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THERMOCHEMICAL STUDY OF ELECTRON DONOR-ACCEPTING POWER OF ETHYLENEDIAMINE IN SOLUTIONS

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Heats of mixing of ethylenediamine with various substances whose electron-donating and electron-accepting powers are known were determined. The conclusion is drawn that ethylenediamine possesses high electron-donating and low electron-accepting power. The donor number is estimated as 50^{+3} .

Ethylenediamine (ETDA) is being extensively used now not only as a classical ligand which gives stable complexes with heavy metal ions, but also as a solvent with considerable basicity, for example for activation of cellulose and other polymers [1,2]. Due to its structure ETDA may act as a donor of electrons (unshared electron pair of nitrogen) and as an acceptor (hydrogen bond via NH_2 protons). In order to elucidate the reactivity of ETDA, the mechanism of processes occurring in this solvent and the nature of its compounds it is necessary to estimate its electron donor-accepting power. We chose the thermochemical method which is widely used in the study of coordination compounds in non-aqueous media [3,4].

The enthalpies of mixing of EDTA with various substances were determined to within $\pm 1.5\%$ in an adiabatic calorimeter under dry nitrogen or vacuum at 298°K according to the technique described in [5,6]. EDTA, organic solvents, and organoelement compounds were purified and

dehydrated following literature methods /7,8/, Fischer's method was used to determine the presence of water. Wood cellulose (crystallinity $\alpha = 65\%$ /1/) and polyvinyl alcohol (acetate group content 1.28%, molecular weight 40,000) (PVA) were dried under vacuum at 373°K and 340°K , respectively.

The most popular scale of donor numbers is based on the comparison of ethalpies of mixing of solvent with antimony pentachloride in dichloroethane /9/. In the case of EDTA this method presents considerable difficulties on due to the intensively proceeding reaction. Following Refs.10,11 we estimated the donor power of EDTA from enthalpies of mixture with chloroform (Fig.1, Table 1).

Table 1
Enthalpies of Mixing of Ethylenediamine with Chloroform
at 298°K

mol %	ΔH cal/mole of mixt.	mol%	ΔH cal/mole of mixt.
10	-160	60	-580
20	-300	70	-570
30	-400	80	-420
40	-500	90	-260
50	-570		

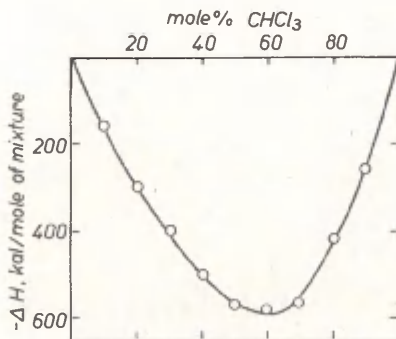


Fig.1 Dependence of EDTA enthalpy of mixing with CHCl_3 on chloroform concentration at 298°K

The enthalpy of mixing of ETDA with an excess of chloroform was -4.0 kcal/mole. Taking into account the association energy of pure ETDA, determined previously from enthalpy of dissolution in hexane, we estimated the energy of the hydrogen bond between ETDA and chloroform, -7.8 ± 0.5 kcal/mole. It is noteworthy that ETDA interacts with pentachloroethane with a thermal effect of -21.5 kcal/mole at component ratio of 1:1. Such a large thermal effect may be due to formation of salt $[\text{H}_2\text{N}(\text{CH}_2)_2\text{NH}_3]^+\text{C}_2\text{Cl}_5^-$ or $[\text{H}_2\text{N}(\text{CH}_2)_2\text{NH}_3]^+\text{Cl}^-$. A considerable thermal effect was also observed when mixing ETDA with such acceptors as $(\text{C}_2\text{H}_5)_3\text{SnCl}$ (1:1) $\Delta H = -13.5$ (a) kcal/mole and $(\text{C}_4\text{H}_9)_3\text{SnCl}$ (1:1) $\Delta H = -11.8$ (1) kcal/mole. The enthalpies of mixing at component ratio of 1:2 were: with phenol -14.2 (s) kcal/mole; with tert.-butyl peroxide -8.8 kcal/mole (in this case side chemical processes of ETDA oxidation occur). A correlation between the enthalpies of mixing of the above acceptors with organic solvents and the donor numbers of solvents ($\text{DN}_{\text{SbCl}_5}$) was reported in /11-14/. Using this correlation we estimated the donor number of ethylenediamine from the data on enthalpy of mixing. $\text{DN}_{\text{SbCl}_5}$ for ETDA was found to be 50 ± 3 . Therefore ethylenediamine is a donor solvent with considerable basicity /15/.

