $k_{\mu\to\infty}$ value (which does not depend on μ) may be used for the evaluation of the purely inductive influence of the

Table 1

N N	R	M.p., °C (alcohol) or b.p. °C/mm	λ_{max}	ε_{274}	ε_{261}
I	$(CH_2)_3N(CH_3)_3^+$	194	274	1020	787
II	$CH_2C{\equiv}CCH_2N(CH_3)_3^+$	155	274	855	646
III		162	274	1020	788
IV	$CH_2C{\equiv}N$	141-4/II	275	1110	802
V	$CH_2C{\equiv}CH$	115/15	274	905	659

Physical and spectral characteristics of benzoates, C_6H_5COOR.

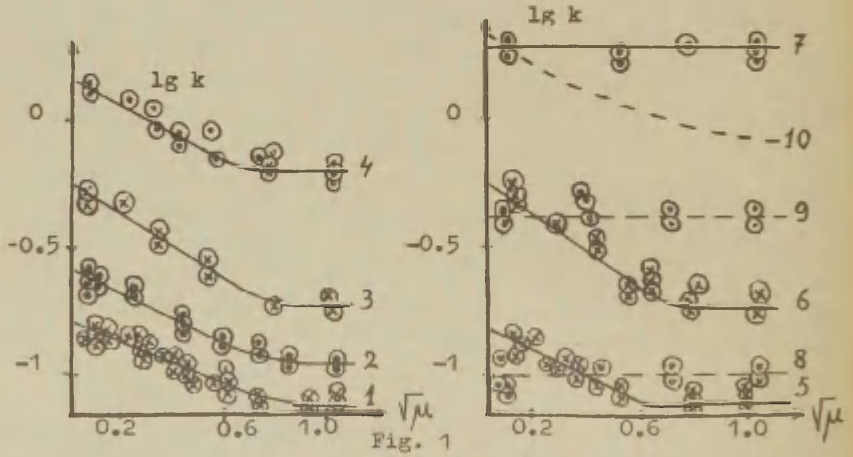


Fig. 1

Dependence of the alkaline hydrolysis rate on the ionic strentgh; 1 = I, 25°, 2 = I, 50°, 3 = II, 25°, 4 = II, 50°, 5 = III, 25°, 6 = III, 50°, 7 = IV, 50°, 8 = V, 8 = V, 25°, 9 = V, 50°, IO = benzoylcholine, 50° (after Püssa et al.)

Table 2

Alkaline Hydrolysis of Cyanmethyl Benzoate (IV) in Water at 50°

C_{ester} mM	C_{OH} mM	C_{KCl} M	k, l/mol·sec		
			pH[x]	UV[x]	Mean
3.94	2.63	-	2.4	3.1	2.75
3.94	0.675	-	2.8	3.3	3.05
3.94	0.631	0.25	2.2	3.1	2.65
0.49	1.29[xx]	0.49[xx]	-	2.9	2.9
3.82	0.30	1.0	2.3	2.9	2.6
3.82	1.59	1.0	3.5	2.7	3.1
0.49	1.29[xx]	0.85[xx]	-	2.3	2.3

x) pH=pH-stat method, UV=spectrophotometric method

xx) In 0.05 M boric buffer pH=8.75

Table 3

Alkaline Hydrolysis of Propargyl Benzoate (V) in Water

25°				50°			
C_{ester} mM	C_{OH} mM	C_{KCl} M	$k^{x)}$ l/mol·sec	C_{ester} mM	C_{OH} mM	C_{KCl} M	$k^{x)}$ l/mol·sec
0.435	0.692	-	0.104	0.740	1.02	-	0.455
0.512	1.29	-	0.076	0.740	0.69	-	0.450
0.512	2.70	-	0.149	0.740	1.26	-	0.382
0.512	6.02	-	0.162	0.656	0.795	0.16	0.508
0.512	6.85	-	0.127	0.656	0.970	0.16	0.390
0.512	3.98	0.16	0.086	0.656	1.48	0.16	0.537
0.512	5.00	0.16	0.131	0.740	1.77	0.5	0.355
0.740	7.60	0.16	0.096	0.740	1.15	0.5	0.402
0.512	3.98	0.5	0.098	0.656	0.933	1.0	0.410
0.512	9.10	0.5	0.113	0.740	1.74	1.0	0.490
0.512	6.02	1.0	0.119	0.512	1.74	1.0	0.405
0.740	6.02	1.0	0.083	0.740	1.15	1.0	0.422
0.740	9.10	1.0	0.113				

x) The rate constants are determined by UV-method

Table 4

Alkaline Hydrolysis of 3-Trimethylammonium Propylbenzoate in Water

C_{ester} mM	C_{OH} mM	C_{KCl} M	$k^{x)}$ l/mol·sec	C_{ester} mM	C_{OH} mM	C_{KCl} M	$k^{x)}$ l/mol·sec
25°							
6.47	1.48	-	0.140	6.45	1.78	0.25	0.0733
10.0	0.775	-	0.160	10.20	0.890	0.25	0.0855
10.15	3.63	-	0.152	6.00	2.53	0.25	0.082
3.62	5.50	-	0.158	6.25	3.02	0.35	0.097
3.46	3.63	-	0.154	3.75	1.32	0.35	0.0775
10.0	0.740	-	0.160	3.75	5.50	0.35	0.089
3.56	0.980	-	0.153	3.26	2.00	0.35	0.104
6.40	1.38	-	0.142	3.34	1.35	0.35	0.117
8.94	4.46	-	0.160	6.30	2.57	0.5	0.076
6.64	1.48	0.03	0.178	3.83	1.48	0.5	0.080
9.55	3.47	0.03	0.176	4.14	5.89	0.5	0.077
4.24	4.06	0.03	0.175	9.90	1.48	0.5	0.065
3.37	2.00	0.04	0.143	9.94	6.30	0.5	0.0745
3.59	1.48	0.04	0.132	6.15	2.30	0.5	0.0685
3.53	4.67	0.04	0.156	6.00	2.53	0.72	0.062
6.05	1.70	0.09	0.124	10.20	1.26	0.72	0.0706
10.10	0.74	0.09	0.103	4.00	7.10	0.72	0.092
4.06	6.75	0.09	0.123	5.52	2.14	1.0	0.103
9.70	4.66	0.09	0.122	3.35	6.45	1.0	0.084
3.88	0.98	0.09	0.133	10.20	5.50	1.0	0.077
6.55	1.56	0.15	0.106	9.60	1.66	1.0	0.0635
10.30	4.90	0.15	0.115	3.44	1.445	1.0	0.077
4.16	5.50	0.15	0.117				
50°							
6.47	0.467	-	0.45	3.44	1.58	0.25	0.28
3.65	1.35	-	0.64	9.60	0.691	0.25	0.22
10.12	0.295	0.04	0.60	6.55	0.575	0.56	0.19
9.55	1.09	0.09	0.37	10.20	1.07	1.0	0.25
3.62	0.561	0.09	0.38	6.50	0.725	1.0	0.20

$^{x)}$ The mean of two methods values.

Table 5

Alkaline Hydrolysis of Benzoate of 4-Trimethylammonium-butin-2-ol-1 in Water

C_{ester} mM	C_{OH} mM	C_{KCl} M	k^x l/mol·sec	C_{ester} mM	C_{OH} mM	C_{KCl} M	k^x l/mol·sec
			25°				
8.40	1.26	-	0.237	7.30	2.09	0.5	0.147
4.54	0.362	-	0.226	6.98	1.10	0.5	0.132
3.83	1.26	-	0.226	7.47	1.38	0.5	0.156
8.12	0.362	-	0.234	5.50	2.14	0.7	0.094
7.19	0.69	-	0.251	4.74	1.15	0.7	0.172
4.99	0.69	-	0.331	6.62	2.14	0.7	0.099
4.30	1.55	0.04	0.227	4.71	0.933	0.7	0.125
4.52	0.835	0.04	0.231	4.16	0.74	0.7	0.108
5.27	1.78	0.16	0.162	5.70	1.15	1.0	0.117
4.45	1.07	0.16	0.173	7.70	0.605	1.0	0.116
6.09	0.63	0.16	0.148	5.80	2.14	1.0	0.121
3.78	1.86	0.3	0.134				
5.16	1.025	0.3	0.141				
			50°				
6.44	0.178	-	1.115	5.73	0.430	0.25	0.92
5.80	0.347	-	1.33	5.45	1.57	0.25	0.606
5.98	0.417	0.04	1.14	5.67	0.466	0.5	0.735
5.55	0.282	0.04	1.04	6.12	0.38	0.56	0.68
6.00	0.355	0.09	1.19	5.70	0.87	0.56	0.80
5.80	0.145	0.09	0.88	5.86	0.65	1.0	0.505
6.40	0.191	0.15	0.595	5.74	0.38	1.0	0.49
5.75	0.436	0.15	0.55	6.00	0.50	1.0	0.54
5.85	0.204	0.15	0.81	6.03	0.802	1.0	0.68
				5.61	0.802	1.44	0.645

x) The mean of two methods values.

II

Table 6

Alkaline Hydrolysis of 4-Hydroxy-1,1-dimethylpiperidinium-benzoate in Water

C_{ester} mM	C_{OH} mM	C_{KCl} M	k^{x} l/mol·seo	C_{ester} mM	C_{OH} mM	C_{KCl} M	k^{x} l/mol·seo
25°							
6.40	1.51	-	0.123	6.05	1.20	0.15	0.068
3.45	1.35	-	0.135	5.85	5.25	0.15	0.0867
6.55	4.17	-	0.139	5.90	2.21	0.15	0.089
3.95	0.811	-	0.110	5.95	1.91	0.25	0.060
5.84	1.78	0.04	0.0965	3.85	1.23	0.25	0.0615
4.11	0.965	0.04	0.0955	6.30	7.10	0.25	0.067
6.35	5.60	0.04	0.102	6.04	3.17	0.56	0.054
6.33	4.68	0.09	0.093	6.24	2.40	0.56	0.058
6.05	1.66	0.09	0.088	5.68	1.59	0.56	0.064
6.10	2.29	0.09	0.0925	3.80	3.02	1.0	0.0545
5.70	5.00	0.09	0.0985	3.92	1.66	1.0	0.046
5.70	0.955	0.09	0.079	6.20	2.95	1.0	0.0575
				5.85	4.90	1.0	0.053
50°							
6.28	0.346	-	0.68	5.55	0.795	0.25	0.164
6.10	0.795	-	0.504	5.70	1.59	0.25	0.202
5.31	0.245	-	0.465	5.05	0.550	0.25	0.17
5.85	0.588	-	0.546	5.76	0.509	0.35	0.216
5.30	0.407	0.04	0.29	5.11	0.338	0.35	0.152
5.90	1.410	0.04	0.396	6.20	0.955	0.35	0.188
5.28	0.742	0.04	0.272	5.20	2.15	0.56	0.238
5.14	0.814	0.15	0.36	5.56	0.760	0.56	0.178
5.95	0.550	0.15	0.285	5.04	0.501	0.56	0.19
5.85	0.347	0.15	0.246	5.07	0.501	1.0	0.163
				5.00	1.20	1.0	0.219

x) The mean of two methods values.

Table 7

Influence of Ionic Strength on Alkaline Hydrolysis of Eeters, C_6H_5COOR, (I-V) in Water

№№	R	t °C	The linear extrapolation range $\sqrt{\mu}$	$-\varphi$	$k_{\mu=0}$ l/mol.sec	$k_{\mu\to\infty}$ l/mol.sec	E_{act} kcal/mol $\mu=0$	E_{act} kcal/mol $\mu\to\infty$
I	$/CH_2/_3\overset{N}{}/CH_3/_3^+$	25 50	0.06-0.5I 0.07-0.5I	0.62±0.08 0.77±0.I6	0.I87±0.009 0.63 ±0.07	0.082±0.007 0.2I ±0.06	9.3	7.2
II	$CH_2C{\equiv}CCH_2\overset{N}{}/CH_3/_3^+$	25 50	0.07-0.4I 0.08-0.5I	0.59+0.I4 0.65±0.20	0.28 +0.02 I.4I ±0.24	0.I2 +0.02 0.57 ±0.I0	I2.4	II.9
III		25 50	0.07-0.5I 0.07-0.40	0.65±0.07 0.84±0.I4	0.I4I±0.007 0.58 ±0.07	0.055±0.005 0.I9 ±0.02	I0.8	9.5
IV	$CH_2C{\equiv}N$	50	-	-	2.7 ± 0.3		-	
V	$CH_2C{\equiv}CH$	25 50	- -	- -	0.II± 0.02 0.44± 0.035		I0.6	

Table 8

Influence of Distance Between the Charges in Transition State upon Alkaline Hydrolysis of Esters, C_6H_5COOR, in Water

N	r, Å		25°, Q = 3.06			50°, Q = 3.21		
	Model[3] referred to	Our model	$-\Delta \lg K_{exp}$	$-QZ_1Z_2/r$ Model[3] referred to	$-QZ_1Z_2/r$ Our model	$-\Delta \lg K_{exp}$	$-Q Z_1Z_2/r$ Model[3] referred to	$-Q Z_1Z_2/r$ Our model
$CH_2N(CH_3)_3^+$ *) $(CH_2)_2N(CH_3)_3^+$ *)	2.4	4.4	> 0.7 ~ 0.75	I.27	0.70	> 0.5 ~ 0.80	I.34	0.76
trans	3.8	5.4		0.8I	0.52		0.84	0.60
gauche	2.85	4.4		I.II	0.70		I.I7	0.73
 $(CH_3)_2^+$	4.3	6.0	0.4I±0.06	0.70	0.5I	0.49±0.09	0.74	0.54
$(CH_2)_3N(CH_3)_3^+$	5.0	6.7	0.36±0.06	0.6I	0.46	0.48±0.I7	0.64	0.48
$CH_2C{\equiv}CCH_2N(CH_3)_3^+$	5.9	7.8	0.37±0.II	0.52	0.39	0.39±0.I5	0.54	0.4I

*) Data of Püssa et al.[2]

charged substituent and the lg k value for the evaluation of his electrostatic effect. Accordingly [3], the letter effect may be also calculated theoretically by means of the Christiansen [10] equation (1):

$$\lg k_{el} = \frac{Q \cdot z_1 \cdot z_2}{r} \qquad (1)$$

where z_1 and z_2 are the charges of agents; r is a distance in A between the charges in transition state; $Q = e^2/2.3\ kT = 3.06$ at 25° and $Q = 3.21$ at 50° (in water).

Unfortunately a direct comparison between the values which were calculated according to Eq.(1) and the experimental $\Delta \lg k_{exp}$ values is no reliable procedure. It is so on the one hand, because of unprecise experimental data with the errors of 10-20% and, on the other hand, because of the uncertainties in the selected transition state structure. We assume,for one of the possible models, that the transition state is similar to the tetrahedric adduct structure and the degree of C-O bond heterolysis is close to zero. This model is in accordance with Ingold's school views [11] according to which the rate-determining step in alkaline hydrolysis of ester is the tetrahedric adduct formation. This view is confirmed by the isotopic exchange data [12] and by the correlation of the aryl esters hydrolysis rate with σ° (See Refs.2,13). As seen from Table 8,this model fits better with experimental data for I-III than that suggested by Palm et al.[3], in which the degree of C-O bond heterolysis in transition state is close to unity. Of course, that is no final criterion of the model choice; this question require further investigations.

In any case, the data obtained are in good qualitative accordance with the hypothesis [3] about influence of the ion pairs on hydrolysis of esters containing charged substituents.It was of interest to try on bases of the experimental data to characterize quantitatively this process. If,as a first approximation, to assume that only the equilibrium (2) between free ions and ion pairs in solution occurs

and that the greater ionic aggregates may be neglected, the observed constant should be described by Eq.(3).

$$R_4N^+ + A^- \rightleftharpoons [R_4N^+A^-] \qquad (2)$$

$$k_{obs} = k_i \cdot x_{iens} + k_{ip} \cdot x_{ion\ pairs} =$$

$$= k_i \cdot x_{ions} + k_{ip} \cdot (1 - x_{ions}) \qquad (3)$$

where $x_{ions} = [R_4N^+]/C_{ester}$, $x_{ion\ pairs} = [R_4N^+A^-]/C_{ester}$. The association constant is expressed by Eq.(4):

$$K_{ass} = \frac{[R_4N^+A^-]}{[R_4N^+] \cdot [A^-]} = \frac{1 - x_{ions}}{x_{ions} \cdot C_{A^-}} \qquad (4)$$

and $x_{iens} = 1/(1 + C_{A^-} \cdot K_{ass})$. (5)

Assuming that $x_{ions} \longrightarrow 1$ at $\mu \longrightarrow 0$ and, consequently, $k_i = k_{\mu=0}$ and $x_{ione\ pairs} \longrightarrow 0$, at $\mu \longrightarrow \infty$ and, consequently, $k_{ip} = k_{\mu \to \infty}$, we will obtain from Eq.(5) and (3), after some transformation, equation (6):

$$\frac{k_{\mu=0} - k_{\mu\to\infty}}{k_{obs} - k_{\mu\to\infty}} = 1 + K_{ass} \cdot C_{A^-} \qquad (6)$$

Thus, between the expression in the left member of Eq.(6) and C_{A^-} $(=\mu)$ should be a linear dependence with slope equal to K_{ass}. Such a dependence calculated from data on alkaline hydrolysis of I at 25° is shown in Fig.2. It can

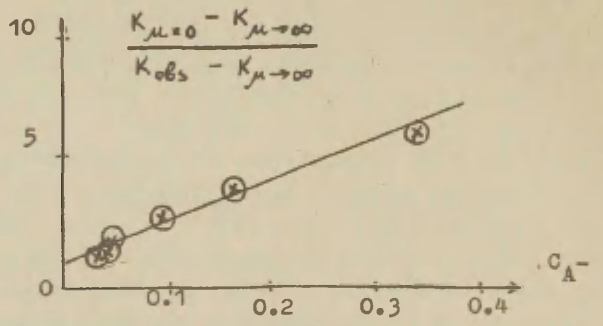


Fig. 2

Examination of Eq.(6) for hydrolysis of ester I

be seen that the dependence is really linear and the K_{ass} value calculated from this dependence is 15 l/mol. The analogous calculation for the data for benzoylcholine [2] gives K_{ass} = 4.5 l/mol. Now, it is difficult to say whether this difference in K_{ass} is real or as a result of the the errors connected with the estimation of $k_{\mu=0}$ and $k_{\mu\to\infty}$ values.

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Substituted Hydrazides of Hydroxylcarboxylic Acids. CII. The Kinetics of Acylation of Phenylhydrazide of Dibutylglycolic Acid with Acid Chlorides of Aliphatic Carboxylic Acids.

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The kinetics of acylation of phenylhydrazide of dibutylglycolic acid with acid chlorides of six aliphatic carboxylic acids in benzene at 25, 40, 55, and 70°C have been studied. A correlation between the lg K values and the σ^*- and E_s^0- constants, characteristic of the inductive and the steric effect of the acyl group of acid chloride, respectively, has been found.

It was established earlier that the nature of the acyl group of an acid chloride of carboxylic acid altered appreciably the reaction rate of acylation of arylhydrazides of disubstituted glycolic acids [1,2]. This article gives a more detailed study of the question. It presents the results of investigation of the kinetics of acylation of phenylhydrazide of dibutylglycolic acid [3] with acid chlorides of six different aliphatic carboxylic acids

$$C_6H_5NHNHCOC(OH)(C_4H_9)_2 + RCOCl \xrightarrow{-HCl} C_6H_5N(COR)NHCOC(OH)(C_4H_9)_2$$

($R = CHCl_2$, $C(CH_3)_3$, CH_2Cl, CH_2CH_2Cl, $n\text{-}C_3H_7$, $CH_2OC_2H_5$)

in benzene at 25, 40, 55 and 70°C. The method of kinetic measurements using quantitative determination of unreacted phanylhydrazide by means of polarography has been described earlier [4].

One can see that such compounds have been used as acylating agents, the acyl groups of which (R) differ substantially in their inductive and steric effects.*

Table 1. The Kinetics of Dichloroacetylization of Phenylhydrazide of Dibutylglycolic Acid at 70°C

Time min	0	2.5	5.0	7.0	10.0
i_l μA	1.216	0.842	0.440	0.327	0.215
K l/mol·sec	-	0.150	0.208	0.192	0.177
$\bar{K}$ l/mol.sec			0.182 ± 0.018		

Table 2. The Kinetics of Acylation with Acid Chloride of Trimethylacetic Acid at 70°C

Time min	0	10	20	40	60	91
i_l μA	1.297	1.011	0.828	0.520	0.351	0.188
K l/mol·sec	-	0.00980	0.00887	0.00903	0.00862	0.00839
$\bar{K}$ l/mol·sec			0.00894 ± 0.00040			

*For the values of σ^*-constants characterizing the inductive effect of the acyl groups (R) see Refs.5,6, and the values of the steric constants E_s^o see Refs. 5,7.

Table 3. The Kinetics of Acylation of Phenylhydrazide of Dibutylglycolic Acid with Acid Chlorides (RCOCl). General Kinetic Information

R	$a \cdot 10^4$ mol/l	$b \cdot 10^4$ mol/l	$\bar{K}$ l/mol·sec 25°C	40°C	55°C	70°C	E_A kj/mol	A l/mol·sec
$CHCl_2$	181.8	9.09	0.0426± ±0.0096	0.0718± ±0.0110	0.128± ±0.015	0.182± ±0.018	27.6	$3.10 \cdot 10^5$
$C(CH_3)_3$	454.5	9.09	0.000839± ±0.000111	0.00181± ±0.00010	0.00409± ±0.00021	0.00894± ±0.00040	43.9	$4.07 \cdot 10^4$
CH_2Cl	9.09	9.09		0.865± ±0.096	1.405± ±0.080	2.150± ±0.300	27.0	$2.83 \cdot 10^4$
CH_2CH_2Cl	45.45	9.09		0.386± ±0.060	0.788± ±0.080	1.290± ±0.046	35.8	$3.83 \cdot 10^5$
$n\text{-}C_3H_7$	90.9	9.09		0.255± ±0.012	0.367± ±0.036	0.553± ±0.013	22.6	$1.61 \cdot 10^5$
$CH_2OC_2H_5$	45.45	9.09		0.550± ±0.040	0.866± ±0.050	1.480± ±0.120	27.8	$2.42 \cdot 10^4$

The typical kinetic data are tabulated (see Tables 1 and 2). Table 3 shows general kinetic information where a and b denote the initial concentrations of acylating agents and phenylhydrazide; K, E_A and A denote the values of the rate constants, activation energies and pre-exponents in the Arrhenius equation, respectively.

The data given in Table 3 testify to the fact that the nature of acyl group of acid chlorides affects substantially the reaction rate of acylation of phenylhydrazide of dibutylglycolic acid. When $R=C(CH_3)_3$ is replaced by $R=CH_2Cl$ the reaction rate becomes by some 500 times greater.

On comparing the values of rate constants for $R=CHCl_2$ and $R=C(CH_3)_3$ when their steric constants are almost equal (-2.20 and -2.14 respectively [5]) one may consider with confidence that the inductive effect of substituents shows itself in the reaction series. If to compare the rate constants for chloro- and dichloroacetylchlorides it becomes clear that the steric effect of the acyl group takes place together with the inductive effect. Indeed, the rate constant for chloroacetylchloride is by one order greater than the rate constant for dichloroacetylchloride though the negative inductive effect of the substituent ($CHCl_2$) is higher than the similar effect of the CH_2Cl-group (Taft σ^* constants of these subetituents are equal to 1.93 and 1.04, respectively [6]).

To value the influence of both inductive and steric effects of the substituents on the reaction rate of acylation of phenylhydrazide the Taft equation was used in form [8,9]:

$$\lg K = \lg K_0 + \rho^* \sigma^* + \delta E_s^0 \qquad (1)$$

where the values of E_s^0-constants [10] characterizing the steric effects of the substituents and not containing the hyperconjugation of both C-H and C-C-bonds were used instead of the values of E_s-constants.

The application of the multiple regression theory [11]

to the determination of the equation (1) parameters gave the following results:

$40^{\circ}C$ $\lg K = 0.073 + 0.695\,\sigma^{*} + 1.186\,E_s^{\circ}$
$R = 0.993;\ S = 0.113.$

$55^{\circ}C$ $\lg K = 0.237 + 0.664\,\sigma^{*} + 1.111\,E_s^{\circ}$
$R = 0.995;\ S = 0.093.$

$70^{\circ}C$ $\lg K = 0.435 + 0.602\,\sigma^{*} + 1.065\,E_s^{\circ}$
$R = 0.995;\ S = 0.094.$

In Figure the values of $\lg K - 1.111\,E_s^{\circ}$ are plotted vs. Taft σ^{*}-constants at $55^{\circ}C$.

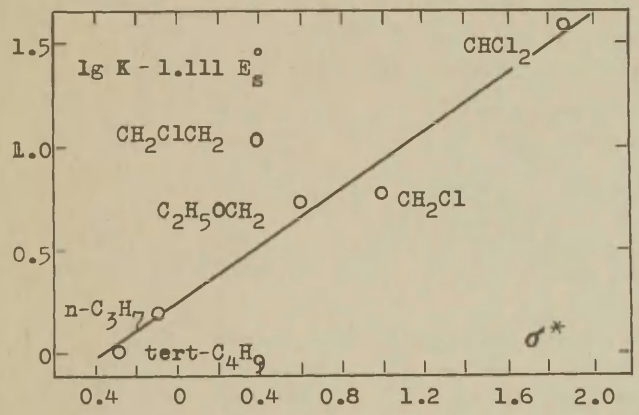

Figure. Plot of $\lg K - \delta E_s^{\circ}$ vs. Taft σ^{*}-constants at $55^{\circ}C$.

As is evident from the Figure, the point corresponding to the acid chloride of β-chloropropanoic acid lies above the regression line. No explanation of this fact is given at present. The point was not considered when parameters of the correlation equation (1) were determined.*

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*If the point is considered, the correlation coefficient becomes lower and the standard deviation becomes higher ($R \approx 0.95$–0.96; $S \approx 0.24$–0.26).

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Substituted Hydrazides of Hydroxylcarboxylic Acids. C111. Study of Basicity of Arylhydrazides of Dibutylglycolic Acid by Potentiometric Method

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The half-neutralization potentials of six arylhydrazides of dibutylglycolic acid were determined in mixture of nitromethane - acetic anhydride (2:1). A linear dependence between the relative values of the half-neutralization potentials ($\Delta E_{1/2}$), characterizing the basicity of compounds, and the Hammet σ- constants was established.

Earlier we studied the basicity of β,β-dimethylhydrazides of disubstituted glycolic and acetic acids by the method of the potentiometric titration in acetonitrile [1]. It was established that phenylhydrazides of disubstituted glycolic acids could not be titrated under given conditions.

This study has been carried out in order to work out the method of the quantitative determination of arylhydrazides of disubstituted glycolic acids and to establish the dependence between the structure and the basicity of these compounds.

It was established by preliminary experiments that the application of amphiprotic (ketones, acetonitrile, alcohols) and some protogenic solvents (acetic acid) did not result in the appearance of the leap of titration. That is why the mixture of nitromethane - acetic anhydride (2:1) was used for measurings. It is known that the application of the

mixture of solvents has some advantages in comparison with individual solvents [2]. In our case the addition of nitromethane to acetic anhydride* results in the improvement of conditions of the titration owing to the decrease of the constant of autoprotolysis, the rise of differentiating properties of the mixture in respect of weak bases and the weakness of the acylating action of acetic anhydride.

Experimental

0.2 mole of arylhydrazide of dibutylglycolic acid was dissolved in mixture of nitromethane (20) ml) and acetic anhydride (10 ml). Solvents were refined and dried as described by Kreshkov et al. [3]. The preparated solution was poured into a thermostated vessel for the titration. The titration was carried out with 0.1 n solution of perchloric acid in dioxan with continuous stirring by a current of dry nitrogen. At ths beginning of the titration the potential values were determined after addition of each portion of 0.2 ml of the titrant, near the equivalence point at intervals in which ths potential of the indicator electrode practically did not change each portion amounted to 0.05 ml. A silver-chloride electrode filled with saturated solution of potassium chloride in acetic anhydride was used as the reference electrode and the glass electrode as the indicator electrode. Measurings were carried out by means of pH-meter millivoltmeter pH-340, at $20.0 \pm 0.2°C$.

Results of Investigations.

Values of the half-neutralization potentials ($E_{1/2}$) for the studied compounds as mean values from 2-3 determinations relative values of the half-neutralization potentials ($\Delta E_{1/2}$) determined as the difference between the E values for the studied compounds and the standard, diphenylguanidine (DFG), are tabulated (see Table 1).

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* These compounds give the leap of titration in the medium of acetic anhydride.

Table 1. The $E_{1/2}$ and $\Delta E_{1/2}$ Values for Arylhydrazides of Dibutylglycolic Acid, $ArNHNHCOC(OH)(C_4H_9)_2$ [4-7]

NN	Ar	$E_{1/2}$ (mV)	$\Delta E_{1/2}$ (mV)
1	C_6H_5	292 ± 3	251 ± 6
2	$p\text{-}CH_3OC_6H_4$	273 ± 2	232 ± 5
3	$m\text{-}BrC_6H_4$	318 ± 3	277 ± 6
4	$p\text{-}BrC_6H_4$	313 ± 2	272 ± 5
5	$m\text{-}CH_3C_6H_4$	293 ± 2	252 ± 5
6	$p\text{-}CH_3C_6H_4$	285 ± 2	244 ± 5
7	DFG	41 ± 3	0

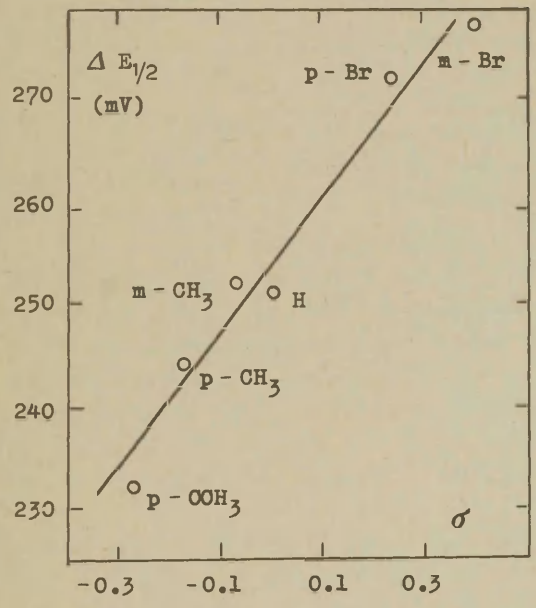

Figure. Plot of $\Delta E_{1/2}$ vs. Hammett σ-constante.

One can see that the nature and the position of the substituent in the benzene ring connected with the atom of nitrogen influence substantially the basicity of aryl-hydrazides of dibutylglycolic acid. This can be represented by the Hammet equation used in the form:

$$\Delta E_{1/2} = \rho\sigma + \Delta E^{o}_{1/2} \qquad (1)$$

In Figure the dependence of $\Delta E_{1/2}$ on the corresponding values of Hammet σ-constants is represented. One can see that the reaction series corresponds to Eq. (1).

The parameters of correlation between $\Delta E_{1/2}$ and σ-constants are shown in Table 2.

Table 2. The Correlation Parameters

SD of mV/σ-unit	SD of mV/σ-unit	r	SD(mV)	$(E^{o}_{1/2})$catc mV
67.2	6.2	0.983	3.4	253

The correlation becomes worse when σ^{o}-constants are used instead of Hammet σ-constants:

r = 0.960; S = 5.3 mV.

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^{13}C NMR SPECTRA AND CONJUGATION IN ALKOXY- AND ALKYLTHIOETHYLENES. II. CORRELATION OF ^{13}C CHEMICAL SHIFTS WITH SUBSTITUENT CONSTANTS

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The nature of relationship between chemical shifts of ^{13}C α- and β-carbon atoms of the vinyl group for twenty alkylthio- and alkoxyethenes and structural constants of appropriate alkyl substituents was studied by correlation analysis methods. Chemical shift ^{13}C variations were found to be moderately described by the linear equations, in which the arguments are inductive, hyperconjugative and steric constants of the substituents. However,the linear ralationship between the arguments does not permit us to draw an unambiguous conclusion on the significance of the influence of different effects.

The closest pair correlations ($r \approx 0.55$) were obtained for β-carbon atoms with steric constants of the CH_2R substituent. Therefore it is possible to suppose that the electron charge distribution in the heterovinyl group can be mostly determined by the steric inhibition of resonance, and that the greater sensitivity of p-π-conjugation in alkyl thioethylenes to the branching of a substituent is probably caused by geometrical conditions of realization of plane conformations as well as by the symmetry of 3d-orbitals.

A detailed analysis of pair correlation equations allows us to discuss some particularities of the participation of sulphur and oxygen atoms as an electron-donating group in the p-π-conjugation with a double bond.

The purpose of the present paper is to seek quantitative relationships between the charge distribution in the vinyl group of CH_2=CHXR (X = O,S, R = alkyl) and the structural characteristics of radicals R, namely their various substituent constants. Such relationships are expected to enable us to estimate the relative role of various structure effects in the polarization of unsaturated bond and to support the assumption of the conjugation in heterovinyl fragments as well as the transmission mechanism through the O and S atoms.

The ^{13}C chemical shifts are well known to be an approximate measure of the total charge density at the appropriate atom C of interest (cf.Ref. 1 and references therein). On this account we have measured ^{13}C chemical shifts for two above-mentioned series of vinyl compounds and processed the data obtained with the help of correlation analysis.

In literature /2-4/ the ^{13}C chemical shifts of some vinyl alkyl ethers (alkoxyethenes) have been described and discussed already, whereas for vinyl alkyl sulphides (alkylthioethenes) that has not been done yet at all. Recently, a series of papers /5-8/ on vinyl aryl ethers and sulphides dealing with the problems like those stated above have been published. In one of these works /6/ ^{13}C chemical shifts have been measured and related to the Hammett σ constants. From the Hammett ρ values, which for sulphide series appeared to be higher than that for ethers, it was concluded that the polar substituent effect on the double bond was transmitted through the S atom better than through the O atom owing to the 3d orbitals participation of the former. However, our results discussed below imply

that it may be not the only possible interpretation.

