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REACTIVITY OF HEXABROMO- AND 5,5-DIMETHOXYTETRABROMOCYCLOPENTADIENES IN THE REACTION OF DIENE SYNTHESIS WITH N-POLYBROMINE-CONTAINING PHENYLMALEIMIDES

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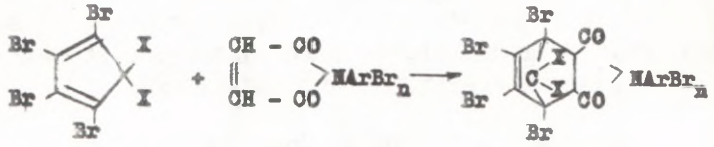
A study has been carried out on the reactivies of hexabromocyclopentadiene and 5,5-dimethoxytetrabromocyclopentadiene in the reaction of diene synthesis with N-polybromine-containing phenylmaleimides. It has been demonstrated that the activities of the systems under study are determined by the whole complex of orbital donor-acceptor interactions and localization energies. In the reactions of N-polybromine-containing phenylmaleimides with hexabromocyclopentadiene and 5,5-dimethoxytetrabromocyclopentadiene an "anomalous" correlation is observed between reagents" activity and selectivity: a more active addend has a higher selectivity.

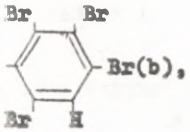
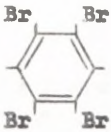
Our earlier study of hexabromocyclopentadiene (HBC) and 5,5-dimethoxytetrabromocyclopentadiene (DMTBC) reactivities in the reaction of diene synthesis with N-arylmaleimides and other dienophiles has shown that in this reaction series the HBC reacts according to the "diene-acceptor, dienophile-donor"-type, while with DMTBC a "diene-donor, dienophile-acceptor" reaction type is observed[1-3].

This work, which is a continuation of the above investigations, concerns the reactivities of HBC and DMTBC in the reaction of diene synthesis with N-polybromine-containing phenylmaleimides (III a-c) in benzene chloride.



I,II III a-c IV a-c, V a-c

where X = Br (I,IVa-c); OCH_3 (II,Va-c); $ArBr_n$ =  Br(a),

 Br(b),  Br(c)

To investigate the electron nature of addends in diene synthesis we have determined in this work the electron-acceptor properties of dienophiles (IIIa-c), which can be defined according to their electron affinity[4].

The electron affinity of dienophiles (IIIa-c) has been determined by the UV-absorption spectra of the charge-transfer complexes of these dienophiles with N,N,N',N'-tetramethyl-para-phenyldiamine as a donor according to the Briegleb[5] equation:

$$E_a = 2.78 - E_{te} \text{ (eV)}$$

where E_a is the electron affinity of the dienophile, and E_{te} is the charge transfer energy of the charge-transfer complexes of these compounds with N,N,N',N'-tetramethyl-para-phenyldiamine. The results obtained are given in Table 1.

First the polarographic behavior of dienes (HBC and DMTBC) and dienophiles was investigated on a dropping mercury electrode in dimethylformamide solutions against the background of tetraethylammonium iodide. It was found that during

the polarography of dienophiles (IIIa–c) two reduction waves were observed: the first one ($E_{1/2}$ = –0.29 to –0.32), corresponding to the bromine atom reduction in the aromatic nucleus, overlapped the HBC reduction wave during their simultaneous determination, while the second wave ($E_{1/2}$ = –1.82 to –1.91) of the double bond reduction remained unaffected. Therefore, during the study of the HBC and dienophile (IIIa–c) interaction, the kinetics of the reaction course was followed by the variation of the second wave height of dienophile reduction. In case of DMTBC, however, overlapping was not observed, and the reaction course was monitored by the decrease of the DMTBC concentration.

Table 1

Electron Affinity of N-Polybromine-containing Phenylmaleimides, HBC and DMTBC

Compound	λ_{max}, nm	hν to, eV	E_a, eV
N-(p-bromophenyl)maleimide (III)*	465	2.66	0.12
N-(2,4,6-tribromophenyl)maleimide (IIIa)	480	2.58	0.20
N-(2,3,4,6-tetrabromophenyl)maleimide (IIIb)	497	2.49	0.29
N-pentabromophenylmaleimide (IIIc)	523	2.37	0.41
Hexabromocyclopentadiene (I)*	600	2.07	0.73
5,5-Dimethoxytetrabromocyclopentadiene (II)*	$\leqslant$400	$\geqslant$3.103	$\leqslant$–0.303

* The data for the compounds (I,II,III) are taken from [1].

In an earlier work the kinetics of the HBC and DMTBC interaction with N-(p-bromophenyl)maleimides was studied spectrophotometrically[4]. We compared the data of the above study with those obtained by means of polarography for the same reaction kinetics. The results of the spectrophotometric and polarographic determinations, as expected, were essentially

identical.

The reaction rate constants were calculated according to method[6], using the kinetic equations for bimolecular reactions[7]. A linear relationship between the logarithms of the reaction rate constants and the reciprocal temperature indicates that the reaction under study obeys the Arrhenius equation, which enabled to determine the kinetic and thermodynamic parameters.

The data on the rate constants for the reaction of HBC and DMTBC with dienophiles (IIIa-c) and the kinetic activation parameters are given in Table 2.

Table 2

Parameters of the Diels-Alder Reaction of Hexabromo- and 5,5-Dimethoxybromocyclopentadienes with N-Polybromine-containing Phenylmaleimides (IIIa-c) in Benzene Chloride

Reagents	$K \cdot 10^5$, l/(mole·s)			E_A, kJ/mole	log A	$\Delta H^{\neq}$, kJ/mole	$-\Delta S^{\neq}$, J/mole·deg
	70°C	80°C	90°C				
I, III	1.54	3.06	5.82	64.0	4.9	60.6	165.5
I,IIIa	0.89	1.74	2.98	67.0	5.2	64.0	195.6
I,IIIb	0.45	0.94	1.91	74.8	6.0	71.9	188.1
I,IIIc	0.25	0.54	1.12	78.2	6.3	74.2	184.3
II,III	40.0	61.8	94.6	43.0	3.2	40.1	201.9
II,IIIa	21.6	33.8	45.1	45.9	2.3	43.0	216.5
II,IIIb	10.7	16.8	30.7	57.3	3.7	54.3	205.2
II,IIIc	6.2	10.5	17.6	59.3	3.8	56.3	203.4

The rate constant values for the reactions of HBC and DMTBC with N-(p-bromophenyl)maleimide (III) are taken from [4].

The reactions are characterized by low activation energies and high negative values of activation entropy, inherent of the Diels-Alder reaction.

As it is seen from Table 2, there is an obvious tendency to the decrease of HBC reactivity with the increase of the electron-acceptor properties of the dienophiles (IIIa-c) (See Table 1), indicative of the "diene-acceptor, dienophile-donor" reaction type.

The decrease of the HBC reactivity as compared with that of DMTBC may be explained by a decrease of the donor-acceptor interaction energies and by an increased conjugation with HBC. Hence, in the diene synthesis reaction with N-polybromine-containing phenylmaleimides the factors of donor-acceptor interaction and the localization effect change symbatically, and the relative activity of addends in this reaction series is determined by the two factors. The substitution of two geminal bromine atoms in HBC by electron-donating methoxy groups leads to the increase of DMTBC reactivity as compared with HBC.

The comparison of the electron-acceptor properties of the reagents (Table 1) shows that the absolute electron affinity value of dienophiles (III a-c) is lower than that of HBC but higher than that of DMTBC, as far as the latter has a higher electron-donating capacity than HBC and compounds (III a-c).

To confirm the donor nature of DMTBC we have studied the "activity-selectivity" ration in the reactions of HBC and DMTCB with dienophiles (III a-c).

It is known that, when the reactivity of addends is monitored by their donor-acceptor properties, it means that a more active reagent should have a higher selectivity.[3]

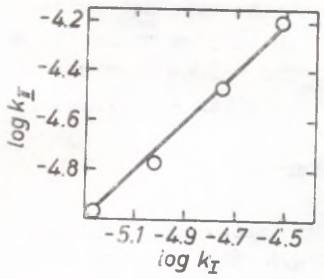


Fig.1. Correlation between the reactivity of DMTBC (II) and HBC (I) in the reactions with N-polybromine-containing phenylmaleimides (III a-c).

The results obtained (Fig.1) show that DMTBC is a more active diene and it is more selective as compared with HBC - the slope of the correlation line equals 1.03, i.e. an "anomalous" correlation is observed between the activity and selectivity. A marked increase of DMTBC reactivity in comparison with that of HBC may be caused both by the increase of the donor-acceptor interaction energy, and by the decrease of the π-delocalization energy of DMTBC.

Experimental

The UV absorption spectra of the charge-transfer complexes of N,N,N',N'-tetramethyl-para-phenyldiamine and the dienophiles (III a-c) were taken on a "SF-18"-type spectrophotometer.

Fresh samples of HBC, DMTBC and N-polybromine-containing phenylmaleimides were used for kinetic determinations. The purity of the starting compounds was checked by the thin-layer chromatography on a non-fixed layer of the "KSK" grade silica-gel in the benzene-dichloroethane-acetic acid (4:1.5:1) system with iodine-vapor development.

The diene synthesis was carried out in ampoules in benzene chloride at 70°, 80° and 90° with molar ratios of 1:2 for HBC to dienophile (III a-c) and 2:1 for DMTBC to dienophile (III a-c).

Second order rate constants were determined polarographically on a polarograph "OH-101" according to the concentration change of addends. The values have been calculated as the mean values of 3-4 parallel experiments.

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Organic Reactivity
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KINETICS OF INTERACTION OF α-HALOGENDESOXYBENZOINES WITH ALIPHATIC AMINES. 3. SIMULTANEOUS EFFECT OF STRUCTURE OF REAGENTS

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Kinetics of reactions of substituted α-bromodesoxybenzoines ($R-C_6H_4-COCHBrC_6H_4-R^*$) with aliphatic amines in acetonitrile at 25°C has been studied. Quantitative regularities concerning substituent effect in substrate and that of amine structure on their interaction rate have been established. The obtained results are in keeping with the assumption that the formation of α-aminoketones proceeds via the Dewar - Winstein complex.

In order to continue our studies[1,2] dealing with effects of various factors (e.g. nucleophile structure, nature of a leaving group in electrophile, temperature, medium) on the rate of nucleophilic substitution reactions in α-halogendesoxybenzoines and to find out their mechanism, simultaneous effect of reagents' structure (substituents at the nitrogen atom in amine and in both nuclei of α-bromodesoxybenzoine) on the kinetics of these processes has been investigated in the present paper.

Interaction of the whole set of substituted α-bromodesoxybenzoines studied in this report with the primary and secondary aliphatic amines proceeds quantitatively and irreversibly in acetonitrile, obeying the following equation:

$$R\text{-}C_6H_4COCHC_6H_4\text{-}R' + 2R_1R_2NH \longrightarrow R\text{-}C_6H_4COCHC_6H_4\text{-}R' + R_1R_2\overset{\oplus}{N}H_2 \cdot \overset{\ominus}{Br} \quad (1)$$

(Br on the first product; NR_1R_2 on the first product)

The equation in case of tertiary amines* is:

$$R\text{-}C_6H_4COCHC_6H_4\text{-}R' + R_1R_2R_3N \longrightarrow R\text{-}C_6H_4COCHC_6H_4\text{-}R' \quad (2)$$

(Br on the first product; $\overset{\oplus}{N}R_1R_2R_3 \cdot \overset{\ominus}{Br}$ on the second product)

The second order rate constants (the first for each individual reagent) for the studied reactions are given in Table 1.

The influence of the nature of the radicals R and R' in α-bromodesoxybenzoines is satisfactorily described (Table 2) by equations (3) and (4):

$$\log k = \log k_o + \rho^o\sigma^o \quad (3)$$

$$\log k = \log k_o + \rho^o\sigma^o + \rho_R^+\sigma_R^+ \quad (4)$$

The ρ^o value found with a rather good reliability (mean error 16%, maximum error 23%) is positive in all cases, which evidences about the assistance of acceptor substituents R and about the hindrance of those of donor substituents on the reaction studied. Similar conclusion can be drawn about the reference of R' substituents according to the induction mechanism. However, comparatively small $\rho^{o'}$ values and great errors in their determination (mean error 33%, maximum error 82%) show that these results cannot be reliable enough. Firmer conclusions about the electronic effect of the R' substituents can be made on the bases of the ρ_R^+ values (mean

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* A reaction with trimethylamine has been studied. For peculiarities of interaction with other tertiary amines see [1].

Table 1

Rate Constants[a] of Reaction of $k \cdot 10^2$(l · mole^{-1}· s^{-1}) α-bromodesoxybenzoines ($R\text{-}C_6H_4COCHBrC_6H_4\text{-}R'$) with Aliphatic Amines in Acetonitrile at 25°C

	Amine	R=R'=H[b]	R' = H				R = H						
			4-CH_3O	4-CH_3	4-C_6H_5	4-Cl	4'-CH_3O	4'-CH_3	4'-Br	4'-NO_2	3'-CH_3	3'-Cl	3'-Br
1	$MeNH_2$	19.6	14.1	15.9	24.7	38.7	91.0	32.8	37.1	45.8	20.5	28.1	27.9
2	$EtNH_2$	7.68	4.48	4.76	8.62	13.6	26.4	10.6	10.8	15.9	9.12	12.3	10.4
3	i-$PrNH_2$	1.18	0.837	0.985	1.44	2.32	4.48	1.68	1.81	2.35	1.13	1.53	1.59
4	$BuNH_2$	8.36	6.13	6.54	11.3	14.1	35.6	13.1	14.8	18.4	8.20	10.7	12.2
5	c-$HexNH_2$	2.18	1.54	1.57	2.71	3.88	8.37	3.04	3.24	4.09	2.09	2.53	2.63
6	Me_2NH	108	63.9	81.9	121	154	464	149	149	145	93.7	103	104
7	Et_2NH	1.67	0.995	1.32	1.82	2.68	8.63	2.76	2.39	2.83	1.61	2.06	2.03
8	MePrNH	19.1	12.3	14.6	20.5	29.9	98.0	31.6	28.4	24.9	17.5	18.3	19.8
9	Bu_2NH	2.00	1.52	1.56	2.30	3.04	10.9	3.39	2.88	3.32	2.01	2.03	2.22
10	i-Bu_2NH	0.731	0.556	0.655	0.792	1.01	4.53	1.29	0.947	0.897	0.742	0.721	0.722
11	Piperidine	93.3	55.0	58.2	93.3	146	382	134	142	113	84.6	102	99.7
12	Me_3N	2.06	1.72	1.57	2.24	3.09	17.1	3.80	3.12	2.07	1.99	1.92	1.93

[a] Errors of constant determination do not exceed 7%

[b] Data of report[2] have been given.

Table 2

Parameters of Equations (3) and (4) in Case of Reactions of α-bromodesoxybenzoines ($R\text{-}C_6H_4COCHBrC_6H_4\text{-}R'$) with Aliphatic Amines in Acetonitrile at 25°C

	Amine	R' = H				R = H				
		log k_o	ρ^o	S	R	log k_o	$\rho^{o'}$	$-\rho_R^+$	S	R
1	$MeNH_2$	-0.67±0.02	0.98±0.13	0.05	0.97	-0.67±0.03	0.45±0.09	1.19±0.13	0.06	0.97
2	$EtNH_2$	-1.13±0.02	1.11±0.16	0.05	0.97	-1.07±0.03	0.37±0.09	0.90±0.14	0.06	0.95
3	i-$PrNH_2$	-1.89±0.02	0.98±0.13	0.05	0.98	-1.92±0.03	0.40±0.07	1.06±0.10	0.05	0.98
4	$BuNH_2$	-1.05±0.03	0.82±0.19	0.07	0.93	-1.06±0.03	0.44±0.08	1.15±0.12	0.06	0.97
5	c-$HexNH_2$	-1.64±0.02	0.94±0.13	0.05	0.97	-1.67±0.03	0.36±0.08	1.07±0.12	0.06	0.97
6	Me_2NH	0.00±0.03	0.78±0.18	0.07	0.93	0.00±0.03	0.22±0.08	1.17±0.12	0.06	0.98
7	Et_2NH	-1.79±0.03	0.88±0.16	0.06	0.95	-1.77±0.03	0.31±0.09	1.25±0.13	0.06	0.98
8	MePrNH	-0.73±0.02	0.83±0.12	0.04	0.97	-0.73±0.03	0.18±0.09	1.26±0.13	0.06	0.98
9	Bu_2NH	-1.69±0.02	0.70±0.10	0.03	0.97	-1.70±0.04	0.25±0.11	1.29±0.17	0.08	0.96
10	i-Bu_2NH	-2.13±0.02	0.51±0.10	0.03	0.95	-2.13±0.03	0.11±0.09	1.33±0.14	0.06	0.98
11	Piperidine	-0.07±0.02	0.98±0.12	0.04	0.98	-0.04±0.02	0.19±0.04	1.10±0.06	0.03	0.99
12	Me_3N	-1.68±0.02	0.64±0.08	0.03	0.97	-1.69±0.02	0.06±0.06	1.57±0.10	0.04	0.99

error 10%, maximum error 16%). The latter shows that the character of such influence is opposite to that of R substituents. It should be stressed that the same phenomenon is observed in case of the interaction of substituted α-bromodesoxybenzoines with p-toluidine in nitrobenzene, where $\rho^{o} = 0.75$[3], $\rho^{o'} = 0.11 \pm 0.04$* and $\rho_{R}^{+} = -1.59 \pm 0.06$*.

Eq. (5) has been employed to quantitatively estimate the structural effect of aliphatic amines on their reaction rate:

$$\log k = \log k_{o} + \rho^{*} \Sigma \sigma^{*} + \delta E_{N} \qquad (5)$$

where $\Sigma\sigma^{*}$ characterizes the inductive effect of hydrocarbon fragments attached to the nitrogen atom; E_{N} is the steric "availability" of this atom, the ρ^{*} and δ values denote the reaction susceptibility to the mentioned effects[5]. It has been shown earlier on the example of aminolysis reactions of unsubstituted α-halogendesoxybenzoines[1,2] that only the data for the primary and secondary alkylamines obey Eq. (5). The latter can be explained by a possible interaction of these amines and the tertiary ones with α-halogendesoxybenzoines according to various mechanisms[1,2]. The result of reactions with participation of tertiary amines do not obey the regularities obtained in case of primary and secondary amines also in case of the processes dealt with in the present paper.

The results of data treatment (Table 1, Nos 1-11) show (see Table 3) that the character of the influence of radicals in primary and secondary amines does not practically depend on the substituents' nature in the aromatic nuclei of α-bromodesoxybenzoines although the ρ^{*} values tend to decrease if the deceptor properties of R' become stronger (Fig. 1). Changes of ρ^{o} and particularly of ρ' (Table 2) during transfer from one amine to another (Fig. 2) are also observed. Thus, it is possible to speak about the joint influence of substituents' electronic effect in amine and substrate (first of all R) on the process rate. In order to evaluate this influence quantitatively, equation (6) was

* Calculated by us according to the data of ref.[4].

used (α_1 and α_2 are the coefficients characterizing the joint electronic effect of substituents in substrate and in amine):

$$\log k = \log k_o + \rho^{o}\delta^{o}(R) + \rho^{o'}\delta^{o}(R') + \rho_R^{+}\delta_R^{+}(R') + \\ + \rho^{\Sigma}\Sigma\delta^{\Sigma} + \delta E_N + \alpha_1\delta^{o}(R)\Sigma\delta^{\Sigma} + \alpha_2\delta^{o}(R')\Sigma\delta^{\Sigma} \qquad (6)$$

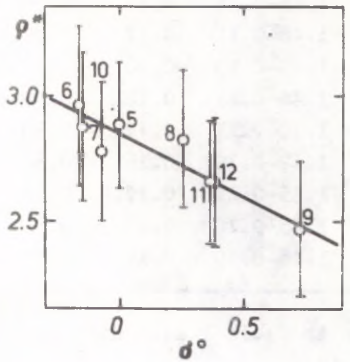


Fig. 1. Dependence of ρ^{Σ} values on δ^{o} of substituents R' in α-bromodesoxybenzoines in case of interaction with amines in acetonitrile at 25°C. Numbers of points correspond to Table 3.