The acceptor power of ethylenediamine was estimated by determining the enthalpies of mixing with organic solvents with the known donor power /9,14/. Enthalpies of mixing of ETDA at component ratio of 1:2 are listed in Table 2. As can be seen from the Table, ETDA does not form stable complexes through H-bonds even with such a strong donor of electrons as hexamethylphosphorus triamide. An exception is the enthalpy of mixture with acetone. In this case the following reaction presumably proceeds:

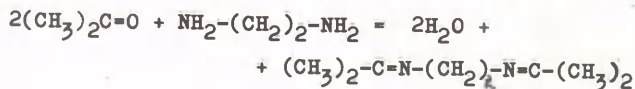


Table 2

Enthalpies of Mixing of Ethylenediamine with Organic Solvents with the Known Donor Power at the Component Ratio 1:1, 298°K

Solvent	ΔH cal/mole	Solvent	ΔH cal/mole
Nitromethane	+410	Dimethylformamide	-105
Acetonitrile	+180	Dimethylsulfoxide	-300
Diethyl ether	+780	Hexamethylphosphorus trisulfide	-300
Tributylphosphate	+890	Acetone	-10600
Diethylamine	+410		
Butylamine	+400		
Pyridine	+370		

Formation of quite stable coordination compounds is observed when mixing ETDA with hydroxyl-containing compounds possessing donor-accepting functional groups and prone to autoassociation by means of H-bonds. The obtained enthalpies of mixture with hydroxyl-containing substances at component ratio of 1:2 are given in Table 3. It follows from the experimental data that in these systems ETDA is an electron donor and alcohols and water are acceptors.

Table 3

Enthalpies of Mixing of Ethylenediamine with Hydroxyl-Containing Organic Solvents at the Component Ratio 1:2, 298°K

Solvent	ΔH cal/mole	Solvent	ΔH cal/mole
Methanol	-3450	tert.-Butanol	-1260
Ethanol	-2520	Phenol	-14200(e)
Ethyleneglycol	-5000	Water	-4250
Glycerol	-3660		

The same type of interaction is observed when mixing ETDA with hydroxyl-containing polymers, e.g. with cellulose and polyvinyl alcohol (Table 4, Figs. 2 and 3).

Table 4

Enthalpies of Mixing of Ethylenediamine with Polyvinyl Alcohol and of Water with Polyvinyl Alcohol at 298°K

PVA concn in conv.mol%*	ΔH cal/conv.mole of mixture	
	ETDA - PVA	H ₂ O - PVA
10	-200	-55
20	-390	-110
30	-580	-155
40	-760	-190
50	-950	-225
60	-1080	-255
70	-920	-280
80	-610	-290
90	-310	-175

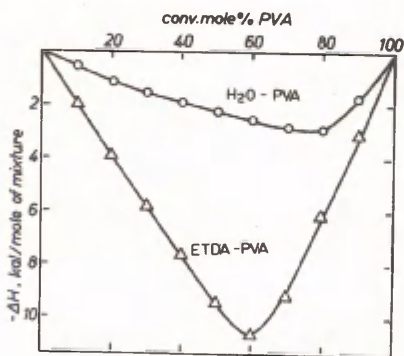


Fig.2 Dependence of enthalpy of mixing of ethylenediamine with polyvinyl alcohol and of water with polyvinyl alcohol on mixture composition at 298°K

The molecular weight of the repeating polymer unit is taken as a conventional mole.