Experimental

The ^{13}C nmr spectra (pure liquid) were taken at 25°C on a Varian XL-100/12 instrument at 25.2 MHz. The signal-to-noise ratio was enhanced by the $^{13}C-\{^1H\}$ noise decoupling. The chemical shifts were measured with the accuracy within $\pm$ 0.01 ppm, $Si(CH_3)_4$ being used as an internal standard ($\sim$ 5% molar) and the lower-field shifts given by positive δ values. Assignments were based on the off-resonance decoupling technique.

Results

The whole body of the experimental data, further processed through computer, is given in Table 1. Therein are also placed the inductive (σ^*), hyperconjugative (Δn)* and steric [$E^o_{S(R)}$, $E^o_{S(CH_2R)}$] constants of substituent R /9/. The ^{13}C chemical shift values (hereafter conventionalized as C^o_α, C^o_β for α and β carbons of vinyl group in the ether series and C^s_α, C^s_β, correspondingly, for that in the sulphide series) as well as their differences ($\Delta C^o = C^o_\alpha - C^o_\beta$, the same for ΔC^s)** were correlated according to the following general multiparametric equation:

$$C^{o(s)}_{\alpha(\beta)} = a_o + a_1\sigma^* + a_2\Delta n + a_3E^o_S \qquad (1)$$

The other equations with all possible combinations of two arguments and the single-argument correlations were also seen about. Two versions - with $E^o_{S(R)}$ and $E^o_{S(CH_2R)}$ - for any such a regression were checked. Least square calcula-

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* $n = n_H + 0.4\,n_C$, where n_H and n_C are numbers of H and C atoms in α-position.

** These C values were used in hope to get rid of, though partly, possible anisotropic effects.

Table 1. ^{13}C Chemical Shifts (ppm) of the Compounds $CH_2=CHXR$ (X = O,S) and the Substituent Constants

№	R	C^O_α	C^O_β	ΔC^O	C^S_α	C^S_β	ΔC^S	σ^*	Δn	$E^\circ_{S(R)}$	$E^\circ_{S(CH_2R)}$
1.	CH_3	153.33	85.13	68.20	133.35	107.71	25.64	0.00	3.0	0.00	-0.27
2.	C_2H_5	152.09	85.70	66.39	132.68	109.74	22.94	-0.10	2.4	-0.27	-0.56
3.	C_3H_7-n	152.25	85.63	66.62	132.98	109.63	23.35	-0.115	2.4	-0.56	-0.59
4.	C_4H_9-n	152.23	85.62	66.61	132.97	109.45	23.52	-0.13	2.4	-0.59	-0.60
5.	C_4H_9-i	152.18	85.64	66.54	133.32	109.38	23.94	-0.125	2.4	-1.13	-0.55
6.	C_4H_9-s	151.10	87.41	63.69	132.02	111.80	20.22	-0.21	1.8	-1.53	-1.13
7.	C_6H_{11}-cyclo	150.49	87.47	63.02	131.90	111.50	20.40	-0.20	1.8	-1.19	-1.18
8.	C_3H_7-i	150.50	87.50	63.00	131.98	112.00	19.98	-0.19	1.8	-0.87	-1.13
9.	C_4H_9-t	146.23	90.55	55.68	130.19	115.69	14.50	-0.30	1.2	-2.14	-1.94
10.	C_5H_{11}-t	145.96	90.55	55.41	129.94	115.62	14.32	-0.31	1.2	-2.20	-1.94

tions[x] were carried out after the special programmes on the computer of the BESM-4 type.

The equation coerficients a_i (or b_i for the single--parameter correlations), their standard deviations $s_{a,i}$ (or $s_{b,i}$), the correlation coefficients R (or r for pair correlations and the net correlations dispersions, s_o, are sumarized in Tables 2-7.

Table 2. The Data of Three- and Twoparameter Correlations for CH_2=CHOR, $E^o_{S(R)}$ Used as a Steric Constant

C^o	a_o	a_1	s_{a_1}	a_2	s_{a_2}	a_3	s_{a_3}	R	s_o
C_α	138.00	-15.64	13.31	5.42	2.31	1.09	0.96	0.946	0.83
	135.91	-12.30	13.81	6.16	2.36			0.938	0.88
	154.37	11.04	8.64			1.73	1.15	0.914	1.03
	145.17			3.11	1.29	0.85	1.00	0.938	0.88
C_β	97.90	12.89	8.30	-4.57	1.44	-0.76	0.60	0.967	0.52
	99.32	10.55	8.71	-5.08	1.49			0.961	0.56
	84.08	-9.60	6.11			-1.29	0.81	0.932	0.74
	91.95			-2.66	0.83	-0.55	0.65	0.958	0.59
ΔC	40.09	-28.53	21.02	9.99	3.65	1.85	1.52	0.958	1.31
	36.57	-22.86	21.98	11.25	3.75			0.951	1.40
	70.28	20.65	14.48			3.03	1.93	0.925	1.73
	53.19			5.77	2.07	1.40	1.62	0.950	1.42

[x] We acknowledge the help of V.V. Keyko and computer center of the Irkutsk State University.

Discussion

Multiparametric correlations

First of all, we will examine the multiparametric correlation data (Tables 2-5). It is seen that, in spite of rather high correlation coefficients, especially for eqs. with $E^{o}_{S(CH_2R)}$ (Tables 3,5, R = 0.94-0.99), and fairly low s_o values (0.4-0.9), some eqs. of the (1)-type and their twoparametric modifications are proving to be uncertain because of the large coefficient variances (s_{a_i}). It refers above all to inductive terms ($a_1\sigma^*$) in nearly all multiple regressions, both for alkoxy- and for alkylthioethenes series. These terms appear to be significant, seemingly by chance, only in the σ^*, $E^{o}_{S(CH_2R)}$ combination

Table 3. The Data of Three- and Twoparametric Correlations for CH_2=CHOR, $E^{o}_{S(CH_2R)}$ as a Steric Constant

C^o	a_o	a_1	S_{a_1}	a_2	S_{a_2}	a_3	S_{a_3}	R	S_o
	163.76	0.97	6.85	-2.98	1.89	7.02	1.17	0.987	0.41
C_α	154.70	-7.72	4.54			5.52	0.77	0.984	0.46
	163.11			-2.76	1.12	6.98	1.11	0.987	0.42
	79.70	1.19	1.38	1.36	0.38	-4.93	0.24	0.999	0.12
C_β	83.82	5.14	1.23			-4.24	0.21	0.998	0.16
	78.89			1.62	0.23	-4.98	0.23	0.999	0.14
	84.06	-0.23	7.45	-4.33	2.06	11.96	1.28	0.995	0.45
ΔC	70.87	-12.88	5.31			9.78	0.90	0.993	0.54
	84.23			-4.39	1.22	11.98	1.21	0.995	0.45

Table 4. The Data of Three- and Twoparametric Correlations for CH_2=CHSR, $E^o_{S(R)}$ Used as a Steric Constant

C^s	a_o	a_1	Sa_1	a_2	Sa_2	a_3	Sa_3	R	S_o
	124.84	-7.02	5.94	3.03	1.03	-0.11	0.43	0.952	0.37
	124.62	-6.70	5.82	3.11	0.99			0.952	0.37
C_I	133.99	7.90	4.23			-0.46	0.56	0.909	0.50
	128.04			2.00	0.58	-0.006	0.45	0.946	0.38
	127.02	16.79	6.59	-6.60	1.14	-0.60	0.48	0.988	0.41
C_p	128.13	14.94	6.91	-7.00	1.18			0.986	0.44
	107.08	-15.65	7.12			-1.37	0.95	0.947	0.86
	119.26			-4.10	0.76	-0.33	0.60	0.980	0.53
	-2.44	-24.36	12.58	9.70	2.18	0.70	0.91	0.979	0.70
	-3.77	-22.30	12.63	10.17	2.16			0.978	0.80
ΔC	26.86	23.37	11.30			1.83	1.51	0.937	1.35
	8.74			6.10	1.33	0.31	1.04	0.971	0.91

for C^o (Table 3, line 5) and for C^s (Table 5, line 4), Student's test being used herewith and thereafter. Further comparison shows that the hyperconjugative terms are more certain throughout than inductive ones. They are entirely certain for all eqs. of Tables 2, 3 (excluding line 1) and 4 as well as in eqs., represented by lines 3,4 in Table 5. It is noteworthy that more close relationships are fulfilled for the sets with $E^o_{S(CH_2R)}$ constants. Even in the 'worst' set of the correlation equations obtained (Table 3, lines 1-3), the only term, which could be considered as statistically certain, is steric one in eqs. with the

Table 5. The Data of Three- and Twoparametric Correlations for CH_2=CHSR, $E^{\circ}_{S(CH_2R)}$ Used as a Steric Constant

C^S	a_o	a_1	S_{a_1}	a_2	S_{a_2}	a_3	S_{a_3}	R	S_o
	136.57	-1.02	2.70	-0.82	0.75	3.02	0.50	0.991	0.15
C_α	134.08	-3.40	1.70			2.61	0.29	0.990	0.16
	137.27			-1.05	0.45	3.08	0.44	0.991	0.15
	113.60	8.00	2.84	-2.23	0.78	-3.64	0.49	0.998	0.17
C_β	106.80	1.49	2.26			-4.76	0.38	0.996	0.23
	108.13			-0.45	0.62	-4.08	0.62	0.996	0.24
	23.15	-9.42	4.75	1.34	1.31	6.78	0.81	0.997	0.28
ΔC	27.23	-5.51	2.96			7.46	0.50	0.997	0.29
	29.58			-0.75	0.92	7.32	0.91	0.996	0.33

Table 6. The Pair Correlation Coefficients for a Mutual Dependence between the Arguments, $x_i = f(x_j)$, (for series of Table 2)

Arguments	$\Delta n_{(R)}$	$E^{\circ}_{S(R)}$	$E^{\circ}_{S(CH_2R)}$
$\sigma^*_{(R)}$	0.98	0.92	0.96
$\Delta n_{(R)}$	1.00	0.93	0.98
$E^{\circ}_{S(R)}$	0.93	1.00	0.93

$E^{\circ}_{S(CH_2R)}$ constants . Apparently, the main reason of all above uncertainties is rather a close linear relationship between the arguments. This is endorsed by the pair correlation coefficient values given in Table 7. It should be noted that such correlations for alkyl substituents were earlier discussed /11-13/, but their physical meaning is so far not clear enough.

In effect, therefore, the results on multiple correlations lead us to the following conclusions:

(i) The dependence of ^{13}C chemical shift for any vinylic carbon of alkoxy and alkylthioethene on the structure of the radical is not expressed adequately when assuming that all three effects appear simultaneously.

(ii) In most cases, such a dependence is well approximated by the twoparametric equations with Δ n and $E^{\circ}_{S(CH_2R)}$ as arguments.

(iii) Closer relationships are observed for the alkylthioethenes series, for the β carbons of the vinyl group and for the substituent constant sets with $E^{\circ}_{S(CH_2R)}$ instead of $E^{\circ}_{S(R)}$.

(iv) The C values, which were used in hope to get rid of, though partly, possible anisotropic effects, give in fact no advantage to $C^{\circ(s)}_{\alpha(\beta)}$ values.

Pair correlations

Now let us go over to the pair correlations (Table 7). They are well in line with the above conclusions. Weaker linear relationships exist in the case of σ^* constants. The ability of the substituent constants to be linearly related with the $C^{\circ(s)}_{\alpha(\beta)}$ values increases in the order:

$$E^{\circ}_{S(R)} < \Delta n < E^{\circ}_{S(CH_2R)}.$$

After Fisher's criterion the correlation equations with

Table 7. The Data of Pair Correlation ($c_i = b_o + b_1 x_i$) for CH_2=CHXR (X = O,S)

C	x_i	b_o	b_1	S_{b_i}	r	S_o^2
C_α^o	Ω^x	154.65	23.00	16.65	0.894	1.47
	Δn	142.27	4.10	0.31	0.933	0.94
	$E^o_{S(R)}$	153.87	3.09	0.28	0.899	1.39
	$E^o_{S(CH_2R)}$	154.84	4.27	0.10	0.979	0.31
C_β^o	Ω^x	83.88	-18.58	8.55	0.914	0.75
	Δn	93.89	-3.32	0.13	0.955	0.40
	$E^o_{S(R)}$	84.52	-2.48	0.15	0.914	0.75
	$E^o_{S(CH_2R)}$	83.75	-3.43	0.02	0.995	0.05
C_α^S	Ω^x	134.07	11.08	3.47	0.903	0.31
	Δn	128.09	1.98	0.06	0.946	0.18
	$E^o_{S(R)}$	133.63	1.43	0.08	0.876	0.39
	$E^o_{S(CH_2R)}$	134.15	2.05	0.01	0.986	0.05
C_β^S	Ω^x	106.86	-25.18	11.23	0.936	0.99
	Δn	120.44	-4.50	0.11	0.980	0.30
	$E^o_{S(R)}$	107.79	-3.30	0.24	0.921	1.22
	$E^o_{S(CH_2R)}$	106.78	-4.54	0.02	0.996	0.06

$E^o_{S(CH_2R)}$ as a single argument are the best, introducing other argument in the pair correlation is not statistically justifi-

able. Consequently, only the following equations should be left under further analysis:

$$C^{o}_{\alpha} = 154.84 + 4.27\ E^{o}_{S(CH_2R)} \qquad (2)$$

$$r = 0.979;\quad S^2_o = 0.31$$

$$C^{o}_{\beta} = 83.75 - 3.34\ E^{o}_{S(CH_2R)} \qquad (3)$$

$$r = 0.995;\quad S^2_o = 0.05$$

$$C^{s}_{\alpha} = 134.15 + 2.05\ E^{o}_{S(CH_2R)} \qquad (4)$$

$$r = 0.986;\quad S^2_o = 0.05$$

$$C^{s}_{\beta} = 106.78 - 4.54\ E^{o}_{S(CH_2R)} \qquad (5)$$

$$r = 0.996;\quad S^2_o = 0.06$$

Since ^{13}C chemical shifts are linearly related to (at least, approximately) the total charge at the relevant C atom, one can refer to the $C^{o(s)}_{\alpha(\beta)}$ values as being a proper measure of electron density near the α- and β-positions of the vinyl group. So Eqs.(2)-(5) indicate unequivocally that, on going to bulkier substituents, electron density is markedly displaced of the β-carbon towards the α-carbon, i.e., the degree of p-π conjugation in the heterovinyl fragment, CH_2=CHX, becomes lower. The slope values of Eqs. (3)and(5) show that the electron withdrawal of the β-carbon in vinyl sulphides is by factor ~ 1.3 (4.54 : 3.34) stronger than that in vinyl ethers (the higher the C_β value the more β-carbon is deshielded). An opposite picture (with factor 2.0) is observed for the α-carbons (cf.Eqs.(2) and (4)). It means that the electron income to the α-position of the vinylthio group does not fit the charge loss from its β-position, especially if this is compared with the substituent-induced electron redistribution in the vinyloxy group. The inversion of the slope magnitudes could be ex-

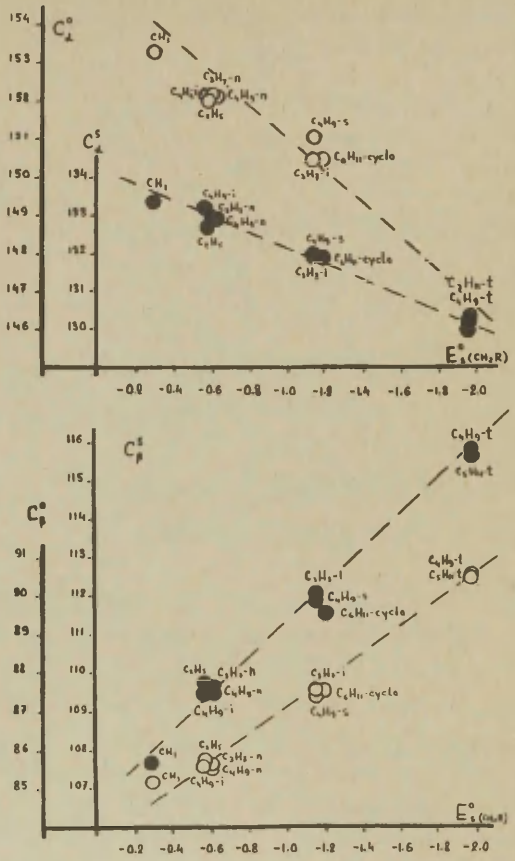

Fig. 1. XC $^{13}C^{\circ(s)}_{\alpha(\beta)}$ vs steric constant $E^{\circ}_{S(CH_2R)}$ relationships

○ = alkoxyethenes; ● = alkylthioethenes

in the pertinent alkyl series though this time it has no-

plicable in terms of electron-attracting nature of 3d sulphur orbitals:

$$\left[CH_2=CH-S-R \longleftrightarrow \overset{+}{C}H_2-CH=\overset{-}{S}-R\right],$$

i.e. the formal charge loss from the double bond could be tentatively accounted for the electron displacement onto vacant orbitals of sulphur. By contrast, in the ether series, the greater slope value of the C^o_α, $E^o_{S(CH_2R)}$ dependence as compared with that of C^o (cf.Eqs.(2)and(3)) might be taken as an evidence of the added electron income to the double bond. The explanation here could be based on the CNDO/2 total charge distribution in methoxyethene /8/:

$$\overset{-0.13}{CH_2}=\overset{0.16}{CH} - \overset{-0.20}{O} - \overset{0.14}{CH_3}$$

It is quite conceivable that the steric inhibition on p-π conjugation may result in levelling of charges along the double bond by the additional electron income to the α-carbon from the neighbouring oxygen atom on which the considerable negative charge is localized (partly as a consequence of p-π conjugation).

The next point deserving special attention is that the sensitivity of the ^{13}C chemical shift of the vinylic carbon to the steric effect in the sulphide series proves to be effectively higher than that for the oxygen homologues (4.54 and 3.34, respectively). It seems to be much similar to the Hammet σ, ρ relationships concerning the ^{13}C chemical shifts in the corresponding sulphur and oxygen aryl series /6/. In this work, as it was mentioned above, the greater value of the sulphur homologues have been explained by an enhanced transmission of the polar effects through the sulphur atom. On the other hand, now one can see that such 'enhanced transmission' of sulphur takes place well in the pertinent alkyl sries thogh this time it has nothing to do with the so-called 'through-conjugation'. As

a matter of fact, the relationships found by us reflect some steric effects. The hindrance of p-π conjugation by the bulkier substituent R is assumed to be the most probable version*.

These inferences agree well with the IR study /14/, in which the higher sensitivity of the infrared intensity of alkylthiobenzenes and alkylthioethenes to the variation of the alkyl structure was also interpreted in terms of steric inhibition of resonance. As it is shown in a work/14/ referred to, the geometrical and the 3d sulphur orbital symmetry requirements are assumed to be such that the steric inhibition of resonance on branching of alkyl radicals should be enlarged faster in the sulphide series. Besides, if the p-π conjugation of α,β-unsaturated sulphides is weaker than that of corresponding ethers, then it would further loose p-π coplanarity in the vinylthio group and make the p-π conjugation in it still more sensitive to any substituent effect. The direct comparison of the ^{13}C chemical shift values of Table 1 enable us to point out that the p-π conjugation in alkylthioethenes is about by 3 times weaker than in alkoxyethenes**. This falls in agreement with the ^{1}H chemical shift values of the vinyl protons and proves to be fully compatible with our previous data /15,16/ on the relative basicity of these two studed series.

Thus, 'the greater transmission efficiency' of the sulphur atom due to the through-conjugation as it has been stated /6/ may be still alternatively explicable by lowering of the rotation barrier around the S-C (vinyl) bond or even by diminishing of the distance between substitu-

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* In the following paper we will show that there is some contribution of steric compression independent of any conjugation effect.

** This part in details is to be published separately.

ent and indicator (resonant nuclei and the like).

Now it becomes evident enough, why just the $E^{o}_{S(CH_2R)}$ constants, not the $E^{o}_{S(R)}$, ensure better correlations: because the key rotation occurs around the C-XR bond, the steric characteristics of the rotated fragment XR as a whole or those of its isosteric analog CH_2R should be very essential.

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A STUDY ON THE MECHANISM OF HYDROLYSIS OF CARBOHYDRAZONES

Report II

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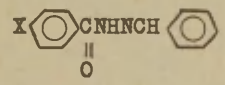
The hydrolysis kinetics of carbohydrazones of a general formula

 where

X = OH, OCH_3, CH_3, H, Cl, NO_2

in the pH range of 1÷14 and in the temperature range of 10 + 50°C was studied. The thermodynamic parameters of the reaction were calculated. At pH ~3 a change with rate-limiting step takes place. In the reaction series studied the isokinetic ratio with the value β = 302°K at pH = 1.15 and β = 290°K at pH = 4.01 was observed. Quantitative estimations were confirmed experimentally. The inversion of substituent influence is shown at "crossing" of β

Proceeding with the investigation of hydrolysis reaction of carbohydrazones we examined the substituent influence in the hydrazide part of the molecule upon the hydrolysis rate constant in the pH range of 1÷14. At pH = 1.15 and 4.01 hydrolysis kinetics was studied in the temperature range of 10-50°C.

The investigation of hydrolysis kinetics and the experimental data processing was carried out by the method described earlier /1/. The data obtained are listed in Table 1. The values of pD in systems with D_2O were calculated by the equation

$$pH = pD + 0.4 \qquad (1)$$

Table 1

Rate Constants and Activation Parameters* of Hydrolysis Reaction of Carbohydrazone of a General Formula $XC_6H_4CONHNCHC_6H_5$

No	pH	X	K_{13}	K_{25}	K_{40}	K_{50}	$\Delta F^{\neq}$ kcal/mol	$\Delta H^{\neq}$ kcal/mol	$\Delta S^{\neq}$ kal/mol.grad
1	1.15	OH	0.04955	0.1648	0.8318	2.333	18.50	18.56	+0.20
2	"	OCH_3	0.05333	0.1722	0.8035	1.986	18.48	17.44	-3.48
3	"	CH_3	0.05888	0.1758	0.7852	1.879	18.47	16.71	-5.89
4	"	H	0.06950	0.1862	0.7161	1.622	18.43	15.95	-8.32
5	"	Cl	0.09183	0.2018	0.6223	1.297	18.38	12.58	-19.48
6	"	NO_2	0.2095	0.2410	0.4898	0.7311	18.28	7.50	-36.16
1	4.01	OH		0.001750	0.004786	0.008790	21.20	11.75	-31.70
2	"	OCH_3		0.001581	0.004169	0.007674	21.26	11.46	-32.85
3	"	CH_3		0.001550	0.003758	0.006546	21.27	10.40	-36.46
4	"	H		0.001429	0.003170	0.004919	21.32	8.73	-42.23
5	"	Cl		0.001349	0.002344	0.003388	21.35	6.42	-50.08
6	"	NO_2		0.001089	0.001259	0.001380	21.48	2.04	-65.05

* All the thermodynamic parameters are calculated for the temperature 298°K by the equations given by Laidler.[3]

Fig.1 shows the dependence of lg of rate constant of pseudo-first-order hydrolysis reaction for the extreme members of reaction series upon pH. In the alkaline solution the rate constant appeared to be higher at pH=13 than it was at pH=10

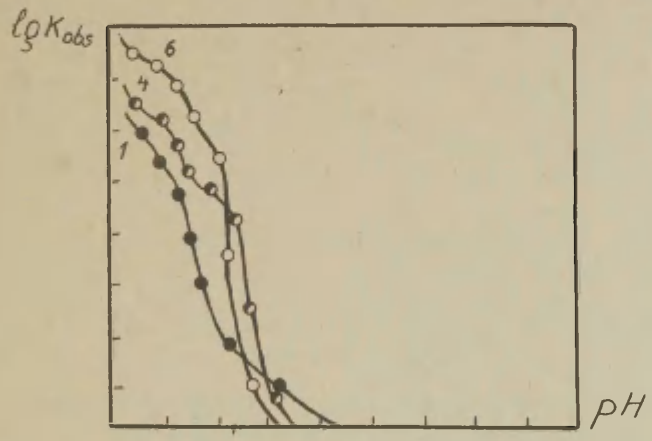
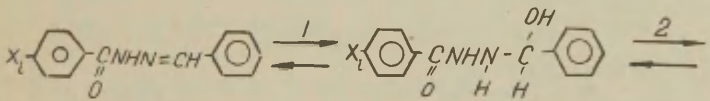
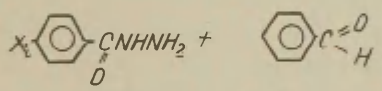


Fig.1. The lg dependence of rate constant of hydrolysis reaction of p-substituted benzoylhydrazones of benzaldehyde upon pH (the substituent order corresponds to Table 1).

The bell form of the dependence curve of rate constant of reaction on the medium pH in some cases /4-7/is explained by change of the limiting step of process





It appears from Table 1 that the substituent influence on the rate constant of hydrolysis is different at various values of pH and temperatures. Electronacceptor substituents

increase hydrolysis in a strong acid medium (see Fig.2) and decrease it in a weak acid one and also at high temperatures in a strong acid medium.

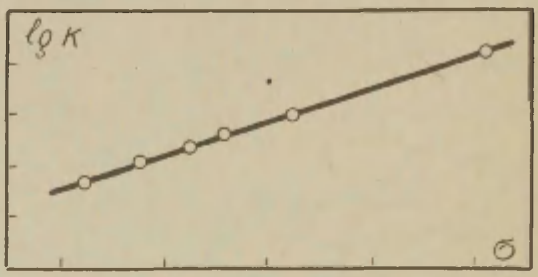


Fig.2. The lg K_h dependence on σ at pH = 1.15, t = 25°C.

The correlation is performed by means of the Hammett σ-constant, hence at step limiting the reaction rate, no stabilization of transition state by means of direct polar conjugation can occur.

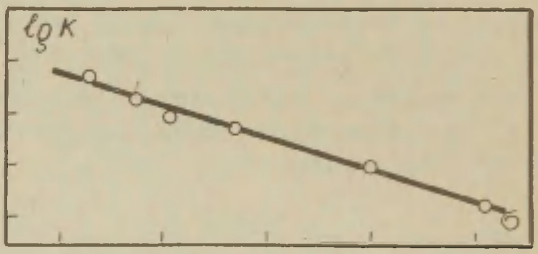


Fig.3. The lgK_h dependence on σ at pH=4.01, t = 25°C.

In case the limiting step is step I, the formation of intermediate compound, the reaction rate should depend on the extent of hydrazone basicity. The more the initial hydrazides basicity the more the latter. In case the limiting step is the second step, hydrolysis step, the less basicity of the leaving hydrazide the easier it is hydrolyzed. The correlation parameters for the hydrolysis reac-

tion of p-substituted benzoylhydrazones of benzaldehyde are listed in Table 2. The analysis of data obtained shows that the influence of substituents upon the rate constant of hydrolysis submits to Hammett's equation over a whole temperature range studied.

Table 2

The Correlation Parameters of $\lg \frac{K}{K_0} = \rho\sigma$ for Hydrolysis

No	°C	pH	$\lg K_0$	ρ	r	S
1	13	1.15	-1.1549±0.0031	+0.4196±0.021	0.998	0.013
2	25	"	-0.7290±0.005	+0.1439±0.020	0.998	0.028
3	40	"	-0.1495±0.007	-0.2087±0.020	0.997	0.073
4	50	"	+0.2020±0.027	-0.4300±0.014	0.998	0.013
5	25	4.01	-2.838±0.005	-0.1679±0.003	0.996	0.042
6	40	"	-2.508±0.008	-0.5065±0.021	0.999	0.008
7	50	"	-2.309±0.005	-0.7106±0.013	0.999	0.005

It appears from Table 2 that at pH=1.15 the influence inversion of the substituent upon the hydrolysis rate /10/ is performed at a temperature change. At pH=4.01 the ρ value is increased (absolute value) at a temperature rise. Low value of the reaction constant shows both low sensitivity of reaction rate to the structural changes in the hydrazide part of the molecule and the proximity of isokinetic temperature to the experimental one, as even little changes of temperature result in a sign change.

The hydrolysis of benzoylhydrazone of benzaldehyde in D_2O/DCl and D_2O/CH_3COOD have been studied. The difference in the dependence of reaction rate on acidity in water and deuterium oxide resulted in the change of the isotope effect of solvent from 1.51 (pH/pD/1.45) to the inverse isotope effect of 0.52 (pH/pD/4.10) /8.9/.

The temperature dependence on the inverse temperature for pH=1.15 (20) and pH=4.01 (3) is given in Fig.4.

The temperature dependence of the reaction constant of the process studied is expressed by Eqs. (2) and (3).

$$\rho = (6.9447 \pm 1.1810) + (-2.1265 \pm 0.3591)\mathbf{I} \qquad (2)$$
$$r = 0.999 \quad S = 0.12$$

$$\rho = (7.0099 \pm 0.5690) + (-2.0317 \pm 0.1769)\mathbf{I} \qquad (3)$$
$$r = 0.998 \quad S = 0.104$$

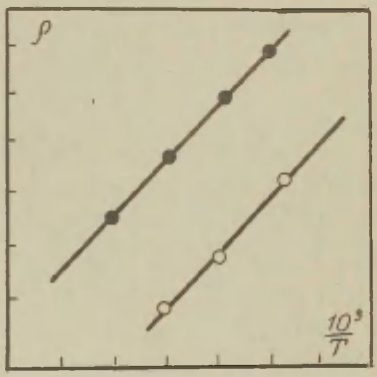


Fig.4. The ρ dependence on $^1/T$.

So, at T = 305°K (pH = 1.15) and T = 290°K at pH = 4.01 ρ becomes 0, i.e. the isokinetic ratio is carried out with the values β =305°K (pH = 1.15) and β =290°K (pH = 4.01). The same conclusion can be drawn when to consider the dependence of lgK_{T_1} on lgK_{T_2} (see Fig.5)

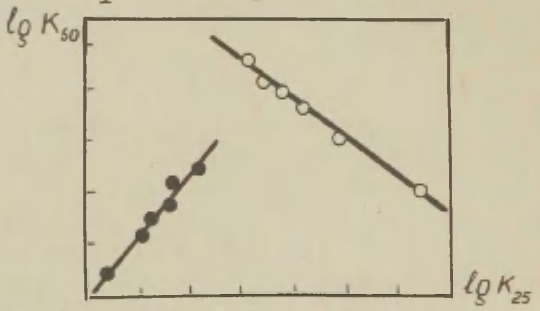


Fig.5. The dependence of $lgK_{50°C}$ on $lgK_{25°C}$

pH=1.15 b= -2.993±0.064 r = 0.999 S = 0.009
pH=4.01 b= 4.133±0.315 r = 0.989 S = 0.05

The calculation by the equation:

$$\beta = \frac{T_1 . T_2 (b-1)}{bT_2 - T_1} \qquad (11,12)$$

resulted in the values of β =304°K (pH=1.15) and 291°K (pH=4.01) which corresponds to the values of β obtained from the temperature dependence of ρ. High coefficients of the correlation prove a good realization of isokinetic ratio.

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SUBSTITUENT EFFECT IN DEHYDROGENATION OF DIHYDROPYRIDINES WITH TRIPHENYL VERDAZYLIC SALTS.

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The kinetics of the dehydrogenation of I,4-dihydropyridines (DP) with triphenyl verdazylic salts (RN^+X^-) in CH_3CN has been studied spectroscopically. The reaction rate depends much on the DP structure and is described by a bimolecular kinetic equation $v=k_2 (RN^+)(DP)$. Substituent effect in the salt and DP upon the reaction rate has been studied.The lgk values correlate well with Hammett σ-constants and $E_{1/2}$ of oxidation of DP and reduction of salts in CH_3CN. It has been concluded that at the rate-determining step a hydrogen transfer from DP molecule to salt RN^+X^- occurs as a result of a charge-transfer complex formatinn.

I,4-dihydropyridines (DP) are the analogs of the most significant and biologically active compounds - of coenzyme NAD (nicotinamide adenine dinucleotide) and dihydrocoenzyme NADH. They possess distinct electron- and hydrogen-donating properties and, besides, they are carriers of hydrogen in biochemical oxidation-reduction processes.[1] DP are also effective antioxidants.[2] The reaction mechanism with the participation of I,4-dihydropyridines is being constantly studied.[3-5] When N-benzyl-I,4-dihydronicotinamide (BDN) and 2,6-dimethyl-3,5-dicarbethoxy-I,4-dihydropyridine (Hantzsch's ether, HE) are dehydrogenated with salts of triphenyl verdazyl radicals (RN^+X^-) the rate of these reactions can be described in terms of a bimolecular kinetic equation $v=k_2(RN^+)_6$ $\cdot$(DP); the rate only slightly depends on the solvent nature.

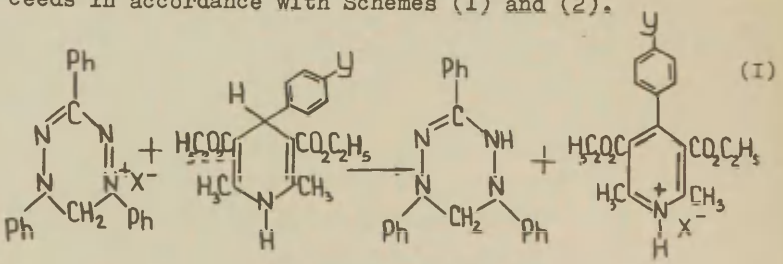
Going on with our research on the mechanism of dehydrogenating DP with triphenyl verdazylic salts [7] we have studied the reaction kinetics of RN^+X^- (X = $C(NO_2)_3$, Br) with 2,6-dimethyl-3,5-dicarbethoxy-(4-p-Y-phenyl)-I,4-dihydropyridines (Y-Ph-HE) (Y = H, CH_3, OCH_3, CI, NO_2) and 2,4,6-trimethyl--3,5-dicarbethoxy-I,4-dihydropyridine (CH_3-HE) in acetonitrile. We have also studied how a substituent in the para-position of a C-phenyl and N-phenyl ring of trinitromethane salts of triphenyl verdazyl influences the reaction kinetics with CH_3-HE.