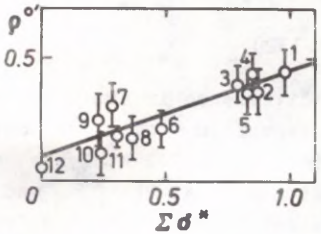


Fig. 2. Dependence of ρ^{o} values on $\Sigma\,\delta^{\Sigma}$ for radicals in the vicinity of nitrogen atom in amines in case of their interaction with substituted α-bromodesoxybenzoines in acetonitrile at 25°C . Numbers of points correspond to Table 2.

Table 3

Parameters of Eq. (6) Describing Structural Effect of Primary and Secondary Amines (N = 11) on Rate of their Reactions with α-Bromodesoxybenzoines ($R\text{-}C_6H_5COCHBrC_6H_5\text{-}R'$) in Acetonitrile at 25°C

No	R and R'	log k_o	$-\rho^{IR}$	δ	S	R
1	4-CH_3O	1.17±0.28	2.75±0.30	1.42±0.11	0.18	0.98
2	4-CH_3	1.80±0.28	2.80±0.30	1.42±0.11	0.18	0.98
3	4-Cl	2.14±0.24	2.72±0.26	1.46±0.10	0.15	0.98
4	4-C_6H_5	1.99±0.26	2.75±0.28	1.45±0.11	0.17	0.98
5	H	2.03±0.26	2.89±0.28	1.48±0.11	0.17	0.98
6	4'-CH_3O	2.68±0.31	2.97±0.33	1.42±0.13	0.20	0.97
7	4'-CH_3	2.18±0.28	2.88±0.30	1.44±0.11	0.18	0.98
8	4'-Br	2.20±0.27	2.83±0.29	1.50±0.11	0.17	0.98
9	4'-NO_2	1.96±0.25	2.47±0.27	1.42±0.10	0.16	0.98
10	3'-CH_3	1.93±0.27	2.78±0.29	1.45±0.11	0.17	0.98
11	3'-Cl	1.95±0.24	2.66±0.25	1.45±0.10	0.15	0.98
12	3'-Br	1.94±0.25	2.66±0.27	1.46±0.10	0.16	0.98

Processing of the data given in Table 1 according to the equation gives the relationship (7):

$$\log k = 1.93 + (1.19\pm0.24)\delta^{o}(R) - (0.16\pm0.19)\delta^{o}(R') - (0.47\pm0.11)\delta_R^{+}(R') - (2.80\pm0.12)\Sigma\delta^{IR} + (1.43\pm0.04)E_N^{+} + (0.13\pm0.65)\delta^{o}(R)\Sigma\delta^{IR} + (0.59\pm0.29)\delta^{o}(R')\Sigma\delta^{IR} \quad (7)$$

(S = 0.24; R = 0.95; N = 132)

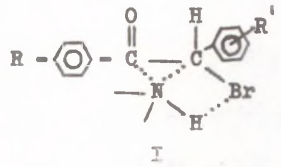
It can be seen that there is no difference in the signs of $\rho^{o'}$ and ρ_R^{+} values which was observed in case of data treatment according to Eq. (4) (see Table 2). Analysis of coefficients in Eq. (7) also indicates that the ρ^{o} and α_1 values are statistically insignificant. Data treatment without taking into account the negligible values of $\rho^{o'}\delta^{o}(R')$ and $\alpha_1\delta^{o}(R)\Sigma\delta^{IR}$ does not practically influence the values of significant parameters (cf. the values of

ρ^{o}, ρ_{R}^{+}, ρ^{*}, δ, α_2 in Eqs. (7) and (8).

$$\log k = 1.94+(1.20\pm0.20)\delta^{o}(R)-(0.54\pm0.11)\delta_{R}^{+}(R') - \\ -(2.78\pm0.11)\Sigma\delta^{*}+(1.44\pm0.04)E_{s}+(0.34\pm0.14)\delta^{o}(R)\Sigma\delta^{*} \quad (8)$$

$$(S = 0.22);\ R = 0.96;\ N = 132)$$

The obtained results have lead to the conclusion that the transition state of studied reactions has got the structure of the Dewar-- Winstein[6] complex (I) where the nitrogen atom simultaneously interacts with carbonylic and α-carbonic atoms. High positive value of ρ^{o} (Table 2; Eq.(8)) shows that the level of nitrogen bond formation with carbonylic carbon is relatively high, exceeding the level of loosening of carbonylic bond (if the latter is influenced during the process), If the $\rho^{o'}$ is close to zero and the ρ_{R}^{+} value is negative, the degree of formation of the bond between nitrogen α-carbonic atoms is much lower than the degree of the C-Br bond breaking. At the same time, the coefficient α_2, considerably diffusing from zero in Eqs. (7) and (8) evidence about the amine interaction with an α-carbonic atom. In case of decreasing of the amine basicity, the positive charge of α-carbonic atom increases and the mentioned interaction becomes stronger (according to the Hammond postulate). The increase of positive charge of nitrogen and the ionization of the C-Br bond in I leads to the formation of the N--H....Br hydrogen bond, promoting the proceeding of the process in aprotic mediums.



I

Experimental

Amines and acetonitrile used were purified according to the known methods. Substituted α-bromodesoxybenzoines were obtained as described in[4,7]. They were purified by means of cristallization from petroleum ether.

Kinetic measurements were carried out under pseudomonomolecular conditions at considerable excess of amine spectrophotometrically (λ = 266-294 nm) and conductometrically.[2]

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Organic Reactivity
Vol. 23 1(81) 1986

SOLVENT EFFECT ON POSITION OF $\pi 1, \pi^*$ ABSORPTION BAND OF DIAMINOANTHRAQUINONES

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Solvent effect on the position of the long-wave $\pi 1, \pi^*$ - absorption bands of 1,2-, 1,4-, 1,5- and 1,8- diaminoanthraquinones is described by means of the Kamlet - Taft and Koppel - Palm equations. Contributions of their different interaction types with solvents are evaluated. Effect of aminogroups position in anthraquinone nucleus is also dealt with.

Aminosubstituted 9,10-anthraquinones have great practical value as synthetic dyes, pigments and luminescent solvents. Recently, they have been used in several new fields of technology: in color photography and television, in the sphere of laser technology, in electro-optical equipment, etc.[1] It also explains the lasting interest in studying certain physico-chemical properties of these compounds, their electronic spectra included[1,2].

We have established[3] that the solvent effect on the position of the long - wave $\pi 1, \pi^*$ bands of some anthraquinone monosubstituents, determining the color of these compounds can be quantitatively characterized by the multiparameter Kamlet - Taft and Koppel - Palm equations based on the conception of linear correspondences of solvation energy.

The present paper deals with the influence of chemical

structure of diaminoanthraquinones on the nature of their interaction with solvents.

The Kamlet - Taft[4] equation has been used in neutral solvents which cannot form intermolecular hydrogen bond in case of all diaminoanthraquinones studied as well as monoamino-substituents:

$$\nu_{max} = \nu_0 + s\pi^* \qquad (1)$$

where ν_0 denotes the position of the $\pi 1$, π^* absorption band in cyclohexane (the standard solvent), π^* is the solvatochromic parameter characterizing the non - specific solvation by a solvent; s denotes the solvatochromic coefficient showing the compounds susceptibility to the nonspecific solvation.

The characteristics of the obtained equations are given in Table 1.

Table 1.

Characteristics of Solvatoochromic Equations (1) According to Kamlet - Taft in Neutral Solvents

Equation	Anthraquinone substituent	$\nu_0 10^{-3}$ cm^{-1}	$-s.10^{-3}$	Number of solvents N	Correlation coefficient r	Standard deviation, cm^{-1} S
1-1	1-amino-	21.96±0.08	0.66±0.13	12	0.963	70
1-2	1,5-diamino-	21.66±0.17	1.01±0.30	6	0.977	80
1-3	1,8-diamino-	21.23±0.25	1.21±0.58	5	0.967	130
1-4	1,4-diamino-	18.60±0.10	0.30±0.23	6	0.875	60
1-5	1,2-diamino-	21.58±0.20	1.13±0.38	5	0.984	70
1-6	2-amino-	26.16±0.36	2.78±0.60	11	0.961	270

Comparison of solvatoochromic coefficients s shows that the susceptibility of α,α-diaminoanthraquinones containing aminogroups to nonspecific solvation is in different benzene rings of anthraquinone nucleus (1,5- and 1,8-) 1,5- - 1,8 times higher than that of 1-aminoanthraquinone. In case of 1,4-diaminosubstituent the susceptibility is, on the

contrary, twice lower than in case of 1-aminoanthraquinone. A low correlation coefficient obtained for this compound has been caused by very small values of the $\pi 1$, π^* band shifts influenced by neutral solvents. In this connection, 1,2-diaminoanthraquinone is closer to 1-aminoanthraquinone (its susceptibility to the non-specific solvation is 1.7 times higher) than to 2-aminoanthraquinone (the susceptibility of the former is 2,5 times lower) 1,2-diaminoanthraquinone is remarkably more susceptible (3.7 times) to neutral solvents than its 1,4-isomer.

The general solvatochromic Kamlet - Taft[4] equation can be applied for the whole set of solvents:

$$\nu_{max} = \nu_0 + s\pi^* + a\alpha + b\beta \qquad (2)$$

where solvatochromic parameters α and β characterise the ability of proton-donor solvent to form the intermoleoular hydrogen bond with the proton-acceptor and a proton-donor dissolved compound, respectively. Solvatochromic coefficients a and b show compound's susceptibility to the corresponding interactions with solvents.

The characteristics of equations (2) are listed in Table 2.

The values of solvatochromic coefficients a evidence about the fact that the introduction of another α - aminogroup into the other benzene ring of the anthraquinone system leads to a 1,2-1.4-time increase of compound's susceptibility to the formation of the intermoleoular hydrogen bond with proton - donor solvents. But the introduction of the α -aminogroup into the same benzene ring turns a compound practically unsusceptible to this type of intermolecular hydrogen bond (aα for 1,4- diaminoanthraquinone is statistically insignificant). 1.2- diaminoanthraquinone is 3.7 times more susceptible than 1- aminosubstituent but its susceptibility is 1.8 times smaller than that of 2-isomer.

It follows from solvatochromic parameters b that the introduction of another aminogroup into position 5 does not practically influence the susceptibility of 1- aminoanthraquinone to the formation of the intermoleoular hydro-

Table 2

Characteristics of General Solvatochromic Equations (2) According to Kamlet - Taft

Equation	Anthraquinone substituent	$\nu_0 10^{-3}$ cm^{-1}	$-s.10^{-3}$	$-a.10^{-3}$	$-b.10^{-3}$	N	Correlation coefficient R	SD cm^{-1}
2-1	1-NH_2-	21.96±0.06	0.64±0.09	0.17±0.09	0.68±0.10	22	0.989	60
2-2	1,5-$(NH_2)_2$-	21.62±0.12	0.92±0.22	0.24±0.18	0.63±0.20	14	0.987	80
2-3	1,8-$(NH_2)_2$-	21.22±0.10	1.14±0.17	0.20±0.17	0.91±0.22	15	0.993	80
2-4	1,4-$(NH_2)_2$-	18.61±0.07	0.28±0.14	(0.02±0.11)	0.45±0.13	16	0.974	50
2-5	1,2-$(NH_2)_2$-	21.59±0.27	1.14±0.47	0.44±0.38	2.33±0.37	14	0.992	160
2-6	2-NH_2-	26.10±0.30	2.71±0.47	0.79±0.34	2.39±0.36	22	0.985	260

gen bond with proton - acceptor solvents, while 1,8-diaminoanthraquinone is 1,3 times more susceptible. 1,4 - diaminoanthraquinone is less susceptible to this interaction type but value a for 1,2-diaminosubstituted anthraquinone does not differ much from that for 2- aminoanthraquinone, i.e. it is determined by the mobility of hydrogen atoms of 8-aminogroup.

For all compounds studied, the contribution of intermolecular hydrogen bond formed by means of hydrogen atoms of the aminogroup is remarkably higher than that of intermolecular hydrogen bond formed on the expense of the hydrogen of proton - donor solvents. As to 1,5- and 1,8- diaminoanthraquinones, dominates nonspecific solvation. In case of 1,4- and particularly of 1,2- diaminoanthraquinones, the contribution of the intermolecular hydrogen bond on the expense of hydrogen atoms of aminogroup is the greatest.

The solvent effect on the position of the $\pi 1$, π^* band of diaminoanthraquinones can be quantitatively described also by means of the Koppel - Palm[5] equation (3), though it usually yields the poorest statistical characteristics (Table 3)

$$\nu_{max} = \nu_0 + y\frac{\varepsilon - 1}{2\varepsilon + 1} + p\frac{n^2 - 1}{n^2 + 2} + eE + bB \qquad (3)$$

where ν_0 denotes ν_{max} in vapor phase, ε is the dielectric constant, n is the refraction indicator; E and B are the parameters of general acidity and basicity of solvents; y, p, e, b are the coefficients depending on the compound structure, which characterize its susceptibility to the effect of the corresponding solvent properties. As a rule, the multiple correlation coefficients R characterizing equations (3) are smaller, while standard deviations and reliable intervals are greater than those in Eq. (2).

According to the Koppel - Palm[5] method, the contributions of different types of interaction with solvents are determined by the decrease in the R value when separate terms are excluded in turn from Eq. (3). The data presented in Table 4 confirm the conclusion that the contribution of sol-

Table 3

Characteristics of Solvatochromic Parameters (3) According to Koppel - Palm

Equation	Anthraquinone substituent	$\nu_0 10^{-3}$ cm^{-1}	$-y.10^{-3}$	$-p.10^{-3}$	-e	-b	N	R	SD cm^{-1}
3-1	1-NH_2-	23.23±0.49	1.48±0.60	3.98±1.71	22±10	1.9±0.6	24	0.986	80
3-2	1,5-$(NH_2)_2$-	22.75±0.86	1.66±0.89	3.83±2.92	27±22	1.7±0.9	14	0.957	148
3-3	1,8-$(NH_2)_2$-	22.63±0.58	1.91±0.79	4.86±2.07	26±15	2.6±0.7	14	0.993	83
3-4	1,4-$(NH_2)_2$-	19.07±0.35	0.59±0.45	1.40±1.23	9±10	1.1±0.4	15	0.968	64
3-5	1,2-$(NH_2)_2$-	22.14±0.62	3.48±2.18	-	60±48	4.6±2.1	13	0.966	343
3-6	2-NH_2-	29.63±2.38	5.77±2.57	10.63±8.22	83±64	6.1±2.4	21	0.974	370

vents' basicity into their specific interaction with diaminoanthraquinone considerably exceeds that of acidity.

If equations (2) enable to evaluate the general contribution of the dissolved compound nonspecific interactions with solvents in comparison with specific interactions, it is possible by means of Eq. (3) to differentiate between the polarity and polarizability effects of solvents.In case of all studied diaminoanthraquinones as well as monoamino-substituents, the contribution of solvents' polarity, which can be characterized by means of the dielectric constant function, predominates over the contribution of solvents' polarizability, characterized by the function of the refraction coefficient. Eqs. (3) enable to specify that, for instance, that the increase of 1,5 - diaminoanthraquinone susceptibility to the nonspecific interactions with solvents in comparison with 1-aminoderivatives is caused by the growth of the contribution of solvents' polarity (coefficient "y" increases from 1.48 to 1.66), while the polarizability contribution even decreases a bit (coefficient p drops from 3.98 to 3.83):

Table 4

Variation of Correlation Coefficient in Case of Exclusion of Terms from Eqs.(3) According to Koppel - Palm

Equation 3-1	Anthraquinone substituent	R 4 parameters are taken into account	R in case of parameter exclusion			
			E	B	f(ε)	f(n)
3-1	1-amino-	0.986	0.959	0.933	0.953	0.958
3-2	1,5-diamino-	0.957	0.933	0.891	0.898	0.928
3-3	1,8-diamino-	0.993	0.980	0.934	0.964	0.970
3-4	1,4-diamino-	0.968	0.959	0.899	0.949	0.954
3-5	1,2-diamino-	0.968	0.947	0.916	0.935	0.966
3-6	2-amino-	0.974	0.958	0.914	0.926	0.959

Eqs. (2) and (3) give an approximate estimation of the contributions of various interactions of diaminoanthraqui-

nones with solvents. E.g., in case of transition from 1-mono to 1,8-diaminosubstituents, the increase of contributions of intermolecular hydrogen bonds forming on the expense of hydrogen atoms of aminogroups can be estimated according to Eqs. (2) as 0.91: 0.68 = 1.34 times; the intensification of the analogous interaction according to Eqs. (3) is 2.6:1.9 =1.37. The minus at the coefficients in Eqs. (1)-(3) refers to the fact that all these interactions with solvents favor the bathochromic shift of the $\pi 1$, π^* absorption band of the studied compounds. Both methods enable to calculate the ν_{max} values in a great number of solvents, in case of which the values of corresponding parameters are known. Eqs.(1) and (2) guarantee better reliability than Eq. (3).

Table 5

Position of $\pi 1$, π^* Band Absorption Peaks of Diaminoanthraquinones in Different Mediums

Medium	ν_{max} 10^{-3} cm^{-1}			
	1,2-	1,4-	1,5-	1,8-
1 2	3	4	5	6
1 Hexane	-	18.69 [2]	21.74 [2]	21.20
2 Cyclohexane	21.60	18.55 [2]	-	21.04
3 Carbon tetrachloride	21.28	18.52 [2]	21.41 [2]	20.83 [2]
4 Toluene	20.92	18.48 [9]	21.00	-
5 Benzene	20.84	18.45 [9]	21.05 [2]	20.48
6 Dichloromethane	20.76	-	20.83 [2]	-
7 Chlorobenzene	-	18.35 [2]	21.05 [2]	20.40
8 Dioxane	20.24	18.28 [2]	20.75 [2]	20.28
9 Ethyl acetate	-	-	20.84	20.24
10 Acetone	19.56	18.28 [2]	20.75 [2]	20.04
11 Triethylphosphate	18.80	18.00	-	19.72
12 Dimethylphormamide	19.34 [2]	18.08 [9]	20.41 [2]	19.60
13 Anisole	18.35 [2]	-	-	-
14 Dimethylsulfoxide	18.52	17.92	20.24	19.36
15 2-Methyl-2-propanole	18.60	-	20.20	-

Table 5 continued

1	2	3	4	5	6
16	Butanol	18.56	18.15 [9]	-	19.68
17	Ethanol	-	18.15 [2]	20.45 [2]	19.72
18	Methanol	19.04	18.15 [2]	20.49 [2]	19.88
19	2-Propanol	18.56	18.02 [2]	20.32 [2]	19.64

Experimental

Compounds and solvents have been obtained and purified according to the known methods. The absorption spectra were taken on spectrophotometers SF-4 and Specord UV Vis, also literature data were used (see Table 5). The values of π^*, α and β were taken from[4], $\mathcal{E}$ and n from[6], B and E from[6]. The calculations were carried out on a computer "Mir-1", the accuracy being 0.95. The authors are grateful to Yu.V. Ivanova and T.M. Kosacheva for their assistance in carrying out calculations.