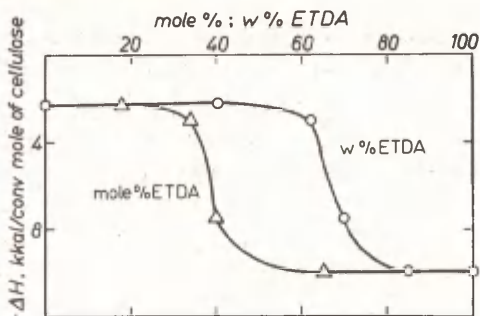


Fig.3 Dependence of the enthalpy of swelling of cellulose on the composition of the water-ethylenediamine mixture at 298°K

Swelling of cellulose in ETDA and its aqueous solutions has been studied in several works [1,16], and it has been shown that considerable swelling takes place only when ETDA content exceeds 62 w/w and is accompanied by reduction of crystallinity. As can be seen from Fig.3, the enthalpy of cellulose swelling in ETDA (-62.5 kkal/g, -10.1 kkal/conv.mole) is considerably higher in absolute value than in water (-14.5 cal/g, 1.35 kkal/conv.mole); water does not interact with the crystalline regions in cellulose [1,17]. The enthalpy of cellulose swelling in aqueous solutions has a region of sharp variation in the range of 60-70 w/w (30-40 mol%) of ETDA. Evidently the presence of ETDA in excess of the composition of complex $\text{ETDA} \cdot 2\text{H}_2\text{O}$ facilitates formation of cellulose complexes and its swelling. A similar pattern is observed when mixing EDTA and water with PVA. The enthalpy of mixture of PVA with an excess of ETDA (-1770 cal/conv.mole) exceeds in absolute value the corresponding value for water (-540 cal/conv.mole). The concentrational dependence of enthalpy of mixing of PVA with water at 298°K displays a maximum at the concentration of devitrification or the region of limited solu-

bility (at given temperature) /18/. In the case of PVA - ETDA mixtures the factor determining the enthalpy of mixing is ETDA-PVA complex formation at molar ratio 2:1.

Hence, the thermochemical method makes it possible to estimate the electron donor-accepting power of ethylenediamine and therefore its ability to form coordination compounds in solutions. The donor number of ETDA at 50^{±3} characterizes it as a donor solvent with considerable basicity.

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THE VALUES OF THE RITCHIE PARAMETERS FOR THE
NUCLEOPHILE - MIXED SOLVENT SYSTEMS

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The kinetics of the formation of triarylcannabinol methyl ethers from triarylmethylcations in mixed solvents is studied. The values of parameters N^+ for nucleophilic systems, such as NaOH/water-organic solvent and CH_3ONa /methanol-organic solvent, are determined.

At the present the Ritchie equation (I) finds wide application in the correlation analysis¹⁻³. The equation connects reactivity of the organic cations with nucleophilic parameters, N^+ , of the nucleophile-solvent system⁴⁻⁶:

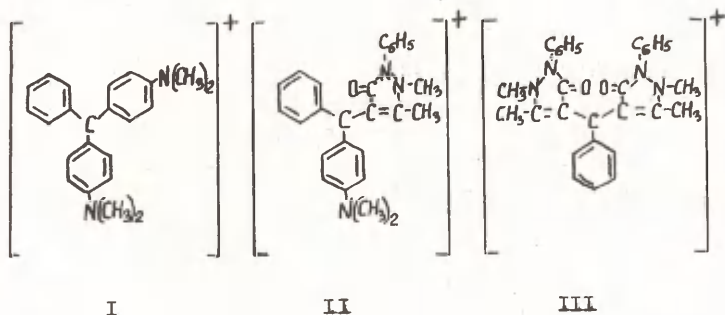
$$\lg k_i = \lg k_{i,0} + N^+ \quad (I)$$

where k_i and $k_{i,0}$ are the rate constants for reactions of i -th cation with the given and standard nucleophilic systems, respectively.

According to Ritchie and coworkers^{5,7-9} the rate constants for the reaction of an electrophilic reagent with different nucleophilic systems can differ from one another by 13 orders of magnitude. Comparison of the experimental rate constants with the calculated ones (equation I) shows that they differ by not more, than one order of magnitude.

The purpose of the present work is to study the possibility of application of the Ritchie equation for nucleophile-mixed solvent systems. The kinetics of the formation

of triarylecarbinol methyl ethers from the cations of Malachite Green (I), Antipyrine Red (II), and Antipyrine Orange (III) was studied in the systems consisting of sodium methylate and mixtures of methanol with (1) acetonitrile, (2) dioxane, and (3) dimethylsulfoxide (DMSO). Table I lists the results obtained.



The values of N^+ were calculated by using the data of Table I by equation (2):

$$N_s^+ = N_m^+ + (\lg k_s - \lg k_m) \quad (2)$$

where s and m are indexes of mixed solvents and methanol, respectively. The value of N^+ for nucleophilic system $^-OCH_3/CH_2OH$ was taken as equal to 7.68 IO .