Experimental

1,4-Dihydropyridines (HE, CH_3-HE, Y-Ph-HE) were synthesized by methods available in literature.[8,9] Para-C--phenyl-substituted trinitromethane salts (Z-RN^+X^-, Z = NO_2, Cl, H, CH_3, OCH_3) were obtained as described earlier.[10] Para-methoxy-N-phenyl-substituted trinitromethane salt were obtained by the synthesis of the corresponding triphenyl verdazyl radical and tetranitromethane, m.p. I27-I28°(λ_{max} = 573 nm, lgε = 4,I6). Kinetic experiments were carried out in the thermostated glass-cell of spectrophotometer "СФ-4". The reaction was observed at λ = 535-575 nm (λ_{max} Z-RN^+X^- Ref.10), where DP and the reaction products practically did not absorb. CH_3CN was thoroughly purified before using.

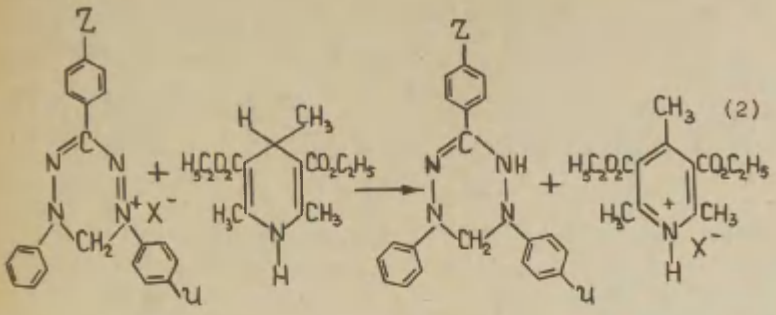
Results and Discussion

The oxidation of I,4-dihydropyridines with RN^+X^- proceeds in accordance with Schemes (I) and (2).



(I)

where Y = CH_3, OCH_3, H, Cl, NO_2, X = $C(NO_2)_3$, Br



(2)

where Z = NO_2, Cl, H, CH_3, OCH_3, U = H, OCH_3.

The formation of a leuco verdazyl (RNH) has been shown by reversible transformation of this leuco base into a radical (when effected with KOH Ref.II); quaternary pyridinium salts have been identified chromatographically.[11]

Figure I represents the kinetic experiments of oxidating OCH_3-Ph-HE with $RN^+\bar{C}(NO_2)_3$ and RN^+Br^-. These experiments have shown that the parallel experiments conform well (exp.I and 2), the nature of the salt anion does not affect the reaction rate (exp.I-3 and 4).

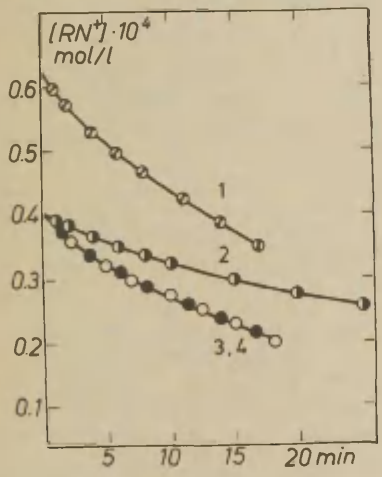


Figure 1

1,2: $RN^+\bar{C}(NO_2)_3$ of 0.40, OCH_3-Ph-HE of 58.6;

3: $RN^+\bar{C}(NO_2)_3$ of 0.40, OCH_3-Ph-HE of 29.3;

4: RN^+Br of 0.62, OCH_3-Ph-HE of 90.7, X 10^{-4} mol/l.

Since the nature of a counterion does not influence the reaction rate we may conclude that the salt is completely dissociated.

The rate of dehydrogenating DP with RN^+X^- can be well described by a bimolecular kinetic equation:

$$v = k_2(RN^+)(DP) \qquad (3)$$

During experiments the values of k_2 change only slightly and conform satisfactorily with those for various initial concentrations of reagents.

The kinetic parameters of the reactions as well as electrochemical oxidation potentials of DP on the graphitic electrode in CH_3CN (Ref.I2) are given in Table I.

Table 1.

The Kinetic Data of Oxidating 2,6-Dimethyl-3,5-dicarbethoxy-(4-p-Y-phenyl)-1,4-dihydropyridine with $RN^+C(NO_2)_3$ in CH_3CN*

Y	10^3 k_2, I/mol sec			E kcal/mol	$-\Delta S^{\neq}$ e.u	$E_{1/2}$
	20°	30°	40°			
OCH_3	106 ± 5	163 ± 7	250 ± 20	7.7	38.7	I.00
CH_3	61 ± 3	96 ± 6	149 ± 7	8.2	38.1	I.07
H	37 ± 2	60 ± 5	94 ± 3	8.6	37.6	I.02
Cl	25 ± 2	44 ± 4	69 ± 2	9.4	35.8	I.06
NO_2	4.9 ± 0.4	9.2 ± 0.7	I7.2 ± 0.9	II.6	3I.5	I.24

*) An arithmetical mean of constants (from 3-5 experiments) with a mean-square error. Error of E does not excced ± 0.5 kcal/mol, $\Delta S^{\neq}$ ± 2 e.u.

Table I shows that the reaction rate (I) depends on the substituent nature in the phenyl ring of DP. When passing from NO_2-Ph-HE to OCH_3-Ph-HE the reaction rate (at 20°) is 22 times as rapid. An excellent linear correlation between the lgk values and the Hammett σ-constants was established.

20° $\lg k/k_0 = -1.216$, $r = 0.995$, $S_0 = 0.050$ (4)

30° $\lg k/k_0 = -1.126$, $r = 0.992$, $S_0 = 0.053$ (5)

40° $\lg k/k_0 = -1.046$, $r = 0.991$, $S_0 = 0.055$ (6)

The rate constants for substituted 1,4-dihydropyridines (without CH_3-HE) can satisfactorily be correlated with $E_{1/2}$ of electrochemical oxidation of DP in CH_3CN:

$$\lg k/k_0 = -4.82\ (E^{x}_{1/2} - E^{o}_{1/2}),\ r = 0.953,\ S_0 = 0.072 \quad (7)$$

where $E^{x}_{1/2}$ refers to substituted DP and $E^{o}_{1/2}$ to not substituted DP. After including CH_3-Ph-HE into Dimroth's equation [13] Eq. (7) becomes as follows:

$$\lg k/k_0 = -4.89\ (E^{x}_{1/2} - E^{o}_{1/2}),\ r = 0.917,\ S_0 = 0.093 \quad (8)$$

Low value of the correlation coefficient in Eq.(8) is probably due to the inaccuracy in determining $E_{1/2}$ for CH_3-Ph-HE in the work of Stradin et al.[12]

Table I shows that the activation energy increases linearly with the increases of $\Delta S^{\neq}$ (compensational effect)

$$E = 523\Delta S^{\neq} + 28.1,\ r = 0.997,\ S_0 = 0.045 \quad (9)$$

Isokinetic temperature is $523^{\circ}K$, i.e. much higher than the used interval of temperature.

Negative value of ρ in Hammett equation (4-6) and α in Dimroth's equation (7 and 8) proves that the increase of electron density in the reaction center stimulates the reaction rate, i.e. DP are electronodonors. The value of $\rho = -1.21$ (at 20°) shows that the reaction is very sensitive to substituent effect. The presence of Hammett and Dimroth's equations and compensational effect point that the reaction mechanism is the same for all substituted Y-Ph-HE (Ref.14).

The rate considerably increases when passing from Y-Ph-HE to CH_3-HE. Table 2 shows the data on the kinetics of the reaction of substituted trinitromethane salts of triphenyl verdazyls with CH_3-HE.

Table 2.

Kinetics Data of Dehydrogenating 2,4,6-Trimethyl-3,5-dicarbethoxy-1,4-dihydropyridine with Substituted Triphenyl Verdazylic Salts in CH_3CN at 25°C

Z	k_2, l/mol sec	$E_{1/2}$, v
OCH_3	1.24 ± 0.03	0.145
CH_3	1.34 ± 0.06	0.150
H	1.60 ± 0.04	0.180
Cl	2.14 ± 0.11	0.205
NO_2	3.56 ± 0.06	0.250
OCH_3 [x]	0.58 ± 0.05	-

x) Substituent is in the para-position of the N-phenyl ring.

The reaction rate depends only slightly upon the substituent nature in the C-phenyl ring of the salt. When passing from NO_2-RN^+ to OCH_3-RN^+ the k_2 value increases only 2.9 times as much. In the N-phenyl ring of the salt the substituent influences the reaction rate much more than in the C-phenyl ring (when passing from H- to OCH_3- the k_2 value decreases 2.1 times as little in the first case and only 1.3 times in the second case). The lgk values correlate excellently with the Hammett σ-constants:

$$\lg k/k_o = 0.456, \; r = 0.998, \; S_o = 0.006 \qquad (10)$$

and the potentials of electrochemical reduction of salts in CH_3CN (Ref.15)

$$\lg k/k_o = 4.27\,(E^x_{1/2} - E^o_{1/2}), \; r = 0.993, \; S_o = 0.010 \qquad (11)$$

Positive value of ρ in Hammet's equation and that of in Dimroth's equation show that the decrease in electronic density at the reaction center of the salt causes an increase in the reaction rate.

Table 1 and 2 and our previous results[7] show that dehydrogenation rate of 1,4-dihydropyridines depends markedly on the substituent nature in the 4-position of DP. When passing from HE to H-Ph-HE the reaction rate with $RN^+C(NO_2)_3$ decreases more than 10^5 times as little.

$$\underset{I}{H\text{-}Ph\text{-}HE} < \underset{35}{CH_3\text{-}HE} < \underset{I,4\cdot10^5}{HE}$$

The dehydrogenation rate, as Table 3 shows, depends mainly upon energetic factors (when passing from HE to CH_3-HE E increases twice as much). When passing from CH_3-HE to H-Ph-HE the activation energy does not change, the differences in the rate are caused by the increasing steric demands for H-Ph-HE in the transition state of the reaction.

Table 3.

Comparison of Kinetic Parameters of the Reaction of $RN^+\bar{C}(NO_2)_3$ with DP

DP	k_2 (20°) l/mol·sec	E kcal/mol	$-\Delta S^{\neq}$ e.u.
HE	$(5 \pm 0.6)\ 10^3$	4.3	29
CH_3-HE	1.3 ± 0.03	8.6	31
H-Ph-HE	0.037 ± 0.002	8.6	38

I,4-dihydropyridines are known [4] to readily form complexes with charge transfer as well as interact with reagents which are the acceptors of only one electron. We believe that at the first stage of the dehydrogenation a complex with a charge transfer between π-electronic systems of DP and RN^+X^- is formed. This complex is probably of a "sandwich" structure since DP is known [5] to be plane and coplanarity for triphenyl verdazyls increases in the order $RN^- < RN^\cdot < RN^+$ (Ref.16). Plane structure of reagents ensures maximal overlap of π-orbitals. This suggestion agrees with the data of $\Delta S^{\neq}$ in Table 3. $\Delta S^{\neq}$ slightly decreases for CH_3-HE (hyperconjugation effect), and for H-Ph-HE, where the phenyl ring is not coplanar with the frame of DP (Ref.17), the steric demands considerably increase. The extent of charge transfer in the complex may probably be great since RN^+X^- are strong acceptors of an electron and DP are donors. Simple calculations show that the reaction $DP + RN^+ \longrightarrow DP^\dagger + RN^\cdot$ is thermodynamically probable*. Very

*Since the electrochemical oxydation potential of H-Ph-HE is 1.02 V and the salt reduction potential is 0.13 V this reaction needs not more than 0.89 V or 1.4 kcal/mol without coulomb and specific interactions.

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important here is the stability of the intermediately formed cation-radicals of DP; this stability increases in the order HE $\lesssim$ CH_3-HE $\lesssim$ Y-Ph-HE which is sympathetic to the activation energy change. At the rate-determining step a hydrogen transfer takes place probably.

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THE INFRARED INVESTIGATION OF ELECTRONIC INTERACTIONS IN DI- AND TRISUBSTITUTED METHANES

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The dependence of frequencies (ν) and band intensities (A) of C-H stretching vibrations in infrared spectra of di- and trisubstituted methanes upon electronic nature of substituents was studied. In the series of disubstituted methanes the A_{CH} and ν_{CH} values were correlated by the sum of σ_p^o constants (when $\sigma_p^o < 0.6$). The parameters of correlations were like those determined for monosubstituted compounds. In the interval $\sigma_p^o = 0.6 + 1.0$ the relations A_{CH}, σ_p and ν_{CH}, σ_p^o gradually inverse their slopes. The change of C-H bond intensity in the series of trisubstituted methanes was also described by the curve with clearly expressed minimum. The observed A_{CH} changes were interpreted according to the formalism of the valence-optical theory developed by Gribov.

In a previous report /1/ infrared spectra of monosubstituted methanes in the range of C-H strectching vibrations of methyl group were studied. The factors determining the frequencies ν_{CH} and intensities A_{CH} changes have been discussed in terms of the electronic effects of substituents. We have now extended the work to the series of di- and trisubstituted methanes.

To minimize the specific intermolecular effects which, as known, have particularly substantial influence on the band intensity /2, 3/, all the measurements were made in inert solvent (CCl_4). Infrared spectra were obtained on "IKS-14" spectrophotometer under conditions similar to those previously specified /1/. The results of measurements of ν_{CH} and A_{CH} are summarized in Tables 1 and 2. The assignements of the bands have already been set up

and their i-r spectra dealt with /2-12/ for most of the compounds listed in Tables. However, there are some cases in which the assignements of bands adopted here is presumable (Nos 3, 4, 14, 15 in Table 1 and No 8 in Table 2), because spectra of these substances were taken for the first time and they have not been interpreted unambiguously yet.

In some cases the bands in question overlap the other bands and the estimation of intensities is rather difficult when such a band-overlapping is pronounced.The overlappind bands were divided graphically into each component by suitable curve resolving and the intensities corresponding to a single vibrational mode were estimated, making allowance for fairly large errors. Additional difficulty in the study of the spectroscopic parameters behaviour was that in some compounds occured favorable conditions for Fermi resonance, which caused displacement of frequencies and redistribution of their intensities /5/. Those conditions were possible because the double frequency of bending vibration, δ_{CH} was approximately equal to the frequency of C-H stretching vibration and because of their identical symmetry. Another problem was caused by the fact that when we took infrared spectra of symmetric disubstituted ethanes we dealt with mixture of conformers with unknown composition. Though the complications mentioned above were the reason of certain differences between measured values and "real" values of ν_{CH} and A_{CH} the differences were, as a rule, less than the changes of ν_{CH} and A_{CH} caused by electronic factors.

Discussion

Disubstituted methanes

Intensities. The behaviour of band intensity of CH symmetric stretching mode of methylene group in the series of disubstituted methanes is greatly analogous to the behaviour of methyl group /1/ in the monosubstituted compounds (Fig. 1a). The change of A^{s}_{CH} in methylene group is correlated with σ^{o}_{p} values of substituents when $\epsilon^{c}_{p} < 0.6$:

Table 1. Ifrared Frequencies and Intensities for CH_2 Group in Disubstituted Methanes[1)]

No	Compound	ν	ε	$\sqrt{A}$	$\sqrt{A^{sum}}$	$\Sigma \sigma_p^o$
1	$NH_2CH_2-CH_2-NH_2$	2855(s) 2930(as)	42.0 51.0	34.6 39.6	51.0	-0.53
2	$OH-CH_2-CH_2-OH$	2880(s) 2945(as)	19.5 23.0	23.0 26.0	33.0	-0.14
3	$(C_6H_5O)_2CH_2$	2895(s) 2916 2950(as) 2975(as)	22.0 24.0 18.7 29.0	26.8	-	0.04
4	$(C_6H_5S)_2CH_2$	2920(s) 2975 3007(as) 3020	12.9 14.2	22.0 12.3	29.0	0.2
5	$CF_3CF_2CH_2OH$	2940(s) 2990(as)	13.7 5.2	20.4 12.0	24.5	0.39
6	$ClCH_2CH_2Cl$	2960(s) 2975(s) 3030(as)	12.5 11.7 1.8	17.8 5.5	18.7	0.38
7	CH_2Cl_2	2987(s) 3054(as)	2.3	12.2 7.3	14.0	0.54
8	CH_2Br_2	2990(s) 3068(as)	1.5 7.9	7.1 15.4	16.8	0.52
9	CH_2I_2	2985(s) 3065(as)	0.9 11.4	5.8 19.0	20.0	0.60
10	$ClCH_2COOCD_3$	2955(s) 3003(as)	9.5 2.0	16.3 7.0	17.8	0.73
11	CF_3CH_2I	2975(s) 3040(as)	7.2 6.7	12.0 13.0	17.5	0.83
12	$CF_3CH_2CCl_3$	2962(s) 3005(as)	4.1 5.7	10.5 13.5	15.9	0.85
13	$(CN)_2CH_2$	2928(s) 2958(as)	16.3 38.6	17.6 27.0	31.4	1.3
14	$(C_6H_5SO_2)_2CH_2$	2926(s) 2983(as)	31.6 22.4	20.0 18.0	26.8	1.38
15	$NO_2CH_2COOCH_3$	2938} 2975}(s) 3032(as)	15.3 12.2 18.0	12.0 17.0	19.0	1.23
16	NO_2CH_2Br	2920 1988(s) 3040} 3067}(as)	7.6 4.0 4.4 8.2	17.9 11.8 20.7	29.6	1.04

1) ν_{CH} are given in cm^{-1}; A_{CH} in $M^{-1}.l.cm.^{-2}$

Table 2. Infrared Frequencies and Intensities for Methyne Group in Trisubstituted Methanes

No	Compound	ν	ε	$\sqrt{A}$	$\Sigma\sigma_p^o$	$\Sigma\sigma_I$	$\pm\mu/\mu_q$ [1]
1	$(C_6H_5O)_3CH$	2955 2925 2900	27.0 63.5	58.5	0.06	1.07	-
2	CHF_3	3040	22.0	28.0	0.51	1.56	-
3	$CHCl_3$	3022	7.2	14.3	0.81	1.41	0.28
4	$CHBr_3$	3030	12.5	20.4	0.78	1.35	0.47
5	CHI_3	3011	24.0	24.0	0.90	1.14	0.57
6	$CF_3(CF_2)_2H$	3000 2990	6.2 4.7	16.1	1.62	1.5	-
7	$CF_3(CF_2)_5H$	3003 2977	6.7 4.3	14.8	1.62	1.5	-
8	CF_2Cl-CF_2Cl- $-(CF_2)_2-CFH-CF_2I$	2960 2985 3005	27.0 41.5 17.4	14.3	1.23	1.4	-
9	$OH(NO_2)_3$	3032	140.0	54.0	2.4	1.89	0.88

1) After Boobyer /2/

$$(A^s)^{I/2}_{CH_2xy} = 23.9 - 22.7 \Sigma\sigma_p^o \quad (r = 0.909,\ n = 9) \qquad (1)$$

There is close coincidence between the starting point and slope of the straight line (1) and the corresponding parameters of the straight line for methyl derivatives /1/:

$$(A^s)^{I/2}_{CH_2X} = 24.7 - 26.4\,\sigma_p^o \qquad (2)$$

After common correlation data processing for mono- and disubstituted methanes the relationship A_{CH}, σ_p^o takes the folloving form:

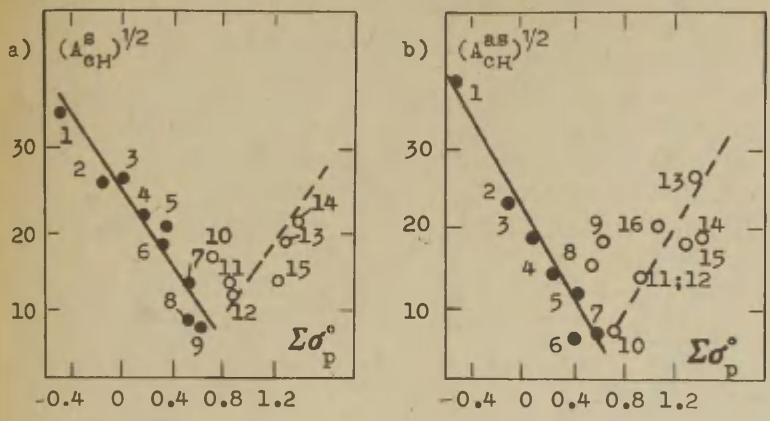

Fig. 1. The plots of A^{s} and A^{as} against σ_{p}^{o} values. The numeration of points is given in correspondence with Table 1. The straigth lines I and II represent Eqs. (3) and (5) accordingly.

o denotes compound not included in correlation treatment.

$$(A^{s})_{CH_3X,CH_2XY} = 24.6 - 24.4\,\Sigma\sigma_{p}^{o} \quad (r=0.926,\ n=28) \qquad (3)$$

It must be noted that the use of the method (11, 13-15) well-known in literature i.e. the discription of the intensity of C-H vibrations by means of inductive σ_{I} values, considerably worsens the quality of correlation. This fact is confirmed by the previous conclusion /1, 16/ about the influence of, at least, two effects - inductive and hyperconjugative - upon spectroscopic parameters of substituted methanes.

It is a feature of the relation between A^{s} and the parameters of substituents in the series of disubstituted methanes that the curve $(A_{CH})^{1/2}$, σ_{p}^{o} gradually changes its slope when passing to the compounds with the strong electron-withdrawing substituents. It means a change in total character of the influence of substituents on A_{CH}: electron-acceptors decrease intensi-

ty on the left branch and increase its values on the right one.

The similar relation between band intensity and electronic structure of substituents has often been noted for organic compounds of different classes /2, 11, 17-21/ and qualitatively related to the change of the sign of dipole moment derivative with respect to the stretching coordinate of C-H bond and to the change of C-H bond dipole moment itself.

More adequate interpretation of the observed form of the curve $A_{CH} - \sigma_p^o$ can be obtained on the base of the valence-optical theory /22, 23/. The band intensity is usually determined as the square of the partial derivative $\partial\mu/\partial Q_i$ of the dipole moment of the molecule with respect to a given normal coordinate Q_i. As is has been stated already /22/, the value $\partial\mu/\partial Q_i$ may be expressed in evident form by the intramolecular parameters (electro-optical coefficients and the form of vibrations). In the first approximation of the theory the changes in absolute band intensity are expressed as follows:

in monosubstituted methanes

$$Y^s_{CH_3} = \frac{\sqrt{3}}{3}\left|\left(\frac{\partial\mu_{CH}}{\partial q} + 2\frac{\partial\mu_{CH}}{\partial q'}\right) - 3\frac{\partial\mu_X}{\partial q}\right|, \qquad (4a)$$

in symmetric disubstituted methanes

$$Y^s_{CH_2} = \frac{\sqrt{6}}{3}\left|\left(\frac{\partial\mu_{CH}}{\partial q} + \frac{\partial\mu_{CH}}{\partial q'}\right) - 2\frac{\partial\mu_X}{\partial q}\right|, \qquad (4b)$$

where μ_{CH} and μ_X are the dipole moments of C-H and C-X bonds, correspondingly; $\partial\mu_{CH}/\partial q$ is the partial derivative of C-H bond moment with respect to its own stretching coordinate; $\partial\mu_{CH}/\partial q'$ is the partial derivative with respect to neighbouring stretching coordinate. The degree of interaction of the CH_3 or CH_2 group with one or two substituents X is determined by the relation between the contributions of the first and

the second terms in the right side of expressions (4a) and (4b).

The estimate of chloro-substituted methanes, performed in the first-order approximation of valence-optical theory /24/, corroborates the assumption about the dominating role of the term $\partial\mu_{CH}/\partial q$ in the change of intensity and about gradual decrease of this value and of the bond moment as the electron-withdrawing influence of substituents increases (Table 3).

Table 3. Bond Moments and Their Derivatives with Respect to Own Stretching Coordinates in Chloro-substituted Methanes /24/.

Parameter	CH_4	CH_3Cl	CH_2Cl_2	$CHCl_3$
μ_{CH}	0.95	0.59	0.13	0.09
$\partial\mu_{CH}/\partial q_{CH}$	0.54	9.34	0.10	-0.06
$\partial\mu_{CH}/\partial q'_{CH}$	0	0	0	0
$\partial\mu_{CCl}/\partial q_{CH}$	-0.28	-0.28	-0.28	-0.28

In Table 3 one can see that the electric fields of the studied molecules have very low interaction coefficients of adjacent C-H bonds; the term $\partial\mu_{CCl}/\partial q_{CH}$ keeps its constant value. The term $\partial\mu_{CH}/\partial q_{CH}$ has the similar change in wider series of substituted methanes (Table 2 and 4). But in this case it is necessary to analyse all the set of terms which determine the absolute intensity of infrared band, because the bond moment derivative corresponding to the cross-term between the internal coordinates is not constant.

The results of calculation of parameter Y (Table 4) prove this conclusion. According to this calculation the change of Y^S value in the series of monosubstituted methanes is of the same type as the above-mentioned relation for experimental A^S_{CH} values. The relation $Y^S, \sigma p^o$, illustrated

Table 4. Electro-optical Parameters for CH_3 and CH_2 Groups of Mono- and Disubstituted Methanes

No	Compound	$\pm Y$		$\pm \partial\mu_{CH}/\partial q$	Ref.
		sym.	asym.		
1	CH_3NH_2	1.8	0.88	1.2	25
2	CH_3-CH_3	1.36	0.43	0.74	26
3	CH_3OH	0.73	0.43	0.53	31
4	$(CH_3)_2CO$	0.65	0.15[x)] 0.15[x)]	0.26[x)]	25 27
5	CH_3Cl	1.11	0.32 0.27	0.06	30 28
6	CH_3Br	1.05	0.23 0.18	-	30 28
7	CH_3F	-	0.57	-	28
8	CH_3I	0.87	0.15 0.12	-	30 28
9	CH_3CN	0.24	0.32	-	29
10	CH_3CHO	-	0.15	-	32
11	$(CH_3)_4Ge$	0.86	0.38	-	33
12	CH_3GeCCl_3	0.41	0.11	-	33
13	CH_3SiCl_3	-	0.19	-	34
14	CH_2CI_2	-	0.18	-	28
15	CH_2Br_2	-	0.09	-	28
16	CH_2I_2	-	0.20	-	28
17	$(OH\text{-}CH_2)_2$	-	0.43	-	31

• Related to one methyl group.

in Fig. 2, corresponds to the left branch of the curve in Fig. 1a.*

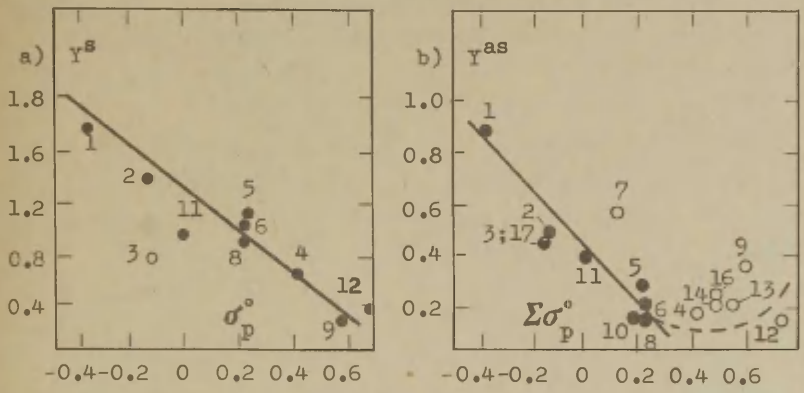

Fig.2. The changes of electro-optical constants Y for: a) symmetric C-H stretching mode of methyl group in monosubstituted methanes; b) asymmetric C-H stretching mode of methyl and methylene groups in mono- and disubstituted methanes. The numeration of points is given in correspondence with Table 4.

Now the lack of calculated data prevents to investigate consequently the fashion of change of parameter Y^s in the series of disubstituted methanes, but the general form of expression (4b) enables us to explain inversion of the order of the intensity changes (Fig.1a) as the result of more intense electronic interactions between CH_2 group and the two substituents X.

As it is shown in Table 1 and in Fig. 1 b the na-

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* The intermolecular effects in the solution CCl_4 result in the change of the terms $\partial\mu/\partial q$, $\partial\mu/\partial q'$, $\partial\mu_x/\partial q$ in comparison with calculated values for gas phase /3, 6/, which leads to the change of intensities of the corresponding bands. But the general form of relation is preserved.

ture of electronic influence on the intensity of asymmetric stretching vibration in disubstituted methanes is analogous to that, which have been determined for A^{s}_{CH} values already. Eq. (5) which can approximate the change of A^{as}_{CH} on the left branch of the curve in Fig. 1 b, has the following form:

$$(A^{as}_{CH})^{1/2}_{CH_2XY} = 22.4-28.2\Sigma\sigma_p^{o} \quad (r=0.956,\ n=7) \qquad (5)$$

The direct comparison with monosubstituted methanes is complicated in this case by significant overlapping of the bands ν^{as} of methyl group, but the identical nature of the relations will be seen, if we correlate the summarized intensities of the bands in the range of stretching vibrations of CH_3 or CH_2 group, accordingly (Fig.3):

$$(A^{sum})^{1/2}_{CH_3X} = 38.0-35.6\,\sigma_p^{o} \quad (r=0.987,\ n=7) \qquad (6)$$

$$(A^{sum})^{1/2}_{CH_2XY} = 33.2-29.5\Sigma\sigma_p^{o} \quad (r=0.964,\ n=8) \qquad (7)$$

$$(A^{sum})^{1/2}_{CH_3X,\,CH_2XY} = 35.2-31.7\Sigma\sigma_p^{o} \quad (r=0.963,\ n=15) \qquad (8)$$

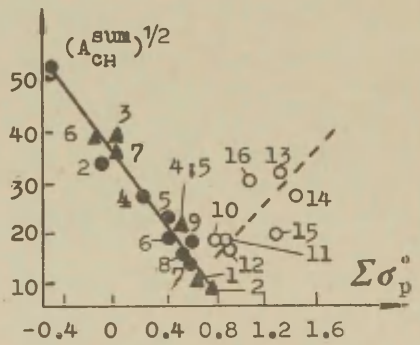

FiG.3.

The changes of total intensity of C-H bands. The numeration of points is given in correspondence with Tables 1,5.
▲ = CH_3X, ● = CH_2XY,
o = compound not included in correlation treatment.

The same is the nature of change of the corresponding electro-optical parameter Y^{as} (Fig.2b) which in the first approximation of the valence-optical theory is expressed by Eq. 9 with one common combination of terms for methylene and methyl groups /22/:

Table 5. Sums of Integral Intensities in the Range of Stretching Modes for Some Monosubstituted Methanes (Solvent; CCl_4)

No	Compound	ν_{CH}	$(A^{sum})^{1/2}$	No	Compound	ν_{CH}	$(A^{sum})^{1/2}$
1	CH_3CN	3026 3000 2938	11.5	5	CH_3COCH_3 2)	3012 2966 2925	23.0
2	CH_3NO_2	3030 2952 2931	9.1 1)	6	CH_3OH	2982 2938 2910	38.0
3	CH_3SCH_3 2)	2990 2970 2917	39.0	7	$(CH_3)_4Ge$ 2)	2980 2910	37.6
4	CH_3SOCH_3	2994 2917	22.0				

1) The i.r. spectrum of deuterated nitromethane is taken also; the correction on the nitro group absorption is made. 2) Values of A_{CH} are calculated for one CH_3 group.

$$Y^{as} = \frac{\partial \mu}{\partial q} - \frac{\partial \mu}{\partial q'} \qquad (9)$$

Vibration frequencies. The above-mentioned regularities of the change of band intensities are relevant for frequencies. As it is shown in Fig. 4, the most studied compounds have the tendency to the change of frequencies ν_{CH}^{s} and ν_{CH}^{as} which is rendered by the sum of σ_p^o values of substituents. If halosubstituted methanes (Nos 6-9) are neglected, as previously /1/, the left branches of ν_{CH}, σ_p^o curves will be approximated as straight lines and the equations will be

$$(\nu_{CH}^{s})_{CH_2Xy} = 2902+90.9\Sigma\sigma_p^o \quad (r=0.993.\ n=18) \qquad (10)$$

$$(\nu_{CH}^{as})_{CH_2Xy} = 2968+85.9\Sigma\sigma_p^o \quad (r=0.996.\ n=11) \qquad (11)$$

After comparison with the results of the analogous correlations obtained for monosubstituted methanes /1/ the same type of electronic effects of substituents is seen in the change ν_{CH}^{as}:

$$(\nu_{CH}^{as})_{CH_3X} = 2975 + 76.6\,\sigma_p^o \qquad (12)$$

This fact enables us to combine the both sets of compounds in one reaction series*

$$\nu_{CH}^{as}) = 2972 + 81.9\Sigma\sigma_p^o \quad (r=0.971.\ n=37) \qquad (13)$$

The curves ν_{CH}, σ_p^o pass through a flat maximum, the place of which respect to the axis of abscissa corresponds the minimumof the curves A_{CH}, σ_p^o (Compare Fig. 1 and 4). The presence of the linear dependence between the values of ν_{CH} and A_{CH} in the studied series of disubstituted me-

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* This conclusion does not concern the frequencies of symmetric C-H mode in the series of monosubstituted methanes, where hyperconjugation affects the change of frequency decisevely, the values ν_{CH}^{s} correlate with σ_R^o constant /1/.