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Organic Reactivity
Vol. 23 1(81) 1986

REGULARITIES CONCERNING CHANGES OF VALUES OF SOLVATOCHROMIC COEFFICIENTS OF SUBSTITUTED 9,10-ANTHRAQUINONES

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It has been shown that between solvatochromic coefficients obtained according to the methods of Kamlet - Taft and Koppel - Palm for 22 substituted 9,10-anthraquinones exist certain linear dependences. Solvatochromic coefficents' values of 1-substituted anthraquinones are in good correlation with the σ_n constants of substituents forming intramolecular hydrogen bonds. Equations enabling to prediot the effect of solvents on the ν_{max} values of this compound series have been given. In case of 2-substituted anthraquinones, analogous regularities are only of approximate nature.

It was shown in report[1] that the effect of solvents on the position of long-wave $\pi 1$, π^* - absorption bands of three 9,10-anthraquinone derivatives oan be quantitatively described by means of the multiparameter Kamlet - Taft[2] (1) and Koppel - Palm[3] equations:

$$\nu_{max} = \nu_o + s\pi^* + a\alpha + b\beta \qquad (1)$$

where π^*, and β are the solvatochromic parameters characterizing the solvent's ability of non-specific solvation of dissolved compounds, that of proton - donor solvent to

form intermolecular hydrogen bonds with proton - acceptor dissolved compounds as well as the ability of proton - accepter solvent to form intermolecular hydrogen bonds with proton - donor solutes, respectively; s, a and b denote solvatochromic coefficients characterizing the susceptibility of a solute to the corresponding solvatochromic parameters; $\nu_0 = \nu_{max}$ are the compounds in cyclohexane in case of which $\pi^* = \alpha = \beta = 0$.

$$\nu_{max} = \nu'_0 + y\,\frac{\varepsilon - 1}{2\varepsilon + 1} + p\,\frac{n^2 - 1}{n^2 + 2} + sE + b'B \qquad (2)$$

where ε is the dielectric constant, n is the refraction index, E and B are the parameters of general acidity and basicity, $f(\varepsilon)$ and f(n) describe the polarity and polarizability effects of solvents, respectively; $\nu'_0 = \nu_{max}$ denote compounds in vapor phase.

It was shown that the both equations give approximately similar evaluation of contributions of specific interactions with solvents into total solvatochromic effect and complementary information on the role of nonspecific interactions. The both methods permit to take into account the ν_{max} values of studied compounds in a great number of solvents. It should be mentioned that the Kamlet - Taft method usually gives more accurate results. The advantage of the Koppel - Palm method is the possibility to bring out the individual contributions of solvents' polarity and polarizability.

The Kamlet - Taft and Koppel - Palm methods are widely used for quantitative characterization of solvent effects on the values of physico-chemical parameters and reactivity of various compounds. However, there are only a few reports where these methods have been used in case of a representative compound series, thus enabling to find out the regularities of changes of solvatochromic coefficients' values.

Up to now we have established that equations (1) and (2) can be employed in case of 22 9,10-anthraquinone derivatives. The obtained values of solvatochromic coefficients are given in Table 1.

Table 1

Values of Solvatochromic Coefficients of 9,10-Anthraquinone Substituents[1,8,9]

Substituted 9,10-anthraquinone	Solvatochromic coefficients according to Kamlet - Taft				Solvatochromic coefficients according to Koppel - Palm				
	$\nu_0 10^{-3}$ cm^{-1}	$s.10^{-3}$ cm^{-1}	$a.10^{-3}$ cm^{-1}	$b.10^{-3}$ cm^{-1}	$\nu_0 10^{-3}$ cm^{-1}	$y.10^{-3}$ cm^{-1}	$p.10^{-3}$ cm^{-1}	$e.cm^{-1}$	$b'.\ cm^{-1}$
1	2	3	4	5	6	7	8	9	10
1-NH_2-	21.96± ±0.06	-0.64± ±0.09	-0.17± ±0.09	-0.68± ±0.10	23.23± ±0.49	-1.49± ±0.60	-3.98± ±1.71	-22±10	-1.9±0.6
1-$NHCH_3$-	20.33± ±0.07	-0.84± ±0.11	-0.30± ±0.08	-	21.97± ±0.65	-1.78± ±0.75	-5.54± ±2.38	-27±20	-
1-NHC_6H_5-	20.23± ±0.08	-0.54± ±0.15	-0.19± ±0.11	0.15± ±0.13	21.30± ±0.39	-0.83± ±0.32	-3.98± ±1.36	-9.8±8.8	-
1-$N(CH_3)_2$-	20.42± ±0.10	-0.98± ±0.14	-0.30± ±0.09	-	21.43± ±0.50	-1.88± ±0.58	-3.24± ±1.68	-	-0.65±0.53
1-NC_5H_{10}-	19.87± ±0.10	-0.83± ±0.15	-0.27± ±0.14	-	21.38± ±0.65	-1.61± ±0.68	-5.21± ±2.27	-23±21	-
1-$NHCOCH_3$-	23.92± ±0.11	0.25± ±0.24	0.55± ±0.20	0.49± ±0.23	24.30± ±0.49	0.79± ±0.71	-2.21± ±1.67	48±12	0.9±0.6
1-$NHCOC_6H_5$-	23.23± ±0.13	1.08± ±0.19	0.69± ±0.14	-	23.00± ±0.37	2.04± ±1.34	-	28±25	-
1-OH-	24.72± ±0.09	-0.17± ±0.16	-	-	-	-	-	-	-

Table 1 continued

1	2	3	4	5	6	7	8	9	10
1-OCH_3	27.10±±0.10	-0.90±±0.18	-0.49±±0.14	-	28.20±±0.91	-	-4.59±3.47	-59±20	-1.1±0.5
2-NH_2-	26.10±±0.30	-2.71±±0.47	-0.79±±0.34	-2.39±±0.36	29.63±±2.38	-5.77±±2.57	-10.63±8.22	-83±64	-6.1±2.4
2-$NHCH_3$-	23.68±±0.22	-1.68±±0.39	-0.64±±0.31	-1.24±±0.34	26.48±±1.74	-4.84±±1.74	-8.38±6.02	-49±43	-2.1±1.7
2-NHC_6H_5-	23.36±±0.16	-1.47±±0.32	-0.49±±0.28	-1.22±±0.30	25.34±±1.48	-3.48±±1.83	-5.81±5.34	-58±44	-2.5±1.6
2-$N(CH_3)_2$-	22.59±±0.19	-1.61±±0.29	-0.66±±0.18	-	25.36±±1.35	-3.72±±1.11	-9.35±4.82	-33±29	-
2-NC_5H_{10}-	22.85±±0.07	-2.23±±0.07	-0.80±±0.05	-	25.89±±1.41	-4.21±±1.57	-10.67±4.73	-47±40	-
2-$NHCOCH_3$-	27.10±±0.18	-0.33±±0.30	0.47±±0.19	-0.62±±0.19	27.59±±0.54	-0.66±±0.49	-	29±11	-1.85±0.44
2-$NHCOC_6H_5$-	27.44±±0.28	-0.43±±0.42	-	-0.78±±0.23	28.66±±0.80	-1.33±±0.81	-3.92±2.45	-	-1.73±0.65
2-OH-	21.14±±0.06	-0.59±±0.05	-0.11±±0.05	-1.41±±0.06	29.36±±0.14	-2.45±±0.64	-2.75±1.74	-30±10	-2.6 ± 0.5
2-OCH_3-	27.97±±0.07	-0.96±±0.11	-0.35±±0.09	-	29.22±±0.57	-	-5.44±2.15	-28±17	-1.87± 0.62

Table 1 continued

1	2	3	4	5	6	7	8	9	10
1,2-$(NH_2)_2$-	21.59± ±0.27	-1.14± ±0.47	-0.44± ±0.38	-2.33± ±0.37	22.14± ±0.62	-3.48± ±2.18	-	-60±48	-4.6±2.1
1,4-$(NH_2)_2$-	18.61± ±0.07	-0.28± ±0.14	-0.02± ±0.11	-0.45± ±0.13	18.96± ±0.40	-	-1.47± ±1.45	-13±11	-1.5±0.4
1,5-$(NH_2)_2$-	21.62± ±0.12	-0.92± ±0.22	-0.24± ±0.18	-0.63± ±0.20	22.75± ±0.86	-1.66± ±0.89	-3.83± ±2.92	-27±28	-1.7±0.9
1,8-$(NH_2)_2$-	21.22± ±0.10	-1.14± ±0.22	-0.20± ±0.17	-0.91± ±0.22	22.63± ±0.58	-1.91± ±0.79	-4.86± ±2.07	-26±15	-2.6±0.7

Comparison of values of solvatochromic coefficients for the same compounds obtained according to Kamlet - Taft and Koppel - Palm revealed the existence of linear dependences between them. In case of coefficients characterizing the compounds' susceptibility to the specific interactions with solvents, this dependence is common for all compounds. Thus, there is a satisfactory correlation between the values of b and b' :

$$b' = (2.20 \pm 0.17) \cdot b \cdot 10^3 cm^{-1} \qquad (3)$$

Number of points N = 20; correlation coefficient r = 0.982; standard deviation SD = $3.4 \cdot 10^{-4}$ cm^{-1}.

It can be seen in Table 1 that the accuracy of determination of coefficients e according to Koppel - Palm is usually negligible. Evidently, for that reason, there is only rough interdependence between the e and a values:

$$e = (0.072 \pm 0.012)a - (9.0 \pm 6.0)\ cm^{-1} \qquad (4)$$

$$N = 19;\quad r = 0.92;\quad SD = 3.3\ cm^{-1}$$

The s coefficients according to Kamlet - Taft are in good correlation with the y values according to Koppel - Palm. The latter values characterize the susceptibility of the compounds' ν_{max} to the influence of solvents' polarity:

$$y = (2.13 \pm 0.27)s\ cm^{-1} \qquad (5)$$

$$N = 19;\quad r = 0.958;\quad SD = 550\ cm^{-1}$$

In case of 1-substituted compounds the dependence is excellent:

$$y_1 = (1.93) \pm 0.19)s_1\ cm^{-1} \qquad (5\text{-}1)$$

$$N = 9;\quad r = 0.990;\quad SD = 210\ cm^{-1}$$

The relationship between the coefficients s and values p which describe the compounds' susceptibility to the polarisability effect of solvents is remarkably weaker according to the method of Koppel - Palm :

$$p_1 = (2.78 \pm 1.20)s_1 - (2740 \pm 790)\ cm^{-1} \qquad (6\text{-}1)$$

$$N = 5;\quad r = 0.953;\quad SD = 460\ cm^{-1}$$

$$p_2 = (3.65 \pm 1.08)s_1 - (1982 \pm 1793)\ cm^{-1} \qquad (6\text{-}2)$$

$$N = 7; \quad r = 0.950; \quad SD = 1110\ cm^{-1}$$

A common interrelationship of these values in case of all studied compounds is also expressed by correlation coefficient 0.926.

The obtained results evidence about the fact that the solvatochromic coefficient s, characterizing the ν_{max} susceptibility of the 9,10-anthraquinone derivatives to the nonspecific solvation by solvents, expresses more the polarity effect than that of the solvents' polarizability.

The interdependence of the ν_0 and ν'_0 values in case of (alkyl, aryl) aminoanthraquinones is satisfactorily described as follows:

$$\nu'_0 = (1.39 \pm 0.19)\nu_0 - (6830 \pm 3900)\ cm^{-1} \qquad (7\text{-}1)$$

$$N = 14; \quad r = 0.980; \quad SD = 562\ cm^{-1}$$

A different straight line is observed in case of oxy-, metoxy- and acylaminosubstituted derivatives:

$$\nu'_0 = (0.753 \pm 0.118)\nu_0 + (5848 \pm 3227)\ cm^{-1} \qquad (7\text{-}2)$$

$$N = 7; \quad r = 0.991; \quad SD = 294\ cm^{-1}$$

which is in good correspondence with the data of [4]. It is possible to calculate rather accurately the position of the long-wave band in vapor phase in case of a substantial number of substituted anthraquinones by means of equations (7-1) and (7-2), proceeding from the ν_{max} values. These calculated values are not easy to obtain experimentally.

We have shown in report[5] that the ν_{max} values of long-wave absorption bands of monosubstituted anthraquinones depend on the electron-donor activity of substituents. It was interesting to find out if such a dependence existed also in case of solvatochromic coefficients.

The correlation analysis of solvatochromic coefficient values of 1-substituted anthraquinone with the substituents forming intramolecular hydrogen bond with oxygen atoms of the nearest carbonylic group of an anthraquinone nucleus

has shown that the best results of the whole set of known substituent σ-constants are obtained using the σ_n constants in accordance with Mac-Daniel[6]. Use of para-constants in case of 1-substituted anthraquinones has been justified in[5]. The figure illustrates the dependence of the values of solvatochromic coefficients s on substituent constants σ_n.

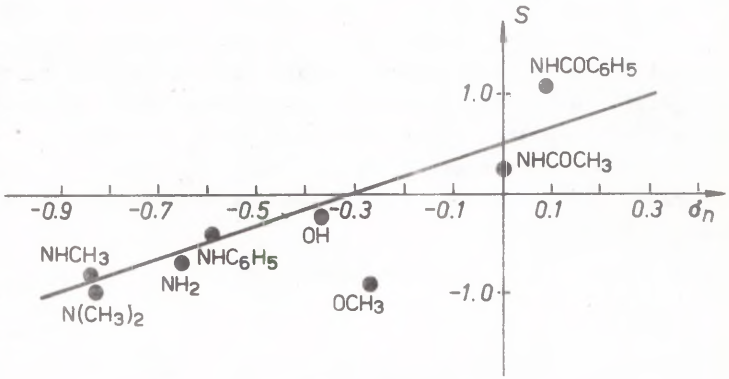

Figure. Dependence of values of solvatochromic coefficients s of 1-substituted anthraquinone on the substituents' σ_n-constants.

As a result of the increase in the electron-donor activity of substituents, the s value deviates from the positive values for acylaminosubstituted anthraquinones up to the growing negative values for 1-substituted anthraquinones with other substituents. The point of 1-methoxyanthraquinone whose structure lacks the intramolecular hydrogen bond, deviates from the regression line towards more negative values. The point for 1-dimethylaminoanthraquinone, on the contrary, obeys the found regularity . The latter is in good correlation with the data of[7], according to which the straight lines of proportional response of the ν_{max} values of 1-and 2-substituted anthraquinones, either forming or not the intramolecular hydrogen bond, intersect in the vicinity of the point for dimethylaminoanthraquinone. The s

value for 1-piperidinoanthraquinone should also obey the established regularity, enabling to estimate the value of σ_n constants for the piperidinogroup (-0.78).

It follows from Eq. (8) (see Table 2) that s=0 if σ_n = = -0.32, i.e.the 1-substituted anthraquinone with a substituent, forming the intramolecular hydrogen bond, whose $\sigma_n \approx -0.32$ cannot be susceptible to the effect of nonspecific interaction with solvents.

Table 2.

Correlation Parameters Characterizing the Relationship of Solvatochromic Coefficients s_k with Substituent Constants σ

$$s_k = k\sigma + c \cdot cm^{-1} \cdot 10^{-3}$$

Equation	Solvatochromic coefficient s_k	σ-constant	N	r	SD cm^{-1}	K $cm^{-1} \cdot 10^{-3}$	C $cm^{-1} \cdot 10^{-3}$
8	s_1	σ_n	7	0.956	230	1.82±0.50	0.59±0.29
9	a_1	σ_n	7	0.944	158	1.11±0.35	0.52±0.20
10	y_1	σ_n	7	0.980	330	3.79±0.70	1.28±0.44
11	p_1	σ_n	5	0.958	440	3.74±1.53	-2.04±0.99
12	e_1	σ_n	6	0.960	9.8	0.075±0.023	0.034±0.014
13	s_2	σ_n^+	8	0.948	240	1.72±0.46	0.74±0.53
14	a_2	σ_n^+	9	0.92	180	1.09±0.34	0.85±0.40
15	y_2	σ_n^+	8	0.958	450	3.63±0.87	1.13±1.00
16	p_2	σ_n^+	7	0.946	1930	14.84±4.70	11.05±5.66
17	e_2	σ_n^+	5	0.86	20	0.10±0.08	0.07±0.09

Such compounds are 1-oxyanthraquinone (σ_n^{OH}= -0.37), whose ν_{max} value does not practically depend on the polarity of neutral solvents,1-substituted anthraquinones having substituents whose $\sigma_n < -0.32$ have the positive solvatochromic effects. Using of substituents with $\sigma_n > -0.32$ leads to negative solvatochromic effects of the corresponding 1-substituted anthraquinones.solvatochromic effects of the corresponding 1-substituted anthraquinones.

The other solvatochromic coefficients of 1-substituted anthraquinones (Table 2) depend similarly on the substi-

tuents' electron-donor activity. Only statistically significant values of solvatochromic coefficients have been included in the calculations. The value of the σ_n constant for piperinogroup, calculated by us, corresponded satisfactorily to the obtained regularities in all cases. In case of 1-dimethylaminoanthraquinone, solvatochromic coefficients a and y obey the general regularity, while p and e deviate towards more negative values. Evidently, different straight lines are characteristic to 1-substituted anthraquinones with substituents both forming or not the intramolecular hydrogen bond. In case of one kind of solvatochromic coefficients the straight lines intersect near the point for 1-dimethylaminosubstituted anthraquinone, in other cases they intersect in a longer distance from it.

The regularities found permit to predict the position of longwave absorption bands in different solvents in vapor phase in case of a large group of 1-substituted anthraquinones having the intramolecular hydrogen bond forming substituents. In case of 2-substituted anthraquinones, the mutual dependence between solvatochromic coefficients and substituents' electron-donor activity is expressed remarkably more vaguely. According to correlation analysis, the electrophilic σ_n^+ substituent constants[5,6] are most suitable for the quantitative description of this dependence, although in such a case the analysis is only approximate (Table 2). Besides, the absolute values of solvatochromic coefficients of 2-aminoanthraquinone turn out to be higher than it follows from the calculations according to Eqs.(13)-(17).

Variations of the b and b' coefficients' values are not determined by the σ substituent constants.

The data available are not sufficient enough to explain all the reasons causing the observed differences in the behavior of solvatochromic coefficients of 1- and 2-substituted anthraquinones.

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AMIDES PROTONATION - A COMPARISON OF pK_{BH^+} AND m^* VALUES ESTIMATED BY THE METHODS BASED ON EXCESS ACIDITY AND ON FACTOR ANALYSIS

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Results of comparison of two methods (viz. based on excess acidity and on target testing factor analysis) for calculating basicity constants pK_{BH^+} and slope parameters m^* of amides from shifting UV spectra are reported.

Most work on amides protonation was performed by using UV spectroscopy. But the maxima of adsorption bands in the amides spectra are shifting with increasing acid concentration and, as a result, the ionization ratio values (I =

= C_{BH^+}/C_B) calculated from these spectra depend on the wavelength chosen. In order to correct such lateral medium shifts, a number of methods have been proposed[1]. Nevertheless, a satisfactory solution to the problem has not yet been achieved and the basicity constants calculated from ionization ratios are not very reliable.