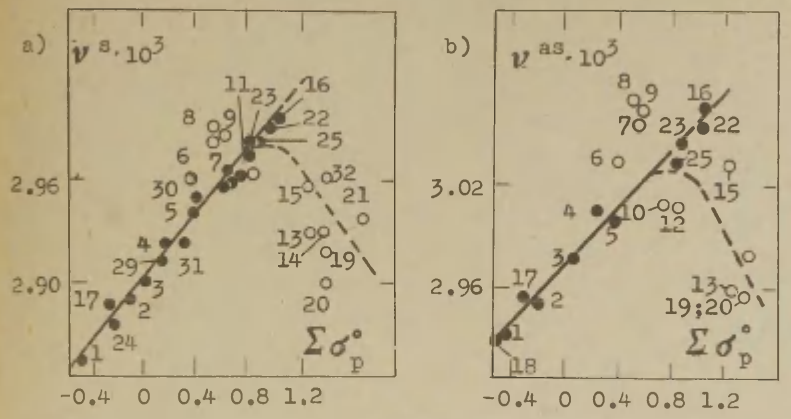

Fig.4. The changes of ν^{s} and ν^{as} in disubstituted methanes. The numeration of points (Nos 1-16) is given in correspondence with Table 1; N 17 = $(CD_3O)_2CH_2^*$ /5/; N 18 = $(CH_3CH_2^*)_3N$ /35/; N 19 = $(CH_3)_3\overset{+}{N}CH_2^*COC_6H_5$ /16/; N 20 = $(CH_3)_2\overset{+}{S}CH_2^*COC_6H_5$ /16/; N 21 = $CH_2(NO_2)_2$ /36/; N 22 = $ClCH_2NO_2$ /36/; N 23 = OF_3CH_2Br /5/; N 24 = $CD_3CH_2CD_3$/5/; N 25 = CF_3CH_2Cl /5/; N 26 = $BrCH_2^*C\equiv CH$ /5/; N 27 = $ClCH_2^*C\equiv CH$ /5/; N 28 = $FCH_2^*C\equiv CH$ /5/; N 29 = CCl_3CH_2OH /5/; N 30 = CF_3CH_2OH /5/; N 31 = $CD_3CH_2^*C\equiv CH$ /5/; N 32 = NO_2CH_2CN.
o = compound not included in correlation treatment.

thanes proves the similar nature of electronic influence on these parameters (Fig.5). Certain deviations in some cases are probably due to factors mentioned above, which distort the original electronic interactions, registered with the change of ν_{CH} and A_{CH}.

The discovered interconnection between the nature of relations ν and A is somewhat unexpected, for in general the intensity of the absorption band and its position in spectrum are the functions of different parameters. The obtained correspondence of the change in A and ν can be explained qualitatively if we assume that in this parti-

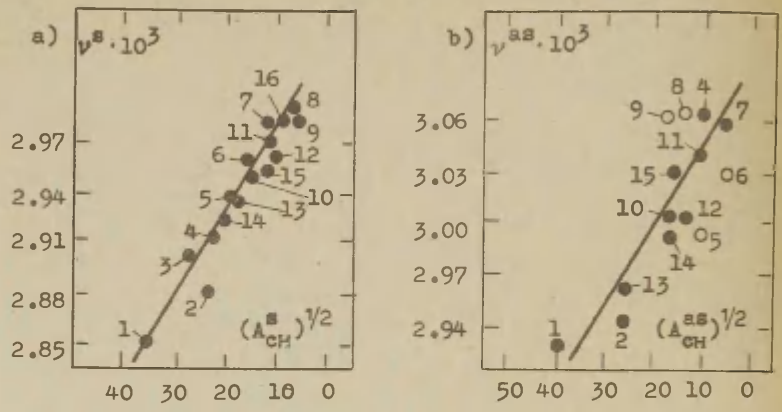

Fig.5. The relation between ν_{CH} and A_{CH}. The numeration of points is given in correspondence with Table 1.

cular case there is a clear-cut relation between the set of the coefficients of potential energy K_{ij}, which characterize the valence force field and the bond moment derivatives $\partial\mu_i/\partial q_j$ with respect to the corresponding bond stretching coordinate. If we assume then that the force constants $K_{1,2}$ and $K_{1,3}$, which describe the interaction between a given C-H bond and neighbouring bonds, reach their maximal values commensurable with the diagonal term $K_{1,1}$, the corresponding elements of the matrix of electro-optical constants $\partial\mu/\partial q_2$ and $\partial\mu/\partial q_3$ reach their maximum too, and vice versa. Some arguments in favor of this view can be found in literature /22,24/.

The experience of estimation of a good number of substituted methanes shows that the frequency shift in spectra is mainly due to the change of the force field of alkyl group; "kinematic" factors are of minor importance (for examples see Refs. 12,37,40).

The application of this approach to explanation of the band intensities of the C-H stretching modes of trisubstituted methanes is complicated by the shortage of experimental data and by the complexity of the observed spectral pattern. The factors, which distort the monotony of ν_{CH} and A_{CH} change comprise the presence of specific intermolecular effects even in such inert solvent as carbon tetrachloride /2, 38/, complex Fermi resonance with two and several combinations and overtones, mechanic unharmonicalness of the studied vibrations /39/ etc.

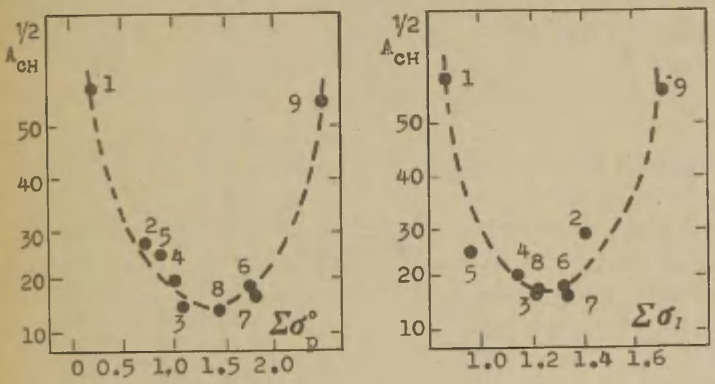

Fig.6. Dependence of A_{CH} of trisuostituted methanes on σ_p° and σ values. The numeration of points is given in correspondence with Table 1.

The data listed in Table 2 are not sufficient for an unambiguous conclusion about the type of dependence of frequencies and band intensities of the stretching vibrations upon the electronic effects. With the given set of substituents we can observe the approximate dependence with both σ_I and σ_p° values (Fig.6). We can only state now that in this case the intensity changes are expressed by the curve with a pronounced minimum. The right branch in Fig.6 is in agreement with the increase of $\partial\mu/\partial q$ when

passing from halogenated compounds to trinitromethane (Table 2).

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THE INFRARED INVESTIGATION OF ELECTRONIC INTERACTIONS IN SUBSTITUTED BENZYLS

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On the basis of the analysis of infrared spectra of some benzyl derivatives as $C_6H_5CH_2X$ and $XC_6H_4CH_2OH$ it was shown that changes of position and intensity of the C-H stretching modes of methylene group due to the influence of the α- substituent and the substituent in aromatic ring could be correlated by the relations analogous to those obtained earlier for monosubstituted methanes and toluene, respectively. Characteristic features of phenyl radical electronic influence on local infrared and nmr spectroscopic parameters of methylene group were discussed. The resulting electronic effect of phenyl ring was determined by its inductive influence and two types of resonance interaction: 1) by means of effect of hyperconjugation with aliphatic C-H bonds which caused the transition of some part of electronic density from group CH_2X to aromatic cycle; 2) by means of effect of hyperconjugation with C-X bond, which caused displacement of electronic density from benzene ring to group CH_2X. The relative contributions of the effects of the first and the second type depended on the studied reaction series and the CH_2X group electronic nature.

In development of the investigation of the mechanism of electronic interactions in substituted methanes /1,2/ and toluenes /3,4/ the study of infrared characteristics of methylene group in substituted benzyls as $C_6H_5CH_2X$ and $XC_6H_4CH_2OH$ was made.

Infrared spectra. The results of the study of benzyl derivatives infrared spectra /5-8/ show that the band within the range of 2900-2930 cm^{-1} generally belongs to the

frequency of symmetric C-H stretching mode of methylene group in the compounds which have electron-withdrawing substituent in α-position; its asymmetric mode is within the range of 2960-3000 cm^{-1}. The problem of assignement of the fundamentals in benzyl spectra which have strong electron-releasing groups (NH_2, $N(CH_3)_2$, OH, OCH_3) is not still settled definitely. We stick to the oppinion stated in 1963 already /7,8/, according to which the symmetric mode has the absorption band at 2860-2880 cm^{-1} and the asymmetric mode has the absorption band at $\sim$ 2930 cm^{-1}. The similarity between benzylamine or benzyl alcohol infrared spectra and those of related structure disubstituted ethanes - ethylenediamine and ethylene glycol - the spectral interpretation of which is enough correct /9,10/ indirectly proves this assignement.

The spectral pattern in the studied range for some compounds is complicated by the Fermi resonance and also by significant overlap of the ν^{as} CH_2-mode with the ν^{s} CH_2-mode or with the ring vibrations. Because of these difficulties we measured both the integrated intensity of separate bands (A^{s} and A^{as}) and the total intensity of bands in the range of stretching modes (A^{sum}). Infrared spectra of solutions of the studied compounds in carbon tetrachloride were obtained on a IKS-14 spectrophotometer under conditions similar to those specified previously /3/.

The results of correlative treatment of the data (Table 1) enable us to conclude that for the compound as $C_6H_5CH_2X$ the observed changes of spectroscopic parameters ν and A of methylene group have some regularities of electronic influences which are qualitatively similar to regularities which have been obtained in the series of monosubstituted methanes /1,2/.

As it is shown in Fig.1a the symmetric CH_2 stretching frequency for benzyl derivatives has linear connection with σ_R^{o} values for the substituents:

$$\nu^{s} = 2917 + 107.6\ \sigma_R^{o} \quad (r=0.966.\ n=11) \qquad (1)$$

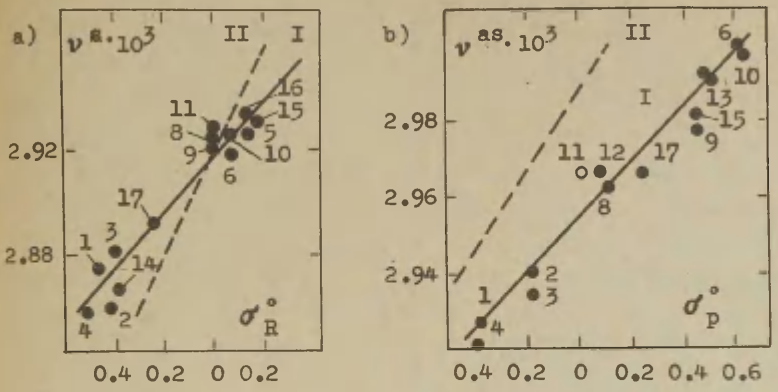


Fig.1. Plots of ν^{s} and ν^{as} for α-substituted benzyls against σ_R° and σ_p° values, respectively. The identification numbers correspond to entries in Table 1. The straight line II represents monosubstituted methanes /1/.

By analogy with our previous work /1/, where the like change of ν^{s}_{CH} in the series of monosubstituted methanes was interpreted on the assumption of the presence of hyperconjugative interaction of methyl group and substituent X, which was capable of σ,π-conjugation, the effect of hyperconjugation is believed to influence the position of the band of ν^{s}_{CH} methylene group in substituted benzyls. Remarkable is the fact that the straight lines I and II in Fig.1a have different slopes and cross at the point for which $\sigma_R^{\circ} = 0$.

The fashion of changes of difference $\Delta\nu^{s} = (\nu^{s})_{C_6H_5CH_2X} - (\nu^{s})_{CH_3X}$ which characterizes the influence upon ν_{CH} values exchanges of one hydrogen atom of methyl group in monosubstituted methanes to phenyl ring, enables us to conclude that depending on the nature of α-substituent the phenyl ring has either electron-withdrawing (X = +M-substituent) or electron-releasing (X = -M-substituent) properties.

Table 1. Frequencies and Band Intensities of Stretching Vibrations of Methylene Group in Infrared Spectra of α-Substituted Benzyls

No	X	ν^{s}_{CH}	$(A^{s}_{CH})^{1/2}$	ν^{as}_{CH}	$(A^{sum}_{CH})^{1/2}$	σ_p^o	σ_R^o
1	$-NH_2$	2876	39.8	2930	58.5	-0.38	-0.48
2	$-OCD_3$	2857	40.5	2940	53.7	-0.16	-0.40
3	-OH	2875	40.5	2930	53.5	-0.16	-0.40
4	$-NHC_6H_5$	2855	46.0	2925	50.5	-0.40	-0.50
5	$-CONH_2$	2925	23.2	-	-	0.25	0.13
6	-CN	2916	13.6	2985 2955	17.8	0.65	0.09
7	-Cl	2965	24.2	-	-	0.26	-0.18
8	$-SC_6H_5$	2927	21.8	2960	27.4	0.1	0
9	$-SOC_6H_5$	2924	17.6	2967	20.0	0.52	0
10	$-SO_2OC_6H_5$	2927	17.2	2982	18.8	0.68	0.06
11	-D	2930	31.6	2964	34.6	0	0
12	-SH	2933	24.8	2965	28.0	0.04	-0.15
13	-SON	2940	13.7	2987	15.5	0.52	-
14	$-OC_6H_5$	2865	(31)	2930	46.0	0.02	-0.36
15	$-COC_6H_5$	2930	(21)	2970	26.4	0.50	0.19
16	$-COOCD_5$	2933	20.0	2980	-	0.50	0.15
17	$-OCOC_6H_5$	2892	20.0	2958	35.4	0.31	-0.23

Our infrared data, which prove the double nature of phenyl ring electronic influence are in certain correspondence with the results of fluorine nmr investigation of meta- and para-fluorine-derivatives of benzyls having α-substituents. According to Adcok and coworkers /11/ the displacement of the ^{19}F signal under the influence of the substituent CH_2X (atom X is more electronegative than carbon) are determined by its inductive effect and by two types of resonance interaction: (i) by electron-withdrawing effect of hyperconjugation of aliphatic α-C-H bonds which causes the transition of some part of electron density from group CH_2X to aromatic cycle; (ii) by electron-releasing effect of hyperconjugation (or simply conjugation) of C-X bond, which causes the displacement of electron density from benzene ring to group CH_2X. Taking into account the said above we can consider the selective sensitivity ν_{CH}^{s} values to resonance effect as the indication to the dominant role of the first type conjugation in the benzyl derivatives where a carbon atom of methylene group has excessive negative charge under the influence of +M substituent in α-position, and, on the contrary, the second type conjugation effect is more obvious when an atom of carbon of methylene group has somewhat cationoid nature under the influence of -M substituent.

In contradiction to the behaviour of ν_{CH}^{s} mentioned above, the changes of asymmetric CH_2 stretching mode correlate by σ_p^{o} values of substituents (Fig.1b).

$$\nu_{CH}^{as} = 2949 + 52.7\ \sigma_p^{o} \quad (r = 0.991.\ n = 12) \qquad (2)$$

The same dependence for monosubstituted methanes is /1/:

$$\nu_{CH}^{as} = 2975 + 76.6\ \sigma_p^{o} \qquad (3)$$

The fact that the frequency ν_{CH}^{as} in substituted methanes exceeds regularly the values of ν_{CH}^{as} in benzyl derivatives ($\Delta\nu \simeq 25\ cm^{-1}$) shows that phenyl ring has electron-releasing influence on ν_{CH}^{as}. In accordance with the interpretation given above this excess may be assumed as the result of the predominance of the second type conjugation

over inductive influence and the effect of σ,π -conjugation of C-H bonds with benzene ring.

One can trace the similar phenomenon in the change of integrated intensities for the CH_2 stretching mode. As it is shown in the Fig.2, the linear relation

$$(A^s)^{1/2}_{C_6H_5CH_2X} = 31.3 - 27.2\ \sigma_p^o \quad (r = 0.976,\ n = 15) \quad (4)$$

has just the same slope as it was for A^s values in substituted methanes /1/:

$$(A^s)^{1/2} = 24.7 - 26.4\ \sigma_p^o \quad (5)$$

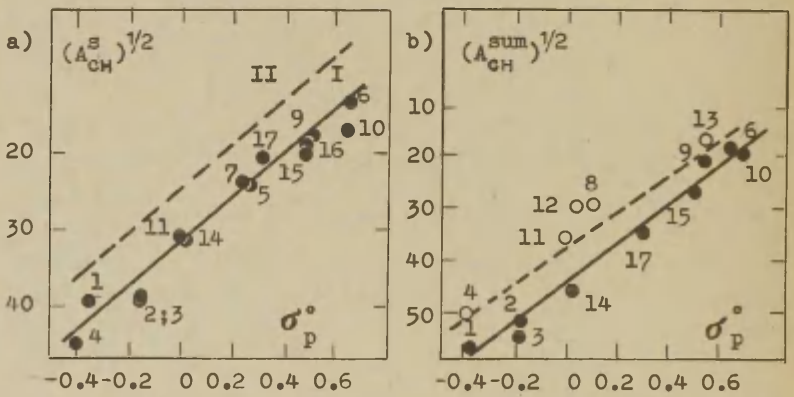


Fig.2. Correlation of intensity of the methylene group stretching modes of α-substituted benzyls with σ_p^o values. The identification numbers correspond to entries in Table 1.

The shift of the straight line (4) relatively (5) towards great values σ_p^o (Fig.2a) shows that in this case phenyl radical acts also as sufficiently strong electron donor.

Here we could not determine the relationship of ν as change because of the difficulties in determination of the change of intensity of significant overlapping bands of asymmetric C-H vibrations. But the higher coefficient of regression in relation (6), comparing with the rela-

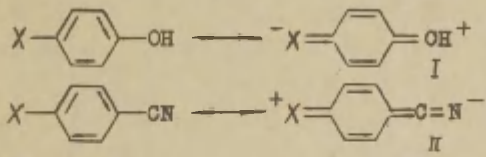
tion (4) - the correlation (6) was obtained for the sum intensity of bands - the value A^{as}_{CH} in the series of substituted benzyls is more sensitive to the change of electronic nature of substituent (and somewhat less sensitive to the influence of phenyl ring) than A^{s} :

$$(A^{sum})^{1/2}_{C_6H_5CH_2X} = 45.0-39.3\sigma_p^{o} \quad (r=0.985.\ n=7) \qquad (6)$$

The analogous relation in the series of substituted methanes is /2/:

$$(A^{sum})^{1/2} = 38.0 - 35.6\,\sigma_p^{o} \qquad (7)$$

The mentioned features of phenyl ring electronic influence are not specific for benzyl derivatives. It is known, in particular, that the exchange of methyl radical to phenyl one in some compounds like CH_3X, where X is electron donor ($-NH_2$, -OH) or electron acceptor (-CO(R), -ON) causes the increase of integral intensity of bands of all the above-mentioned groups. Taking into consideration that in the first case electron-releasing substituents reduce infrared intensities, and in the second case they increase it /12/ we can explain the observed changes in terms of the valence bond method by the increase of relative weight of resonance structures I and II respectively /12/:



Since limiting polar structures are stabilised by resonance the presence of phenyl ring increases band intensity in both cases due to its ability to conjugate with reaction centre either of +M- or -M-type.

The data of the present work show that the redistribution of electron density in α-substituted benzyls under the influence of polar substituent is like this which can be determined by changes of band intensity of the C=O and

CN groups. It corresponds to an accepted assumption /1, 12, 13/ which says that electronic interactions registered by the A_{CH} values characterize the condition of vibrating nuclei, which meets the polarisation of C-H bond towards C^{+}-H^{-}. The fact that effective value $\sigma_{C_6H_5} \approx -0.26$ taken from relations (4)-(5), is close to the σ^{+} value, proves the resonance nature of electron-releasing influence of phenyl radical upon infrared parameters of methylene group.

The results listed in Table 2 allow us to consider the peculiarities of electronic interactions in benzyl derivatives which have a varying substituent in aromatic ring.

Table 2. Frequencies and Band Intensities of Stretching Vibrations of Methylene and Hydroxyl Groups in Infrared Spectra of Substituted Benzyl Alcohols

No	X	ν^{s}_{CH}	$(A^{s}_{CH})^{1/2}$	ν^{as}_{CH}	$(A^{as}_{CH})^{1/2}$	$(A^{sum}_{CH})^{1/2}$	$(A_{OH})^{1/2}$
1	H	2875	40.5	2930	36.0	53.5	45.5
2	m-NH_2	2872	39.6	2920	39.6	56.5	40.5
3	m-F	2875	35.0	2930	33.0	46.5	48.5
4	m-Cl	2873	35.0	2925	31.0	46.5	50.0
5	m-I	2882	34.4	2935	31.4	47.5	47.5
6	m-NO_2	2870	34.0[2)]	2925	30.0[2)]	45.5[2)]	55.5
7	p-NO_2	2870	31.2[2)]	2925	32.4[2)]	45.5[2)]	55.0

1) Intensities of bands 3617 and 3635 cm^{-1}. 2) Taking into account correction for absorption of the nitro group.

The data obtained show that introduction of substituent is of almost no influence upon the frequencies of methylene and hydroxylic groups in benzyl alcohol, but it seriously changes their intensity.

As it is seen in Fig.3a the change of A^{s}_{CH}

in the series of substituted benzyl alcohols is rendered by σ_p^o values of the substituent:

$$(A^s)^{1/2} = 38.7 - 10.1\ \sigma^o \quad (r=0.991,\ n=8) \qquad (8)$$

$$(A^{sum})^{1/2} = 53.0 - 14.0\ \sigma^o \quad (r=0.935,\ n=6) \qquad (9)$$

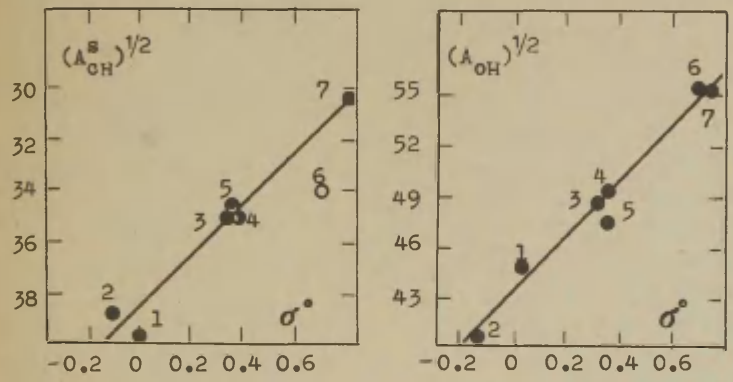


Fig.3. Plots of A_{CH} and A_{OH} for substituted benzyl alcohols against σ^o values. The identification numbers correspond to entries in Table 2.

The coefficient of regression in Eq. (8) is half the value of that of Eq.(4); practicaly it coincides with the values which were found earlier /3/ for intensity of methyl group in the series of substituted toluenes (ρ = 12,7). Thus in this case the total electronic influence on the A_{CH} value is determined by additive contributions of electronic effects which are caused by hydroxylic group and the substituent in aromatic ring.

Relation (10) describes changes of the band intensities of OH group in ring substituted benzyl alcohols (Fig.3b):

$$(A_{OH})^{1/2} = 43.7 + 15.3\ \sigma^o \quad (r=0.973,\ n=7) \qquad (10)$$

It follows from the comparison (10) with the analogous dependence in the series of substituted phenols*

* The values of A_{OH} are taken from Stone et al./14/.

$$(A_{OH})^{1/2} = 72.0 + 11.5\,\sigma^{\circ} \quad (r=0.970.\ n=10) \qquad (11)$$

that introduction of methylene "bridge" in accordance with the given above interpretation sharply decreases the intensity of OH vibrations; it blocks the transmission of the direct resonance interaction but it is of almost no influence upon A_{OH} sensitivity to inductive and mesomeric effects of substituent X.

FMR-spectra. As in the case of infrared parameters, the question of the nature of electronic influence of phenyl radical on the magnitude of proton chemical shift of methylene group necessitates to employ substituted methanes as the standard series of comparison. The nearly constant shift of proton signal of methylene group towards the weaker field comparing with methyl group in corresponding methanes (Table 3) is characteristic of the most substituted benzyls. This shift reflects not only electronic influence of phenyl radical, but the influence of ring current and anisotropic effect of $C_{C_6H_5}$ - C(H) bond. Corrections for paramagnetic effect of C-X bond in group CH_2X are known for some of studied benzyl derivatives /15/. For the reason that after elimination of for all the mentioned here "magnetic" effects, chemical shifts are correlated by the relation (12) which has been determined for substituted methanes (15):

$$\Sigma\sigma^{*} = 0.92 + 0.85\,\delta_{CH_3} \qquad (12)$$

we can say that in this case the phenyl group has the features of some weak electron acceptor of -I-type ($\sigma^{*}_{C_6H_5} = 0.6$).

Approximate constancy of $\Delta\delta$ value for the most part of substituted benzyls (Table 3) proves indirectly the possibility to apply this conclusion to some more compounds. Certain "exceeding" of $\Delta\delta$ values occurs only if there is strong electron-releasing substituent in the molecule (X = = $N(CH_3)_2$, OCH_3, OH, F). The possible explanation is that electronic interactions in the compounds of this type include both the inductive influence and the effect of hy-

Table 3. Chemical Shifts for Monosubstituted Methanes and Benzyls[1)]

X	CH_3X	$C_6H_5CH_2X$		7)
	δ_{CH_3} 2)	δ_{CH_2}	$\delta^*_{CH_2}$ 3)	$\Delta\delta$
-CN	1.99	3.74 4)	2.09	-0.1
-COOH	2.07	3.64 4)	1.99	0.08
$-SCH_3$	2.08	3.66 4)	2.01	0.07
$-SC_6H_5$	2.47	4.11 4)	2.46	0.01
$-CH_3$	0.87	2.60 2)	0.95	-0.08
$-C_6H_5$	2.34	3.92 2)	2.27	0.07
-Br	2.68	4.46 5)	2.81	-0.13
-Cl	3.05	4.57 5)	2.92	0.13
-F	4.26	5.31 5) 5.24 6)	3.66 3.59	0.60 0.67
-OH	3.38	4.69 4)	3.04	0.34
$-OCH_3$	3.24	4.46 4)	2.81	0.43
$-N(CH_3)_2$	2.12	3.32 4)	1.67	0.45

1) Chemical shifts are given in p.p.m. with respect to tetramethylsilane as internal reference. 2) Taken from Refs.16, 17. 3) Correction for magnetic anisotropy and ring current of phenyl group is introduced ($\Delta\delta' = -1.65$ /15/). 4) Taken from Ref. 17. 5) Taken from Ref. 18. 6) Taken from Ref. 19. 7) $\Delta\delta = \delta_{CH_3} - \delta^*_{CH_2}$.

perconjugation of the first type arising as the result of intensification of electron-withdrawing capability of phenyl ring in the presence of strong +M-substituent.

Completing the discussion of the whole set of spectral data, we can state that the phenyl radical in substituted benzyls can change significantly its electronic influence. Its resultant effect is determined by the relation between the inductive effect and the effects of hyperconjugation of the first and the second type the relative contributions of which are not constant and depend upon the kind of the studied reaction series and the electronic nature of group CH_2X.

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ISOTOPE EXCHANGE OF HYDROGEN IN SUBSTITUTED METHANES AND RELATED COMPOUNDS

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Kinetics of the base-catalyzed deuterium exchange of aliphatic CH bonds in halogen derivatives of saturated hydrocarbons, α-substituted benzyls, some organosulfur and organophosphorus compounds is studied. It is shown that the change of kinetic CH-acidity of the studied compounds and of most other substituted methanes (with kinetic data available in literature) is rendered satisfactorily by means of σ^--values of substituents.

In one of the previous works /1/ we applied the method of the base-catalyzed deuterium exchange to quantitative investigation of substituent electronic influence on the mobility of hydrogen atoms in substituted methanes and in the compounds of $(CH_3)_nM$ or $C_6H_5M(CH_3)_{n-1}$ type, where M was heteroamom or atomic group. It was snown that the change of kinetic CH-acidity depended on the total electronic influence of substituent (J, M, C-effects) and it could be correlated by nucleophilic σ^- values. But because of the shortage of kinetic data correlation parameters were estimated on the base of the reaction series with relatively small specific weight of the compounds which were characterized by σ^- values within the range of values 0.2 ÷ 0.9. Further accumulation of experimental information of deuterium exchange kinetics of methanes and similar compounds, which has been obtained by us and by others /2-9/, enables us to provide more uniformity in selection of objects for correlation treatment by means of additional insertion of some compounds of the following classes: 1) halogen substituted

aliphatic hydrocarbons (Table 1), 2) some organosulfur and organophosphorus compounds (Tables 2, 3), α-substituted benzyls (Table 4). Table 5 gives the data of relative mobility of hydrogen in methanes, taken from our previous work /1/. The most part of kinetic data refer to alcoholic (ROD + HO^-, R = CH_3, C_2H_5, t-C_4H_9) or aqueous solutions (D_2O, DO^- + D_2O). Sometimes basic solvent-alcohol-DMSO system or alkaline metal amide solution in liquid ammonia were used. It follows from the data obtained that, as a rule, the change of solvent causes certain alteration of rate which is nearly constant; it depends on the nature of substrate slightly and it is eliminated in comparison of the relative values of rate constants.

In order to determine the place of the studied compounds in the whole CH-acidity scale, kinetics of deuterium exchange of some of them was measured in several media. The value lgf = Δ lgK, estimated for toluene as standard compound, was used as correlated variable. The fact that the kinetic CH-acidity changes in separate groups of compounds can be described by practically the same relations, shows that we can study them within one and the same reaction series (Fig.1).

The relationship for the great part of the data summarized in the Tables 1-5 is*

$$\lg f = 0.5 + 14.6 \Sigma \sigma^- \qquad (1)$$

(r=0.987, S=1.2, n=70)

The Taft-Lewis relation (1a):

$$\lg f = -0.3 + 15.6 \Sigma \sigma_I + 14.8 \Sigma \sigma_R^- \qquad (1a)$$

(R=0.985, S=1.2, n=41)

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* Certain deviations from the perfect correlation may be partially refered to incomplete comparability of the data, obtained by different authors; then, they may be the result of secondary chemical processes in the solution, and also they may be explained as the performance of the solvent differentiating effect.

Table 1. Kinetics of Exchange Reaction in Halogenated Methanes and Similar Compounds

Ho	Compound	Solvent[1]	t°C	$K \cdot 10^5$. sec^{-1}	Relative rate	lgf[2]	$\Sigma\sigma$ [3]	Ref.
1	2	3	4	5	6	7	8	9
1	CH_2Cl_2	A(1N)	36	0.02	$8.0 \cdot 10^{-7}$	8.9	0.52	7
2	CH_2Br_2	A(1N)	36	0.23	$1.0 \cdot 10^{-5}$	10.0	0.54	7
3	CH_2I_2	A(1N)	36	0.25	$1.0 \cdot 10^{-5}$	10.0	0.54	7
4	CF_3H	A(0.2N)	70	0.1	$8.0 \cdot 10^{-6}$	9.9	0.51	3
5	CF_3CF_2H [4]	A(0.3N)	85 70 55 25	35 9.2 2.3 0.15	$1.3 \cdot 10^{-4}$	11.1	0.76	-
6	$CF_3(CF_2)_3H$ [4]	A(0.3N)	85 70 55 25	13.0 3.0 0.63 0.03	$3.2 \cdot 10^{-5}$	10.5	0.76	-
7	$CF_3(CF_2)_5H$ [4]	A(0.3N)	85 70 55	20.0 3.8 0.57	$1.2 \cdot 10^{-4}$	11.2	0.76	-
8	$CF_3(CF_2)_6H$	A(0.3N)	70	2.9	$3.1 \cdot 10^{-5}$	10.5	0.76	3
9	CF_3CFHI [4]	A(0.03N)	25	0.4	$4.0 \cdot 10^{-3}$	12.6	0.85	-

Table 1 (cont.)

1	2	3	4	5	6	7	8	9
10	$(CF_3)_2CH_2$ 4)	A(0.03N)	25	0.6	$5.0 \cdot 10^{-3}$	12.7	0.84	-
11	$(CF_3)_3CH$	A(0.001N)	45	-	$8.0 \cdot 10^{3}$	18.9	1.26	3
12	$(CF_3)_2CHF$	A(0.001N) B	 37	 -	 1	15.0	1.01	3 2
13	$(CF_3)_2CHBr$	B	37	-	2600	18.4	1.11	2
14	$(CF_3)_2CHCl$	B	37	-	756	17.9	1.10	2
15	$(CF_3)_2CHI$	B	37	-	179	17.3	1.11	2
16	CF_3CHCl_2	B	37	-	2.7	15.4	0.94	2
17	CF_3CHBr_2	B	37	-	3.5	15.6	0.96	2
18	$(CF_3)_2CHC_6H_5$	B	37	-	1.2	15.1		2
19	$CH_3^*COOCH_3$	A(0.042N) E(0.57N)	25 35 25	0.6 4.1 48.0	$4.0 \cdot 10^{-3}$	12.6	0.74	-

1) Adopted symbols (Table 1-5): A=$CH_3ONa+CH_3OD$; B=0.08N $(C_2H_5)_3N+(CH_3OD+DMSO-D_6)$ (1:1 by volume); C = $C_2H_5OK(Na)+C_2H_5OD$; C' = $C_2H_5OK(Na)+C_2H_5OH$; D = 0.1N t-BuOK+t-BuOD(^3H); E = 0.1N $C_2H_5OK+(C_2H_5OD+DMSO-D_6)$ (1:5); E' = 0.1N $C_2H_5OK+(C_2H_5OH+DMSO$) (1:5); F = KND_2+ND_3; G=NH_3. Concentration of base is given in brackets. 2) Methyl acetate (No 19) is used as intermediate reference in course of lgf calculation; its rate constant is compatible with those for compounds Nos 1-12 and for toluene (No 42 in Table 4). 3) It is effective value σ =0.42 for CF_3 substituent (from Eq.(1) calculated); for halogens $\sigma^- = \sigma^0$. 4) Rates were determined by us and V.P.Dushina.

Table 2. Kinetics of Exchange Reaction in Organosulfur Compounds

No	Compound	Solvent[1]	t, °C	K.10^5. sec^{-1}	lgf	$\Sigma\sigma^-$	Ref.
1	2	3	4	5	6	7	8
20	CH_3SCH_3 [2]	E	150	0.49	-1.3		-
		F'(0.45N)	0	30.0	-1.3		5
	[2]	D	160	0.02	2.1	0.17	-
21	$C_6H_5SCD_3$ [2]	F'(0.01N)	-60	130.0	4.2	0.29	5
		E	125	11.0			
			110	2.3	(2.0)		-
			95	0.45			
			138	1.1			
			120	0.24	4.1		-
22	$C_6H_5SCD_2CH_3$	F'(0.06N)	-60	14.0	2.6	0.14	5
23	$C_6H_5SCD(CH_3)_2$	F'(0.06N)	-60	0.06	0.15	-0.01	5
24	$(C_2H_5S)_2CH_2$	D	120	12.5	5.2	0.34	5.6
25	$(C_2H_5S)_2CDC_6H_5$	C'(0.1N)	50	0.35	8.8	0.53	6
26	$(C_2H_5S)_2CD(C_2H_5)$	D	138	0.47	3.7	0.21	5
			120	0.31			
27	$(C_6H_5S)_2CH_2$ [2,3]	C(0.1N)	70	7.5	9.9		-
			55	1.1			
			40	0.14			
		G	120	0.6	10.1	0.58	5

Table 2 (cont.)

1	2	3	4	5	6	7	8
28	$(C_6H_5S)_3CH$	G	120	20.0	11.4	0.87	5
29	$(C_2H_5S)_3CD$	C'(0.1N)	138 120 60 100 80 50	$7.0.10^3$ $2.5.10^2$ 36.0 15.9 1.74 0.038	7.9	0.48	- 6
30	CH_3SOCH_3 2)	C (0.1N)	50 25	3.0 0.25	10.0	0.73	1
31	$C_6H_5SOCD_3$ 2,3)	C' (0.1N)	65 50 35	21.0 4.1 0.77	11.0	0.83	-
32	$CH_3SO_2CH_3$ 2)	C (0.1N) D_2O	0 25	5.0 0.0033	17.7 16.7	1.05	- 1
33	$C_6H_5SO_2CD_3$ 2)	C'(0.1N)	0	11.0	18.0	1.05	-
34	$(CH_3)_3S^+I^-$ 2)	0.26N OD^- +D_2O	26.8	3.0	13.2	1.16	1

1) See footnote at Table 1. 2) Rates were determined by us. 3) Activation parameters (E, kcal.M^{-1}; lgA) for compounds Nos 21, 27, 31 equal 31.3, 13.2; 28.3, 13.9; 22.8, 11.0, respectively.

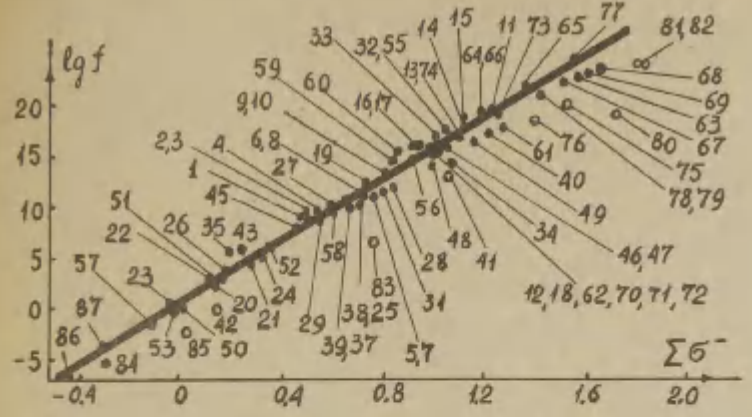

Fig.1. Plot of the relative rate constants of deuterum exchange against σ^- values. The numeration of points is given in correspondance with Tables 1-5.

o denotes the compound which is not included in correlation treatment.

corroborates almost equal sensitivities of reaction centre to resonance and inductive influences of substituents.

The reaction constant ρ^- of Eq.(1) has a higher degree of precision than the ρ^- value estimated in our previous paper /1/. This distinction lets in force the principial conclusions concerning the range of existence of Eq.1 and mechanism of substituent electronic influence on the mobility of hydrogen atoms in various groups of substituted methanes and similar compounds.

The next corrections must be incorporated however in those conclusions:

A) The substituent effect upon the exchange rate of methane derivative is enhanced more than in two times compared with one in the substituted toluenes /11/ ($\rho_{CH_3X} / \rho_{CH_3C_6H_4X} \simeq 1.9$).

B) CH-Acidity changes of sulfoxides and phosphine oxides (Nos 30, 31, 37-39) are rendered satisfactorily by

Table 3. Relative Rate Constants for Exchange in Organophosphorus Compounds /9/

No	Compound	Solvent[1)]	lgf	σ^-
35	$(CH_3)_3P$	E(0.57N)	5.0	0.20
36	$(C_6H_5)_2PCH_3$	E(0.57N)	4.7	0.29
37	$(CH_3)_3PO$	E(0.57N)	8.7	0.66
38	$(C_6H_5)_2P(O)CH_3$	E(0.57N)	9.3	0.68
39	$(C_6H_5)_2P(S)CH_3$	E(0.57N)	8.4	0.62
40	$[(C_6H_5)_2P(O)]_2CH_2$	$C_6H_5ND_2$	17.3	1.26 [2)]
41	$[(CH_3)_4P^+]J^-$	$0.26NDO^-+D_2O$	12.2	1.06

1) See footnote at Table 1. 2) $\Sigma\sigma = \sigma^- + \sigma^0$.

Eq.(1).There is certain discrepency between observed and calculated from Eq.(1) rate constants for compounds in which a positive charged substituent is bonded with CH_3 group (Nos 34, 41, 83), but the use of Eq.(1) instead the early obtained relation diminishes the differences between these magnitudes.

In general the results obtained indicate that the electronic influences of substituents are independent and additive. There are only the following deviations from additivity rule. Firstly, unadditivity arisesif the two strong electron-withdrawing substituents are bonded with reaction centre ("saturation effect"). Secondly, in the case of combination with strong -C-substituent the halogens are more electron-releasing (Nos 69, 75, 76, 80-82) than would be predicted by their σ values (so-called "α-effect" /1, 12, 13/). The description of electronic effects of two -C-substituents in the first case is possible by the plot of lgf against the sum of σ^- and σ^0 values (Nos 40, 63-68, 73); electronic effect of two nitro groups

Table 4. Kinetics of Exchange Reaction of α-CH Bonds in Benzyls [1]

No	Compound	Solvent[2]	t°C	K·10⁵ sec⁻¹	E	lgA	-lgK₂₅₀[3]	lgf	σ_x^-	Preparation
1	2	3	4	5	6	7	8	9	10	11
42	$C_6H_5CH_3$	E	150	10.0						
			135	2.3	33.7	13.4	(11.3)[4]			
			120	0.49						
		E'	150	6.5	-	-				-
		C(0.57N)	25	-	-	-	15.9[5]	0	0	
		F(0.03N Na)	-30	2.0	-	-				
			-45	0.5						
		(0.05N K)	-35	6.9	-	-				
			-45	1.8	-	-				
43	$C_6H_5CH_2SCH_3$	C(0.57N)	125	11.0						
			110	2.1	32.8	14.1	10.0	5.9	0.17	14,15
44	$(C_6H_5CH_2)_2S$	C(0.57N)	90	11.0						
			75	2.2	29.3	12.7	8.8	7.1	-	-
45	$C_6H_5CH_2SC_6H_5$	E	10	94.0	-	-		(9.6)		
		C(0.57N)	90	11.0						
			75	2.5	23.9	10.44	7.1	8.8	0.29	16
			60	0.56						
46	$C_6H_5CH_2SO_2CH_3$	C(0.002N)	10	130.0	17.3	10.4	(-0.27)[4]	16.2	1.05	17
			-5	18.0						
47	$C_6H_5CH_2SO_2C_6H_5$	C(0.002N)	-5	66.0						
			-20	11.0	(16.0)	(9.9)	(-0.65)[4]	16.5	1.05	17
		C(0.1N)	0	420						

Table 4 (cont.)

1	2	3	4	5	6	7	8	9	10	11
48	$C_6H_5CH_2SOCH_3$	C(0.1N)	0	4.7	-	-	-	13.4	0.83	18
49	$C_6H_5CH_2CN$	C(0.002N)	0	40.0	-	-	-	16.0	0.99	-
50	$C_6H_5CH_2OC_2H_5$	E	160 145 130	13.0 3.2 0.58	35.8	14.2	(12.0)[4]	-0.7	-0.16	-
		C(0.57N)	180		no exchange					
51	$C_6H_5CH_2OC_6H_5$	E	110 95 80	7.5 1.4 0.25	30.5	13.3	(9.1)[4]	(2.2)		19
		C(0.57N)	180 140	4.0 0.74	(33.2)	(11.6)	12.8	3.1	0.02	
52	$(C_6H_5)_2CH_2$ /23/	E	45 30 18	14.0 2.6 0.58	21.4	10.9	4.8	(6.5)		
		C(0.57N)	-	-	30.1	12.2	9.9	6.0	0.19	-
53	$C_6H_5CH_2CH_3$	E	135	0.93	-	-	-	-0.4	-0.15	-
54	$(C_6H_5CH_2)_2$	E	140	8.3	-	-	-	0.4	-	-
55	$C_6H_5CH_2COO_6H_5$	C(0.002N)	-20 -35	64.0 18.0	-	-	-	17.0	0.87	20
56	$C_6H_5CH_2COOC_2H_5$	C(0.01N)	0	(40.0)			1.1	14.8	0.74	-
57	$C_6H_5CD(CH_3)_2$ /5/	F'	-	-	-	-	-	-1.6	-0.30	-
58	$(C_6H_5)_3CH$ /23/	C(0.57N)	90 75	0.97 0.22	-	-	8.1	7.8	0.38	-

1) Rates were determined by us and Yu.L.Kaminsky. 2) See Table 1. 3) Solvent C. 4) Solvent E. 5) Calculated from Hammett relation /11/.

Table 5. Relative Rate Constants of Exchange in Some Substituted Methanes

No	Compound	Solvent	lgf	$\Sigma\sigma^-$
1	2	3	4	5
59	CH_3COCH_3	D_2O $D_2O + DO^-$	14.9	0.87 [1]
60	$C_6H_5COCH_3$	$DO^- + D_2O$ 0.001N $C_2H_5OK + C_2H_5OD$	15.3	0.87 [1]
61	CH_3NO_2	D_2O	17.3	1.27
62	CH_3CN	D_2O	15.0	0.99
63	$CH_2(CN)_2$	D_2O	22.3	1.62
64	$CH_2(COOC_2H_5)_2$	D_2O	19.6	1.2 [2]
65	$CH_2(COCH_3)_2$	D_2O	22.4	1.37 [2]
66	$CH(COCH_3)_2CH_3$	D_2O	20.1	1.22 [2]
67	$CH_2(COOC_2H_5)NO_2$	D_2O	22.0	1.52 [2]
68	$CH_2(CH_3CO)NO_2$	D_2O	23.1	1.65 [2]
69	$CH(CH_3CO)_2Br$	D_2O	22.6	1.64 [2]
70	$(CH_3CO)CH_2Cl$	D_2O	15.2	0.99
71	$CH_3CH(NO_2)C_2H_5$	D_2O	15.2	0.99
72	$(C_2H_5)_2CHNO_2$	D_2O	14.8	1.01
73	$C_6H_5CH_2NO_2$	D_2O	18.7	1.27
74	$CH_3CH_2NO_2$	D_2O	16.8	1.12
75	$BrCH_2NO_2$	D_2O	19.6	1.53
76	$CH(CH_3CO)Cl_2$	D_2O	18.1	1.41
77	$CH_2(NO_2)_2$	D_2O	24.1	1.56 [3]
78	$C_2H_5CH(NO_2)_2$	D_2O	21.0	1.43 [3]

Table 5 (cont.)

1	2	3	4	5
79	$CH_3CH(NO_2)_2$	D_2O	21.1	1.41 3)
80	$FCH(NO_2)_2$	D_2O	18.4	1.73
81	$BrCH(NO_2)_2$	D_2O	23.9	1.83
82	$ClOH(NO_2)_2$	D_2O	23.8	1.82
83	$(CH_3)_4N^+I^-$	0.26N DO^- +D_2O	6.2	0.77
84	CH_3OCH_3	0.7N KND_2 +ND_3	-5.9 4)	-0.27
85	$C_6H_5OCD_3$	0.06N KNH_2 +NH_3	-2.5	-
86	$(CH_3)_3N$	0.6N KND_2 + ND_3	-6.8 4)	-0.44
87	$(C_6H_5)_2NCH_3$	0.06N KND_2 + ND_3	-3.7	-0.29

1) The effective σ^-values for the $COCH_3$ and COC_6H_5 substituents ($\sigma^- \simeq 1.0$) estimated from Eq.(1) exceed the standard values. There is the same enhancement their electron-withdrawing properties during deuterium exchange of CH_3 group in the series of substituted toluenes; for 4-methylbenzophenone $lgk_{25°}=-6.6$ in solution 0.57N $C_2H_5OK+C_2H_5OD$ ($\rho=7.6$ /11/, 2)$\Sigma\sigma^-_{p-x}+\sigma^\circ_{p-y}$, 3)$\Sigma\sigma=2\,\sigma^\circ_{p-NO_2}+\sigma^\circ_{n-x}$.
4) Recalculated values are referred to the rate constant of toluene in KND_2 + ND_3 solution.

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in dinitrometnane and its derivatives is rendered approximately by the sum of two $\sigma^\circ_{p-NO_2}$ values.

/1/ we should point out that in the exchange reaction of α-substituted benzyls we can see clearly electron-withdrawing effect of phenyl group (effective σ^- value estimated from Eq. (1) is 0.19). As far as we know /21, 22/, phenyl ring can show electronic amphoteric character which depends on the nature of reaction centre and the type of reaction series. Electron-withdrawing action of phenyl ring in exchange reaction is determined by

both its inductive influence and the capability of more effective delocalisation of electron density from electron release sp^2-hybrid carbon atom in carbanion transition state of $C_6H_5CH^-X$ type to aromatic cycle.

Experimental

The part of compounds were used as commercially obtained; other compounds were prepared according to the methods reported in the literature (the methods of preparation are given in Table 4).

The rate constants for isotopic exchange reaction were determined as previously described /24/. Deuterium content was measured by the method of low-voltage mass spectrometry. As a rule, mass spectrometric analysis was performed by molecular ion; for compounds Nos 5, 6, 7, 10, 48 - by fragment ions, the masses of which are 51, 51, 51, 133, 138, correspondingly.

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THE BASE-CATALYZED DEUTERIUM EXCHANGE IN SOME ORGANOPHOSPHORUS AND ORGANOARSENIC COMPOUNDS

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On the bases of the results of investigation of kinetics of the deuterium exchange of alkyl and alkylphenyl derivatives of phosphine, arsine, their oxides, sulfides, phosphonium and arsonium salts, which are supplemented with measurements of infrared and proton magnetic resonance spectra the analysis of the influence of electronic effects of substituents and medium on kinetic CH-acidity of organophosphorus and organoarsenic compounds is made.

Though the study of the organic compounds of phosphorus and arsenic has been conducted by many authors by using different physical and chemical methods /1-15/, the problem of electronic interactions in those is far from being solved. In order to achieve more information on this question electronic factors affecting the rate of the basic deuterium exchange and some spectroscopic characteristics of methyl-phenyl derivatives of phosphine and arsine, their oxides, sulfides and onium compounds are examined in this work. The published data on the kinetic CH-acidity of organophosphorus compounds (OPC) /11, 14, 15/ are incomplete; it is difficult to compare their relative rates because of great differencies in experimental condition. The data concerning the CH-acidity of organoarsenic compounds (OAC) are restricted to one compound, tetramethylarsonium iodide /15/. The present work is a part of complex study of kinetic and spectroscopic parameters of CH-acids which have different structure /16-20/.

Results and Discussion

The most part of the kinetic measurements has been carried out in solution of potassium ethoxide in ethanol-D or in mixture of dimethyl sulfoxide ($DMSO-D_6$) and ethanol-D. In some cases employed solvents were water and liquid ammonia (sodium hydroxide and sodium amide were used as catalyst). Tables 1 and 2 summarize the kinetic data obtained.

Organophosphorus compounds Estimating the relative mobility of hydrogen of alkyl groups we must take into account the possible appearence of solvent differentiating effect. As it is shown in Table 1, the addition of DMSO to alcohol solution gives the rate of deuterium exchange of trimethylphosphine oxide ten times as large approximately, but it has just no influence on the process of exchange in trimethylphosphine. The observed relation between the rate of deuterium exchange and the properties of the medium is connected with the presence of the basic centre in molecules of OPC (atom P or P(O)-group), the degree of specific solvation of which by alcohol molecules changes affected by DMSO. Like studied earlier nitrogen heterocycles /20/ behaviour of which in this respect is analogous to OPC there must be considered two types of the rate changes due DMSO addition for interpretation of the data obtained:

$$C_2H_5O^-...DOC_2H_5 + DMSO \rightleftharpoons C_2H_5O^- + C_2H_5OD...DMSO \qquad (1)$$

$$^{+s}P...DOC_2H_5 + DMSO \rightleftharpoons P + C_2H_5OD...DMSO \qquad (2)$$

In this, if ethoxide-ion desolvation (Eq.(1)) increases its nucleophilicity and, consequently, the reaction rate, substrate desolvation (Eq.(2)), decreasing the positive charge on phosphorus atom, causes the opposite effect. The higher basicity of substrate, the more important role plays Eq.(2).

The data obtained for trimethylphosphine show that the influence of DMSO addition on the processes described by

Table 1. Kinetics for the Base-catalyzed Deuterium-hydrogen Exchange Reactions of Alkyl Groups in OPC

No	Compound	Solvent[1]	Temp., °C	$k.10^5$, sec^{-1}	E kcal, mol^{-1}	lgA	$-lgk_{25°}$	lgf	Method of preparation
1	2	3	4	5	6	7	8	9	10
1	$(CH_3)_3P$	A(0.57N) B	160 150	0.4 0.26	-	-	-	5.0 (-1.4)	21
2	$(C_6H_5)_2P(OH_3)$ 2)	A(0.57N)	160	0.2	-	-	-	4.7	22
3	$(CH_3)_3PO$	A(0.1N) B C(0.25N)	115 95 80 75 60 45 135 120 105	17.0 3.1- 0.76 10.0 1.9 0.28 8.5 2.4 0.62	24.2 26.1 27.6	9.8 12.4 10.7	7.9 6.8 9.5	8.7 (4.5)	23
4	$(C_6H_5)_2P(O)CH_3$	A(0.1N)	115 105 90	9.1 3.8 1.0	27.8	13.0	7.4	9.3	24
5	$(C_6H_5)_2P(S)CH_3$	A(0.1N)	95 85 70	9.5 3.2 0.51	29.3	13.2	8.3	8.4	25

Table 1 (cont.)

1	2	3	4	5	6	7	8	9	10
6	$(CH_3\dot{C}H_2)_3PO$	A(0.1N)	180 160	3.4 0.54	-	-	-	5.8	-
7	$(C_3H_7\dot{C}H_2)_3PO$	A(0.1N)	180 160	3.0 0.78	-	-	-	6.0	-
8	$[(C_6H_5)_2P(O)]_2CH_2$	$C_6H_5ND_2$	50	3,7 [3]	-	-	-	17.4	
9	$[(CH_3)_4P]^+I^-$	C(0.25N)	25	0,2 [4]	-	-	-	12.2 [4]	-
10	$[C_6H_5P(CH_3)_3]^+I^-$	C(0.25N)	25	3,2 [4]	-	-	-	13.4 [4]	-
11	$[(C_6H_5)_2P(CH_3)_2]^+I^-$	C(0.25N)	20	9.7	-	-	-	(14,2) 14.5 [4]	26
12	$[(C_6H_5)_3PCH_3]^+Br^-$	C(0.01N)	20 10 1	8.0 1.6- 0.26	26.5	15.7	3.7	15.5	-
13	$C_6H_5CH_3$ /16/	A(0,57H) B	- -	- -	- -	- -	15.9 11.3	0	-

1) Adopted symbols: A = $C_2H_5OK + C_2H_5OD$; B = 0,1N $C_2H_5OK + (C_2H_5OD$ + DMSO - $D_6)$ (1:5 by volume); C = HaOD + D_2O. 2) lgf for exchange of $(C_6H_5)_2PCD_3$ and $C_6H_5P(CD_3)_2$ in $KNH_2 + NH_3$ solution (-30°) were also estimated /11/; they equalled 1.4 and 1.1, respectively.
3) Taken from Ref./27/; in order to evaluate lgf value we measured the rate constant of deuterium exchange of nitromethane under the same conditions ($k=3.10^{-5}$ sec^{-1}); for the latter lgf = 17.3 /18/. 4) After Ref. /14/ the rate constants of exchange reaction of the compounds Nos 9-12 in the DO^-+D_2O solution are in relation as $k_9:k_{10}:k_{11}:k_{12}=1:17:240:2400$.

Table 2. Kinetics for the Base-catalyzed Deuterium-hydrogen Exchange Reaction of Alkyl Groups in OAO.

Compound	Solvent[1]	Temp.. °C	$K \cdot 10^5$. sec^{-1}	Igf
$(CH_3)_3As$	A(0.57N)	160	0.01[2]	-
$C_6H_5As(CH_3)_2$	A(0.57N)	160	0.01 [2]	
	D	20	22.0	-1.0
		0	2.3	
$C_6H_5As(S)(CH_3)_2$	A(0.1N)	110	11.0 [3]	
		95	3.1	8.8
		80	0.68	
$(CH_3\overset{*}{C}H_2)_3AsO$	A(0.1N)	160	3.2	(6.3)
$[C_6H_5As(CH_3)_3]^+I^-$	C(0.25N)	62	4.2 [4]	12.9
		45	0.32	

1) See footnote to Table 1; D = 0.03 N $NaND_2$ + ND_3. 2) No isotope exchange at heating for 60 hours was observed 3) E = 24.5 kcal.mol^{-1}; lgA=10.1. 4) Rate constant of exchange in $(CH_3)_4As^+I^-$ is equal to $7.2.10^{-6}$ sec^{-1} under the same condition /15/.

Eqs. 1 and 2 practically completely compensate each other. In the case of trimethylphosphine oxide when basicity and specific solvation are notably lower,* desolvation effect of ethoxide-ion predominates. This effect determines the acceleration of the exchange process as a whole. This acceleration nevertheless is lower than in the case of aromatic compounds, which are practically uncapable to appear basic properties.**

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* The pKa values of trimethylphosphine and its oxide as the base are 8.7 and 0, correspondingly /28/.

** For illustration note that similar changes in the medium composition increase the deuterium exchange rate of the methyl derivatives of naphthalene /19/ and of α-substituted benzyls /18/ by 10^3 - 10^4 times.

Table 1 and Fig.1 illustrate very wide range of the kinetic acidity OPC depending on the electronic structure of molecules ($\Delta lgk \simeq 10$). For internal consistency, measured values have been recalculated relatively to the rate constant for toluene ($lgf = \Delta lgK$). The change of relative rate constants in general is rendered by linear relation (3), determined earlier for deuterium exchange of substituted methanes /18/*:

$$lgf = 0.5 + 14.6 \Sigma\sigma^{-} \qquad (3)$$

In this, as, before /17, 18/, methyl and methyl-phenyl derivatives of IV-VI group elements are considered as the derivatives of methane CH_3X where X is composite substituent $(CH_3)_nM$ or $(C_6H_5)_mM(CH_3)_{n-m}$.

The necessity of the use of nucleophilic σ^{-}-constants proves that the kinetic CH-acidity of methyl group, which is directly bonded to phosphorus, is determined by the total electronic influence of phosphorus-containing substituent (I^{-}, M-, C-effects).

In accordance with the assumption about absense or unsufficiency of electron-releasing effect of p,π-conjugation in OPC /1/, all the studied compounds substitute hydrogen of their methyl groups to deuterium of solvent with greater rate than methane. The knowledge of σ-constants of different kind of phosphorus-containing substituents is necessary for more detail information about relative role of inductive and resonance effects in the activation mechanism of exchange process. A number of ways to determine these constants are known at present /1,4-8/. Unfortunately

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* Like other "onium" compounds /17/ rate constants of deuterium exchange of phosphonium salts are somewhat lower ($\Delta\sigma \sim 0.3$) than one could expect to obtain from Eq. (3). One possible reason of this is the influence of anion, which partially compensates the positive charge on phosphorus atom /8, 9, 17/.

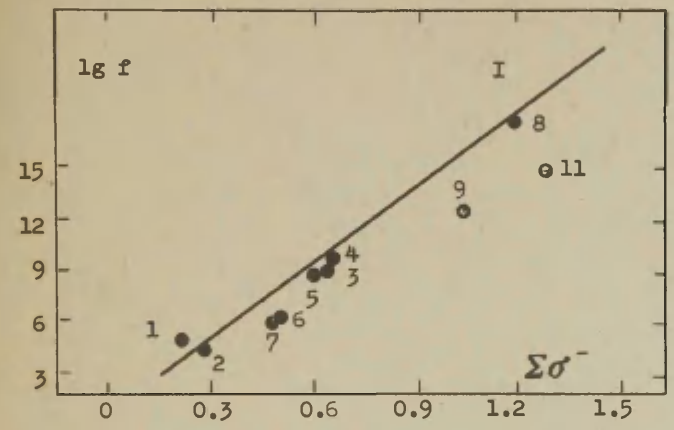

Fig.1. Plots of the relative rate constants of deuterium exchange against σ^- values. The numeration of points is given in correspondance with Table 1. The straight line I meets Eq.(3.)

the available sets are not complete enough. Then, the values of some constants are estimated by a single method and naturally they must be checked up indenpendently. To obtain additional data on this question, we used some spectroscopic reaction series showing selective sensitivity to electronic effect of different nature for evaluation of σ -constant for phosphorus-containing substituents.

The σ_R^0 values are estimated from relation reflecting their connection with infrared intensities of the ring-stretching bands in monosubstituted benzenes /29, 30/:

$$A_{CC} = 17600(\sigma_R^0)^2 + 100 \qquad (4)$$

The σ_I -constants are estimated on the assumption of possible application of the linear relation between the proton chemical shifts in substituted methanes and Taft's inductive constants /31/* to series of OPC:

$$\Sigma \sigma^* = 0.92 + 0.85\ \delta_{CH} \qquad (5)$$

* Estimating inductive constants by the results of

Table 3. The i.r.-Spectroscopic Parameters of OPC and OAC[1)]

No	Compound	Solvent	ν^{as}_{CH}	ν^{s}_{CH}	$(A^{s}_{CH})^{1/2}$	ν_{cc} [2)]	A_{cc}
1	$(CH_3)_3P$	CCl_4	2960	2898	19.0	-	-
2	$(C_6H_5)_2PCH_3$	CCl_4 CD_3OD	2970 2970	2905 2909	18.0 17.3	1592	218
3	$(CH_3)_3PO$	CCl_4 CD_3OD	2985 2990	2917 2919	12.0 13.4	-	-
4	$(C_6H_5)_2P(O)CH_3$	CCl_4	2970	2918	9.5	1596	165 [3)]
5	$(C_6H_5)_2P(S)CH_3$	CCl_4	2988 2956	2918	17.8	-	-
6	$[(C_6H_5)_2P(CH_3)_2]^+I^-$	CD_3OD	3000	2920	30.8	-	-
7	$[(C_6H_5)_3PCH_3]^+Br^-$	CD_3OD	2990	2915	36.0	1598	265
8	$(CH_3)_3As$	CCl_4	2980	2910	26.2	-	-
9	$C_6H_5As(S)(CH_3)_2$	CCl_4	3015	2930	13.1	1617 1585	320
10	$C_6H_5As(CH_3)_2$	CCl_4	2990	2919	27.0	1587	320
11	$[(CH_3)_4As]^+I^-$	CD_3OD	3017	2930	12.5	-	-
12	$[C_6H_5As(CH_3)_3]^+I^-$	CD_3OD	3015	2925	24.2	-	~ 0

1) ν_{CH} in cm^{-1}, A_{CH} and A_{cc} in $M^{-1}.l.cm^{-2}$. 2) In $CHCl_3$. 3) For $(C_6H_5)_3PO$ A_{cc} = 143.

The σ_p^o values are estimated from correlations which describe the changes of band intensity of the symmetric C-H mode of methyl group in infrared spectra of substituted methanes /17/:

$$(A_{CH}^s)^{1/2} = 24.7 - 26.4\ \sigma_p^o \qquad (6)$$

The data necessary for estimation of σ -constants from infrared spectroscopic parameters of the studied OPC are obtained in this work (Table 3); the published δ_{CH} values for $(CH_3)_3P$, $(CH_3)_3PO$, $(CH_3)_4P^+I^-$ are equal 0.9, 1.9, 2.5, respectively /21, 32, 33/.

As it is shown in Table 4, our estimations of inductive and resonance σ -constants of phosphine, phosphoryl and thiophosphoryl groups are, in general, in reasonable correspondence with the results of commonly used methods of determination. Estimation of σ values of phosphonium groups is more complex. Considerable discrepancy in numerical evaluations of σ -constants of onium substituents results, primarily, from the strong dependence of their values upon the properties of solvent /5 - 9,34/. We can hardly say that Eq.(6) fits for determination of σ_p^o values for phosphonium groups. It is explained not only by extremely high sensitivity of A_{CH} to the properties of solvent, but also by the fact that the A_{CH} changes in substituted methanes may be approximated by the linear dependence (6) only when the σ_p^o values are smaller than 0.6 /17/. For all these difficulties, the further and more precise definition of σ values of phosphonium groups from the data of other reaction series is necessary.

Though it follows from Table 4 that there is cer-

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measurements δ_{CH} corrections for ring current and anisotropic effects were neglected, for, as it follows from literature /21,32/ those corrections were negligible and chemical chift in POC was defined nearly completely by electronic influence of phosphorus-containing group.

Table 4. σ-Values of Phosphorus-containing Substituents

Substituent	σ_m	σ_p	σ_p^-	σ_p^o	σ_I	σ_R^o	σ_R^- d)
1	2	3	4	5	6	7	8
$(CH_3)_2P$-	0.09 [1] 0.03 [2]	0.23 [2]	0.18 [1] 0.22 [1]	0.22 [3] (0.05) [9]	0.07 [2] 0.11 [4]	(-0.02) [2] 0.08 [6]	
	0.06±0.03	0.23	0.20±0.02	0.22	0.09±0.02	0.08	(0.11)
$(C_6H_5)_2P$-	0.12 [1] (0.23) [2] 0.11 [5]	0.19 [5] 0.19 [2] (0.31) [2]	0.26 [1] 0.32 [1]	0.26 [3] 0.20 [9]	0.21 [2] 0.05 [5] 0.09 [11]	(-0.01) [2] 0.08 [6]	
	0.11±0.01	0.19	0.29±0.03	0.23±0.03	0.13±0.08	0.08	(0.16)
$(CH_3)_2PO$	0.41 [1] 0.42 [2]	0.62 [2] 0.34 [10]	0.62 [1] 0.70 [10]	0.48 [3] 0.63 [8] 0.50 [9]	0.35 [2] 0.25 [4] 0.31 [7]	0.15 [2]	
	0.41±0.01	0.48±0.14	0.66±0.04	0.54±0.09	0.30±0.05	0.15	(0.36)
$(C_6H_5)_2PO$-	0.43 [2] 0.38 [5]	0.62 [2] 0.50 [2] 0.53 [5]	0.68 [1]	0.58 [3] 0.58 [8] 0.51 [9]	0.30 [2] 0.37 [5] 0.27 [7] 0.27 [7]	0.14 [2] 0.09 [6]	
	0.41±0.03	0.55±0.07	0.68	0.55±0.03	0.3±0.07	0.12±0.03	(0.38)
$(C_6H_5)_2PS$-	0.47 [2] 0.29 [5]	0.49 [2] 0.57 [2] 0.47 [5]	0.62 [1]	(0.26) [3] 0.51 [8] 0.51 [9]	0.40 [2] 0.23 [7] 0.27 [7]	0.11 [2]	
	0.38±0.09	0.51±0.06	0.62	0.51	0.3±0.1	0.11	(0.32)

Table 4 (cont.)

1	2	3	4	5	6	7	8
$[(CH_3)_3P]^+I^-$	0.84[1] 0.47[2]	0.63[2] 0.73[a]	1.02[1] 1.14 0.98[10]	0.63[9]	0.40[a] 0.43[2] 0.33[a] 0.38[12]	0.2[2] 0.08[6]	-
	0.66±0.2	0.68±0.05	1.06±0.08	0.63	0.39±0.06	0.14±0.06	(0.67)
$[(C_6H_5)_2PCH_3]^+I^-$ -	1,13[10]	1.01[2] 0.33[2]c) 1.39[2]e) 1.18[10]	1.28[13]	-	0.6[2]c) (1.14)[2]	-	
	1.13	1.1±0.3	1.28		(0.6)		
$[(C_6H_5)_3P]^+Br^-$ -	-	-	-	-	0.75[7] 0.52[12]	0.074[6]	-
					0.64±0.12	0.074	

a) Reaction series, used for determination of σ values: 1) pKa of phenols /1.38/; 2) ^{19}F chemical shifts for a variety of aryl fruorides /5,6,9/; 3) A^s_{CH} in i.r. spectra of substituted methanes (Eq.(6)); 4) S_{CH} in p.m.r. spectra of substituted methanes (Eq.(5)); 5) pKa of benzoic acids /1.41/; 6) A_{CC} in i.r. spectra of substituted benzenes (Eq.(4)); 7) pKa of substituted acetic acids /44/; 8) alkaline hydrolysis of phenyl acetates /42/; 9) $\sigma_p^o = \sigma_I + \sigma_R^o$ (from series 2); 10) S_{CH_3} in p.m.r. spectra of substituted toluenes /8/; 11) deuterium exchange in substituted benzenes /12/; 12) taken from Ref./46/; 13) taken from Ref./40/.
b) For $[(C_4H_9)_3P]^+I^-$. c) Solvent = DMSO. d) $\sigma_R^- = \sigma^- - \sigma_I$. e) Solvent = CF_3COCH_3.

tain discrepancy in absolute values of σ -constants of phosphorus-containing substituents, these results enable us to conduct, on the bases of the following from Eq. (3) equality of reaction constants $\rho_I \simeq \rho_R^0 \simeq \rho_R^- \simeq \rho^-$ discussion of the semiquantative relation between contributions of separate electronic effects to the change of free energy of activation of exchange reaction.

The data obtained show that sharp increase of CH-acidity of methyl group during transition from original phosphine to corresponding oxide (or sulfide) and then to phosphonium salt is due mainly to inductive effect; as the charge on the central phosphorus atom increases the role of d-orbital stabilization of the intermediate carbanion increases also.