In this situation, recently, two new methods have been suggested for treating spectra that reflect protonation and medium shift simultaneously. The first method proposed by R. Cox and K. Yates[2] is based on the concept of excess acidity and the second (Ü. Haldna and A. Murshak[3]) uses the target testing factor analysis.

According to the Cox-Yates method the unprotonated B and protonated BH^+ forms of base are considered to exist in two states ($B_{(1)}$, $B_{(2)}$ and $BH^+_{(1)}$, $BH^+_{(2)}$) differing by the states of hydration. Then with increasing acidity two simultaneous processes take place: protonation and transition of the more hydrated state into the less hydrated state. In the case of amides which protonate in relatively dilute sulfuric acid only the splitting of the BH^+ form into the more hydrated $BH^+_{(1)}$ and the less hydrated $BH^+_{(2)}$ states should be taken into account. It is assumed that the absorption spectra of the species $BH^+_{(1)}$ and $BH^+_{(2)}$ — $\varepsilon_{BH^+(1)} = f(\lambda)$ and $\varepsilon_{BH^+_{(2)}} = f(\lambda)$ do not depend on acid concentration and can be expressed by the spectrum of BH^+ in water ($\varepsilon_{BH^+aq} = f(\lambda)$) and the medium shift ($\delta\varepsilon_{BH^+} = f(\lambda)$).

The equilibrium between base and its conjugate acid BH^+

$$B + H^+ \rightleftharpoons BH^+; \qquad K_{BH^+} = \frac{a_{H^+} \cdot a_B}{a_{BH^+}}$$

in the Cox-Yates approach is given by Eq. (1)[4]

$$\lg I = \lg C_{H^+} + m^{\pm}X + pK_{BH^+} \qquad (1)$$

where C_{H^+} is the molar concentration of the solvated protons; X is the excess acidity (X-function) and $m^{\pm}$ is the slope pa-

6

rameter.

The equilibrium between states (1) and (2) $BH^+_{(1)} \rightleftharpoons BH^+_{(2)}$ is also described using excess acidity[2]:

$$\lg I_A = \lg \frac{c_{BH^+(2)}}{c_{BH^+(1)}} = \Delta m^*_A X$$

where Δm^*_A is a difference between m^* values for $BH^+_{(2)}$ and $BH^+_{(1)}$.

The expression derived for variations in amides molar absorptivity with changing acidity at a given wavelength is Eq. (2)[2]

$$\varepsilon = \frac{\varepsilon_B + I\,(\varepsilon_{BH^+} + \delta\varepsilon_{BH^+} I_A)}{I + 1} \qquad (2)$$

where $I_A = (I_A - 1)/(1 + I_A)$.

According to the method based on the target testing factor analysis[3,5] the experimental data matrix $[D]$ is decomposed into two abstract matrices: the row matrix $[R]_{PCA}$ and the column matrix $[C]_{PCA}$

$$[D] = [R]_{PCA} \cdot [C]_{PCA}. \qquad (3)$$

In target testing we make use of a number of supposed pK_{BH^+} and m^* values and each combination of them yields us a test vector $\bar{\bar{R}}$ in accord with Eq. (4) ($\bar{\bar{R}}$ is a column vector serving as a target in the transformation procedure).

$$\bar{\bar{R}} = c_{BH^+} / (c_{BH^+} + c_B). \qquad (4)$$

Next, for each test vector the respective predicted vector $\bar{R}$ is calculated:

$$\bar{R} = [R]_{PCA} [\lambda]^{-1}_{PCA} [R]_{PCA} \bar{\bar{R}}$$

where $[\lambda]_{PCA}$ is the diagonal matrix with eigenvalues of the $[D]$ matrix on the main diagonal.

If the test vector $\bar{\bar{R}}$ is a real one, i.e. fits the measured set of UV spectra, each element of $\bar{\bar{R}}$ will be reasonably close to the corresponding element of $\bar{R}$ yielding $z = \sum(\bar{\bar{r}}_{i1} - \bar{r}_{i1})^2 = \text{minimum}$ where $\bar{\bar{r}}_{i1}$ and $\bar{r}_{i1}$ are the elements of $\bar{\bar{R}}$ and $\bar{R}$, respectively. The pair of pK_{BH^+} and m^* values used to calculate $\bar{\bar{R}}$ with the minimal z is considered to be the best choise from a given set of pK_{BH^+} and m^* values.

Ultimately, the abstract solution (Eq. (3)) can be converted into the real one. Postmultiplying $[R]_{PCA}$ by transformation matrix $[T]$ and premultiplying $[C]_{PCA}$ by the inverse of the transformation matrix $[T]^{-1}$ the transformed solution can be obtained

$$[R]_{TFA} = [R]_{PCA} \cdot [T]$$

$$[C]_{TFA} = [T]^{-1} \cdot [C]_{PCA}$$

The transformation matrix $[T]$ is given by the equation

$$[T] = [\lambda]^{-1}_{PCA} \cdot [R]^{T}_{PCA} \cdot [\bar{\bar{R}}]$$

where $[\bar{\bar{R}}]$ is the $[R]_{PCA}$ matrix in which the first column has been replaced by the test vector $\bar{\bar{R}}$ corresponding to the minimal z value.

Since the actual values of pK_{BH^+} and m^* are not known, we cannot verify the validity of each of the methods separately. But as the first approximation, the validation can be made by comparing the results obtained by the two methods based on completely different initial concepts. That is why our objective was to compare the pK_{BH^+} and m^* values calculated from the available experimental data on the UV absorption spectra of amides in aqueous sulfuric acid solutions using the methods described above. The amide spectra used were taken from supplementary materials of the paper[5] and the benzamide spectrum was measured by the authors. Benzamide was purified by recrystallization from an ethanol-water

mixture and the m. p. was 127.8–128.1°C. Dissolving benzamide in ethanol the standard solution with a concentration of about 1% (w/w) was prepared. The sample solution was made by adding the weighted amount of the standard solution (ca 0.1 g) to 20 ml of sulfuric acid solution. The reference solution was prepared by adding to 20 ml sulfuric acid solution the volume of pure ethanol equal to that of the added standard solution. Spectrophotometer "Specord M40" and the cuvettes with a matched path length (0.2–0.5 cm) thermostatted at 25°C were used for UV measurements in the region of 210–275 nm. Practically no corrections for the chemical reactions of benzamide in sulfuric acid during the measurement time were necessary to be made.

In order to calculate the pK_{BH^+} and m^* values according to the excess acidity method[2] it was necessary to solve a set of equations (2) with the following unknowns: pK_{BH^+}, m^* and three unknowns (ε_B, ε_{BH^+aq}, $\delta\varepsilon_{BH^+}$) at each of the wavelength used. This was performed using the Newton iterations method in which the difference between the experimental and calculated ε values (S_ε) was minimized ($S_\varepsilon = \sum(\varepsilon_{exp.} - \varepsilon_{calc.})^2 / NF$, where NF are the degrees of freedom). Calculations were performed using two similar programs: an original program[2] (was kindly supplied by R. Cox) and that of the authors. In the original program a general-purpose curve-fitting subroutine CURFIT adapted from Bevington[7] was utilized.

In calculations all experimental data were taken into account (no points were rejected) and in each run Δm_A^* had a fixed value which was varied by a step of 0.01 until the minimal S_ε was reached (in the case of N-isopropyl- and N-isobutylbenzamide the minimum was not observed: S_ε diminished with decreasing Δm_A^*). It should be noted that the original Cox program enables us to find the final solution with worse initial values of unknowns than our program, but the final results obtained by both programs are practically the same.

Factor analysis calculations were made using the computer

program described by Haldna et al[3]. An additional condition was set up that in the most concentrated sulfuric acid solution used the fraction of the protonated form (Eq. (4)) must be $\geqslant 0.99$. All calculations were performed on EC-1052 computer and the results are presented in Tables 1 and 2.

From a comparison of the pK_{BH^+} values calculated by both methods (Table 1) a conclusion can be made that ΔpK_{BH^+} values have a normal distribution[8] with the mean $\overline{\Delta pK_{BH^+}} = -0.024$ and a standard deviation of the arithmetical mean $S_{\overline{X}} = 0.025$. With a probability of 37% we may state that $\Delta\overline{pK} = 0$.

By comparing the m^* values (Table 2) we excluded Δm^* for N,N-diisopropylbenzamide because it deviated from the mean by an almost triple standard deviation. In this way we obtained $\overline{\Delta m^*} = 0.083$ and $S_{\overline{X}} = 0.027$, i.e. factor analysis gives lower m^* values than the excess acidity method (a statistical hypothesis that $\Delta m^* = 0$ should be rejected because its probability is $< 1\%$).

The values of pK_{BH^+} and m^* obtained in this report permit the calculation of the sulfuric acid concentration in which the base is half-protonated. The data in Table 3 demonstrate that the above methods are in rather satisfactory agreement (excluding N,N-diisopropylbenzamide, the mean difference of half-protonation concentrations calculated by the two methods is $\pm 1.6\%$ H_2SO_4).
Using the obtained pK_{BH^+} and m^* values (Tables 1 and 2), and Equation (1) we also calculated the ionization ratios of amides at various H_2SO_4 concentrations. To exemplify this, Table 4 presents some results.

From the foregoing, we can draw a conclusion that the methods based on the excess acidity and on target testing factor analysis proved to be suitable for calculating the pK_{BH^+} and m^* values of amides (Factor analysis gives m^* on an average 0.08 unit lower than the Cox-Yates method). Since both methods are based on different initial ideas, such an agreement is quite notable and serves as a good approach to reality.

Table 1

Basicity Constants of Amides Calculated by Methods Based on the Excess Acidity (I Method) and on Factor Analysis (II Method)

Substance	I method		II method	$\Delta pK_{BH^+}=pK_{BH^+}(1)-pK_{BH^+}(II)$
	pK_{BH^+}	Δm^*_A	pK_{BH^+}	
1.Benzamide	-1.48±0.03	0.11	-1.38	-0.10
2.N-Ethylbenzamide	-1.57±0.10	0.22	-1.50	-0.07
3.N-Isopropylbenzamide	-1.55±0.08	0.01-0.05	-1.56	+0.01
4.N-Isobutylbenzamide	-1.56±0.04	0.01-0.05	-1.66	+0.10
5.N-sec-Butylbenzamide	-1.53±0.03	0.05	-1.45	-0.08
6.N-tert-Butylbenzamide	-1.32±0.06	0.10	-1.34	+0.02
7.N-Benzylbenzamide	-1.76±0.07	0.15	-1.61	-0.15
8.α-Methyl-N-benzylbenzamide	-1.52±0.06	0.11	-1.44	-0.08
9.N,N-Diethylbenzamide	-1.11±0.08	0.10	-1.08	-0.03
10.N,N-Diisopropylbenzamide	-0.62±0.04	0.13	-0.74	+0.12
11.Benzoyl piperidine	-0.94±0.03	0.10	-0.94	0.00

Table 2

Slope Parameters of Amides Calculated by Methods Based on the Excess Acidity (I Method) and on Factor Analysis (II Method)

Substance	I method		II method	$\Delta m^{H} = m^{H}(I) - m^{H}(II)$
	m^{H}	S_{ε} a)	m^{H}	
1. Benzamide	0.58±0.03	0.186	0.55	0.03
2. N-Ethylbenzamide	0.52±0.10	0.028	0.51	0.01
3. N-Isopropylbenzamide	0.62±0.11	0.017	0.58	0.04
4. N-Isobutylbenzamide	0.39±0.03	0.017	0.40	-0.01
5. N-sec-Butylbenzamide	0.65±0.03	0.011	0.52	0.13
6. N-tert-Butylbenzamide	0.66±0.06	0.011	0.65	0.01
7. N-Benzylbenzamide	0.66±0.06	0.012	0.45	0.21
8. α-Methyl-N-benzylbenzamide	0.45±0.05	0.010	0.30	0.15
9. N,N-Diethylbenzamide	0.59±0.08	0.009	0.54	0.05
10. N,N-Diisopropylbenzamide	0.71±0.01	0.008	0.23	0.48
11. Benzoyl piperidine	0.53±0.06	0.010	0.32	0.21

a) root mean square error between experimental and calculated ε values (except benzamide ε means optical density)

Table 3

Sulfuric Acid Concentrations at Half-Protonation Calculated by Methods Based on the Excess Acidity (I Method) and on Factor Analysis (II Method)

Substance	H_2SO_4 % w/w		Difference Δ % = = %(I) - %(II)
	I method	II method	
1.Benzamide	34.20	32.90	1.30
2.N-Ethylbenzamide	37.80	36.60	1.20
3.N-Isopropylbenzamide	34.55	35.80	-1.25
4.N-Isobutylbenzamide	42.50	44.55	-2.05
5.N-sec-Butylbenzamide	33.45	35.20	-1.75
6.N-tert-Butylbenzamide	29.25	29.85	-0.60
7.N-Benzylbenzamide	37.45	41.15	-3.70
8.α-Methyl-N-benzylbenzamide	39.04	43.75	-4.71
9.N,N-Diethylbenzamide	26.40	26.70	-0.30
10.N,N-Diisopropylbenzamide	15.53	24.40	-8.87
11.Benzoyl piperidine	23.80	28.10	-4.30

Table 4

Ionization Ratios of Some Amides Calculated at Various H_2SO_4 Concentrations

H_2SO_4 % w/w	log I			
	I method	II method	I method	II method
	Benzamide		N-Isopropylbenzamide	
14	-0.99	-0.91	-1.05	-1.07
20	-0.69	-0.60	-0.73	-0.77
26	-0.40	-0.32	-0.43	-0.48
32	-0.11	-0.04	-0.13	-0.19
38	0.19	0.25	0.18	0.11
44	0.50	0.54	0.51	0.42
50	0.83	0.85	0.85	0.75
	N-tert-Butylbenzamide		N,N-Diethylbenzamide	
12	-0.92	-0.95	-0.73	-0.72
18	-0.59	-0.61	-0.41	-0.41
24	-0.27	-0.30	-0.12	-0.12
30	0.04	0.01	0.18	0.15
36	0.36	0.33	0.47	0.44
42	0.70	0.66	0.78	0.72
48	1.05	1.01	1.11	1.03
	N-Isobutylbenzamide		α-Methyl-N-benzyl-benzamide	
18	-0.96	-1.06	-0.89	-0.88
24	-0.71	-0.81	-0.63	-0.66
30	-0.48	-0.57	-0.38	-0.45
36	-0.25	-0.34	-0.13	-0.25
42	-0.02	-0.10	0.13	-0.06
48	0.22	0.14	0.39	0.14
54	0.47	0.39	0.67	0.35
60	0.74	0.67	0.97	0.56
66	1.04	0.98	1.32	0.81

We thank Dr. G. Sapir for his kind assistance in obtaining some literature sources.

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Organic Reactivity
Vol. 23 1(81) 1986

THE CENTRAL CARBON ATOM CHARGE INFLUENCE ON THE REACTIVITY OF THE CONJUGATED IONS OF TRIARYLMETHANE SERIES

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It is shown on the basis of semiempirical calculations (CNDO/2 method) of some conjugated carbonium ions of triarylmethane series and experimental data concerning the thermodynamics and kinetics of ionic reactions with their participation that there is a correlation between the δ^+-charge of the central carbon atom of the cations studied and the values of log k and pK_{R^+} of these reactions. The investigation carried out proved the validity of the idea of the central carbon atom δ^+-charge value being the determining factor of the charge of the triarylmethyl ions reactivity towards nucleophilic reagents.

It is known that the idea of the determining role of reagents' molecule charge distribution character which re-

flects the structural peculiarities of the reagents and the nature of their interactions with a medium is one of the basic conceptions in the modern reactivity theory[1-3].

All extensive experimental material accumulated by the present time, concerning the reactions with the participation of the conjugated ions of triarylmethane series[2,4,5] shows the central carbon atom δ^+-charge value to be the most important factor determining the thermodynamic and kinetic behavior of these ions in the reactions with nucleophilic reagents. It is from this position that one can explain a number of quantitative tendencies observed in the series of triarylmethyl ions: linearity of free energies, the isokinetic interrelation etc.

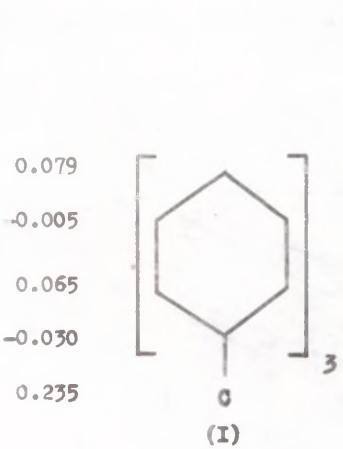
It seemed to be interesting to carry out an independent estimation of the δ^+-charge value in the series of substituted triarylmethyl ions in order to compare the results obtained with the experimental thermodynamic and kinetic data.

For that purpose we carried out semiempirical calculations (CNDO/2 method[6,7]) of triphenylmethylcation (I) and its derivatives containing from one to three $N(CH_3)_2$-groups in para-position to the central carbon atom (II)-(IV).

The use of the literature data for the semiempirical calculations of the triarylmethyl ions by means of the Hückel method and the PPP method[8] was regarded to be inexpedient because the allvalent method CNDO/2 permitted to calculate the electronic structure of organic objects more successfully than the π-electronic methods[6,7].

It follows from the analysis of the results obtained (see schemes) that the maximum of the positive charge is localized on the central carbon atom, which agrees with the qualitative ideas of the electronic structure of triarylmethyl ions. A clear tendency towards the decrease of this charge is observed. At the same time, a number of electron-releasing substituents taking part in the delocalization of positive charge of the conjugated ion is decreasing.

The comparison of calculation data with the results, obtained from the kinetic study of the interaction of cations (II)-(IV) with sulfite-anion (H_2O, 298 K, $\mu = 0$), en-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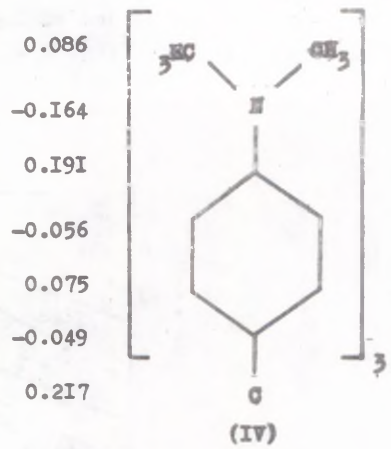
-0.005
0.065
-0.030
0.235
3
C

(I)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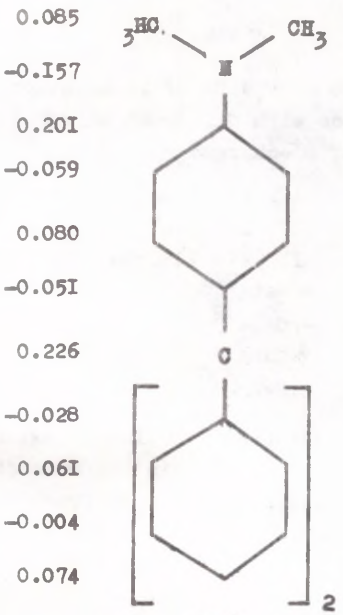
0.191
-0.056
0.075
-0.049
0.217
3HC
CH3
N
3
C

(IV)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0.080
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0.226
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0.061
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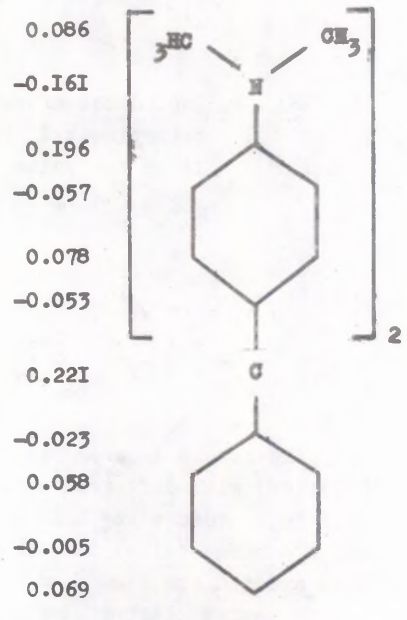
0.074
3HC
CH3
N
C
2

(II)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-0.161
0.196
-0.057
0.078
-0.053
0.221
-0.023
0.058
-0.005
0.069
3HC
CH3
N
2
C

(III)

abled us to establish the existence of the linear correlation between the values of log k and the δ^+-charge for the corresponding ions (Fig. 1).

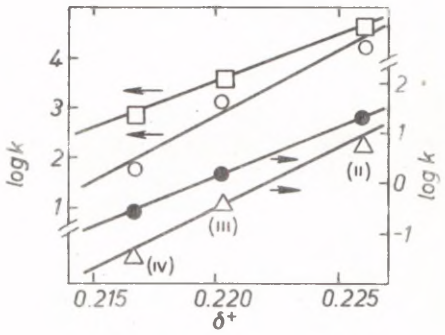

Fig. 1. Dependence of rate constants of interactions of triarylmethyl ions with different anions (298 K) on the value of δ^+-charge:

× - SO_3^{2-} (H_2O) II. $k = 4.38 \cdot 10^4$ l/(mole·s)
III. $k = 3.87 \cdot 10^3$ l/(mole·s)
IV. $k = 7.90 \cdot 10^2$ l/(mole·s)
• - OH^- (H_2O) - data[9-11]
○ - CH_3O^- (CH_3OH) - data[12,13]
△ - CN^- (H_2O) - data[14,15] (293 K)

Literature data on the interaction kinetics of cations (II)-(IV) with different anions are showed in the same figure. In all cases log k is the increasing linear function of the δ^+-charge value. The meanings of pK_{R^+}[16,17] of the cations studied are also found to be in the linear dependence on the central carbon atom charge value (Fig. 2).

It results from the aforesaid that the dependence of log k (or pK_{R^+}) on the δ^+-charge value can be described by

the equation of the straight line:

$$\log k = A\delta^{+} + B, \qquad (1)$$

where k is the rate or equilibrium constant for the reaction of triarylmethyl ions, A and B denote the coefficients of the straight line.

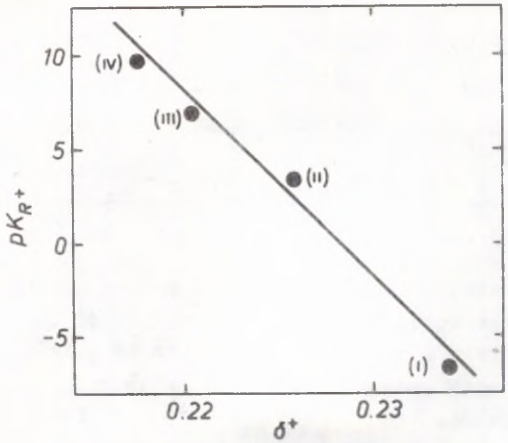

Fig. 2. Central carbon δ atom charge influence on the value of pK_{R^+} (296 K) of triarylmethyl ions (I)-(IV):

$$pK_{R^+} = (200 \pm 20) - (880 \pm 90)\delta^{+};$$

$$r = 0.990;\ s = 1.256;\ n = 4.$$

The values of A and B for the reactions considered are listed in the Table and in the note to Fig. 2. It results from the data of the Table that the value of coefficient A for the kinetic series slightly depends on the nature of a nucleophile. Such a result is in good agreement with the idea of isolation of the "cationic" fragment of the activated complex from its "anionic" part, postulated for reactions of this type (the "early" transition state)[18,19].

Having used Eq. (1), we carried out an estimation of the rate constants of a number of reactions with the partic-

Table

Parameters of Correlation Equation of Type log k
log k = $A\delta^+$ + B for Interactions of Cations
(II)-(IV) with Different Anion (298 K)

Anion	(solvent)	A	-B	r	S
SO_3^{2-}	(H_2O)	188±3	38±1	0.999	0.019
OH^-	(H_2O)	209±6	46±1	0.999	0.042
CH_3O^-	(CH_3OH)	259±35	54±8	0.991	0.232
CN^-	(H_2O)[a]	237±15	53±3	0.998	0.102

[a] 293 K

ipation of cation (I) which could not be obtained experimentally because of the high reactivity of this cation. The obtained values of log k appeared to be 3.12±0.05 for the reaction with hydroxide anion and 6.18±0.05 for the reaction with sulfite anion.

Thus, the study carried out, completely proved the validity of the idea that the δ^+ charge of the central carbon atom has a decisive role in the thermodynamics and kinetics of the reactions with the participation of the conjugated ions of triarylmethyl series.

The data on the structure of triarylmethyl ions were taken from literature[20].

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Organic Reactivity
Vol. 23 1(81) 1986

SALT-DEPENDENT PROMOTION OF *p*-N,N,N-TRIMETHYLAMMONIUM-*trans*-CINNAMOYL-CHYMOTRYPSIN DEACYLATION

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The influence of KCl and CsCl on the *p*-N,N,N-trimethylammonium-*trans*-cinnamoyl-chymotrypsin (TMAC-CT) deacylation rate constant has been studied in the presence of modifiers, indole and acetonitrile, that bind in the hydrophobic slit of the active center of this acylenzyme. It is shown that the salt dependence of the deacylation rate constant of the TMAC-CT complexes with the modifiers is greatly different from that of TMAC-CT and coincides with the common salt dependence of the deacylation of the acyl-chymotrypsins in which the acyl group interacts with the hydrophobic slit in the active site of the enzyme. The change in the type of the deacylation salt dependence associated with the introduction of the modifier molecule into the hydrophobic slit appears as the promotion of the reaction. The extent of the promotion depends on the concentration of salt in the reaction mixture.

In previous communications from this laboratory[1,2] it has been shown that the interaction of the acyl-chymotrypsin acyl group with the hydrophobic slit in the active site of the enzyme makes a definite contribution to the parameters of the kinetic salting effect in the deacylation reaction; accordingly, two types of the deacylation reaction salt dependence can be discerned depending on whether or not the acyl group interacts with the hydrophobic slit of the active site of the acyl-enzyme. In Fig. 1 the salt dependence of

the deacylation rate constant for cinnamoyl-chymotrypsin, 3-(2-furyl)acryloyl-chymotrypsin, N-acetyl-L-tyrosyl-chymotrypsin and *p*-N,N,N-trimethylammonium-*trans*-cinnamoyl-chymotrypsin (TMAC-CT) is shown. The influence of KCl on the deacylation rate constant of these acyl-enzymes is mostly due to the kinetic salting effect[1] according to the equation

$$\log k_3 = \log k_3^o + \Delta\varkappa_{k_3} c + \Delta B_{k_3} c^2 \quad , \qquad (1)$$

where c is the salt concentration while $\Delta\varkappa$ and ΔB denote the difference in the salting parameters of the ground and transition states of the reaction (a detailed analysis of the influence of salts will be published elsewhere). Fig. 1 shows that the data for cinnamoyl-chymotrypsin, 3-(2-furyl)-acryloyl-chymotrypsin and N-acetyl-L-tyrosyl-chymotrypsin in which the Ser-195-linked acyl group interacts with the hydrophobic slit in the active site of the enzyme, constitute a common dependence. In TMAC-CT the hydrophobic slit is vacant as indicated by the possibility of the promotion of its deacylation in 3 M KCl solution by indole[6] which, owing to the capacity of binding in the hydrophobic slit of the enzyme, is a typical competitive inhibitor in α-chymotrypsin reactions with specific substrates. Fig. 1 demonstrates that the salt dependence of the TMAC-CT deacylation rate constant clearly differs from that of other acylenzymes.

Taking into consideration that the kinetic salting effect in acyl-chymotrypsin deacylation depends on the interaction between the hydrophobic slit of the enzyme and the acyl ligand it is of interest to study how the kinetic salting effect reflects the interaction between the hydrophobic slit and the molecule of an individual substance, the non-covalent modifier. To clarify the point, we have investigated the dependence of the promotion of the TMAC-CT deacylation upon salt concentration.

The deacylation reaction of an acyl-enzyme EA in which the acyl group is not bound in the hydrophobic slit can be accelerated (promoted) by adding a modifier M due to the formation of a complex EAM with increased reactivity[7,8]

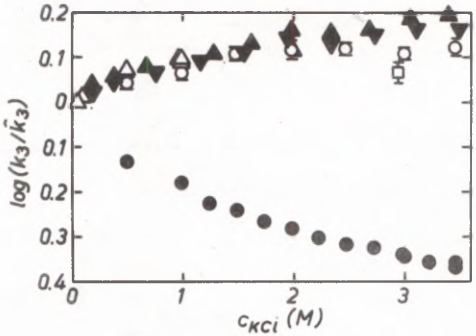


Fig.1. Dependence of acyl-chymotrypsin deacylation on KCl concentration: ▼ - cinnamoyl-chymotrypsin[1]; ▲ - 3-(2-furyl)acryloyl-chymotrypsin[2]; △ - N-acetyl-L-tyrosyl-chymotrypsin (the data about KCl influence on k_{cat} in the reaction of α-chymotrypsin with N-acetyl-L-tyrosine ethyl ester[3]; in this reaction $k_{cat} \approx k_3$[4,5]); ● - TMAC-CT (for data see also[6]); ○ - the complex of TMAC-CT with indole; □ - the complex of TMAC-CT with acetonitrile. The data are normalized, $\hat{k}_3$ is the rate constant in the absence of KCl (in the case of N-acetyl-L-tyrosyl-chymotrypsin - in 0.01 M KCl).

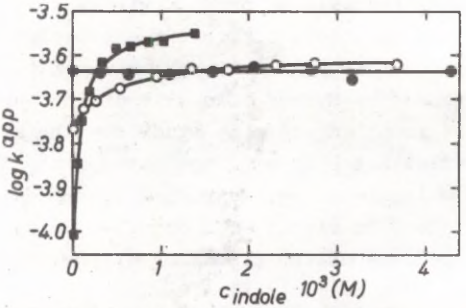
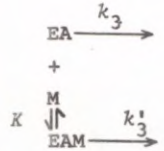


Fig.2. Dependence of TMAC-CT deacylation on indole concentration: ● - in the absence of KCl; ○ - in 0.496 M KCl; ■ - in 3.46 M KCl. The curves show the fit of the data to Eq. (3). For experimental conditions see Table 1.



(2)

where K is the dissociation constant of the complex EAM.

The dependence of the parameters of Scheme (2) on the concentration of KCl and CsCl in the reaction mixture was studied; indole and acetonitrile were used as modifiers. The obtained data were fitted into Eq. (3)

$$k^{app} = \frac{k_3 + k_3' \frac{[M]}{K}}{1 + \frac{[M]}{K}} \qquad (3)$$

which is derived from Scheme (2). In Fig. 2 representative dependencies of log k^{app} on indole concentration at three KCl concentrations are shown. Fig. 2 shows that in the absence of salt, indole has no influence on the reaction rate constant ($k_3' = k_3$) while the data measured in the presence of KCl fit well into Eq. (3). The results of data-processing by Eq. (3) are given in Table 1.

Table 1 shows that all parameters of Scheme (2) depend on salt concentration. Deacylation rate constants of the complex of TMAC-CT with indole at various KCl concentrations are shown in Fig. 1. On the basis of the figure it can be said that they fall fairly well on the upper dependence. In other words, upon saturation of TMAC-CT with indole the points in log ($k_3/\hat{k}_3$) *vs.* c_{KCl} plot rise from the lower dependence to the upper one. The same conclusion can be drawn from the comparison of the data about CsCl influence on cinnamoyl-chymotrypsin deacylation[1], and on the promotion of TMAC-CT deacylation by indole (Table 1).

With the aim to investigate whether the salt-dependent promotional effect is sensitive to the choice of the modifier, the influence of acetonitrile on TMAC-CT deacylation was measured under the same set of conditions. Like indole,

Table 1

Influence of Salts on the Promotion of the TMAC-CT Deacylation by Indole[a]

Salt	c_{salt} (M)	$k_3 \cdot 10^4$ (s^{-1})	$K \cdot 10^4$ (M)	k_3'/k_3
	0	2.320±0.004	no promotion	
KCl	0.496	1.718±0.017	5.26±0.64	1.48±0.02
	0.991	1.531±0.023	4.08±0.56	1.76±0.04
	1.48	1.324±0.019	2.96±0.23	2.24±0.04
	1.98	1.217±0.026	3.25±0.34	2.49±0.06
	2.47	1.109±0.015	2.14±0.12	2.74±0.04
	2.99	1.036±0.011	1.78±0.09	2.84±0.04
	3.46	0.983±0.019	1.63±0.13	3.10±0.07
CsCl	0.601	1.444±0.016	4.88±0.44	1.78±0.03
	1.20	1.281±0.014	4.69±0.33	2.11±0.03
	2.19	1.164±0.024	4.41±0.46	2.59±0.06
	3.40	1.133±0.022	3.96±0.39	2.60±0.06
	4.63	1.158±0.013	4.22±0.31	2.71±0.05
	5.85	1.461±0.029	2.29±0.33	2.11±0.06

[a]Pseudo-first-order kinetics at 25.0±0.2 °C were measured spectrophotometrically at 299 nm, pH was maintained by 0.05 M carbonate buffer at 9.10 (at this pH value the influence of salts on the ionogenic equilibria in the enzyme[1,6] does not appear in the kinetics of the deacylation reaction). The rate constants were determined in duplicate or triplicate at 9 or 10 indole concentrations in each salt solution, the weighted means of the rate constants were fitted to Eq. (3) (in logarithmic form), the modifier concentration was calculated by the equation $[M]=0.5\{[M]_o-[EA]_o-K+\sqrt{(K+[EA]_o-[M]_o)^2+4K[M]_o}\}$, where the subscript "zero" refers to the initial concentrations. Parameter values ± S.E., calculated by the non-linear regression method[9], are given.

acetonitrile did not promote the reaction in the absence of salt, while in 2.94 M KCl solution its influence could be described by Eq. (3) with the following parameter values: $k_3 = (1.06 \pm 0.03) \cdot 10^{-4}$ s^{-1}, $K = 0.37 \pm 0.06$ M, $k_3' = (2.7 \pm 0.2) \cdot 10^{-4}$ s^{-1}. The comparison of the deacylation rate constant of the complexes of TMAC-CT with indole and acetonitrile (Fig. 1) reveals that both modifiers promote the reaction to approximately the same extent although, as it can be seen from Table 1, the indole binding constant is about 2000 times better than that for acetonitrile.

To summarize, it can be concluded that the type of the dependence of the acyl-chymotrypsin deacylation rate constant on salt concentration is determined by whether there is a ligand, or an acyl group or a molecule of a non-covalent modifier, in the hydrophobic slit of the enzyme. If the acyl group of the acyl-enzyme leaves the hydrophobic slit vacant, the change in the type of the deacylation salt dependence upon introduction of the modifier molecule into the hydrophobic slit will appear as the salt-dependent promotion of the reaction.

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Organic Reactivity
Vol. 23 1(81) 1986

EFFECT OF LEAVING GROUP AND SOLVENT NATURE ON THE RATE OF FORMATION OF α-AMINOKETONES

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Interaction kinetics of α-halogenacetophenones with piperidine has been examined in a great number of solvents at 30° C. Different quantitative regularities concerning the effects of various solvent properties (polarity, polarizability, etc.) on the rate of the bimolecular reactions of α-piperidine-acetophenone formation have been found and discussed.

Conformational structure of α-chloroacetophenone has been studied at various stages of the reaction with piperidine.

The formation rate of α-aminoketones in α-bromoacetophenones reactions with various amines considerably depends on the nucleophile structure as well as on the solvent nature[1]. In addition to that, it is the solvent properties and the substituent in the α-position with regard to the carbonyl group of α-halogenacetophenone molecules that remarkably determine their rotamerization character[2,3]. Thus, it is quite natural that interrelations between the conformations of an electrophile and its behavior in the mentioned

reactions are examined if the solvent nature directs the variation of both spectroscopic and kinetic characteristics of the electrophile.

The present work is aimed at studying the influence of the leaving group nature and solvent properties on the rate of α-aminoketones' formation reaction. The conformational appertaining of α-chloroacetophenone at various stages of the reaction with piperidine has also been found out.

Experimental

α-halogenacetophenones, piperidine and solvents were purified as described in[4].

Reaction (1), proceeding like[1] was followed according

$$PhCOCH_2Hal + 2C_5H_{10}NH \rightarrow PhCOCH_2NC_5H_{10} + C_5H_{10}\overset{+}{N}H_2\overset{-}{Hal} \quad (1)$$

to the method of argentometric potentiometric titration of the forming haloide ions. Rate constants of second order reactions were calculated according to formula (2).

$$k = \frac{1}{(b-2a)t} \ln \frac{a(b-2x)}{(a-x)b} \quad (2)$$

where a and b (M) denote the initial concentration of α-halogenacetophenone and piperidine, respectively; x(M) is the reaction products' concentration at time t (s).

The validity of Eq.(1) in case Hal=Cl was proved by means of separation of the products of α-chloroacetophenone reaction with piperidine in conditions close to critical. The chlorohydroxide of α-piperidineacetophenone, obtained from cyclohexane, dioxane and nitrobenzene solutions turned out to have characteristics similar to those got earlier[5].

The reaction rate constants, calculated according to Eq.(2) remain constant during the process in case of all solvents used and do not depend on the initial concentration of the reagents. However, in cyclohexane, in the case of α-chloroacetophenone, the constants increase monotonically in the course of the process, while in case of α-bromoacetophenone the opposite effect is observed (Table 1).

Table 1

Interaction Kinetics of Different α-Halogenacetophenones with Piperidine in Cyclohexane at 30°C

$t \cdot 10^{-5}$ s	Yield %	$k \cdot 10^{5}$ $M^{-1} \cdot s^{-1}$	$t \cdot 10^{-3}$ s	Yield %	$k \cdot 10^{3}$ $M^{-1} \cdot s^{-1}$
HaI=Cl; a=0.0103M; b=0.0416M;			HaI=Br; a=0.0251M; b=0.0308M		
1.51	6.8	1.14	0.30	3.8	2.62
2.42	12,9	1.42	0.60	6.6	2.32
3.45	20.6	1.70	1.20	12.4	2.29
4.80	33.8	2.27	2.40	21.0	2.10
5.89	46.3	2.92	4.32	33.8	2.15
6.87	59.4	3.84	5.04	37.6	2.14
6.89	60.1	3.91	6.90	48.2	2.29
7.57	67.2	4.46	9.00	53.8	2.13
			13.9	66.8	2.14
$k_o = 9.9 \cdot 10^{-6}$ $M^{-1} \cdot s^{-1}$			$k_o = 2.71 \cdot 10^{-3}$ $M^{-1} \cdot s^{-1}$		

It evidences about the fact that in cyclohexane, a series of interactions which do not obey Eq.(2) is carried out in addition to the main bimolecular reaction flow. They will be studied later on. In order to characterize these processes, extrapolated to zero time, reaction rate constants

(k_o) have been used. The k_o values will not practically change if the concentrations of α-halogenacetophenones is varied, depending linearly on the initial concentration of piperidine (Table 2). The latter refers to its catalytic influence on the rate of the reaction studied.