The fact that electron-withdrawing effect of $(C_6H_5)_2P(O)$ and $(C_6H_5)_2P(S)$ group is much weaker than the electron-withdrawing influence of onium substituents is evidently the result of decrease of positive charge on phosphorus atom due to electrostatic and conjugative (p,d-interaction) effects of oxygen (or sulfur) atom bonded with it. As it is known /2/, phosphorus d-orbitals are situated rather favourably in relation to P=O bond of phosphine oxide, thus providing the possibility of simultaneous overlapping of two 3d-orbitals with lone electron pairs of oxygen. For this reason d-levels are to have difficulties in bonding with the other radicals, composing electronic environment of phosphorus atom. And really, judging by the fact that the substitution electron-donor methyl radicals to electron-withdrawing phenyl groups in trimethylphosphine oxide has comparatively weak acidifiing influence upon reaction centre, the exchange process activation for the studied compounds is defined primarily by the electronic nature of heteroatomic P=O and P=S groups, which essentially block interactions between valent non-bonded parts of molecule. The same conclusion follows from the results of measurements of equilibrium CH-acidity: the pK_a^{CH} values of diphenylmethylphosphine

oxide and dimethylphenylphosphine oxide are close (according to MSED scale they are 31.7 and 31.3 correspondingly /35/).

But if the change of electronic structure of OPC occurs in the fragment of molecule, which is not separated from reaction centre by phosphorus atom, the rate constants of deuterium exchange vary in accordance with the properties of introduced substituent. This is clearly seen from the comparison of the data on the CH-acidity of methylene groups in symmetric alkylphosphine oxide:

$HCH_2^*P(O)(CH_3)_2$ $CH_3CH_2^*P(O)(C_2H_5)_2$ $C_3H_7CH_2^*P(O)(C_4H_9)_2$

The observed here almost 1000 times decrease of rate constants results from the effect of destabilization of transition state of reaction under the influence of electron-donor methyl or n-proply substituent. The possibility of application of the relation (3) to the description of observed rate constant changes by plot of their values against the sum $(\sigma^-_{R'_2PO} + \sigma^0_{R'})^*$ demonstrate the additive nature of electronic effects of both substituents, which are bonded directly with the reaction centre. In accordance with Zatsepina and coworkers /18/, the electronic influence of two -C-substituents on kinetic CH-acidity of tetraphenylmethylenediphosphine dioxide (N 8 in Table 1) is correlated by the sum of $(\sigma^- + \sigma^0)$ values of phosphoryl group.

In contradistinction to phosphoryl derivatives the electronic effect of phosphonium groups greatly depends on the nature of hydrocarbon radicals bonded with positively charged phosphorus atom. As it is shown in Table 1, successive substitution of three methyl radicals

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*Nucleophilic σ^--constants of $(C_2H_5)_2P(O)$ and $(C_4H_9)_2P(O)$ substituent are not known. Because the nature of alkyl radical bonded with the phosphorus atom has insignificant influence on the total electronic effect of phosphorus containing substituent, we used σ^--constant of group $(CH_3)_2P(O)$ for describing of electronic effect of those substituents.

to phenyl radicals causes acceleration of the exchange process of methyl group in onium compounds more than in 2000 times. One of the possible reasons of the observed rise of sensitivity is that in phosphonium salts there is no competition between phenyl group and substituent with lone pair of electrons for bonding of vacant d-orbitals. In this case the substitution of methyl group to phenyl one is accompanied by additional shift of electronic density from the phosphorus atom to the ring, and this fact, in its turn, causes the contraction of d-orbitals and intensification of their capability to participate in resonance interaction with the reaction centre of +C-type.

Organoarsenic compounds The kinetic and spectroscopic data obtained for the OPC and OAC (Tables 1-3) indicate that phosphorus- and arsenic-containing substituents are similar with respect to their electronic effects and hence all that we conclude from the study of OPC concerning the role of specific solvation and the trends of changes of inductive and resonance contributions to the total electronic effect caused by increasing the positive charge at the central atom or by the replacement of phenyl radical by methyl one are valid for OAC. However the effects of R_2As and R_3As^+ groups are considerable smaller as well as $R_2As(O)$ and $R_2As(S)$ groups are larger than in the cases of their phosphorus analogues.* The situation is comparable to that

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* Since σ^- values for arsenic-containing substituents are unavailable their electronic effects upon CH-acidity cannot be interpreted by using Eq.(3). In addition to the σ-constants which are available in literature/12,13/we are giving now some σ values calculated from Eqs.(4) and (6): σ_ρ° values for $C_6H_5AsCH_3$ and $C_6H_5As(S)CH_3$ substituents are equal -0.09 and 0.44; σ_R° values for $(CH_3)_2As$ and $(CH_3)_2As(S)$ substituents are - 0.11 and 0.11, respectively.

found recently for some other properties of the OAC /12, 13/. It seems likely that the decreased CH-acidity is related to a smaller inductive effect of central atom As^{+5} or As^{+5} primarily through its lesser electronegativity and larger atomic radius as well as the more weak $2p_{\pi} - 4d_{\pi}$ resonance interaction in the OAC than $2p_{\pi} - 3d_{\pi}$ conjugation in the OPC. One reason of the described behaviour $R_2As(O)$ and $R_2As(S)$ substituents may be that their inductive effects outweigh those of phosphorus derivatives. It probably arises from the more positive arsenic's atomic charge because of the double bond's degrees of As=O and As=S are smaller than those of P=O and P=S respectively. From the comparison of the relative rate constants of the studied OPC and OAC with available in literature /1,15,17, 18/ kinetics data on deuterium exchange in the compounds of nitrogen and sulfur which have the like structure it follows, that by intensity of electron-withdrawing influence on the reaction centre posphorus- and arsenic-containing substituent take intermediate place.

As it is shown in Fig.2, there is a linear relation between the rate constants of deuterium exchange of methyl group in 'onium compounds like $(C_6H_5)_nM(CH_3)_{4-n}$ where M=P, As, S (but the case M=N) and the pK_a^{CH} values of the analogous phenacyl derivatives /36, 37/.The latter indicates the same type of electronic influence of the studied charged substituents on kinetic and equilibrium CH-acidity.

Experimental

The compounds studied were prepared by methods available in literature (Table 1).The general procedure of kinetic experiments adopted in this work has been described earlier /45/. Deuterium content was determined by the method of low-voltage mass spectrometry.

Infrared spectra were taken on a "IKS-16" spectrophotometer. Concentration of substance in the solution

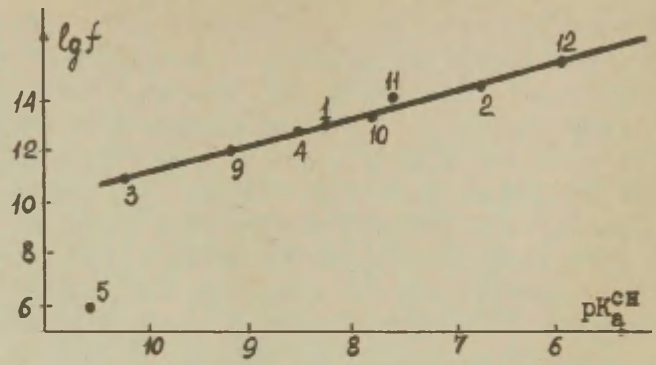

Fig.2. Dependence between rate constants of deuterium exchange of methyl groups in ›onium compounds and the pK_a^{CH} of their phenacyl derivatives.
The numeration of points Nos 9-12 is in correspondance with Table 1; No 1 = $(CH_3)_3S^+ I^-$ /17, 18/; No 2 = $|C_6H_5S(CH_3)_2|^+ClO_4^-$ /17,18/; No 3 = $(CH_3)_4As\ ^+I^-$ /15/; No 4 = $|C_6H_5As(CH_3)_3|^+I^-$; No 5 = $(CH_3)_4N\ ^+I$ /15/.

CCl_4 was 0.005–0.05 mol.l^{-1} (layer was 0.5–2.0 cm) in the solution $CHCl_3$, CD_3OD and DMSO-D_6 0.2–0.5 mol.l^{-1} layer was 0.01–0.02 cm).

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KINETICS OF HYDROLYSIS FOR ESTERS WITH A VARIABLE ALCOHOLIC PART

III* Alkaline Hydrolysis of Esters of p-Nitrobenzoic Acid in Water

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Alkaline hydrolysis rate constants of seven p-nitrobenzoates in water at 25° have been estimated spectrophotometrically. Correlation parameters for the dependence of the obtained rate constants on the inductive and steric substituent constants in the alcoholic part of esters have been calculated. The results obtained are compared with the data for analogous reaction series from literature and it is shown that correlation parameters do not depend on the nature of the acylic residue of ester.

The kinetics of alkaline hydrolysis for esters with a variable acylic part has been investigated rather extensively. Nevertheless few years ago one could get but scrappy findings concerning the alkaline hydrolysis kinetics for esters with a variable alcoholic part and, moreover, in most cases only saturated hydrocarbonic substituents with rather a narrow range of δ^* variation had been varied in the alcoholic part of ester molecule. That made

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* For reports I and II, see Refs. 1 and 2.

it difficult to obtain reliable data for the inductive and steric effects of the alcoholic part on the reactivity of esters. The introduction of but a few compounds with electronegative substituents into a reaction series improves the correlation. [1,3,4] At the same time it is still questionable whether it is possible to consider together electronegative and saturated hydrooarbonic substituents. The terminology referring to the separation of substituents into two groups is rather arbitrary. It is known that the polar effects of substituents containing either heteroatoms (C, O, N, etc.) or unsaturated groups (C = C, C ≡ C, aromatic residues) referred generally to as electronegative or electronoacoepting (it means that $\sigma^* > 0$) differ in its mechanism and quantitative regularities from the polar effect of saturated hydrocarbonic substituents (CH_3, C_2H_5, $i\text{-}C_3H_7$, eto.)[5]. However, even the sign of σ^* for the latter substituents is disputable: according to Taft[6] for those $\sigma^* \leq 0$ while from the data cited elsewhere[7] for all the alkyls $\sigma^* > 0$. That is why we avoid referring to them as electronodonating or electronoacoepting substituents. Therefore it is preferable to consider the reaction series containing electronegative substituents only. Some of these series are described in literature: i) for alkaline hydrolysis of methacrylates in water at 25°, $\mu = 0.5$; see Ref.4; ii) for alkaline hydrolysis of benzoates in water at 15°, 25°, 40° and 50°, $\mu \leq 0.05$ (acidic hydrolysis has been studied at 50° as well), see Ref.8; iii) for alkaline and acidic hydrolysis of acetates in water at 25° (the data obtained by various authors have been summarized and discussed) see Ref.7.

The series of alkaline hydrolysis of benzoates studied elsewhere [1,2] may not be presently discussed owing to the lack of reliable data on steric constants, E_s, for $OCH_2C{\equiv}CH$ and $OCH_2C{\equiv}N$ groups; the values employed earlier [1,2] appear to be incorrect.

It is of interest to extend the number of reaction

series and, particularly, to elucidate to what extent the correlation parameters ρ* and δ for esters with a variable alcoholic part depend on the nature of acylic residue. In connection with it, the present investigation has been performed keeping in mind the study of the kinetics of alkaline hydrolysis in water* for p-nitrobenzoates with electronegative substituents in the alcoholic part of esters. β-Phenylethyl (I), benzyl (II), β-methoxyethyl (III), methyl (IV), β-ohloroethyl (V), phenyl (VI) and chloromethyl (VII) esters of p-nitrobenzoic acid have been chosen for the present investigation. As a matter of faot, the alkaline hydrolysis kinetics for esters of p-nitrobenzoio acid has not been examined up to date. The only data quoted in literature are the hydrolysis rate constants for methyl-p-nitrobenzoate (K = 5.6 l/mol·seo,** see Ref.10) and ethyl-p-nitrobenzoate (K = 3.78**, Ref.10; 0.39, Ref.11; 0.59, Ref.12; 0.54 l/mol·sec, Ref.13).

Experimental

Esters of p-nitrobenzoic acid. Esters (I-VI) have been synthesized by the Schotten-Bauman and Einhorn[14] methods via the interaction of p-nitrobenzoyl chloride with the proper alcohol and reorystallized from hexane. β-Methoxyethyl ester of p-nitrobenzoic acid (III) is not described in literature: For this compound is m.p. 45-46°(hexane). Calculated for $C_{10}H_{11}NO_5$: C 53.33; H 4.92; N 6.22. Found: C 53.57; H 5.00; N 6.07.

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*When attempting to investigate the alkaline hydrolysis kinetics for esters of p-nitrobenzoic acid in 30% aqueous solution of ethanol we have observed a decrease in the rate constant in the course of reaction. This appears to be connected with a partial transetherifioation of p-nitrobenzoates.

**The values at 30° reported by Sharma[10] seem to be doubtful.

Chloromethyl-p-nitrobenzoate (VII). A mixture of p-nitrobenzoylchloride (15g), paraforme (2.4g) and anhydrous zink chloride (1.7g) was heated in a sealed ampoule at 100° for 4h. The reaction mixture was washed with hexane. The insoluble precipitate was filtered, the product crystallyzed during cooling was twice recrystallized from hexane. The yield of chloromethyl p-nitrobenzoate (VII) (in literature not described as yet) was 12.2g (70%), m.p.87-88°(hexane). Calculated for $C_8H_6ClNO_4$: C44.57; H 2.80; N 6.50; Cl 16.44. Found: C 44.67; H 2.92; N 6.39; Cl 16.52.

Experimental and analytical procedures and results of kinetic measurements. Hydrolysis of esters I-VII was carried out in a 0.05 M borate buffer solution[15] in the pH range of 8.8 to 11.4 at 25° (μ = 0.15). The pH's of solutions were measured at 25° by a pH meter pH-340 using a glass electrode ЭСЛ-IIГ-04 and a silber chloride electrode ЭВЛ-IМ. Owing to the low solubility of p-nitrobenzoates I-VII in water the stock solutions (2 to $6\cdot10^{-3}$ mol/l) in ethanol were initially prepared and then used to prepare aqueous $1 \div 10\cdot10^{-5}$ mol/l solutions of esters I--VII as described by Pūssa et al.[16] The concentration of ethanol in solutions used for measurements did not exceed 1 per cent (V). Alkaline hydrolysis rate constants for p-nitrobenzoates were determined using spectrophotometric technique.[17] The reaction was carried aut in a temperature-controlled quartz cell of a СФ-4А spectrophotometer with the pathlenghth of 1 to 5 cm depending on the solubility of the ester under study. The UV-spectra of equeous solutions of potassium p-nitrobenzoate and the esters under study (I-VII) had been studied in the wavelength range of 230 to 320 nm. For kinetical measurements the wavelengths, λ, 263 nm (or 264 nm) and 300 nm were used. The formulae for calculating the degree of substance conversion are cited in our earlier paper,[17] the procedure of estimating the C_{OH^-}. The reaction was carried out up to about 70 per cent of conversion. At least five parallel runs varying

Table 1

Properties and Parameters of UV-Spectra for $p\text{-}NO_2C_6H_4COOX$

№	Substituent X	*Melting point °C	UV-spectrum λ max nm	UV-spectrum ε lg max	ε at 263 nm	ε at 300 nm
I	$C_6H_5CH_2CH_2$	61-62 [22]	263	3.99	9750	2210
II	$C_6H_5CH_2$	84-85 [22]	263	4.05	11240	2540
III	$CH_3OCH_2CH_2$	45-46	263	4.01	10230	2270
IV	CH_3	96 [23]	264	4.08	11980**	2720
V	$ClCH_2CH_2$	55-55.5 [24]	263	4.10	12490	2670
VI	C_6H_5	127-128 [22]	263	4.11	12950	3230
VII	$ClCH_2$	87-88	263	4.12	13170	2760
	$p\text{-}NO_2C_6H_4COO^-$	-	273	4.00	9220	5270

*Crystallized from hexane

**Corresponds to 264 nm

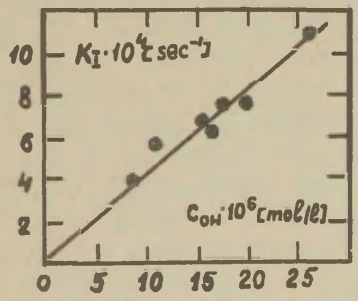

Fig.1. Plot of pseudo-monomolecular alkaline hydrolysis constants for chloromethyl-p-nitrobenzoate (VII) vs alkali concentration in water at 25°

the concentrations of alkali and ester for each rate measurement were performed, the kinetical curves being made up from 5 to 7 experimental points. The ranges of concentrations variation are presented in Table 2. The values of bimolecular hydrolysis rate constants obtained and their confidence interval are presented in Table 2, as well.

Evaluation of the reproducibility of the data. The final values of bimolecular alkaline hydrolysis rate constants for esters I-VII were estimated by Eq(1) as the weighted mean of all the measurements.

$$K = \frac{1}{m}\sum_{i=1}^{m}\left(\frac{1}{n_i}\sum_{j=1}^{n_i} K_{ij}\right) = \frac{1}{m}\sum_{i=1}^{m} K_i' \quad , \qquad (1)$$

where K_{ij} is a result at jth measurements in ith parallel run, K_i' is the arithmetical mean in ith run, n_i is the number of measurements in ith run, and m is the number of a run.

The reproducibility of the value obtained is expressed by the confidence range, ΔK, calculated from Eq.(2).

$$\Delta K = \frac{t(p,f)\cdot S_o}{\sqrt{N}} \quad , \qquad (2)$$

where t is the Student-test at the confidence level, $p = 0.95$ and the number of degrees of freedom, f, $N = \sum_{i=1}^{m} n_i$ is the total number of measurements, and S_o is the root-mean square deviation. To calculate S_o the uniformity of dispersions in individual experiments had been preliminarily checked by G-criterion[18] or by the Bartlet criterion[19] and after that total uniformity of the numerical values was determined by comparing the dispersion, $\bar{S}_n^2$, characterising the error in calculation during the run and given by Eq. (3) and the dispersion $\bar{S}_m^2$ characterising the range of deviations from run to run and estimated by Eq.(4)

$$\bar{S}_n^2 = \frac{\sum\sum (K_{ij} - K_i')^2}{N - m} \quad , \qquad (3)$$

$$\bar{S}_m^2 = \frac{\sum n_i (K_i' - K)^2}{m - 1} \qquad (4)$$

Table 2

Bimolecular Alkaline Hydrolysis Rate Constants for p-Nitrobenzoates $p\text{-}NO_2C_6H_4COOX$ (I-VIII) in Water at 25° and Characteristics of Alcoholic Groups

N°	Substituent X	Limits of variation		Number of measurements	K ± ΔK l/mol·sec	σ^*_X	$-E^s_{CH_2X}$
		C_{ester} M·10⁵	C_{OH^-} M·10⁴				
I	$C_6H_5CH_2CH_2$	1.0-1.3	4.2-30.0	36	0.50 ± 0.01	0.08	0.45
II	$C_6H_5CH_2$	1.1-1.2	1.7-11.0	25	0.91 ± 0.03	0.215	0.38
III	$CH_3OCH_2CH_2$	1.4-1.9	3.1-16.3	36	0.98 ± 0.02	0.19*	0.42**
IV	CH_3	7.9-11.6	0.5-3.0	30	1.7 ± 0.2	0.205[7]; 0.0	0.07
V	$ClCH_2CH_2$	8.5-11.6	0.6-3.5	72	3.4 ± 0.1	0.385	0.48**
VI	C_6H_5	1.0-1.6	0.2-1.3	42	9.0 ± 0.8	0.600	0.38
VII	$ClCH_2$	1.5-1.9	0.1-0.3	36	42. ± 4.	1.05	0.90
VIII	C_2H_5	-	-	-	0.59[12]	0.048[7]; -0.1	0.36

*Calculated at $\sigma^*_{CH_2OCH_3}$ = 0.52, Ref.6, in consideration of $Z^*_{CH_2}$ = 0.36; the rest σ^* are taken from alsewhere.[6]

**Taken from Ref.25; the rest E_s are taken from, Ref.6.

If a significant difference between $\bar{S}_n^2$ and $\bar{S}_m^2$ values was observed (checked by F criterion[18,19]), the value of S_o was taken to be equal to $\bar{S}_m$ (in this case f = m-1); if such a difference lacked, S_o was calculated by Eq. (5), (f = N-1).

$$S_o = \sqrt{\frac{\sum\sum (K_{ij} - K_i')^2 + \sum n_i (K_i' - K)^2}{N - 1}} \qquad (5)$$

The regression parameters were calculated by the least-squares method using computer "МИР-I". The data are presented in Table 3.

Results and discussion

According to Ingold[20] alkaline hydrolysis of esters as a rule follows the $B_{AC}2$ mechanism. When examining the alkaline hydrolysis of p-nitrobenzoates (I-VII) the proportionality between lg (1-X), where X is a degree of conversion, and the time, τ, is observed. That confirms the first-order kinetics in respect of ester. At the same time the calculated first-order rate constants, K_I, depend linearly on the OH^- concentration and consequently, the first-order kinetics in respest of alkali is the case (pseudomonomolecular reaction). An illustration of such a dependence for chloromethyl p-nitrobenzoate (VII) is given in Fig.1. Though in case of this compound a secondary substitution reaction of chlorine atom by the S_N2 mechanism might be expected we failed to discover it; probably it is due to the fact that rate of the latter process is much lower than that of hydrolysis.[8] Thus, the data obtained support the bimolecular nature of the alkaline hydrolysis reaction for all the examined esters of p-nitrobenzoic acid (I-VII). This allows us to compare the results of this work and the data from literature, because the reaction mechanism appears to be the same in all the cases.

Several approaches to analyse the dependence of alka-

Table 3

Parameters for Hydrolysis Rate Constants Correlation with Inductive and Steric Constants of Substituents in the Alcoholic Part of Ester Molecule

N°	Reaction series	Method of calculation	lg K_o	ρ^*	δ	r	s	Reference
1	$p\text{-}NO_2C_6H_4COOX$, 25°, μ=0.15	B	−0.20±0.13	2.32±0.21	0.63±0.37	0.995	0.095	–
	X=$C_6H_5(CH_2)_2$, $C_6H_5CH_2$, C_6H_5, $CH_3O(CH_2)_2$, $Cl(CH_2)_2$, $ClCH_2$	C	−0.20±0.04	2.24±0.08	(0.54)	0.996	0.073	–
2	C_6H_5COOX, 25°, $\mu \leq 0.05$, X=$ClCH_2$, $Cl(CH_2)_2$, $CH_3O(CH_2)_2$, $C_6H_5CH_2$, C_6H_5	B	−1.26±0.07	1.98±0.14	0.85±0.23	0.998	0.052	6.7
3	C_6H_5COOX, 50°, X-the same as for (2)	A*	−0.91±0.02	2.08±0.01	(0.54±0.11)	0.999	0.001	6.7
		B	−0.71±0.09	2.03±0.19	0.78±0.31	0.996	0.069	
4	CH_3COOX, 25°, X=$ClCH_2$, $Cl(CH_2)_2$	A*	–	2.20±0.09	–	0.997	0.076	7
	C_6H_5, $Cl(CH_2)_3$, $CH_3O(CH_2)_2$, $CH_3O(CH_2)_3$	B	−0.90±0.11	1.99±0.17	0.43±0.30	0.997	0.069	
5	$CH_2=C(CH_3)\text{-}COOX$, 25°, μ=0.5, X=$(CH_3)_2N(CH_2)_2$, $(CH_2)_2OC_2H_5$, $CH_3O(CH_2)_2$, $C_6H_5CH_2$, $Cl(CH_2)_2$	C	−1.32±0.10	1.61±0.42	(0.54)	0.910	0.094	4

*The parameters of these correlations have been calculated by Palm et al[7]; the rest of calculations are made by us using the data from other papers.[4,6,7]

line hydrolysis rate constants for esters on the inductive and sterio effects of substituents in the alcoholic part of their molecules may be applied, namely:

A) A combined analysis of rate constants for alkaline and acid hydrolysis using the Taft postulates according to which the rate of acid hydrolysis does not depend on the inductive effect ($\rho^*_H = 0$) and the steric effect in acid hydrolysis is the same as in the alkaline one ($\delta_H = \delta_{OH}$, see Ref.6); in this case Eq.(6) is valid.

$$\lg K_{OH} - \lg K_H = (\lg K^o_{OH} - \lg K^o_H) + \rho^* \sigma^* \qquad (6)$$

This approach was used[7] for the analysis of data on the hydrolysis of the acetates, CH_3COOX, and the benzoates, C_6H_5COOX.

B) If the data on the acid hydrolysis are missing, the two-parameter Taft equation (7) may be applied to analyse the data for the alkaline hydrolysis.

$$\lg K_{OH} = \lg K^o_{OH} + \rho^* \sigma^* + \delta E_s \qquad (7)$$

Using the data for acetates and benzoates it was shown (see Table 3) that the parameters ρ^* and δ, obtained by method B), do not significantly differ from those obtained by techniques A) (they are not so precise, though). That allowed us to apply method B) to the analysis of data obtained by us for the series of p-nitrobenzoates.

C) Method A) cannot be employed for the analysis of methacrylate hydrolysis data[4] because of the lack of information on the acid hydrolysis, and Method B) is not applicable either as the E_s-values in the range studied do not practically change. Therefore the data were treated proceeding from the assumption that the δ-value is essentially independent of the structure of the acylic part of ester (and the temperature as well). Consequently, we may assume $\delta = 0.54$ as calculated for benzoates.[9] Then the equation becomes

$$\lg K_{OH} - 0.54E_s = \lg K^{o}_{OH} + \rho^{*}\sigma^{*} \qquad (8)$$

The results of kinetic measurements in the series of p-nitrobenzoates were also treated according to Method B) and it was shown that the regression parameters obtained by Methods B) and C) did not differ significantly.

The data presented in Table 3 exhibit that i) Eq.(7) is well satisfied for the series of p-nitrobenzoates studied by the authors, and ii) that the values of ρ^{*} and δ found for all the reaction series studied (1-5) coincide within the range of the ir experimental uncertainties.* This supports the conclusion made elsewhere[21] concerning the additive effect of acidic and alcoholic parts of ester molecules on their reactivity.

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*The narrowness of the reaction series (σ^{*} varies from 0.08 to 0.385) is responsible for the low correlation coefficient for the methacrylate series (5).

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Infra-Red Spectra and Electronic Effects.III.Influence of Substituent on the Frequencies of the Stretching Band and the Basicity of Aromatic Amino Group

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The influence of substituent on the position of IRstretching bands (νNH_2) and the basicity (pKa) of 4'-R-substituted-4-aminodiphenyls and 4'-R-substituted-4-aminodiphenyloxides were studied.

The calculated reaction constants (ρ)(Table 3), show that the diphenyloxydes transmit the overall influence of the substituent in one ring to the reaction centre of the other, worse than the diphenyls do. Simultaneously the transmission of the electronic effect by the inductive effect is enhanced when an oxygen atom is introduced between the aromatic rings (Table 4).

It was demonstrated that in the aniline and the 4-aminodiphenyl series there was a direct polar conjugation between the amino group and the electron-withdrawing substituent, while for the diphenyloxydes the inductive effect predominated. The Yukawa-Tsuno coefficients for the first two series are equal to ca 0.8 and ca 0,5, respectively, while for the diphenyloxide series it is rather small (ca 0.1). For diphenyloxides the transmission factor (γ') depends on the reaction centre under consideration and the method of investigation (Table 5).

The problem of transmission of electronic effects in diphenyl systems containing heteroatoms continues to attract the attention of many investigators.[1-3] However, the use of different methods gives contradictory results.[4-7]

Earlier [8,9] we have reported the influence of the substituent on the C=O stretching frequencies of substituted benzoates and substituted 4-methoxy carbonyl diphenyloxides. It was of interest to study the electronic behaviour of so strong an electron-releasing centre as the amino group. As a measure of the substituent's influence were chosen the acid-base properties (pKa) and stretching frequencies (νNH_2) of the amino group.

A great deal of data on the frequencies νNH_2 and ionization constants of anilines has been accumulated.[10-14] It has been shown that their νNH_2 values correlate better with σ - scales, while frequencies of other functional groups (OH, CN, CO) correlate better with the $\sigma^-(\sigma^+)$-constants.[13] Possibly this is due to the fact that for the pertinent correlation νNH_2 vs. σ, as extreme substituents were chosen the OCH_3 and OC_2H_5 groups, which badly fall out from the linear relationship.[10,15] This incited us to reexamine the available data [12,13,15,16] on the substituent's influence upon the frequencies νNH_2 in aniline derivatives (Table 1). The points for OCH_3 and OC_2H_5 groups, deviating from the common relationship (Fig.1) and the parameters for C_6H_5, a much stronger acceptor than can de anticipated from its σ - values [17,18] were not considered in the correlation. In the case of substituent p-I, 0,276 was chosen as the σ -value.[19] The least-squares analysis of the available data (Table 3) indicate that in the anilines, as well as in other cases [13] the best correlations are observed with σ^- constants. Therefore, here again is a direct conjugation between the electron-withdrawing substituent and an electron-releasing reaction centre. This is further substantiated when considering published [14,20] data on the basicity of aniline derivatives (Table 1). It is noteworthy that the ρ-value for the relationship between pKa and σ^- (-2.78, Table 3)

Table 1

NH_2-Stretching Frequencies (in CCl_4) and Ionization Constants (in H_2O) of p-Substituted Anilines

NN	R	pK_a [14,20]	$\nu_s NH_2$ cm^{-1} [15]	$\nu_{as} NH_2$ cm^{-1} [15]
1	$N(CH_3)_2$	-	3378	3455
2	NH_2	6.08	3377	3453
3	OCH_3	5.30	3382*	3460*
4	OC_2H_5	5.25	3381*	3459*
5	$C(CH_3)_3$	-	3391	3474
6	CH_3	5.12	3390	3470
7	$CH(CH_3)_2$	-	3392	3474
8	H	4.58	3396	3481
9	CH_3S	4.40	-	-
10	F	4.65	3394	3474
11	CH_2CN	-	3401	3487
12	CI	4.00	3398	3482
13	Br	3.91	3399	3485
14	J	3.78	3402	3490
15	$COOC_2H_5$	-	3408	3500
16	$COCH_3$	-	3410	3502
17	SON	-	3410	3500
18	CN	1.74	3412	3505
19	CH_3SO_2	1.48	-	-
20	NO_2	1.02	3416	3509

*Not considered in the correlations.

agrees well with the published[21] ρ-value (-2.767).

The treatment of Table 1 data by a two-parameter Yukawa-Tsuno equation, modified by Yoshioka, Hamamoto and Kubota,[22] where $\Delta\bar{\sigma}_R = \bar{\sigma} - \sigma$, gives the following expressions (1-3):

$$pK_a = (4.58 \pm 0.024) - (2.52 \pm 0.080)(\sigma + 1.37 \cdot \Delta\bar{\sigma}_R), \quad r = 0.997 \quad s = 0.042 \quad (1)$$

$$\nu_s NH_2 = (3394.4 \pm 0.23) + (22.0 \pm 0.62)(\sigma + 0.47 \cdot \Delta\bar{\sigma}_R), \quad r = 0.992 \quad s = 0.47 \quad (2)$$

$$\nu_{as} NH_2 = (3477.8 \pm 0.25) + (31.4 \pm 0.68)(\sigma + 0.61 \cdot \Delta\bar{\sigma}_R), \quad r = 0.984 \quad s = 1.02 \quad (3)$$

High values of Yukawa-Tsuno constants confirm the existence of a very strong polar conjugation of an electron-withdrawing substituent with an electron releasing reaction centre, the relative contribution of the conjugation being bigger in the reaction state (pK_a) than in the ground state (νNH_2).

In Table 2 are listed the experimental values for the ionization constants and NH_2 frequencies of 4-amino-4'-R-diphenyls (II) and 4-amino-4'-R-diphenyloxides (III). The correlation parameters (Table 3) show that for the 4'-substituted-4-aminodiphenyls, both the ionization constants and the NH_2 frequencies correlate better with $\bar{\sigma}$-values than with the σ- or σ^0-values. Hence, in the diphenyl system, there is a direct polar conjugation between the amino group in one ring and the electron-withdrawing substituent in the other. This is substantiated by the data[23,24] where it is shown that the introduction of two methyl groups into 2,2'- or a phenyl group into 2-position results in a decrease in electronic conductivity of the diphenyl system.

The calculated (Eqs.(4)-(6)) Yukawa-Tsuno coefficients are equal to ca 0.5-0.6:

$$pK_a^T = (4.37 \pm 0.030) - (0.56 \pm 0.084)(\sigma + 0.59 \cdot \Delta\bar{\sigma}_R), \quad r = 0.986 \quad s = 0.025 \quad (4)$$

$$\nu_s NH_2 = (3388.7 \pm 0.21) + (5.6 \pm 0.59)(\sigma + 0.69 \cdot \Delta\bar{\sigma}_R), \quad r = 0.993 \quad s = 0.18 \quad (5)$$

$$\nu_{as} NH_2 = (3474.1 \pm 0.23) + (8.3 \pm 0.65)(\sigma + 0.58 \cdot \Delta\bar{\sigma}_R), \quad r = 0.992 \quad s = 0.28 \quad (6)$$

Table 2

The Stretching Frequencies in Dichloroethane (DCE) and Ionization Constants (in H_2O) of Amino Group for 4-NH_2-4--R-diphenyls (II) and 4-NH_2-R-diphenyloxides (III)

No	Series	R	pK_a^T	$\nu_s NH_2$	$\nu_{as} NH_2$
1	II	NH_2	4.70	3385	3468
2		OH	4.65	3386	3472
3		OCH_3	4.48	3388	3472
4		H	4.40	3369	3474
5		Cl	4.20	3390	3475
6		J	4.27*	3390	3477
7		$COOCH_3$	3.98	3392	3479
8		$COCH_3$	4.00	3393	3480
9		NO_2	3.78	3395	3483
1	III	NH_2	5.30	3379	3455
2		OCH_3	5.19	3380	3457
3		CH_3	5.08	3381	3458
4		H	5.06	3382	3461
5		Cl	4.80	3384	3462
6		$COOCH_3$	4.77	3385	3464
7		$COCH_3$	4.70	3385	3465
8		NO_2	4.54	3387	3469

*Determined in aqueous EtOH (20%) and corrected to 2% EtOH according to Hall.[25]

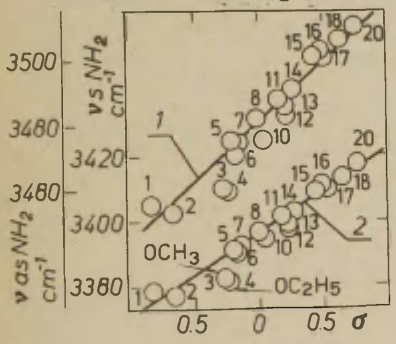

Fig.1.Relationships between asymmetric (1) and symmetric (2) stretching frequencies of amino group in substituted anilines and the Hammett σ-constants, solvent CCl_4. For numerals see Table 1.