The comparison of the obtained reaction rate constants (Table 3) shows that the reactivity of α-bromoacetophenone exceeds more than 100 times that of α-chloroacetophenone. The comparison of the k_{Cl} and k_{Br} values yields a straight line having good statistical characteristics, thus evidencing about the identical mechanisms of the studied reactions:

$$\log k_{Br} = (1.88 \pm 0.05) + (8.85 \pm 0.16) \cdot 10^{-1} \log k_{Cl} \quad (5)$$

$S = 0.05(1.60\%)$, $r = 0.999$, $n = 11$.

Table 2.

Values of Rate Constants (k_o) Extrapolated to Zero Time of Reactions of α-Halogenacetophenones with Piperidine in Cyclohexane in Case of Different Reagent Concentrations at 30°C.

a, M	b, M	$k_o \cdot 10^5$, $M^{-1} \cdot s^{-1}$	a, M	b, M	$k_o \cdot 10^3$, $M^{-1} \cdot s^{-1}$
	HaI = Cl			HaI = Br	
0.00516	0.0416	1.17	0.00503	0.0406	3.24
0.0103	0.0416	0.99	0.100	0.0406	3.18
0.0175	0.0416	0.87	0.167	0.0406	3.19
0.0258	0.0416	1.20	0.0250	0.0406	3.23
0.0250	0.0105	0.46	0.0251	0.0103	1.77
0.0250	0.0316	0.90	0.0251	0.0308	2.71
0.0250	0.0632	1.51	0.0251	0.0612	4.17
0.0250	0.105	2.15	0.0251	0.102	6.33

$k_o = (3.16 \pm 0.57) \cdot 10^{-6} + (1.78 \pm 0.09) \cdot 10^{-4} b$, (3)
$S = 6,4 \cdot 10^{-7}$ (3.8%), $R = 0.997$

$k_o = (1.20 \pm 0.07) \cdot 10^{-3} + (4.98 \pm 0.11) \cdot 10^{-2} b$, (4)
$S = 7.9 \cdot 10^{-5}$ (1.7%), $R = 0.999$

$$\log k_{Br} = (1.88 \pm 0.05) + (8.85 \pm 0.16) \cdot 10^{-1} \log k_{Cl} , \quad (5)$$

$$S = 0.05\ (1.60\%),\quad r = 0.999,\quad n = 11.$$

It was established[1] in the course of examining the solvent effect on the rate of the α-bromoacetophenone interaction with primary and secondary amines that in electron--donor solvents (acetone, dioxane, benzene), the reaction rate undergoes substantial positive deviations from the Kirkwood equation. This speaks about the fact that the reaction studied is rather susceptible to the variation of polarizability and specific properties of the reaction medium. For that reason, we used a four - parameter Koppel-Palm equation[6] in order to quantitatively characterize the influence of the factors on the reactivity of various α-halogenacetophenones.

Table 3

Values of Reaction Constants of Second Order Reactions of α-Halogenacetophenones with Piperidine in Different Solvents at 30°C

No	Solvent	$k_{Cl} \cdot 10^4$, $M^{-1} \cdot s^{-1}$	$k_{Br} \cdot 10^{-2}$, $M^{-1} \cdot s^{-1}$
1.	Cyclohexane	0.0316±0.0057	0.120±0.007
2.	Mesitylene	1.29 ±0.02	2.50 ±0.03
3.	Toluene	3.18 ±0.04	6.41 ±0.08
4.	Benzene	5.30 ±0.09	9.83 ±0.15
5.	Chlorobenzene	14.5 ±0.2	21.4 ±0.2
6.	Dioxane	17.9 ±0.3	29.1 ±0.3
7.	1,2-Dichlorobenzene	22.6 ±0.3	31.6 ±0.1
8.	Nitrobenzene	151 ±6	236 ±2
9.	Benzonitrile	216 ±4	255 ±2
10.	1,4-Dimethylbenzene	2.26 ±0.08	3.85 ±0.06
11.	1,2-Dimethylbenzene	3.00 ±0.07	5.44 ±0.04

The following regression dependencies have been obtained[7]

$$\log k_{Cl} = -(14\pm2) + (6.6\pm1.6)Y + (20\pm5)P + (4.8\pm2.0)\cdot10^{-3}B + (3.7\pm1.1)\cdot10^{-1}E, \quad (6)$$

$$S = 0.20\ (5.1\%),\quad r = 0.99,\quad n = 9;$$

$$\log k_{Br} = -(9.8\pm1.7) + (6.3\pm1.6)Y + (16\pm5)P + (3.8\pm2.0)\cdot10^{-3}B + (3.4\pm1.1)\cdot10^{-1}E, \quad (7)$$

$$S = 0.020\ (6.0\%),\quad r = 0.99,\quad n = 9.$$

Equations (6) and (7) show that both nonspecific and specific solvation influence positively the reaction rate. Besides, the susceptibility of the reactivity of various α-halogenacetophenones to the variation of specific and non-specific properties in the studied solvent series turned out to be statistically similar.

Examination of absolute contributions of any individual solvation effect into the variation of reactivity of α-halogenacetophenones at the transition from the gas phase ($\log k_{Cl} = -14$, $\log k_{Br} = -9.8$, $Y = P = B = E = 0$) to any reagent used confirms a predominating influence of the polarizability. Thus, the transition from gas phase to toluene ($Y = 0.23949$, $P = 0.38285$, $B = 58\ cm^{-1}$, $E = 1.3$) is accompanied by solvatochromic effects on the cvalues of $\log k_{Cl}$ and $\log k_{Br}$, which are equal to 1.6, 7.7, 0.28, 0.48 and 1.5, 6.1, 0.22, 0.44, respectively.

It should be pointed out that a similar predominance of the polarizability factor was observed[7] also when studying the medium effect on the conformational shifts of C=O stretching frequencies of α-chloroacetophenone which seem to be caused by a direct participation of the carbonyl group of the electrophile molecule in the reaction.

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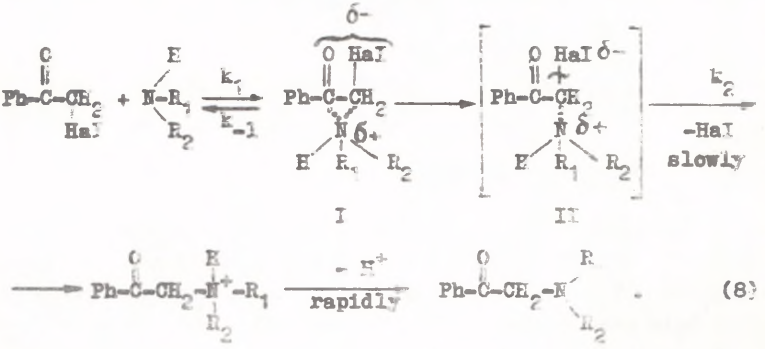
[7] Absence of parameters B and E for solvents 10 and 11 (Table 3) made us include into Eqs. (6) and (7) solvents 1-9 only.

Earlier[1] a scheme of the mechanism of α-bromoacetophenone reactions with different amines has been suggested:



A problem concerning the conformational type of an α-halogenacetophenone molecule at different reaction stages arises while studying the scheme.

During the first stage of a rapid formation of the Deward-Winstein complex (I) (see scheme (8)) nucleophilic solvation of the substrate by means of an amine molecule should alter its conformation. As it has been shown already[3], such a solvation type transforms the substrate into the cis- state. Consequently, in the Deward-Winstein complex, the relations C=O and C - Cl are in the cis- position, in case the former can be observed in the reaction studied.

A further progress of the amine molecule attack, leading to the formation of transformation state (II), can hardly bring about any remarkable conformational changes of the electrophile, since the repulsive interactions of C=O and C-Cl relationships, characteristic to its eclipsed state, should favor the rupture of the halogen-carbon bond in the rate limiting step of the reaction. It can to a certain extent be proved by Eq. (9)

$$\log k_{Cl} = (0.3\pm2.1) - (1.7\pm15)\cdot10^{-2}(\nu^{\text{gauche}}_{C=O} - 1700) - (3.8\pm0.8)\cdot10^{-1}(\nu^{\text{cis}}_{C=O} - 1700). \quad (9)$$

$$S = 0.23 \quad (5.9\%), \quad r = 0.98, \quad n = 11$$

proceeding from the comparison of the reaction rates (see Table 3) with the carbonylic absorption frequencies of α-chloroacetophenone conformers.[7] The latter show that the free activation energy of α-chloroacetophenone reaction with piperidine correlates with the value of the cis- form carbonylic bond order only. The relative log k_{21} susceptibility to the variation of the C=O stretching frequencies of α-chloroacetophenone cis- form can most probably be explained by the destabilization of the transition state (II), resulting from the decrease of the carbon α-atom positive charge in the case of the increase of the carbonylic bond order. As it follows from Eq. (9), changes in the C=O bond order of the α-chloroacetophenone of conformer, do not practically influence the activation energy of the reaction studied.

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A STUDY OF DECOMPOSITION KINETICS OF JANOWSKY δ-COMPLEX IN TETRAHYDROFURAN-WATER MIXTURE

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Dependence of the Janowsky δ-complex decomposition rate on the composition of the tetrahydrofuran-water mixture has been studied. It has been established that the rate constants' value is affected by the shift of the ion-pairing solvation equilibria, as well as by the changes of the solvent structure.

In order to study the mechanism of the reactions of the activated nucleophilic aromatic substitution, attention should be paid to finding out the influence of different medium effects on the stability of the intermediate products - anionic δ-complexes.

According to the earlier investigations[1], the association level of the Janowsky δ-complexes in tetrafuran is rather high, which must also influence their spectral characteristics and decomposition rate.

Proceeding from the aforesaid, the mechanism of the solvent effect on the decomposition kinetics of the Janowsky (1) δ-complexes has been studied in the binary hydrofuran (THF)-water system, in case the components' molar fraction varies from 0 to 1.

The reaction rate was measured spectrophotometrically according to the decreasing of the σ-complex solvent optical density in time, thus, it was necessary to find out the dependence of its spectral characteristics on the solvent composition.

Table 1

Dependence of Kinetic and Spectral Characteristics of the Janowsky σ-Complex on Solvent Composition in Tetrahydrofuran-Water Mixture

% H_2O	N_{H_2O}	$k \cdot 10^5 s^{-1}$	λ, nm	$\varepsilon \cdot 10^{-3}$ l/mole·cm
0	0	4.15	550	13.54
sat.sol.of Crown Ether	0	1.98	562	15.20
2.5	0.10	6.56	558	14.58
5.0	0.19	8.00	561	15.94
7.5	0.27	9.50	562	15.63
10.0	0.33	10.64	563	15.31
12.5	0.39	10.94	564	14.38
15.0	0.44	11.45	563	13.76
20.0	0.53	11.96	560	12.71
25.0	0.68	12.23	558	12.50
40.0	0.75	11.94	551	11.56
50.0	0.82	10.64	552	11.46
60.0	0.87	8.69	550	10.21
75.0	0.93	4.18	530	7.71
90.0	0.98	3.10	493	6.35
95.0	0.99	22.74	487	6.25
100.0	1.0	1.58	480	

As it can be seen from Table 1, adding THF (up to 12.5%) to water leads to a slight bathochromic shift of the maximum to the rising of the absorption intensity. In case of a further increase of the water quantity, a remarkable hypsochro-

mic shift of the absorption band, reaching to 70 nm in pure water is observed. A simultaneous broadening of the band and a considerable drop of the absorption coefficient (Table 1, Fig. 1) takes place.

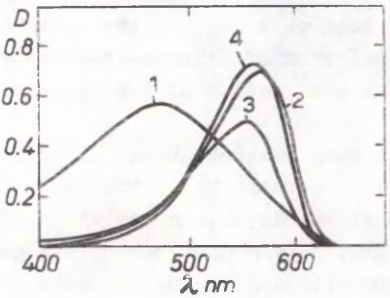
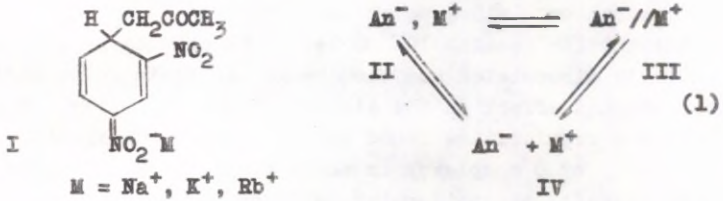


Fig. 1. Absorption spectra of Janowsky complex in THF-water system: 1 - water; 2 - 12.5 % H_2O; 3 - THF; 4 - THF + dibenzo-18-crown-6 ether.

The established regularities can be explained by the ion-pair equilibrium shift (1) as well as by the influence of the medium polarity on the electronic transfer energy, while in case of low concentrations, the former effect prevails in the proton component solution.



Really, due to the fact that a more remarkable longwave absorption[1] corresponds to free ions, the bathochromic shift taking place in the electronic spectra, evidences about the ion-pair equilibrium (I) shift from the contact (II) and solvent-separated (III) ion pairs towards free ions (IV), which is in keeping with the increase of the complex's sdissociation constant[1]. Connection between the ion-pair equilibrium shift and changes of the electronic absorption spectra is also proved by the long wave λ_{max} shift at taking into the tetrahydrofuran solution of dibenzo-18-crown-6 ether б-complex, favoring the distruction of ion associations (Fig. 1, Table 1).

In case of a complete б-complex dissociation, which is reached if the water percentage of the solution is 10^{1}, is another factor that mainly influences the state of the absorption peak - namely, the increase of the energy and the decrease of the probability of the corresponding electronic transfer with the system's growing polarity. It is revealed by the absorption band hypsochromic shift.

It should be mentioned that in dioxan-water systems[2], analogical changes of spectral characteristics of б complexes took place.

As dioxan is a less polar solvent than THF (their dielectric permittivities being 7.34 and 2.21[3], respectively), the bathochromic shift of the absorption band is observed in case of high water concentrations (up to the molar fraction of 0.50-0.70). At the same time, in the mixtures of water and acetone or acetonitrile the б complex absorption band undergoes the bathochromic shift already at an insignificant water concentration[2], since under these conditions (the б complex concentration reaches 10^{-4} mole/l) the complex is practically entirely dissociated and the changes in the spectra reflect the solvent effect on the electron transfer energy, only.

The regularities found should evidently influence the stability of б complexes in these systems. In all cases, the б complex (I) absorption intensity decreases in time, while the optical density logarithm depends linearly on time. It enabled to calculate the rate constants of the pseudofirst

order decomposition reaction of the dyed product. Their values turned out to be constant if the initial concentration of the σ complex is changed, thus proving that the reaction proceeds in the pseudomonomolecular conditions. The values of probable rate constants of the first order decomposition reaction of the Janowsky σ complex in case of different solvent composition are given in Table 1.

The analysis of the obtained results shows that the addition of small quantities of water to the THF leads to a remarkable acceleration of the decomposition reaction. If the molar fraction changes within the range of 0.3–0.8, the reaction rate constant remains practically unchanged, while further adding of water into the mixed solvent causes a considerable stabilization of the σ complex. The nature of the dependence between the decomposition rate constant logarithm (log k) and the function of dielectric permittivity 1/D[*] shows that it cannot be linear in the whole range of changes of the THF-water mixture (Fig. 2).

It was also noticed that one component of the binary solvent (Fig. 3) substantially deviates from the log k linear dependence on the molar fraction (N). According to the assumptions of Palm[6], these data prove that it is not the dielectric effects that play the most significant role in case of the specific solvation of the reagent and the activated complex by the protic solvents.

We have shown earlier [1,7] that the decomposition of the Janowsky σ complex in a mixed solvent (polar aprotic-protic) represents a bimolecular process and a protic component being a specific solvating medium paricipates in the reaction as and attacking agent (Scheme 2). According to the scheme, first takes place a rapid solvation of the molecules of the complex by water because of the formation of hydrogen bonds

[*] As in case of the D values, the Kirkwood function $(D-1)/(2D\pm2)$ and 1/D are in linear dependence[4], we have drawn the graphs within the coordinates log k vs. 1/D. Dependences of the dielectric permittivity on the molar fraction of water in THF[5] were used.

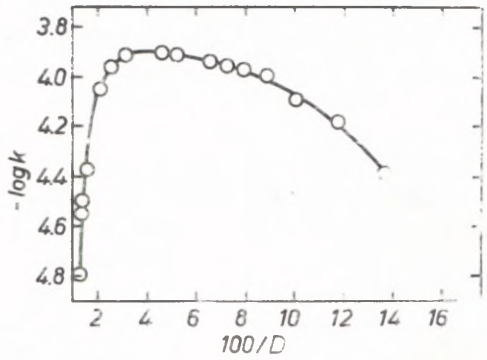


Fig. 2. Dependence of log k on the 1/D value.

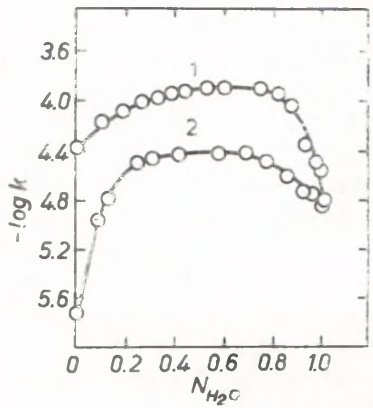
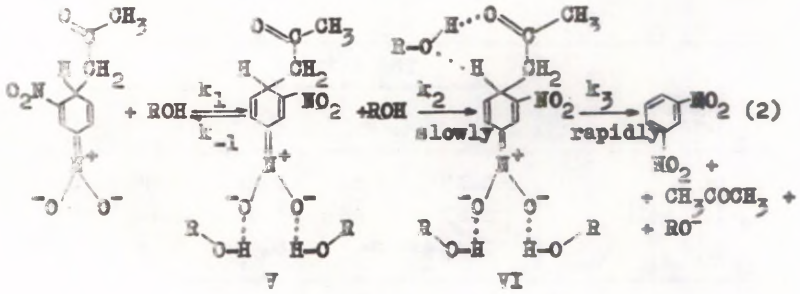


Fig. 3. Dependence of the Janowsky δ complex decomposition rate constant logarithm (1) on the molar fraction of THF (1) and acetone (2).

and then in both nitrogroups. If the solvation product (5) is attacked by a protic component of the solvent, a transition complex (6) will be formed, in which the C-C bond of

the tetrahedral carbon atom is weakened because of hydrogen bonds with water, which favors its shift from the formation of m-dinitrobenzene.



According to the given scheme, increasing of the amount of water in the solution leads to the growth of the Janowsky complex decomposition rate constant. The non-linear character of the log k dependence on the molar fraction of water seems to be caused by the shift of the solvation equilibrium to the right as well as by the σ complex stabilization owing to the hydrogen bonds (V). Evidently, at low concentrations of the protonic component in the binary system, the reaction rate is affected also by the ion-pair equilibrium (1) shift from the ion pairs to the solvated ions. The latter have turned out to be less reactive than the corresponding ion pairs. It is also proved by the fact that the Janowsky σ complex decomposition rate in tetrahydrofuran is due to the ion-pairing much higher than in acetone (Table 2), where the dissociation of the complex is practically completed.

Investigation into the THF-acetone system shows that with the increase of acetone percentage in the mixture, the decomposition trate constant of the complex is dropping parallel to the growth of its dissociation constant. Consequently, the introduction of the crown ether σ complex into the tetrafuran solution leads to the slowing-down of the process (Table 1). Moreover, the decomposition rate in acetone does not depend on the σ complex cation nature, while in THF it

Table 2

Constants of Decomposition and Dissociation Rates (Kd) and Dissociation Level of Janowsky б Complex in THF-Acetone System

Parameter	THF % in acetone				
	100	75	50	25	0
$k \cdot 10^5, s^{-1}$	4.15	3.56	2.21	0.99	0.26
$K_d \cdot 10^4$, mole	2.65	-	3.68	12.6	28.5
	0.32	-	0.45	0.66	0.77

remarkably rises during the transition from sodium chloride to rubidium chloride (Table 3). It has been shown conductometrically[1] that in the б complex THF solution the fraction of contact ion pairs will increase if the radius of the cation increases. Symbatic changing of the decomposition rate constant Na < K < Rb is in keeping with the assumption that the iron pairs participating in the б complex decomposition reaction are more active than its specifically solvated anions.

Table 3

Decomposition Rate Constants of Janowsky б Complexes ($k \cdot 10^5$ s^{-1}) in Tetrahydrofuran and Acetone

Cation of the complex	Na	K	Rb
THF	3.19	4.15	5.11
Acetone	0.381	0.379	0.373

It should also be pointed out that in the mixtures of acetone and alcohols, in case of a small proton-donating component content, the first order rate constant depends

linearly on the molar concentration of either alcohol or water[7].

Changes in the solvent's inner structure can also play a significant role in aqueous solutions. According to mechanism (2), the decomposition of the σ complex is caused by the action of the "free" water molecules. Therefore, its tendency towards self-association as well as the possibility to associate with aprotic components at $N_{H_2O} > 0.3$ (e.g. with acetone[8,9], DMSO[10]) weakens the effective concentration of the attacking agent in the system and causes the reaction to slow down. Formation of a three-dimensional structure in case $N_{H_2O} \geqslant 0.8$[11,12] leads to a smaller activity of water in the decomposition reactions of the σ complex.

The nature of a mixed solvent effect on the Janowsky σ complex kinetic and spectral characteristics concerns also the mixtures of water with acetone, acetonitrile or dioxane, studied earlier[2]. Bends have been found in the same concentration range ($N_{H_2O} \approx 0.3$ and 0.8).

Thus, the mechanism of the Janowsky σ complex decomposition reaction in a mixed solvent (protic-aprotic) remains unchanged in case of all systems studied. The observed kinetic regularities can be explained by the ion association and specific solvation effects as well as with the processes of structural formation in a binary solvent.

Experimental

The synthesis of the Janowsky σ complexes with cations of different alkaline metals was carried out according to the earlier described methods[13].

Solvents were purified and dried by the known methods[14]. The binary mixtures used were made mixing the corresponding volumes of water and THF. The decomposition reaction kinetics was studied at 25.0±0.1° C.

Kinetic data were treated according to the first order equation: $\log k = 2.303(\log A_1 - \log A_2)$.

In mixed solvents, electronic absorption spectra of the σ complex were taken on a spectrophotometer Specord -

-UV-Vis. The optic density in time was measured on a spectrophotometer SF-14.

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Organic Reactivity
Vol. 23 1(81) 1986

KINETIC STUDY OF ALKALINE HYDROLYSIS OF SUBSTITUTED PHENYL TOSYLATES. XV HYDROLYSIS OF m- AND p- SUBSTITUTED TOSYLATES IN CONCENTRATED AQUEOUS $n\text{-}Bu_4NBr$ SOLUTIONS.

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The kinetics of alkaline hydrolysis of m- and p- substituted phenyl tosylates $CH_3C_6H_4SO_2OC_6H_4\text{-}X$ (X=4-NO_2, 3-NO_2, 3-Cl,H) in 2.25 M solution of tetra-n-butylammonium bromide solution has been studied at 40, 50, 75 and 85°C and in 1 M $n\text{-}Bu_4NBr$ solution at 75°C.

The dependence on the tetra-n-butylammonium hydroxide concentration was also investigated (X=4-Cl, 3-NH_2, H). When passing from water to concentrated tetra-n-butylammonium bromide or hydroxide solutions the susceptibility towards the substituent effect ρ^o increases. So in 2.25 M $n\text{-}Bu_4NBr$ solution the $\rho^o_s - \rho^o_{H_2O}$ value was found to be about 0.9 units of ρ^o at 75°C.

It was found on the bases of data on the acidic dissociation of benzoic acids and phenols as well as on the alkaline hydrolysis of phenyl benzoates that the susceptibility towards the substituent effect (ρ^o) is increasing considerably when passing from water to the concentrated tetra-n-butylammonium bromide solutions [1-4].

At the same time, the additions of salts, like NaCl and $NaClO_4$ decrease the ρ^o value in comparison with the same value for water[5,6].

The purpose of the present work was to determine the ρ^o value in 2.25 M $n\text{-}Bu_4NBr$ solution, depending on temperature on the bases of the phenyl tosylates alkaline hydrolysis data set.

Experimental

The kinetics of the alkaline hydrolysis of substituted phenyl tosylates $CH_3C_6H_4SO_2OC_6H_4\text{-}X$ (X=4-NO_2, 3-NO_2, 3-Cl, H) in 2.25 M tetra-n-butylammonium bromide solutions was studied at 40, 50, 60, 75 and 85°C as well as in 1M $n\text{-}Bu_4NBr$ solution at 75°C .

The dependence of the rate constants on the tetra-n-butylammonium hydroxide concentration was studied at 75°C (X=4-Cl, 3-NH_2, H).

The preparation and characteristics of the phenyl tosylates studied[7] and the purification of hydroxide and tetra-butylammonium bromide have been described earlier[4].

The kinetic measurements were carried out under pseudo-monomolecular conditions. The process was followed spectrophotometrically using an apparatus CF-4 and CF-4A, equipped with a photoelectric multiplier and a LP type recorder.

The alkaline hydrolysis kinetics of phenyl tosylates $CH_3C_6H_4SO_2OC_6H_4\text{-}X$ was measured on the following wavelengths:

X	λ (nm)
4 - NO_2	410
3 - NO_2	430
3 - Cl	306
4 - Cl	300
3 - NH_2	295
H (unsubstituted)	296

The second order rate constants k_2 were calculated by dividing pseudofirst order rate constants k_1 by the alkali concentration. The measurements at each salt concentration

were repeated and the arithmetic means of the corresponding second order rate constants k_2 were calculated.

The rate constants $k(M^{-1} \cdot sec^{-1})$ for alkaline hydrolysis of phenyl tosylates $CH_3C_6H_4SO_2OC_6H_4$-X in the presence of n-Bu_4NBr additions are given in Table 1.

The analogous rate constants for various n-Bu_4NOH concentrations at 75°C are listed in Table 2.

The activation parameters E and log A calculated from the relationship between log k and $^1/T$ (Fig. 1) are given in Table 3.

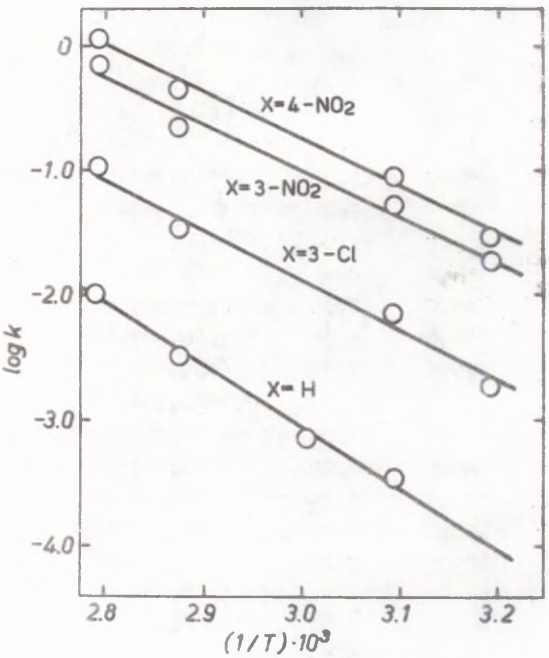

Fig. 1. Dependence of log k on $^1/T$ for alkaline hydrolysis of phenyl tosylates $CH_3C_6H_4SO_2OC_6H_4$-X in 2.25 M n-Bu_4NBr solution.

Table 1

Rate Constants k ($M^{-1} \cdot sec^{-1}$) for Alkaline Hydrolysis of Substituted Phenyl Tosylates $CH_3C_6H_4SO_2OC_6H_4$-X in the Presence of n-Bu_4NBr Additions (C_{OH^-} = 0.0658)

X	Temperature °C	C_{salt} (M)	k($M^{-1} \cdot sec^{-1}$)	n[M]	Notes
4-NO_2	40.0	2.25	$(3.11 \pm 0.34) \cdot 10^{-2}$	10	
	50.0	2.25	$(9.32 \pm 0.30) \cdot 10^{-2}$	5	
	75.0	2.25	$(4.16 \pm 0.07) \cdot 10^{-1}$	5	
			$(3.82 \pm 0.40) \cdot 10^{-1}$	5	C_{OH^-}=0.0329
		1.00	$(1.86 \pm 0.09) \cdot 10^{-1}$	4	
	85.0	2.25	1.13 ± 0.06	4	
3-NO_2	40.0	2.25	$(1.80 \pm 0.11) \cdot 10^{-2}$	6	
	50.0	2.25	$(6.25 \pm 0.27) \cdot 10^{-2}$	5	
	75.0	2.25	$(1.99 \pm 0.19) \cdot 10^{-1}$	4	
		2.25	$(2.58 \pm 0.34) \cdot 10^{-1}$	4	C_{OH^-}=0.0329
		1.00	$(8.16 \pm 0.25) \cdot 10^{-2}$	5	
	85.0	2.25	$(7.61 \pm 0.22) \cdot 10^{-1}$	5	
3-Cl	40.0	2.25	$(1.99 \pm 0.10) \cdot 10^{-3}$	4	
	50.0	2.25	$(7.22 \pm 0.50) \cdot 10^{-3}$	4	
	75.0	2.25	$(3.47 \pm 0.16) \cdot 10^{-2}$	3	
			$(3.48 \pm 0.70) \cdot 10^{-2}$	3	C_{OH^-}=0.0329
		1.00	$(1.39 \pm 0.31) \cdot 10^{-2}$	4	
	85.0	2.25	$(1.09 \pm 0.08) \cdot 10^{-1}$	4	
H	50.0	2.25	$(3.55 \pm 0.26) \cdot 10^{-4}$	3	
	60.0	2.25	$(7.37 \pm 0.23) \cdot 10^{-4}$	4	
	75.0	2.25	$(3.30 \pm 0.31) \cdot 10^{-3}$	4	
			$(2.34 \pm 0.54) \cdot 10^{-3}$	5	C_{OH^-}=0.0329
		1.00	$(1.10 \pm 0.24) \cdot 10^{-3}$	5	
	85.0	2.25	$(1.04 \pm 0.05) \cdot 10^{-2}$	4	

[M] Number of parallel measurements at the salt concentration considered.

Table 2

Rate Constants k ($M^{-1} \cdot sec^{-1}$) for Alkaline Hydrolysis of Substituted Phenyl Tosylates $CH_3C_6H_4SO_2OC_6H_4$-X in Case of Various n-Bu_4NOH Concentrations at 75°C

X	c_{OH^-}	$10^3 \cdot k$ ($M^{-1} \cdot sec^{-1}$)	Notes
4-Cl	0.0111	19.5±0.1	
	0.0557	19.2±1.2	
	0.378	11.5±1.2	
H	0.0121	5.71±0.11	
		6.82±0.24	c_{NaOH} = 0.015-0.075[5]
	0.0658	5.08±0.13	
	0.378	3.39±0.02	
	0.581	2.15±0.31	
3-NH_2	0.0658	3.16±0.23	
		4.83±0.22	c_{NaOH} = 0.04-0.10[5]
	0.378	1.08±0.05	
	0.658	0.386±0.005	

Table 3

Values of log A and E for Alkaline Hydrolysis of Substituted Phenyl Tosylates $CH_3C_6H_4SO_2OC_6H_4$-X for 2.25 M Aqueous n-Bu_4NBr and Water[8] (C_{OH^-} = 0.0659)

X	2.25 M n-Bu_4NBr				Water	
	log A	E(kcal/mole)	s^o	r	log A	E(kcal/mole)
H	11.55± ±1.10	22.15± ±1.70	0.152	0.988	8.47± ±0.21	16.85± ±0.31
	10.29± ±1.41[x]	21.76± ±2.18[x]	0.199	0.981		
3-Cl	10.28± ±1.09	18.40± ±1.66	0.179	0.983	8.64± ±0.25	16.13± ±0.38
3-NO_2	9.90± ±1.64	16.60± ±2.50	0.296	0.955	8.15± ±0.20	14.35± ±0.29
	10.11± ±1.37[x]	16.81± ±2.07[x]	0.243	0.970		
4-NO_2	10.22± ±0.87	16.75± ±1.38	0.157	0.988	8.47± ±0.15	14.61± ±0.23

x At calculation of log A and E values the data for C_{OH^-} = 0.0329 were included

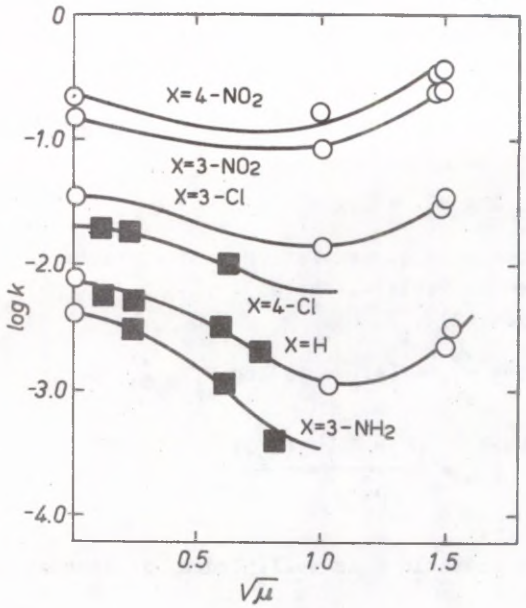

Fig. 2. Dependence of log k on $\sqrt{\mu}$ for alkaline hydrolysis of phenyl tosylates $CH_3C_6H_4SO_2OC_6H_4$ - X at 75°C.

○ - in presence of Bu_4NBr
■ - in presence of Bu_4NOH

Discussion

The dependence of log k on $\sqrt{\mu}$ for the alkaline hydrolysis of substituted phenyl tosylates in presence of n-Bu_4NBr and Bu_4NOH at 75°C is shown in Fig. 2.

Dependences of log k on $\sqrt{\mu}$ go through the minimum which is observed at 1 M electrolyte concentration. When passing from water to the 1 M concentration of tetra-n-butylammonium bromide, solution in the case of all phenyl tosylates negative salt effects were detected, whose values increased with a decrease in the ρ_s^o value for the corresponding substituted

phenyl radical. In the case of tetra-n-butylammonium hydroxide concentrations studied, the dependence of log k on $\sqrt{\mu}$ coincide with a similar curve for tetra-n-butylammonium bromide additions.

The ρ°_{s} and $(\log k^{\circ}_{s})_{calc}$ values found according to equation

$$\log k^{x}_{s} = \log k^{\circ}_{s} + \rho^{\circ}_{s} \sigma^{\circ}_{x} \qquad (1)$$

for various salt concentrations and at various temperatures are listed in Table 4. The a_{js}, $\rho^{\circ}_{H_2O}$ and b_{js} values found by equation (2)

$$\log k^{x}_{js} = (a_{js} + 1) \log k^{x}_{j(H_2O)} + b_{js} \qquad (2)$$

where

$$a_{js} = \frac{\rho^{\circ}_{js} - \rho^{\circ}_{j(H_2O)}}{\rho^{\circ}_{j(H_2O)}}$$

are given in Table 4 as well. Index j denotes reaction and s- medium.

The additions of n-Bu_4NBr to aqueous solution increases the ρ° value for the alkaline hydrolysis of phenyl tosylates in comparison with the same value for water (see Fig. 3, Table 4). For 2.25 molar n-Bu_4NBr solution (corresponds to 6.6 molal solution)

$$\Delta\rho^{\circ}_{s} = \rho^{\circ}_{s} - \rho^{\circ}_{H_2O} \approx 0.9$$

at 75°C.

It follows from the data given in Table 4 that the ρ°_{s} value as well as the $\rho^{\circ}_{H_2O}$ value itself considerably depends on temperature, changing by 0.47 units of ρ° in the temperature range from 50°C to 85°C. At the same time the ρ°_{s} value in the same temperature range decreases only by 0.23 units of ρ°.

An analogous increase in the ρ° value when passing from water to 7.75 molal n-Bu_4NBr solution was found for alkaline hydrolysis of phenyl benzoates[4], acidic dissociation of aromatic carboxylic acids and phenols[3,5] (see Fig. 4, Ta-

Table 4

Values of $\rho^{\circ}_{H_2O}$, ρ°_{s}, $(\log k^{\circ}_{s})_{calc}$, s°, $\Delta\rho^{\circ}$, a_{js}, $\rho^{\circ}_{H_2O}$ and b_{js}

Temperatura °C	$\rho^{\circ}_{H_2O}$	ρ°_{s}	$(\log k^{\circ}_{s})_{calc}$,	s°*	$\Delta\rho^{\circ}$	a_{js}, $\rho^{\circ}_{H_2O}$**	b_{js}**	Notes
			Alkaline hydrolysis of phenyl tosylates**					
50	1.85 ±0.04	3.01±0.18	-3.382±0.104	0.120	1.16	1.05	1.267±0.295	
75	1.74 ±0.05	2.54±0.09	-2.457±0.051	0.070	0.80	0.74	0.560±0.137	
		2.66±0.09	-2.514±0.052	0.069	0.92			1)
		2.75±0.11	-2.580±0.052	0.069	1.01			C_{OH^-} = 0.0329
		2.66±0.12	-2.920±0.071	0.075	0.92			
85	1.61 ±0.07	2.54±0.09	-1.950±0.053	0.072	0.93	0.88	0.842±0.060	
			Alkaline hydrolysis of phenyl benzoates[4]					
50	1.12 ±0.06	2.02±0.051			0.90			
			Acidic dissociation of benzoic acids[3,5]					
25	0.944±0.017	2.09±0.08			1.15			
			Acidic dissociation of phenols[3,5]					
25	2.36 ±0.06	3.27±0.091				0.91		2)

* s° - Standard error when calculating values of ρ°_{s} according to equation (1)

** Concentration of n-Bu_4NBr = 2.25 M (6.6 molal solution)
and n-Bu_4NOH = 0.0659 M

Table 4 continued

Notes

1. The k values for C_{OH^-} = 0.0325 were included when calculating the ρ_s^o value
2. 7.75 molal solution of n-Bu_4NBr

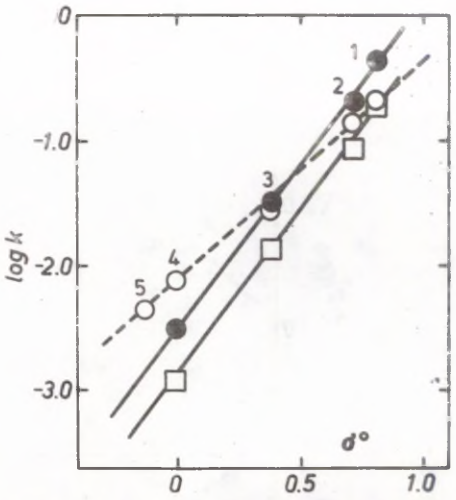

Fig. 3. Dependence of log k on σ° for alkaline hydrolysis of phenyl tosylates $CH_3C_6H_4SO_2OC_6H_4$-X at 75°C,

○ - in water

● - in 2.25 M n-Bu_4NBr solution

□ - in 1 M n-Bu_4NBr solution

1. X = 4-NO_2, 2. X = 3-NO_2, 3. X = 3-Cl, 4. X = 4, 5. X = 3-NH_2

ble 4):

$$\rho_j^{\circ}(Bu_4NBr) = (1.11\pm0.19) + (0.93\pm0.11)\rho_j^{\circ}(H_2O) \qquad (3)$$

$n/n_0 = 6/6$, $s = 0.132$, $r = 0.956$

Both activation energy E and log A considerably increase when passing from water to the 2.25 M solution of Bu_4NBr (see Table 3). Activation energy E for unsubstituted derivative grows by 5 kcal/mole.