Table 3

The Correlation Parameters of Equations $y = y_o + \rho\sigma$.

Correlation	$\rho \pm \Delta\rho$	$y_o \pm \Delta y_o$	r	s	n
		4-R-anilines			
pK_a, σ	-3.72±0.115	4.35±0.047	0.973	0.36	13
pK_a, σ^-	-2.78±0.086	4.46±0.053	0.994	0.17	12
ν_s, σ	25.4±0.48	3395.5±0.22	0.987	1.88	16
ν_s, σ^-	19.2±0.35	3393.8±0.23	0.992	1.73	14
ν_{as}, σ	36.9±0.50	3479±0.23	0.975	3.65	16
ν_{as}, σ^-	28,4±0.38	3477.1±0.25	0.985	3.22	14
		4-amino-4-R-diphenyls			
pK_a, σ	-0.66±0.048	4.34±0.022	0.976	0.07	9
pK_a, σ^-	-0.51±0.036	4.38±0.023	0.985	0.06	9
ν_s, σ	6.8±0.22	3389.1±0.10	0.982	0.53	9
ν_s, σ^-	5.1±0.18	3388.8±0.11	0.991	0.55	9
ν_{as}, σ	9.9±0.26	3474.5±0.12	0.983	0.90	9
ν_{as}, σ^-	7.4±0.19	3473.9±0.12	0.990	0.72	9
		4-amino-4-R-diphenyloxides			
pK_a, σ	-0.55±0.056	4.99±0.026	0.983	0.05	8
pK_a, σ^o	-0.64±0.061	5.03±0.027	0.988	0.05	8
ν_s, σ	5.9±0.22	3382.9±0.10	0.988	0.46	8
ν_s, σ^o	6.9±0.26	3381.7±0.11	0.992	0.39	8
ν_{as}, σ	9.7±0.26	3460.3±0.12	0.985	0.86	8
ν_{as}, σ^o	11.3±0.30	3459.5±0.12	0.987	0.79	8

y_o=value of y for $\sigma = 0$, r= the correlation coeffficient, s= the standard deviation, n=the number of points involved in the correlation. For the values of σ-, σ^- and σ^o-constants see Ref.21

Comparison with the calculated data for aniline (1) - (3), indicates that there is a similar contribution of direct polar conjugation to the interaction between donor and acceptor groups, though there is a marked (three- or four-fold) decrease in the reaction constants.

With the diphenyloxide derivatives (III) correlation coefficients with σ^{o}-values (Table 3) are higher than when using the Hammett constants (σ) or the nucleophilic constants (σ^{-}).

Two-parameter correlations (7)-(9) give low values for Yukawa-Tsuno coefficients.

$$pK_a^T = (4.99\pm0.034) - (0.52\pm0.10)(\sigma + 0.14.\Delta\sigma_R^-), \quad r=0.986,\ s=0.024 \qquad (7)$$

$$\nu_s NH_2 = (3382.2\pm0.25) + (5.7\pm0.72)(\sigma + 0.08.\Delta\sigma_R^-), \quad r=0.989,\ s=0.22 \qquad (8)$$

$$\nu_{as} NH_2 = (3460.0\pm0.28) + (8.3\pm0.75)(\sigma + 0.12.\Delta\sigma_R^-), \quad r=0.990,\ s=0.36 \qquad (9)$$

For a comparison of electronic conductivity in the studied systems we have determined, as it is customary,[26] the transmission factors $\pi' = \frac{\rho}{\rho_{ref.}}$ with the diphenyls used as reference.

Table 4

The Values of Transmission Factors π_1' and π_2'.

Series	pK_a		$\nu_s NH_2$		$\nu_{as} NH_2$	
	π_1'	π_2'	π_1'	π_2'	π_1'	π_2'
I	4.2	-	3.6	-	3.7	-
II	I	I.	I	I	I.	I.
III	0.83	1.14	0.86	1.23	0.98	1.36

The tabulated numerical values for π_1' (Table 4) were calculated from ρ-values for the Hammett σ-constants, and they show that in the diphenyloxide series the electronic effect is transmitted more poorly than in the diphenyl series.

The results permit us to evaluate the role of the so-called "positive bridge effect" (PBE) (see Ref.4) in the

investigated system. PBE, by its definition [27] reflects the transmission of the substituent's inductive influence from one ring of the diphenyl system to the reaction centre of the other ring. In other words, the existence of PBE in a given system must be demonstrated by comparing ρ^{o}-values[28] and in the case of diphenyls, where the contribution of conjugation is substantial, it is necessary to separate the inductive effect by the use of a two-parameter correlation. Whereas for the diphenyloxide series a one-parameter correlation must be used (with σ^{o}), as in this case the contribution of conjugationis limited. It is known[27] that in the case of a reaction centre (+R) and a substituent (-R), $\sigma = \sigma^{o}$; therefore the reaction constant, ρ, deduced from a two-parameter correlation (4)-(6) equals ρ^{o}, the inductive component of the reaction constant in the Yukawa-Tsuno equation.[29] From the $\bar{\nu}_2'$-values, obtained by dividing ρ^{o}_{III} (one-parameter correlation) by ρ_{II} (two-parameter correlation) (Table 4) it follows that in the diphenyloxides PBE does really exist.

It is of interest to estimate the influence of the reaction centre[30] on the extent of transmission of electronic effects by the oxygen bridge. In Table 5 are summarized the transmission factor values against diphenyl ($\bar{\nu}_1'$) and benzene ($\bar{\nu}_3'$) systems, calculated from published and experimental data, the latter being correlated with the Hammett σ-constants.

The results show that for a given reaction centre (amino group) the magnitude of $\bar{\nu}'$-value depends on the method of investigation. The lowest $\bar{\nu}'$- values are observed for the ionization constants, slightly higher for NH_2 frequencies and still higher for the acylation rate constants (K).

This is mainly due to the fact that each method of investigation corresponds to a different state of the system studied. But the transmission of electronic effects is much more seriously affected by the character of the reaction centre. Thus, when changing the electron-releasing hydroxy-

and amino groups for electron-withdrawing nitro and carbomethoxy-groups, a sharp increase of the $\mathcal{W}'$-values is observed. This is probably due to the appearance of a direct polar conjugation between the studied electron-releasing bridge and electron-withdrawing reaction centre, thereby sharply increasing the electronic conductivity of the system under investigation.

Table 5

The Values of $\mathcal{W}_1'$ and $\mathcal{W}_3'$.

Reaction Centre	Correlated parameter	Solvent	$\mathcal{W}_1'$	$\mathcal{W}_3'$	Ref.
NO_2	Reduction rate constant	Dioxane	-	0.767	31
	E 1/2	Ethanol	-	0.425	31
OH	pK_a	50% ethanol	0.48	0.135	30
$COOCH_3$	$\nu C=O$	CCl_4	-	0.361[a]	9
	A (C=O)	-"-	-	0.434	9
	E 1/2	DMFA	-	0.525[b]	9
NH_2	K	Benzene	1,05	0.286[c]	32
	pK_a	50% ethanol	0.78	-	30
	pK_a	H_2O	0.83	0.147	-
	$\nu_s NH_2$	DCE	0.86	0.232	-
	$\nu as NH_2$	-"-	0.98	0.263	-

a for benzene systems[9]: ν CO=1726.9 + 14.2 σ

b for benzene[9] : E1/2 = 1.861 - 0.817 σ

c Calculated from ρ-values, determined by equation[32] $\rho = - \lg f/\sigma_{NO_2}$.

At the same time in the kinetic study of chemical reactions the electronic character of the reaction centre may change sharply in the transition state depending on the components interaction mechanism and thereby change the extent of its interaction with the whole aromatic system and the substituent.

Experimental

All the studied compounds were prepared and purified

by the usual methods; their characteristics corresponded to those published already.[33] IR spectra were taken at least five times in purified[34] dichloroethane (DCE), on a UR-20 spectrophotometer. The instrument was invariably calibrated against dry ammonia and polystyrene. Amine concentration in DCE was ca 5×10^{-3} mol/l and the path length 4mm. Ionization constants were determined spectrophotometrically[14] in sodium acetate/acetic acid buffers ($C_{am} = 5 \times 10^{-5}$ mol/l) containing 2% ethanol. With correction for ionic strength, were obtained the thermodynamic ionization constants (pK_a^T).

The correlation parameters were calculated by the least-squares technique on a computer M-222.

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BASICITY AND STRUCTURE OP AZOMETHINES AND THEIR STRUCTURAL ANALOGS

XV. DIALKYLHYDRAZONES OF AROMATIC ALDEHYDES [x]

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The ionization constants of two series of dialkylhydrazones of aromatic aldehydes were measured by means of potentiometric titration in acetonitrile at 25°.

The correlation analysis revealed the difference between the hydrazones and their similar azomethinee in the protonation reaction. This could be explained by different character of the reaction centers: iminic in azomethines and aminic in hydrazones. The validity of such conclusions is confirmed by the spectra.

In order to compare the behaviour of hydrazones of aromatic aldehydes and alkyl aromatic azomethines III in the protonation reaction we prepared the hydrazones of substitu-

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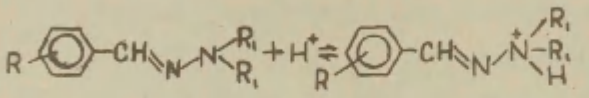
[x] For Communication XIV see Ref.1

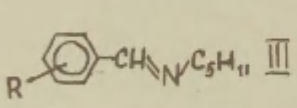
ted benzaldehydes I, II and determined their basicities.



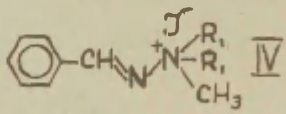
(1)

I, IIa I, IIb

I: $R_1=CH_3$, II: $R_1R_1=C_5H_{10}$ R = H, p-OH, p-OCH_3, p-Cl, p-Br, m-Br, p-NO_2, m-NO_2



III



IV

For elucidating a position of protonation in the molecules I, II with aminic and iminic nitrogens as reaction centers we studied the electronic absorption and IR spectra of hydrazones I, II, IV, V. There is a distinct evidence[2-5] that the methylation of hydrazones I, II occurs at the aminic nitrogen which is assumed to be more nucleophilic than the iminic one. It is not completely clear , however, which of these centers is more basic although protonation of aminic nitrogen is most preferable.[5-7] In some cases conjugated acid may form at an iminic center.[8]

EXPERIMENTAL

The hydrazones I, II were prepared by condensation of the respective aldehyde and hydrazine and purified by vacuum distillation and multiple recrystallization from the alcohol.

Iodomethylates IV were obtained from hydrazones and methyl iodide in absolute benzene. IV $R_1 = CH_3$; m.p. 245°; $R_1R_1 = C_5H_{10}$, m.p. 158°. Perchlorates V were prepared by action of 72% perchloric acid on benzene solution of the respective hydrazone. V $R_1 = CH_3$, m.p. 78°; $R_1R_1 = C_5H_{10}$, m.p. 124°. For synthesis of azomethines III see Ref. 9.

All the compounds were analyzed, the data of elemental analysis corresponded to the formulae. The m.p.'s and b.p.'s of compounds I and II are listed in Table 1.

Table 1. Characteristics of Compounds I, II.

Charac.	H	p-OH	p-OCH_3	p-CH_3	p-Cl	p-Br m-Br	m-NO_2	p-NO_2
Compound I								
M.p.	120°/10mm	155°	110–	-	68°	- -	55°	110°
B.p.	Hg		115/10 mmHg					
pK_a^t	10.14	11.13	10.95	-	9.61	- -	8.41	7.78
Compound II								
M.p.	58–60°	160°	48–50°	117°/	-	68– 117/	67°	88–
B.p.				6–7mmHg		70° 7mm Hg		90°
pK_a^t	11.26	12.34	12.10	11.71	-	10.70 10.46	9.64	9.22
Compound III								
pK_a^t	13.29	14.80	14.76	13.83	12.68	- -	11.31	10.0

The thermodynamic ionization constants of conjugated acids of hydrazones and azomethines were measured as before.[9,10] The pK_a^t's are listed in Table 1. The IR spectra were taken on Specord IR-71. The electronic absorption spectra were registered on Specord UV-Vis (DDR).

Table 2. The Spectral Characteristics of Compounds I, II, IV, V.

Compound	Solvent	UV-spectrum λ max, nm ($\varepsilon 10^3$)	IR spectrum ν cm^{-1} in vaseline oil
I (H=H)	M	227 (8.1) 302 (17.2)	
	DMSO	305 (17.0)	1580, 1620
	H_2SO_4	210 (10.5) 303 (20.1)	
IV (R_1=CH_3)	CH_3CN	255 (15.7)	1580, 1615, 1632
V (R_1=CH_3)	M	255 (27.8)	
	CH_3CN	250 (8.4)	1590, 1620, 1632
II (R=H)	M	225 (7.8) 305 (16.8)	1570, 1600
	H_2SO_4	215 (9.8) 300 (19.9)	
IV (R_1R_1= C_5H_{10})	CH_3CN	257 (16.5)	1595, 1620, 1640
V (R_1R_1= C_5H_{10})	M	260 (29.6)	1595, 1620, 1642
	CH_3CN	250 (30.6)	

DISCUSSION

The electronic absorption spectra of compounds I and II

(R=H) are completely identical and exhibit two bands at 225 and 330 nm (Table 2, Figure 1).

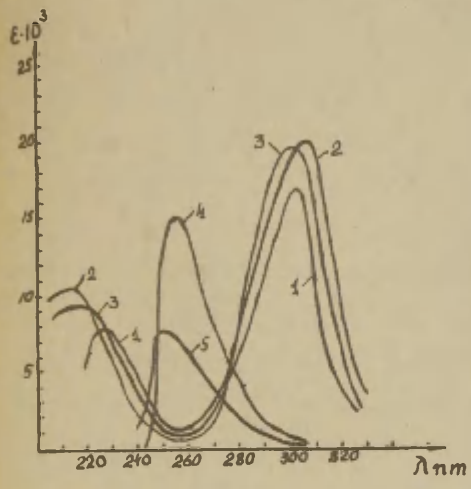


Fig.1. The absorption spectra.

1 - compound I in the alcohol (R=H),

2 - compound I in H_2SO_4 (R=H),

3 - compound II in H_2SO_4 (R=H)

4 - compound IV in acetonitrile ($R_1=CH_3$),

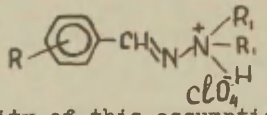
5 - compound V in acetonitrile ($R_1=CH_3$)

When pH is sufficient for shifting the equilibrium (1) completely to the right the spectra of solutions of these hydrazone perchlorates show the absorption of protonated molecules I, IIb which coincides with the electronic spectra of quaternary salts having the structure IV (Fig.1).

Upon dissolving in concentrated sulfuric acid there probably occurs the salt formation at both nitrogen atoms with bathochromic shift (λ=300 nm) of the long wave band with respect to that of monoprotonated compound V. In the same manner the absorption frequency decreases when the iminic nitrogen in azomethines III[13] is protonated.

The presented data enable to assume that the primary pro-

tonation of molecules I, II occurs analogously to the quaterniary salts formation at the aminic nitrogen and that the titration in acetonitrile afforded no diprotonation with the structure of hydrazones I, II conjugated acids corresponding to formula V:



V

The validity of this assumption could be confirmed by analysis of IR spectra of compounds I, II, IV, V.

The spectra of hydrazones I, II show the bands at 1600–1620 cm^{-1} which along with 1580–1590 cm^{-1} frequencies correspond to C=N and C=C modes of the aromatic cycle. In iodomethylates IV and perchlorates V these characteristic bands are shifted to the short-wave region (Table 2) the vibration spectra of V being completely identical to those of IV (the latter are known to have an ammonium structure). Thus, analogously to methylation, the protonation touches aminic nitrogen instead of the C=N bond.

Potentiometric titration of hydrazones I, II with perchloric acid showed a single jump. Hence in these molecules the aminic nitrogen is protonated first with sharp decrease in basicity of its adjacent iminic nitrogen atom.

From the values of pK_a^t's shown in Table 1 one may conclude that the basicities of compounds I and II are below those of alkylimines III (the same aldehyde derivatives). A considerable decrease in the hydra-

zones I and II basicities with respect to dimethylamine (pK_{CH_3CN}=18.73, pK_{H_2O}=10.64) and piperidine (pK_{CH_3CN}=18.92, pK_{H_2O}=11.22) manifests essential electron attractive action of the arylazomethine group on the reaction center (aminic nitrogen). The basicities of aminopiperidine hydrazones II are nearly 1.2-1.4 pK unit above those of the respective dimethylhydrazones I which corresponds to the higher basicity of piperidine with respect to dimethylamine.[14] The ionization constants of conjugated acids of hydrazones in both reaction series I and II provide the best correlation with σ-constants of substituents R, thus the role of conjugation effects in compounds I, IIa and their conjugated acids I, IIb is rather negligible. At the same time in the azomethines III conjugated acids the effect of direct polar conjugation of p-substituents with the reaction center is considerably stronger. This could be evident from an excellent correlation between pK_a's of III and electrophilic σ^+-constants.

Table 3. The Correlation Parameters of Yukawa-Tsuno Equation (2)

Reaction series	ρ°	r_{Y-Ts}	R	S	δ_{pK}	δ_{ρ°	pK°_{cal}
I	2.787	0.284	0.992	0.27	0.17	0.316	10.13
II	2.453	0.367	0.995	0.21	0.08	0.165	11.25
III	2.926	0.603	0.995	-	0.09	0.181	13.20

The results of multiparameter correlations by equations (2), (3) and (4), (Tables 3,4) demonstrate most obviously the difference of reaction series I and II from III.

$$\log K/K^{\circ} = \rho^{\circ}(\sigma^{\circ} + \tau \Delta\sigma_c^{+}) \qquad (2)$$

$$\log K/K^{\circ} = \rho_I \sigma_I + \rho_c \sigma_c^{+} \qquad (3)$$

$$\log K/K^{\circ} = \rho_I \sigma_I + \rho_c \sigma_c^{+} + \rho_{Ic} \sigma_I \sigma^{+} \qquad (4)$$

Attention could be drawn at a considerable value of parameter τ specifying the degree of substituents conjugation with the reaction center for the imine series III and at an approximately twice lower τ for hydrazones I and II (Table 3). The inductive reaction constants ρ_I are nearly the same for all reaction series I-III but the constant ρ_c^{+} corresponding to the total conjugation effect is again larger in series III (Table 4).

Table 4. The Correlation Parameters of Equations (3) and (4)

Reac. ser.	Eq.	ρ_I	ρ_c^{+}	ρ_{Ic}	R	S	δ_{pK}	δ_{ρ_I}	$\delta_{\rho_c^{+}}$	$\delta_{\rho_{Ic}}$	pK°_{cal}
I	3	2870	1533		0989	031	022	0431	0186		1013
	4	2778	0467	3958	0997	013	013	0249	0368	1307	1013
II	3	2485	1463	-	0992	028	011	0237	0123	-	1126
	4	2596	0767	2508	0996	015	009	0189	0323	1114	1135
III	3	2841	2130	-	0996	-	009	0179	0071	-	1323
	4	2835	2138	0046	0996	-	009	0204	0119	0473	1323

The correlations by Eq.(4) (Table 4) reveal quite clearly another difference of the series I and II from azomethines III. It is pronounced in the high values of ρ_{JC} constants specifying the degree of mutual dependence in transmittance of I and C-effect in hydrazones I and II. Introduction of the cross term $\rho_{JC}\sigma_J\sigma_C^+$ into equation (4) desreases sharply the conjugation constant ρ_C^+ for series I and II but it practically does not change the inductive constant ρ_J (cf. correlation by Eq.(3)). This may serve as an evidence that in transmittance of the substituents electronic effects on the reaction center in hydrazones the break of additivity principle involves generally the conjugation component.

Such mutual influence of C and I effects could be explained by specific spatial structure of hydrazones when the p-electrons of edge nitrogen responsible for basicity may interact with π - and σ -cores of the remaining molecular part[5].

The different behaviour of compounds I, II with respect to III may be due to various types of the reaction center iminic in III and aminic in I and II. The electron donor substituents in hydrazones I, II produce rather strong mesomeric effect, their inductive effect being small and comparable to that of the direct polar congujation by its magnitude.

The electron attractive substituents (Cl, Br, NO_2) interact generally by an inductive mechanism with the reaction center.

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BASICITY AND STRUCTURE OF AZOMETHINES AND THEIR STRUCTURAL ANALOGS

XIV. THE TRANSMITTANCE OF ELECTRONIC EFFECTS OF SUBSTITUENTS IN THE POLYENIC AROMATIC AZOMETHINES[x)]

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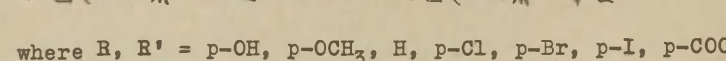
The thermodynamic ionization constants of several series of the polyenic aromatic azomethines were measured by means of potentiometric titration (in acetonitrile at 25°). The results obtained were subjected to the multiparameter correlational analysis. The role of inductive effect in transmittance of electronic influence from an aldehyde part of the molecule to the reaction center was found to be rather great. Its fading is comparatively weak at an increasing number of the vinylenic units separating the substituent and the reaction center. The values of bridge effects of the vinylenic units were estimated for different electronic interactions.

Earlier we have studied the effect of substituents R and

[x)]For Communication XIII see Ref.1.

R' on basicities of vinylogs of aromatic azomethines A (n=1) in an acid-base equilibrium (1)



(1)

where R, R' = p-OH, p-OCH_3, H, p-Cl, p-Br, p-I, p-$COOC_2H_5$ m-NO_2, p-NO_2, p-$\overset{+}{N}(CH_3)_3$

The present study is concerned with:

1. Estimation of an electronic influence from the side of different substituents R in the reaction series A with n=2.

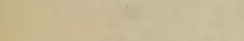
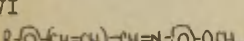
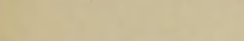
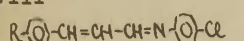
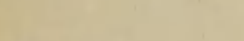
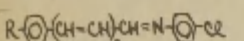
2. Elucidation of the role of various electronic effects and the influence of elongation of a conjugation chain (n = 0,1,2) upon transmittance of the effect of substituent R to the reactive azometine center by comparing the parameters of correlation equations.

For this purpose we prepared the polyenic aldehydes R-C_6H_4-$(CH=CH)_n$-CHO (n=1,2) using the procedures of Yanovskaya[2,3], where R=H CH_3O, Br, Cl, NO_2. Condensation of these compounds with the respective aromatic amines yield-id azomethines A, for the latter the ionizatsion constants of their conjugated acids, pKa^t, were determined in anhydrous acetonitrile as described earlier.[4]

Melting points of the earlier unknown azomethines and their pK_a^t are listed in Table 1. The elemental analysis of the compounds referred to composition A.

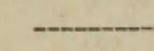
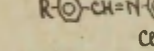
For other reaction series the pK_s^t's of their azomethines were taken from the previous papers.[4,5,6]

Table 1. Melting Points and $pK_a^{t'}$s (25°) of Azomethines in Acetonitrile

Reaction series	Property	H	p-OCH_3	p-CH_3	p-Br	p-Cl	m-NO_2	p-NO_2
III 	M.p. °C	107-108	145		139-140	126-127		149-150
	pK_a^t	12.33	12.75		12.14	12.20		11.79
VI 	M.p. °C	147	198-199		189-190	175		209
	pK_a^t	12.99	13.53		12.84	12.90		12.46
VIII 	M.p. oC	111	134	130-131			99	164
	pK_a^t	10.84	11.67	11.42			10.07	9.82
IX 	M.p. °C	132	161-162		154	163-164		178-179
	pK_a^t	11.57	12.11		11.45	11.48		10.97
XI 	M.p. °C	132	148	196	192-193		192	205
	pK_a^t	12.45	13.29	12.78	12.01		11.60	11.35
XIII 	M.p. °C	79-80	129	124			128	143-144
	pK_a^t	12.01	12.88	12.37			11.06	10.82
XV 	M.p. °C	91-92	101		135		103	173-174
	pKa^t	10.44	11.24		10.00		9.62	9.33

501

Table 1 (continued)

1		2	3	4	5	6	7	8	9
XVI	M.p.	237-	233-	247-	265	238-		191-	209-
	°C	258	234	248		239		192	210
	pKa	7.56	8.98	8.16	6.94	7.04		6.18	5.70
XVII	M.p.	242-	251-	242	264-			228-	239-
	°C	243	252		265			229	240
	pK_a^t	9.38	10.46	9.88	9.07			8.39	8.17

17 reaction series of compounds of the type A were included into the analysis, their designations are shown in Table 2.

Table 2. The Correlation Parameters of Equation (2) for the Reaction Series A[x)]

Series No.	R'	n (in A)	m	ρ^o	τ_{u-T}	R	s	$\delta\rho^o$
1	2	3	4	5	6	7	8	9
I	H	0	9	2.556	0.640	0.992	0.17	0.152
II	H	1	6	1.321	1.343	0.994	0.11	0.328
III	H	2	5	0.700	0.727	0.997	0.04	0.065
IV	OCH_3	0	9	2.564	0.670	0.997	0.08	0.088
V	OCH_3	1	6	1.566	0.856	0.996	0.14	0.266
VI	OCH_3	2	5	0.671	1.054	0.998	0.03	0.055
VII	Cl	0	5	2.477	0.683	0.999	0.06	0.098

Table 2 (continued)

1	2	3	4	5	6	7	8	9
VIII	CI	1	5	1.393	0.631	0.993	0.13	0.158
IX	Cl	2	5	0.765	0.880	1.000	0.01	0.010
X	OH	0	4	2.611	0.596	0.999	0.03	0.064
XI	OH	1	6	1.309	0.827	0.993	0.14	0.140
XII	CH_3	0.	5	2.537	0.875	0.996	0.23	0.191
XIII	CH_3	1	5	1.450	0.734	0.999	0.05	0.061
XIV	$COOC_2H_5$	0	10	2.260	0.890	0.996	0.09	0.085
XV	$COOC_2H_5$	1	5	1.270	0.828	0.990	0.15	0.207
XVI	$\overset{+}{N}(CH_3)_3$	0	9	2.143	1.005	0.993	0.28	0.211
XVII	$\overset{+}{N}(CH_3)_3$	1	7	1.538	0.915	0.997	0.11	0.101

x) m is the number of compounds in the reaction series

R is the correlation coefficient,

s is the standard deviation

δ is the mean square error

$\eta_{u-\tau}$ is the parameter of Eq.(2)

DISCUSSION OF RESULTS

All discussed series I-XVII have a varied substituent R in an aldehyde nucleus and their properties can be compared in groups with the same R' (e.g. I-III, IV-VI, X-XI etc.) and in the view of substituents R' effects, the latter may vary quite widely: from the electron donors (CH_3, OCH_3) to electron acceptors ($\overset{+}{N}(CH_3)_3$, $COOC_2H_5$).

We have already discussed the dependence of basic properties of azomethines upon increase of conductive effect of the bridge over the -CH=CH- group for the reaction series I-II and IV-V.[6] It should be noted that in all series with the same R' the basicities of the respective azomethines increase upon introducing one or (to the greater extent) two vinylenic groups.

The ionization constants of conjugated acids of azomethines in each reaction series I-XVII correlate best of all with the constants corresponding to a considerable effect of the direct polar conjugation of electron donors R with the immonium group in B when using the multiparameter equations (2-5).This demonstrates the same type of substituents R effect on the free energy change in reaction (I) indenpendent of the number of vinylenic units between R and the reaction center. In the molecules A with the same R' an increase of n leads to a decrease of all reaction constants which could be explained by removal of the reaction center from the substituents (Tables 2,3)

$$\log K/K^{\circ} = \rho^{\circ}(\sigma^{\circ} + r\,\Delta\sigma_c^{+}) \qquad (2)$$

With an increasing number of -CH=CH- units the r value in Yukawa-Tsuno equation (2) somewhat increases for the series with electron donors R' (OH, OCH_3) and remains comparable or decreases for the neutral or acceptor constant substituents.

A comparison of the inductive and mesomeric (ρ_J and ρ_c^{+}) reaction constants (Table 3) obtained by the two-parametric

Table 3 . The Correlation Parameters of Equations (3) and (4)

Series No.	ρ_3	ρ_c^+	R	S	$\delta\rho_3$	$\delta\rho_c$
I	2.609	1.925	0.991	0.14	0.163	0.086
II	1.566	1.576	0.993	0.13	0.371	0.122
III	0.730	0.578	0.998	0.03	0.046	0.024
IV	2.669	1.989	0.999	0.07	0.067	0.035
V	1.798	1.367	0.997	0.09	0.222	0.073
VI	0.701	0.681	0.998	0.03	0.056	0.030
VII	2.456	2.014	0.999	0.08	0.135	0.070
VIII	1.437	1.084	0.993	0.13	0.171	0.118
IX	0.758	0.714	0.999	0.01	0.019	0.010
X	2.585	1.989	0.999	0.09	0.193	0.098
XI	1.390	1.136	0.995	0.12	0.132	0.093
XII	2.807	2.264	0.997	0.26	0.285	0.149
XIII	1.477	1.221	0.999	0.05	0.064	0.044
XIV	2.426	1.907	0.996	0.09	0.123	0.086
XV	1.394	1.096	0.993	0.13	0.206	0.116
XVI	2.333	2.075	0.994	0.27	0.218	0.117
XVII	1.615	1.418	0.998	0.09	0.093	0.065

Table 3 (continued)

ρ_{Ft}	ρ_{Rz}	R	s	$\delta\rho_{Ft}$	$\delta\rho_{Rz}$	Series N°
3.084	2.224	0.984	0.20	0.411	0.201	I
1.526	1.483	0.994	0.11	0.230	0.125	II
0.755	0.666	0.984	0.09	0.179	0.098	III
3.133	2.254	0.984	0.20	0.404	0.198	IV
1.834	1.367	0.989	0.15	0.320	0.174	V
0.700	0.791	0.982	0.10	0.212	0.115	VI
2.417	2.397	0.999	0.08	0.196	0.106	VII
1.464	1.332	0.992	0.13	0.280	0.173	VIII
0.767	0.836	0.993	0.07	0.135	0.074	IX

correlation (3) enables to conclude that they both decrease over approximately the same value with increasing number of polyenic units , the value ρ_{Ft} always being greater

than ρ_c^+ for any R'.

$$\log K/K^\circ = \rho_3\sigma_3 + \rho_c^+\sigma_c^+ \qquad (3)$$

The nature of results does not change even with the use of Swain and Lupton equation (4) for the series of correlating σ^+.[7]

$$\log K/K^\circ = \rho_{Fi}F{\cdot}f + \rho_{R\cdot i}R{\cdot}r \qquad (4),$$

where F.f and R.r are specifying the inductive and resonance effects of substituents, respectively, ρ are their respective reaction constants.

Here, however, the resonance effects dominate negligibly over the inductive ones in the series VI and IX.

Thus the analysis using multiparameter equations (3) and (4) also manifests some predominance of the inductive over mesomeric effects in spite of the greater number of -CH=CH- units separating the substituent from the reaction center.

Such weak fading of I-effect leads to an idea of a considerable role of the π-electronic orbitals in transmittance of substituents inductive effect over the system of conjugated bonds by- σ-interaction mechanism which agrees with similar opinion of the authors[8].

As a check of additivity principle and independence of of the electronic effects transmittance in series A in reaction (1) we carried out the correlation using multiparameter equation (5) with $\rho_{3c}\sigma_3\sigma_c^+$ as a measure of nonadditive interactions:

$$\log K/K^\circ = \rho_3\sigma_3 + \rho_c^+\sigma_c^+ + \rho_{3c}\sigma_3\cdot\sigma_c^+ \qquad (5)$$

Table 4. Correlation by Equation (5)

Series No.	ρ_I	ρ_C^+	$\rho_{I,C}$	R	S	δ_{ρ_I}	δ_{ρ_C}	$\delta_{\rho_{I,C}}$	$\delta_{\rho^{ex}}$
III	0.729	0.640	-0.212	0.999	0.02	0.045	0.063	0.200	0.02
VI	0.698	0.784	-0.354	0.999	0.02	0.040	0.056	0.177	0.02
VII	2.445	1.684	1.156	1.000	0.01	0.036	0.056	0.184	0.02
VIII	1.417	1.594	1.813	0.996	0.08	0.163	0.457	1.576	0.09
IX	0.759	0.672	0.144	1.000	0.00	0.001	0.001	0.003	0.00
XI	1.355	1.368	0.791	0.996	0.09	0.138	0.264	0.839	0.07
XVII	1.579	1.626	0.725	0.998	0.06	0.089	0.165	0.525	0.04

As it can be seen from Table 4 for the most typical reaction series the $\rho_{I,C}$-values are almost always slightly lower than ρ_I and ρ_C^+, and it is quite often that the mean square errors are great and comparable to $\rho_{I,C}$'s. Thus the additivity principle and an independent transmittance of I- and C-effects of R-substituents in the reaction series I-XVII are both valid.

Earlier we have estimated a contribution of each substituent in reaction series A (n=0, 1) into the free energy change in protonation (1) via the inductive, mesomeric mechanisms and through the direct polar conjugation[4,6].

Table 5 shows similar data on the series III, VI and IX with two -CH=CH- groups. Here again the pattern of energy components is retained. E.g. the electron donor substituents (OCH_3) exhibited strong mesomeric action and the direct

Table 5. The Inductive (I) and Mesomeric (M) Free Energy Components and the Direct Polar Conjugation (C) Component, kcal/mol

Reaction series	Effect	H	p-OCH_3	p-Cl	p-Br	p-NO_2
III	I	0	-0.249	-0.469	-0.448	-0.627
	M	0	0.401	0.210	0.200	-0.070
	C	0	0.490	0.081	-0.011	-0.039
VI	I	0	-0.239	-0.449	-0.430	-0.603
	M	0	0.385	0.202	0.193	-0.065
	C	0	0.590	0.124	0.033	-0.055
IX	I	0	-0.258	-0.486	-0.465	-0.651
	M	0	0.425	0.204	0.194	-0.111
	C	0	0.570	0.159	0.108	-0.057

polar conjugation effect, the p-Cl and p-Br substituents act generally via inductive and M-effects , the electron acceptor p-NO_2 interacts with the reaction center almost entirely through an inductive component.

Table 6 shows the bridge effects of electronic transmittance (π_{1f}) and (π_{2f}) of the groups -CH=CH-

$$\pi = \frac{\rho_n}{\rho_0} ,$$

where ρ_0 is the reaction constant of the series with the number of -CH=CH- groups n = 0, 1 ,

ρ_n is the reaction constant of the series with the number of -CH=CH- groups n = 1, 2.

Table 6. The Values of Bridge Effects [x] of One and Two (π^{κ}_{1F} and π^{κ}_{2F}) -CH=CH- Groups

Series No.	π^{o}_{1F}	π^{o}_{2F}	π^{J}_{1F}	π^{J}_{2F}	π^{c}_{1F}	π^{c}_{2F}	π^{Fl}_{1F}	π^{Fl}_{2F}	π^{Rz}_{1F}	π^{Rz}_{2F}
II	0.55		0.60		0.82		0.49		0.67	
III	0.53	0.27	0.47	0.28	0.37	0.30	0.50	0.24	0.45	0.30
V	0.61		0.67		0.69		0.59		0.61	
VI	0.43	0.26	0.39	0.26	0.50	0.34	0.38	0.22	0.58	0.35
VIII	0.56		0.58		0.54		0.60		0.56	
IX	0.55	0.31	0.53	0.31	0.66	0.35	0.53	0.32	0.63	0.35
XI	0.50		0.54		0.57					
XIII	0.57		0.53		0.54					
XV	0.56		0.57		0.57					
XVII	0.72		0.70		0.68					

x) The superscript κ in π^{κ} correspond to ρ-type in the correlation equations (2-4).

The analysis of bridge effects leads to the following conclusions.

Independently of ρ's taken for calculation the values of all π_{1F} are usually within the limits 0.5-0.7. These values agree with obtained estimations of the -CH=CH- group conductivities in the polyenic carbonylic compounds.[9]

The reaction series III and IV with R' = H and OCH_3 revealed a decrease of transmission properties of the second group -CH=CH- via inductive $(\pi^{J}_{IF})_{III} < (\pi^{J}_{IF})_{II}$, $(\pi^{J}_{IF})_{VI} < (\pi^{J}_{IF})_{V}$ and mesomeric mechanisms $(\pi^{c}_{IF})_{III} < (\pi^{c}_{IF})_{II}$, $(\pi^{c}_{IF})_{VI} < (\pi^{c}_{IF})_{V}$.

At the same time for the series VIII-IX with R'=Cl a somewhat lowered inductive conductivity of the second vinylenic bridge in series IX is levelled by the gain in conductivity through π-bonds with respect to the VIII series. The same is evident from a comparison of $\pi^{F,I}_{IF}$ and $\pi^{R,T}_{IF}$ in these reaction series.

The electronic effects transmittance via the two vinylenic groups are also in good agreement . They usually range from 0.25 to 0.35 which agree with those obtained by Yanovskaya [9] and co-workers.

Generally the electronic effects in azomethines A (B) are equally transmitted via one and two vinylenic bridges respectively independently of the R electronic effect and the nature of R'.

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On Applicability of the Electrostatic Theory to the Kinetics of Reactions of Triarylmethane Anions

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The kinetic data, obtained for alkaline fading of oxitriphenylmethane dyes, permit interpretation on the basis of the simple electrostatic theory of Brönsted, Christiansen and Scatchard.

The question of charge-type influence on the kinetic parameters of ionic reactions is one of the most important aspects of the problem, concerning applicability of the simple electrostatic model for quantitative interpretation of such processes.

We have studied kinetics of alkaline fading of a number of oxitriphenylmethane dyes namely: Bromphenol Blue (BPB); 3',3''-Dimethoxybenzaurine (DMBA) and its 4-nitro-derivative (NDMBA) in a binary water-acetone solvent system. The results of the spectrophotometric study are given in Table I.

As it should be expected for a reaction of likely charged ions,[I-3] the decrease of the dielectric constant causes the decrease of the rate constant, which is the result of electrostatic repelling of the reagents, the rate constant dependence on I/ε being expressed by a straight line (Fig.).

Table 1

BIMOLECULAR RATE CONSTANTS AND ACTIVATION PARAMETERS
FOR INTERACTION OF OXYTRIPHENYLMETHANE DYES WITH HYDROXIDE ION IN AQUEOUS ACETONE

Dye	ε	Rate constants, 1/mol.sec.				$(H^{\ddagger})_{\varepsilon}$ kcal./mol	$-(\Delta S^{\ddagger})_{\varepsilon}$ e.u.
		20^0	30^0	35^0	40^0		
BPB	H_2O	$2{,}52.10^{-5}$	$5.62.10^{-5}$	$8.51.10^{-5}$	$1.21.10^{-4}$	13.2	35
	75	$1.13.10^{-5}$	$4.07.10^{-5}$	$7.94.10^{-5}$	-	23.2	-2
	70	$4.52.10^{-6}$	$1.62.10^{-5}$	$3.44.10^{-5}$	$7.05.10^{-5}$	24.0	-1
	65	$1.75.10^{-6}$	$7.11.10^{-6}$	$1.41.10^{-5}$	$2.64.10^{-5}$	24.4	-2
	60	$5.05.10^{-7}$	$2.22.10^{-6}$	$4.57.10^{-6}$	$8.75.10^{-6}$	25.5	-1
DMBA	H_2O	$8.1.10^{-3}$	$1.19.10^{-2}$	$1.53.10^{-2}$	$1.98.10^{-2}$	6.0	47
	75	$2.83.10^{-3}$	$7.69.10^{-3}$	$1.33.10^{-2}$	-	17.5	10
	70	$1.18.10^{-3}$	$3.55.10^{-3}$	$5.83.10^{-3}$	$9.26.10^{-3}$	18.3	10
	65	$3.44.10^{-4}$	$1.04.10^{-3}$	$1.74.10^{-3}$	$2.94.10^{-3}$	19.0	10
	60	$7.86.10^{-5}$	$2.42.10^{-4}$	$4.21.10^{-4}$	$7.52.10^{-4}$	20.0	9
MDMBA	H_2O	$1.85.10^{-2}$	$2.36.10^{-2}$	$2.65.10^{-2}$	$3.08.10^{-2}$	3.9	58
	75	$8.24.10^{-3}$	$1.58.10^{-2}$	$2.24.10^{-2}$	-	11.4	29
	70	$4.67.10^{-3}$	$9.63.10^{-3}$	$1.37.10^{-2}$	$2.07.10^{-2}$	12.4	25
	65	$2.05.10^{-3}$	$4.75.10^{-3}$	$7.24.10^{-3}$	$1.07.10^{-2}$	14.0	22
	60	$9.66.10^{-4}$	$2.25.10^{-3}$	$3.58.10^{-3}$	$5.12.10^{-3}$	14.8	22

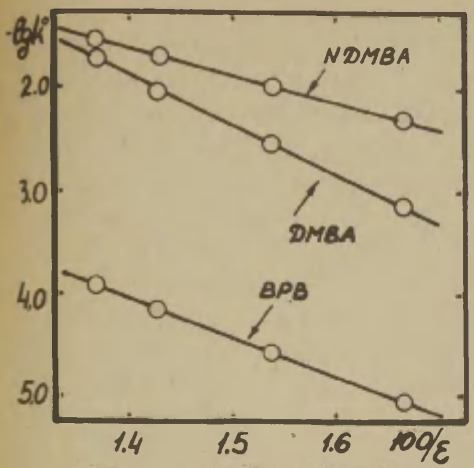

Fig. Dielectric constant influence on the molarization rate constants of oxytriphenylmethane dyes in water-acetone mixtures at 40°C.

Thus, solvent effect on the rate constant of the reactions studied is found to be described by the Brönsted-Christiansen-Scatchard equation, which in case of likely charged ions at infinite dilution takes the following form:[1-3]

$$\lg k = \lg k_{\substack{\mu=0 \\ \varepsilon=\infty}} - \frac{|Z_R| Ne^2}{2.303RTr\varepsilon}$$

The fact that the rate constants, obtained in pure water, reveal no deviation from the straight-line dependence, allows us to conclude that any specific effect of the organic component of the mixed solvent is absent. Such a result is in full agreement with the concept of the high degree of the carbonium charge delocalization due to the direct polar interaction of the negatively charged groups with the reaction cite.

The small values of activated complex radii, found for the reactions studied, probably, may be interpreted as the result of the decreased solvation of the reaction cite relative to that in aminotriphenylmethane and antipyrine series.[4-6]

The pattern of solvent effect on the activation parameters also agrees with predictions of the Electrostatic Theory. In accordance with the theory, isodielectric enthalpies of the process under consideration are found to be increased as soon as the dielectric constant becomes lower. This reflects the increase of electrostatic repelling of the reagents, carrying charges of the same sign, dependence of these parameters on the reciprocal dielectric constant being that expressed by the straight line.

Introduction of electron-withdrawing substituents should be noted to decrease the height of the energy barrier of the process studied, this being the result of positive charge localization on the carbonium centre (see Table 1).

As it should be expected for a reaction of such a type, isodielectric enthalpies exceed those, found under isocomposition conditions, differences of the named parameters being close to their theoretical values, calculated by means of the Warner equation (Table 2). [1,7]

Table 2.

Comparison of Isodielectric and Isocomposition Activation Enthalpies for the Oxytriphenylmethane Dyes Molarization Kinetics in Water-acetone Solvent System

ε	Wt.% acetone in water-organic	$(\Delta H^{\neq})_{\varepsilon} - (\Delta H^{\neq})_{c}$, kcal/mol					
		BPB		DMBA		NDMBA	
		theor.	exptl.	theor.	exptl.	theor.	exptl.
75	0.0	10.2	10.0	12.2	11.5	6.8	7.5
75	9.6	10.2	10.1	12.2	11.9	6.8	7.4
70	18.0	10.9	11.1	13.1	12.6	7.3	7.9
65	26.0	11.8	12.5	14.1	14.0	7.8	8.2
60	34.0	12.8	13.1	15.3	15.4	8.5	8.4

In accordance with Electrostatic Theory, large values of isocomposition activation entropies are the result of ordering of the system through the increased solvation of the activated complex, formed by ions of the same charge.

Thus, mixed solvent influence on molarization kinetics of oxytriphenylmethane dyes can be described by the equations of The Electrostatic Theory, considering solvent as if it were structurless isotropic medium.

Experimental

Bromphenol Blue - a commercial indicator (Kalbaum) has been used.

3',3" -Dimethoxybenzaurine, as well as its 4-nitro-derivative, has been prepared and separated as chloride in accordance with published data.[10]

Preparation of the solutions of the reagents as well as the method of following the kinetics have been described earlier.[11,12]

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A Study on Structure and Solvent Effects on Molarization Kinetics of Oxytriphenylmethane Dyes

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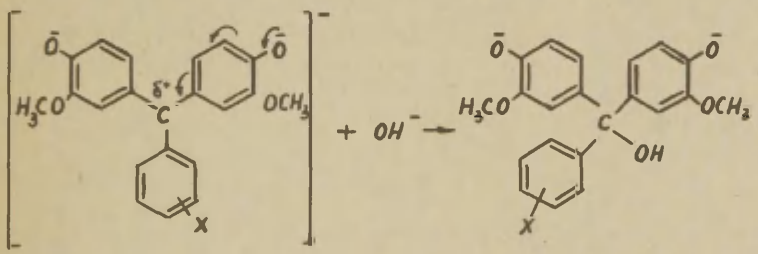
The kinetic results, obtained by spectrophotometric investigation of oxitriphenylmethane dyes alkaline fading in water-acetone mixtures, may be quantitavely interpreted on the bases of the electrostatic and linear free energy relationships.

In proceeding of the study of the problem, connected with the nature of structure and medium effects on conjugated carbonium ions reactivity, we investigated molarization kinetics of a number of 3',3''-Dimethoxibenzaurine derivatives, substituted in 3- or 4-position, in water-acetone solvent system at 20°C:



X: p-CH_3, m-CH_3, H, p-Br, m-Cl, m-NO_2, p-NO_2.

The results obtained are presented in Table 1, in which normalized rate constants[I,2] at infinite dilution

Table 1

BIMOLECULAR RATE CONSTANTS FOR THE REACTION BETWEEN OXYTRIPHENYLMETHANE DYES AND HYDROXIDE ION IN WATER-ACETONE SOLVENT SYSTEM AT 20^0 C.

Wt.% acetone / X	0.0	9,6	I8.0	26.0
p-CH_3	$6.65.10^{-3}$	$1.93.10^{-3}$	$7.24.10^{-4}$	$2.06.10^{-4}$
m-CH_3	$6.67.10^{-3}$	$2.22.10^{-3}$	$8.39.10^{-4}$	$2.57.10^{-4}$
H	$8.1.10^{-3}$	$2.83.10^{-3}$	$1.18.10^{-3}$	$3.44.10^{-4}$
p-Br	$1.11.10^{-2}$	$3.66.10^{-3}$	$1.67.10^{-3}$	$5.93.10^{-4}$
m-Cl	$1.26.10^{-2}$	$5.07.10^{-3}$	$2.37.10^{-3}$	$8.23.10^{-4}$
m-NO_2	$1.75.10^{-2}$	$6.88.10^{-3}$	$3.48.10^{-3}$	$1.51.10^{-3}$
p-NO_2	$1.85.10^{-2}$	$6.24.10^{-3}$	$4.67.10^{-3}$	$2.05.10^{-3}$

are represented.

As it follows from the Table I, mixed solvent effect on the kinetics of the process studied is in all cases in complete agreement with the Electrostatic Theory prediction for a reaction between ions of the same charge. For all of the dyes studied dielectric constant effect on the rate constant can be described by means of the Brönsted-Christiansen-Scatchard equation, which for such a reaction at infinite dilution takes the following form:[I-4]

$$\lg k = \lg k_{\substack{\mu = 0 \\ \varepsilon = \infty}} - \frac{Ne^2}{2.303RTr\varepsilon}$$

The correlation analysis of the results obtained allows us to conclude the substituent effect on the rate constant is described by the Hammett equation, the low value of the reaction constant being the result of a high degree of the charge delocalizatsion on the central carbon atom.[5,6]

As it may be stated from the data of Table 2, the reaction constant is increased at low dielectric constants, being a linear function of the reciprocal values of this parameter. Such a result is in complete agreement with the theoretical concept and reflects increased interaction between the substituent and the reaction cite.[4]

Thus, structure and medium effects on the kinetics of the reaction studied are found to be adequately described by means of the electrostatic and linear free energy relationships.

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Kinetical Detection of Conducting and Nonconducting Ion Pairs in Reactions of HCl with Methanol and Ethanol

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The kinetical data connected with reactions of HCl with methanol and ethanol, and respective conductometric data reported previously and those obtained in present work are discussed. Using the new model of electrolyte solutions suggested by Palm and Karelson proceeding from the data for aqueous solutions an attempt is made to specify the nature of the solutions of HCl in alcohol and the mechanism of the reaction occurring between HCl and alcohol. It is proved that the conductometric data for solutions of HCl in methanol or ethanol over a wide range of concentrations and temperature are quantitatively described by equations established for electrolytes in aqueous solutions. From conductometric data it can be concluded that two different states of ion pairs are present - the conducting and nonconducting ones. The kinetical data are consistent with the conductometric ones. The observed reaction rate results from two pathways via conducting and nonconducting ion pairs, respectively. For solutions of HCl in methanol the nonconducting ion pairs react 5 times faster as compared with the conducting ones. This figure sharply decreases for the ethanol solutions of HCl being equal to 1.5.

In our recent report[1] it was once more confirmed that in the region of the HCl concentrations low enough it could be observed a linearity between the first-order rate constants (k) for the reactions of HCl with saturated aliphatic alcohols, and the equivalent conductivities Λ of respective solutions. This dependence was interpreted as a proof of the proportionality between the reaction rate and the concentration of ion pairs $ROH_2^+ \cdot Cl^-$. Nevertheless, at higher concentrations of HCl the deviations from the linearity between k and Λ were observed. For methanol the value of k even exceeds the k_o-value obtained by the extrapolation of this linearity to $\Lambda = 0$.

This study was performed to obtain additional data for more concentrated solutions of HCl in ethanol and to attempt to interpret the deviations from the linearity between k and Λ.

Experimental

Methods of the purification of alcohols and the preparation of solutions of HCl were described in preceding papers.[2,3] For the conductometric procedure see Ref.1. The effective rate constants k for high concentrations of HCl were determined using titrimetric method.[3]

The respective experimental data for methanol are listed in Tables 1 and 2 and for ethanol in Tables 3 and 4. The data obtained in this study are denoted by asterisk. All other data are taken from our preceding paper.[1]

Table 1

Equivalent Conductivities Λ ($cm^2 . \Omega^{-1} . g\text{-}equiv^{-1}$) for Solutions of HCl in Absolute Methanol

[HCl] (mol/l)×10^3	$\Lambda_{25°}$	$\Lambda_{80°}$	[HCl] (mol/l)×10^3	$\Lambda_{25°}$	$\Lambda_{80°}$
2,000	54.3[M]	68.4	108	119.3	164.2
1,360	-	86.3	54	132.5	183.9
1,100	73.5[M]	-	27	143.6	211.4
849	-	101.0	13.5	154.4	225.2
750	-	104.0	6.7	164.8	247.2
493	82.3	113.5	3.3	171.4	265.9
214	-	145.8	1.6	181.1	279.5

Table 2

Effective Rate Constants k (sec^{-1}) for the Reaction of HCl with Absolute Methanol at 80°C

[HCl] (mol/l)×10^3	k×10^5	[HCl] (mol/l)×10^3	k×10^5	[HCl] (mol/l)×10^3	k×10^5
3,660	34.3	754	16.2	4.2	1.67
2,900	34.5	712	16.2	3.6	1.53
2,750	33.7	447	15.3	2.7	1.29
1,960	28.0	345	13.3	1.9	0.91
1,400	23.1	144	10.8	1.3	0.66
1,280	23.3	99	9.50	0.9	0.43
1,070	21.3	55	7.85		
920	18.5	21.6	4.76		

Table 3

Equivalent Conductivities Λ ($cm^2 . \Omega^{-1} . g\text{-}equiv^{-1}$) for Solutions of HCl in Absolute Ethanol

[HCl] (mol/l)×10^3	$\Lambda_{25°}$	$\Lambda_{80°}$	[HCl] (mol/l)×10^3	$\Lambda_{25°}$	$\Lambda_{80°}$
1,500	12.4*	26.0*	53	37.5	48.6
1,360	13.6*	25.9*	26.5	43.7	59.2
880	17.3*	32.0*	13.3	52.2	74.7
640	17.7*	32.2*	6.63	59.9	91.8
501	-	31.5	3.31	65.9	107.5
342	20.8*	34.2*	1.66	69.1	126.4
220	27.3*	35.7*	0.83	71.6	149.5
212	-	33.6	0.41	74.5	164.2
135	31.2*	38.5	0.21	76.4	191.3
106	32.2	35.9			

Table 4

Effective Rate Constants k (sec^{-1}), for the Reaction of HCl with Absolute Ethanol at 100°C

[HCl] (mol/l)×10^3	k×10^4	[HCl] (mol/l)×10^3	k×10^4
2,320	2.1*	13.3	1.3
1,500	2.0*	6.63	1.2
1,360	1.9*	3.31	1.0
954	1.8*	1.66	0.81
524	1.7	0.83	0.72
106	1.6	0.41	0.51
53	1.5	0.21	0.38
26.5	1.4		

Discussion

As it is obvious from Fig. 1 in the case of ethanol there can also be detected deviations from the linearity between k and λ at higher concentrations of HCl. Although these deviations are less in magnitude as compared with those observed for methanol. This observed relationship between k and λ cannot be explained proceeding from generally accepted conceptions on the nature of the electrolytes solutions.

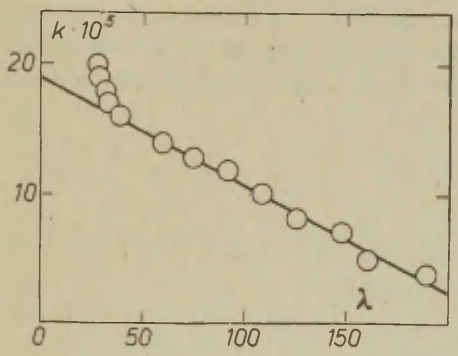

Fig. 1. Plot of k vs. λ for the solutions of HCl in ethanol at 100°C.

On the other hand, recently it has been suggested a new model for solutions of strong electrolytes.[4] According to that model in any case the formation of ion pairs plays an important role and the simpliest modification of Ostwald dilution law (activity coefficients and mobilities of ions do not depend on their total concentration) can be, in principle, applied. The ion pairs (associates) are considered to be present in two different states, one of them being and another not being able to conduct electrical current.

The relative concentrations of these two states are determined by a simple probability law [4] and the Čeleda's relationship [5] is obeyed:

$$\Lambda = \Lambda_0 \times e^{-2.3V''c} \quad \text{or} \quad \lg \Lambda = \lg \Lambda_0 - V''.c \quad (1)$$

where Λ is the equivalent conductivity of the solution of electrolyte, c denotes the concentrations of electrolyte (in g-equiv/l), Λ_0 and V" are constants characteristic for given electrolyte at definite temperature.

The positive deviations from the Čeleda relationship observed in the region of low electrolyte concentrations could be quantitatively interpreted as a consequence of the dissotiation of ion pairs in accordance with the Ostwald dilution law:

$$K = \frac{\alpha^2 c}{1-\alpha} \quad (2)$$

if the degree of dissotiation α was equalized to the

$$\text{ratio } \alpha = \frac{\Delta \Lambda}{\Delta \Lambda_\infty} \quad (3)$$

$$\text{where } \Delta \Lambda = \Lambda - \Lambda_{\check{c}} \quad (4)$$

$$\text{and } \Delta \Lambda_\infty = \Lambda_\infty - \Lambda_{\check{c}} \quad (5)$$

By Λ_∞ the limiting equivalent conductivity is denoted. $\Lambda_{\check{c}}$ is the value of Λ extrapolated to the given concentration of electrolyte using the Čeleda relatioship defined for the region of more concentrated solutions.*

The applicability of Eqs. (2) and (3) for a given set of experimental data can be prooved using the criterion of the linear dependence of $\Delta \Lambda^2 c$ on $\Delta \Lambda$:

$$-\Delta \Lambda^2 c = K \Delta \Lambda_\infty^2 - K \Delta \Lambda_\infty \Delta \Lambda \quad (6)$$

---

* In diluted solutions the $\Lambda_{\check{c}}$ values are close to Λ_0 and $\Delta \Lambda_\infty \cong \Lambda_\infty - \Lambda_0 = \text{const}$

Such a linearity is observed for a number of aqueous solutions of strong electrolytes.[4]

If this model for the solutions of strong electrolytes is relevant for solutions of HCl in alcohol it should be reflected in the applicability of equations (1) and (6).

As one can see from Figs. 2 and 3, Eq. (1) is hold for solutions of HCl both in methanol and ethanol in the range of concentrations of HCl exceeding 0.2 M. Respective values of Λ_o are listed in Table 5. For more diluted solutions the positive deviations $\Delta\Lambda$ from straight lines defined by Eq. (1) are observed (see Fig. 4).

The $\Delta\Lambda$ values so obtained satisfy Eq.(6)(see Table 6). This means that the deviations considered can be quantitatively interpreted as a consequence of the dissociation of ion pairs.

Table 5

The Values of Λ_o Estimated by Linear Extrapolation by Least Squares Treatment from Eq. (1) (r is correlation coefficient, s% = SD x 100/ ΔA_{max}, where SD = standard deviation, ΔA_{max} = range of variable parameter A, in that case A = lg Λ , n is the number of experimental points)

Reagents	Temp. °C	[HCl] M	Λ_o	V"	r	n	s%
HCl CH_3OH	25	0.5-2.0	97.0±3.9	-0.12±0.02	0.991	3	9.6
	80	0.5-2.0	134.0±1.3	-0.15±0.01	0.999	5	1.8
HCl C_2H_5OH	25	0.3-1.5	24.0±0.8	-0.19±0.02	0.989	5	7.0
	100	0.2-1.5	36.9±1.5	-0.10±0.01	0.949	8	16.5

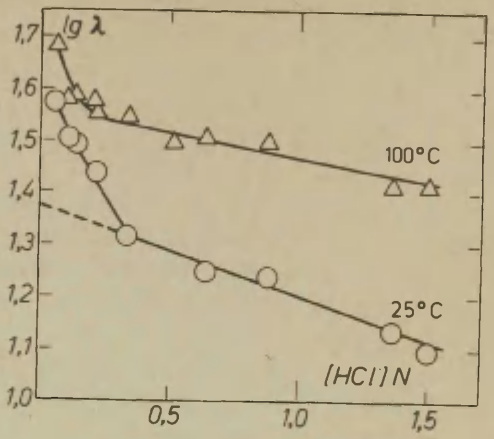

Fig. 2. Plot of lg λ vs. [HCl] for the solutions of HCl in methanol at 25 and 80°C according to the Čeleda relationship

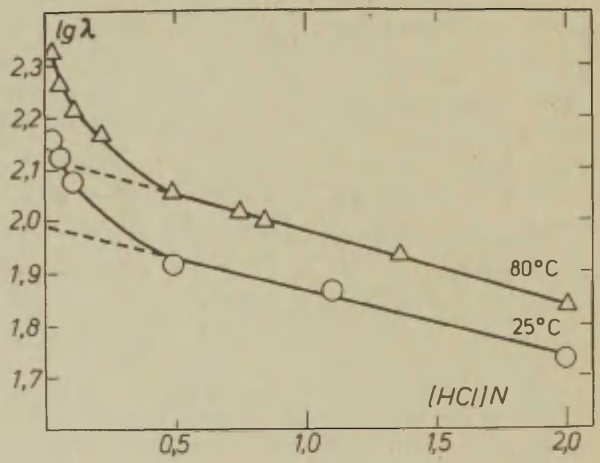

Fig. 3. Plot of lg λ vs. [HCl] for the solutions of HCl in ethanol at 25 and 100°C according to the Čeleda relationship

Table 6

The Values of $\triangle\lambda_{\sim}$ and K Calculated Using Eq. (6) for the solutions of HCl in Methanol and Ethanol

Reagents	Temp. °C	[HCl], M	$\triangle\lambda_{\sim}$	K	r	n	s%
HCl CH_3OH	25	8×10^{-4}-5.4×10^{-2}	90.2±0.4	(1.49±0.04)$\times10^{-2}$	0.997	7	3.2
	80	1.6×10^{-3}-2.7×10^{-2}	163.8±5.7	(1.06±0.03)$\times10^{-2}$	0.982	5	8.5
HCl C_2H_5OH	25	2.1×10^{-4}-6.6×10^{-3}	52.9±0.5	(9.21±0.58)$\times10^{-3}$	0.989	6	6.3
	100	4.1×10^{-4}-6.6×10^{-3}	167.2±6.0	(1.05±0.04)$\times10^{-3}$	0.992	5	5.7

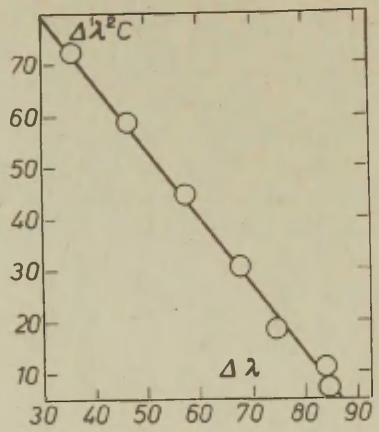

Fig. 4. Relationship in the coordinates of Eq. (1) for the solutions of HCl in methanol at 25°C

From K-values listed in Table 6 the following enthalpy (ΔH) and entropy (ΔS) changes for the ion pair dissociation could be calculated:

Alcohol	ΔH kcal/mol	ΔS e.u.
methanol	-1.23	-12.5
ethanol	-6.24	-30.6

The values of ion pair dissociation constants K calculated in this work are in principle noncomparable with values calculated proceeding from assumption that the degree of dissotiation simply equals the ratio Λ / Λ_∞ (all ion pairs are unable to conduct the electrical current) and using the ions activity coefficients calculated according to the Debye--Hückel theory. The respective numbers (at 25°C)available in literature for methanol [6,7] are quite different as com-

pared with values listed in Table 6. Although for ethanol the values from literature[7-9] are close to those in Table 6 this coincidence shall be considered as fortuitous.

The results obtained make it possible to conclude that the new model for electrolyte solutions is applicable to the solutions of HCl in methanol or ethanol over a wide range of concentrations and temperature.

This conclusion can be additionally prooved using the kinetical data obtained in this work. If the ion pairs are really able to exist in two states detectable conductometrically and the reaction rate is limited by the decomposition of ion pairs it is quite logical to suppose that different states of ion pairs are reacting at different rates. If this is true the following dependence must be valid:

$$k/(1-\alpha) = k_{nc} + (k_c - k_{nc})\,\alpha_c^{v}, \qquad (7)$$

where by k the effective value of rate constant is denoted, k_c and k_{nc} are the rate constants for conducting and non-conducting states of ion pairs, $\alpha = \frac{\Delta\lambda}{\Delta\lambda_\infty}$ (see Eq. (3)) and $\alpha_c^{v} = \frac{\lambda_c^{v}}{\lambda_0}$

The results of the least-squares treatment of respective data according to Eq. (7) are represented in Table 7 and in Fig. 5. One can conclude that the linear dependence between $k/(1-\alpha)$ and α_c^{v} is held both for methanol and ethanol. In the first case Eq. (7) can be tested in range of HCl concentrations from 0.03 to 2 M involving a 5-fold change in the k-value. For ethanol the concentration range is somewhat reduced (from 0.05 to 1.5 M) and k is changed only by a factor of 1.3.In these relations the considerable decrease in the difference between k_c and k_{nc} values is reflected when ethanol ($k_{nc}/k_c \approx 1.5$) is considered instead of methanol ($k_{nc}/k_c \approx 5$). To put in other words the sharp levelling of the rate constants for conducting and nonconducting ion pairs is observed when ethanol is substituted for methanol.

Table 7

Rate Constants k_c and k_{nc} Calculated from Eq.(7) and k_o as Established Earlier [1] for Reactions of HCl with Methanol or Ethanol

ROH	$k_{nc}x10^4$	$k_c x10^4$	r	s%	$k_o x10^4$
CH_3OH 80°C	5.07±0.13	1.16±0.02	0.995	3.7	2.47±0.06
C_2H_5OH 100°C	2.65±0.11	1.70±0.02	0.951	3.0	1.87±0.02

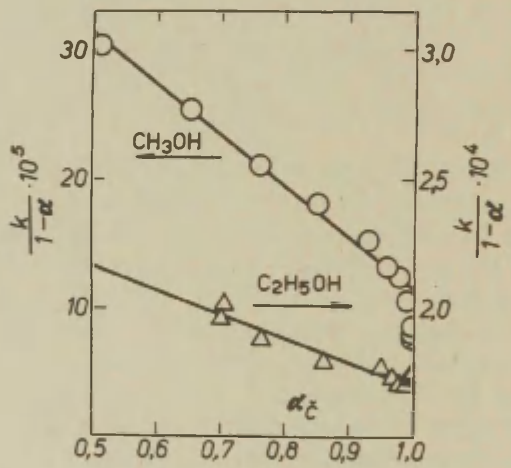

Fig. 5. Relationship in the coordinates of Eq. (7) for the reactions of HCl with methanol at 80°C and with ethanol at 100°C

Newertheless in both cases the nonconducting state is of greater reactivity.

The k_o-values extrapolated using the data for diluted solutions (see Ref. 1 and Table 7) are a sort of effective value intermediates between k_c and k_{nc}.

The same is true for activation energies calculated for different concentrations of HCl (see Table 8 and Ref. 11). As not only the ratio k_{nc}/k_c but also the degree of dissociation of ion pairs can be considerably dependent on temperature the deviations from Arrhenius equation are possible, too.

Previously we have drawn a conclusion[12] that the bimolecular interionic reaction and the unimolecular decomposition of ion pairs are kinetically indistinguishable. In the paper referred to it was stated that the rates of both reactions are in all cases exactly equal to each other.

Table 8

Activation Energy for Reactions of HCl with Methanol or Ethanol at Various Concentrations of HCl with Accuracy of ± 0.5 kcal/mol

Reagents	Temp. °C	[HCl] M	k	E(kcal/mol)
HCl	40-100	0.099		26.5[10]
CH_3OH	70-90	1.3		23.1[10]
	70	3.6*	1.5×10^{-4}	21.6
	80	"	3.4×10^{-4}	
	90	"	1.3×10^{-3}	
HCl	65-95	0.03		31.0[11]
C_2H_5OH	"	0.09		28.8[11]
	100-130	0.5		27.4[3]
	100	1.5*	1.98×10^{-4}	26.8
	110	"	5.47×10^{-4}	
	120	"	12.0×10^{-4}	

For the present this wiewpoint seems not to be any more justified. It would be possible to speak about only the indistinguishability of these reaction pathways. But one has to take into consideration that in the reaction two different kinds of ion pair are taking part and that the concentration ratio for those different ion pairs is determined by the probablity law. Therefore the analysis as it has been based on the mass action law only, is not consistent with the reaction mechanism modified in this work and our earlier conclusion turns out to be not necessarily categorical.

The reactions mechanism between HCl and some other alcohols will be considered in a separate publication.

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