In case of the multiple regression treatment of log k values for alkaline hydrolysis of phenyl tosylates in 2.25 M Bu_4NBr solution at various temperatures, according to equation

$$\log k_T^X = \log k_0^{\circ} + C_X\sigma_X^{\circ} + C_T(1/T) + C_{XT}\sigma_X^{\circ}(1/T) \qquad (4)$$

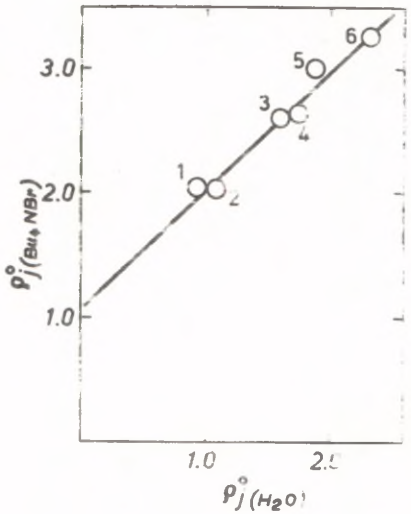

Fig. 4. Relationship between ρ°_{j} (Bu_4NBr) and $\rho^{\circ}_{j}(H_2O)$

1. Acidic dissociation of X-C_6H_4COOH at 25°C.
2. Alkaline hydrolysis of $C_6H_5COOC_6H_4$-X at 50°C.
3. Alkaline hydrolysis of $CH_3C_6H_4SO_2OC_6H_4$-X at 85°C.
4. The same reaction at 75°C
5. The same reaction at 50°C
6. Acidic dissociation of X-C_6H_4OH at 25°C

the term $C_X\delta^{\circ}_X$ was excluded as statistically insignificant. The obtained equation can be written as follows:

$$\log k^X_T=(10.27\pm0.57)-(4.417\pm0.195)(1/T)+(0.933\pm0.031)\delta^{\circ}_X(1/T) \quad (5)$$

$$n/n_0 = 16/16,\ s^{\circ}=0.119,\ r = 0.993$$

In case of water the analogous equation can be represented as:

$$\log k^X_T=(8.37\pm0.12)-(3.645\pm0.038)(1/T)+(0.594\pm0.062)\delta^{\circ}_X(1/T) \quad (6)$$

It follows from relationships

$$E^X = 2.3R(C_T + \rho_{xT}\sigma^o_{xT}) \quad (7)$$

$$\log A^X = \log k^o_0 + C_x \sigma^o_x \quad (8)$$

that activation energy in the 2.25 M Bu_4NBr solution depends a bit more on substituent than in the case of water. At the same time, the dependence of free activation energy on the substituent is completely caused by the changes in activation energy, i.e., the reaction studied corresponds to the isoentropic relationship like in water.

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Organic Reactivity
Vol. 23 1(81) 1986

AN ATTEMPT OF QUANTITATIVE DESCRIPTION OF COMBINED TEMPERATURE AND SOLVENT EFFECTS FOR DIENE CONDENSATION

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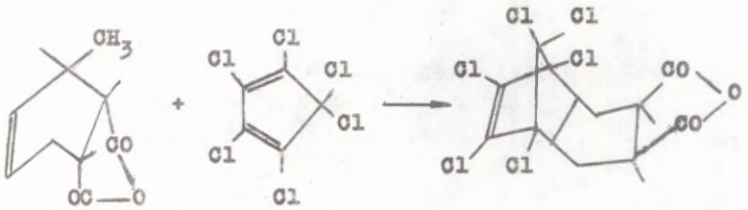
Kinetic data for the diene condensation reaction of hexachlorocyclopentadiene with the anhydride of cis,cis-3-methyl-4-cyclohexene -1,2-dicarboxylic acid in seven solvents at different temperatures have been processed. The negligible contribution of the specific solvation is established. Data for five solvents are represented by the equation which takes into account the contribution of the polarity and polarizability terms into both enthalpy and entropy terms of the total medium effect. The reaction under consideration belongs to the isokinetic ones with close isokinetic temperatures in case of polarity and polarizability effects of the medium.

The data for DMSO are incompatible with the equation for the five solvents. As to benzoic aldehyde, rather large deviations are observed in case of four temperatures of the total five covered by the experimental values of rate constants.

It has been established in the previous studies[1-12] of the diene synthesis reaction that the solvent effects are rather insignificant[7-12] in case of this process. This agrees with the molecular mechanism accepted [13,14] for this reaction. According to this point of view, the activated state could be represented by the charge transfer complex between the addends with an insignificant degree of charge separation[15].

Corresponding data for the reactions with participation of hexachlorocyclopentadiene (HCCPD) are rather scarce[5,11,16,17]. Nevertheless, the rate constants for the reaction between HCCPD and cis-, cis-3-methyl-4-cyclohexene--1,2-dicarbocylic anhydride (cis-, cis-3-Me-4-CHDA) have been determined for seven solvents at different temperatures[16,17]. For the anhydride cited, the reaction is considered[18] to be a stereospecific one and only the endo-exo-adduct is formed due to the bowsprit conformation of the methyl group:



The data for this reaction are reproduced in Table 1. A relatively narrow range of the medium and temperature effects is observed. The results of the least-square treatment of these data in the framework of the coordinates of the Arrhenius equation are listed in Table 2. For 5 solvents (2,3,5-7 from Table 1) the relationships of the log k values on the reverse temperature are linear without doubt. But in case of the benzoic aldehyde (4), a distinct break of the linearity at 130°C is observed and two crossing straight lines appear. For DMSO (1) only 3 experimental values at different temperatures are available, forming also a broken

line.

The combined effects of the medium and temperature could be represented in a most rough approximation by an isokinetic relationship, applied to the total solvent effect. The data available enable one to use a plot of E vs. log A, only.

Table 1.

The Values of the Rate Constant Logarithms for Diene Synthesis with Participation of HCCPD and Cis-,cis-Me-CMDA in Different Solvents and at Various Temperatures.

The estimated relative errors of rate constants range up to 5 per cent.

Temperature °C	log k for Solvents						
	DMSO	DMFA	Cyclohexane	C_6H_5CHO	C_6H_5Cl	Dioxane	Toluene
70	5.03	-	-	-	-	-	-
80	4.85	-	-	-	-	-	-
90	4.61	-	-	-	-	5.17	-
100	-	4.86	4.66	-	-	5.02	5.12
110	-	4.60	4.40	4.90	4.89	4.84	4.93
120	-	4.37	4.13	4.80	4.74	4.65	4.76
130	-	-	-	4.68	4.54	-	-
140	-	-	-	4.49	4.42	-	-
150	-	-	-	4.31	-	-	-

The linear dependence can be represented by the equation (the point for DMSO (1) is omitted):

$$E = (8.80 \pm 0.08) + (1.624 \pm 0.024) \cdot \log A, \text{ kcal/mole} \quad (1)$$

$$n = 6, \quad s = 0.11, \quad r = 0.9995$$

The point for DMSO deviates from this relationship by -1.0 kcal/mole.

The slope (1.624±0.24) of this line corresponds to the isokinetic temperature $\beta = 355 \pm 5°K$ (82°C). This value lies in the range of temperatures which can be obtained experiment-

Table 2

Values of Activation Parameters. The values calculated based on Equation (3) are obtained without using the data for DMSO and C_6H_6CHO

No	Solvent	log A		E		Temperatures taken into account
		Arrhenius equation	Equation (3)	Arrhenius equation	Equation (3)	
1.	DMSO	2.74±0.22	4.68±0.58	12.2±0.4	16.5±1.2	70, 80 and 90
		1.30		9.9		70 and 80
2.	DMFA	4.75±0.09	4.76±0.6	16.4±0.2	16.4±1.2	100, 110 and 120
3.	Cyclohexanone	5.86±0.17	4.43±0.5	18.4±0.3	15.9±1.1	100, 110 and 120
4.	C_6H_5CHO	1.27±0.59	4.16±0.5	10.9±1.1	15.9±1.1	110, 120, 130, 140 and 150
		-0.65±0.26		7.4±0.5		110, 120 and 130
		3.16±0.17		14.5±0.3		130, 140 and 150
5.	C_6H_5Cl	1.65±0.30	3.15±0.3	11.5±0.6	14.2±0.7	
6.	Dioxane	1.67±0.38	1.35±0.5	11.4±0.5	10.8±1.1	
7.	Toluene	2.09±0.40	1.41±0.5	12.31±0.06	11.2±1.1	

ally. Nevertheless, it is different from the mean value (113°C) of the temperatures represented by the data available.and one has no reason to conclude that the "error slope" (see Ref. 19) is observed.

An attempt can be made to describe the influence of separate terms (polarity (Y), polarizability (P), general acidity (E) and general basicity (B)) of the total medium effect in the framework of the corresponding general relationship[19,20]. There is not any single temperature value in case of which experimental data for all solvents studied would be available. Nevertheless, for 110 and 120°C the data cover all six solvents, with the exception of DMSO. The medium effect could be represented by equation:

$$\log k = \log k_0 + yY + pP + eE + bB \qquad (2)$$

The following values were accepted as the medium polarity and polarizability constants:

$$Y = (\varepsilon - 1)/(2\varepsilon + 1)$$

$$P = (n^2-1)/(2n^2 + 1)$$

The E values from paper[21] were used.

Either the original values (B_o)[20], can be used as the basicity constants B or the corrected ones (B_{corr})[22].

The values of solvent parameters used are listed in Table 3.

In the course of the data treatment the influence of the solvent parameters E and B turned out to be insignificant. The real measuring of the E values for the solvent set under consideration is difficult to explain (dioxane appears to be the most powerful acceptor). But the conclusion about the insignificance of the general basicity parameters needs some comments.

Exclusion of the general basicity scale results for 110°C in the increase of the standard deviation (s) from 0.010 (for B_{corr}) or 0.006 (for B_o) up to 0.015. For 120°C analogical figures are 0.040 or 0.026 and 0.049, respectively. The conclusion about the insignificance of this scale results

from the fact that only two statistical degrees of freedom are available. Therefore, proceeding from the data available there is no statistical reason to introduce the general basicity term of the medium not to mention the preference of the B_o-values in comparison with the B_{corr} ones. However, it is not fully guaranteed that the situation would not change if some additional data were obtained.

The values of parameters $\log k_o$, y and p and the corresponding statistics are listed in Table 4. The values of log k for DMSO calculated from these data strongly differ from those extrapolated to 110 and 120°C using the Arrhenius equation.

The simultaneous treatment of all the data available is possible in the framework of the equation which contains the products of the solvent parameters and the reverse temperature (of cross terms). The data were processed making use of the cross terms formed from the centered argument scales[23]:

Table 3.

Values of Solvent Parameters Used.

Nr.	Solvent	Y	P	B_o	B_{corr}	E
1.	DMSO	0.4848	0.2207	193	362	3.2
2.	DMFA	0.4798	0.2044	159	291	2.6
3.	Cyclohexanone	0.4601	0.2121	118	242	0.5
4.	C_6H_5CHO	0.4590	0.2402	105	180	-
5.	C_6H_5Cl	0.3775	0.2337	50	38	0.0
6.	Dioxane	0.2230	0.2094	129	237	4.2
7.	Toluene	0.2395	0.2263	54	58	0.0

$$\log k = \log k_o + C_1Y + C_2P + C_3B + C_nQ + C_5(Y-\bar{Y})(Q - \bar{Q}) +$$
$$+ C_6(P-\bar{P})(Q-\bar{Q}) + C_7(B - \bar{B})(Q - \bar{Q}), \qquad (3)$$

where $Q = 1000/T$ and $\bar{Y}$, $\bar{P}$, $\bar{B}$ and $\bar{Q}$ denote the mean values

Table 4

Results of the Data Treatment at 110 and 120°C According to Equation (2).

Parameter[a]	Scaling			
	Normed		Natural	
	110°C	120°C	110°C	120°C
log k_o			-3.41±0.119	-2.48±0.34
y	0.62±0.05	0.50±0.12	0.75±0.06	0.82±0.19
p	-0.78±0.05	-0.85±0.12	-7.55±0.48	-11.1 ±1.5
Stand. dev-n	0.12	0.28	0.015	0.05

a/ Parameters s and b are statistically insignificant

of the corresponding parameters for the solvents' set used.

During the processing of the data listed in Table 1, according to equation (3), the points for DMSO at 80 and 90° and for benzaldehyde at 140 and 150° were excluded as significantly deviating on the risk level of 0.03. The parameter C_3 appeared to be statistically insignificant and the standard deviation equals 0.025 and 0.036 in case B_o or B_{corr} values were used, respectively.* These results lead to the conclusion that the isokinetic temperature for the basicity scale is indistinguishable from the mean temperature of the experiment. Besides that, for DMSO and benzaldehyde unreasonably low values of activation energy (less than 5 kcal/mole) and negative values of log A are predicted. All this gives rise to the assumption that the formal significance of the B-scale is caused by the possibility to describe better the

* When using B_{corr}, the value of C_5 is insignificant, too; the point for DMSO at 80°C is not excluded while that for benzaldehyde at 130°C is excluded.

points for DMSO and benzaldehyde otherwise incompatible with the remaining data.

Actually, if the data for those two solvents are excluded from the set processed, both coefficients, C_3 and C_7, appear to be insignificant in equation (3). As a result, the medium basicity does not remain among the factors influencing the reaction rate. The corresponding values of parameters and the statistics are listed in Table 5.

Table 5.

Results of Data Processing According to Equation (3). Points for DMSO and Benzaldehyde are Omitted.

Coefficients for all terms containing E or B values are statistically insignificant. Total number of data points in set equals 17.

Parameter	Scaling	
	Normed	Natural
$\log k_0$	-	4.56 ± 0.34
C_1	0.34 ± 0.03	0.88 ± 0.08
C_2	-0.35 ± 0.03	- 8.6 ± 0.8
C_4	-0.90 ± 0.03	- 2.98 ± 0.11
C_5	-0.14 ± 0.03	- 4.9 ± 1.0
C_6	0.11 ± 0.03	31.8 ± 8.5
γ	-	0.3494
F	-	0.2177
σ	-	2.585
Stand. dev.-n	0.11	0.031
SPUR[a]	0.39	

[a] The value of the trace of the reverse correlation matrix divided to the total number of rows (experimental points) in the set. It is a characteristic showing the magnitude of the "overpumping" effect (of nonorthogonality). The values of SPUR < 1 correspond to the practical absence of this effect.

The experimental values of log k for DMSO deviate from the calculated ones, proceeding from these parameters, by 0.76, 0.65 and 0.61 log units at 70, 80 and 90°C, respectively. For the benzaldehyde solution the corresponding deviation range is -0.014, -0.10, -0.17, -0.14 and -0.12 log units at 110, 120, 130, 140 and 150°C, respectively.

The values of activation parameters calculated proceeding from these parameters are listed in Table 2.

Using the parameters of Table 5, the isokinetic temperatures for polarity and polarizability scales could be calculated, as follows:

$$\beta_y = 362 \pm 29^\circ K \ (89^\circ C)$$

$$\beta_p = 372 \pm 37^\circ K \ (99^\circ C)$$

In their uncertainty range, these values are indistinguishable from each other as well as from the isokinetic temperature (82°C) for the total solvent effect cited above.

The parameters given in Table 5 were used for calculation of the values of parameters and their standard deviations of the equation with cross terms formed from natural (noncentered) argument scales:

$$\log k = (18.01 \pm 4.86) + (13.6 \pm 2.6)Y - (90.7 \pm 21.9)P + \\ + (8.19 \pm 1.88)Q - (4.9 \pm 1.0)QY + (31.8 \pm 8.5)QP \qquad (4)$$

Discussion.

Equation (3) with the values of the parameters from Table 5 accurately enough describes the data for 5 solvents. The medium effect is caused by the combined influence of the polarity and polarizability. The relative contributions of those two effects at the mean experimental temperature are represented by the corresponding values of the normed coefficients $y = 0.34$ and $p = -0.35$. The tendency towards the mutual compensation of the corresponding effects is observed in the result of the increase of both medium parameters. Therefore the most prominent relative medium effects could be observed when the

polarity increases and the polarizability simultaneously decreases (and vice versa). For example, in the case of chlorobenzene, the total calculated relative solvent effect using toluene as standard, equals 0.08 (0.02) log units, being the algebraic sum of the polarity and polarizability terms, equal 0.15 and -0.07 units, respectively. But for DMFA and cyclohexanone (at 120°C) both terms have the same signs (polarity increases and polarizability decreases, when compared with toluene): 0.20 + 0.20 = 0.40 (0.39) and 0.18 + 0.13 = = 0.31 (0.36), respectively. In parentheeis, the corresponding differences between the experimental values of log k for the given solvent and toluene are given.

At mean values of the temperature, polarity and polarizability (for the range studied) the calculated total medium effect equals -1.56 units. Contributions of the polarity and polarizability into this value range to 0.307 and -1.87, respectively. The value of log k extrapolated for the mean experimental temperature (113.7°C) equals -3.14 in case of gas phase. It can be concluded from these figures that the substitution of the condensed phase for the gas phase brings about the drop of reaction rate (a 1.5 powers of ten), caused by the increase of the medium polarizability. This effect exceeds the opposite one, related to the increase of the medium polarity. The deviations cited above for the experimental points for DMSO, from the log k values predicted by equation (3) show that the rate constants measured for this medium should rather be related to some different process or pathway than it is in the case of the five solvents used for the parametrization of equation (3). The data for benzaldehyde at 120 ÷ 150°C may testify to the presence of another process whose distorting influence becomes significant in this temperature range. An analogous conclusion may be drawn from the characteristic break of the Arrhenius plot cited above.

In general, the results of processing of the data from Table 1 show that the reinvestigation of the kinetics for two solvents cited as well as the data for a more numerous solvent set and broader temperature range are needed.

Technique of Data Processing

For the statistical data treatment the automatic procedure of multiple regression analysis was used. The corresponding program written by one of the authors of this paper in FORTRAN for a computer "Norsk Data 100" was employed. A more detailed description of this procedure will be published separately.

The detection of the significantly deviating rows (points) on the given risk level is performed using the values of the statistics obtained as a result of the data processing of the set from which the point under consideration is excluded.

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