Table 2 represents the values of N^+ for the nucleophilic systems $^-OCH_3$ /mixed solvent. The same Table lists parameters of nucleophilicity for the systems ^-OH /mixed solvent calculated by the analogous procedure using the data from Ref. 11, the value of N^+ for nucleophilic system $^-OH/H_2O$ being taken as equal to 4.75 IO .

We have checked the possibility to apply the obtained values N^+ for description of the reactivities of II and III by equation (1). As a result, the following equations were obtained:

Table I

The Rate Constants of the Formation of Triarylcarbinol Methyl Ethers in the Systems $\text{C}_6\text{H}_5\text{OCH}_3/\text{Methanol-Organic Solvent}$ (25°C)

Solvent	Content of methanol, %mass.	Rate constants, $\cdot 10^{-3} \text{ l./mol. sec}$		
		I	II	III
Aceto-nitrile-methanol	83.4	1.58	0.68	3.39
	76.4	1.60	-	3.44
	68.2	1.78	0.71	3.64
	58.9	2.02	0.84	3.98
	36.8	3.93	1.73	7.36
	10.1	24.2	17.0	33.6
Dioxane-methanol	60.0	3.89	2.69	10.0
	50.0	7.24	4.47	18.3
	40.0	12.6	7.24	24.0
	30.0	28.8	11.9	61.7
DMSO-methanol	72.5	3.52	1.39	8.15
	53.0	7.66	3.91	15.7
	50.0	9.44	6.50	18.5
	25.0	27.9	19.2	39.8

Table 2

The Values of N^+ for the Systems $\text{C}_6\text{H}_5\text{OCH}_3/\text{Binary Solvent}$

I	X_{N^+}	0.135 7.79	0.267 7.83	0.352 7.89	0.572 8.12	0.874 8.97
2	X_{N^+}	0.135 8.17	0.194 8.44	0.267 8.68	0.352 9.04	
3	X_{N^+}	0.135 8.13	0.267 8.47	0.291 8.56	0.551 9.03	
4	X_{N^+}	0.002 4.91	0.005 4.95	0.011 5.15	0.038 5.86	0.087 5.99

Note: 1. $\text{CH}_3\text{OH}-\text{CH}_3\text{CN}$; 2. $\text{CH}_3\text{OH}-\text{dioxane}$; 3. $\text{CH}_3\text{OH}-\text{DMSO}$;
4. $\text{H}_2\text{O}-\text{HMPA}$; $\text{X}-\text{m.p.}$ 2-nd component.

for Antipyrine Red (p-dimethylaminodiphenylantipyrilmethyl cation)

$$\lg k = -4.132 + 0.912 N^+ \quad (3)$$

$$\pm 0.158 \quad \pm 0.021$$

$$r=0.995; s=0.139; n=21.$$

the nucleophilic systems: $^-\text{OCH}_3(\text{CH}_3\text{OH}-\text{CH}_3\text{CN}, \text{CH}_3\text{OH-dioxane}, \text{CH}_3\text{OH-DMSO}), ^-\text{OH}(\text{H}_2\text{O-HMPA})$

for Antipyrine Orange (diantipyrilphenylmethyl cation)

$$\lg k = -3.536 + 0.911 N^+ \quad (4)$$

$$\pm 0.318 \quad \pm 0.038$$

$$r=0.989; s=0.068; n=15.$$

the nucleophilic systems: $^-\text{OCH}_3(\text{CH}_3\text{OH}-\text{CH}_3\text{CN}, \text{CH}_3\text{OH-dioxane}, \text{CH}_3\text{OH-DMSO}).$

The above analysis allowed us to state that, within the limitations, formulated elsewhere^{12,13}, the Ritchie equation can be applied for kinetic data obtained in systems nucleophile-mixed solvent.

As one can see the values of the slope in Eqns. (3) and (4) differ markedly from unity (see Eqn. 1) and depend on the nature of the electrophile. Thus, quite possible that this coefficient could be a quantitative measure of electrophilic properties of a substrate, e.g. triarylmethylcation. Similar idea was suggested in Ref. 14.

Thus, the scale of nucleophilicity parameters, N^+ , can be used to foretell the reactivity of organic cations not only in the individual solvents but in mixed solvents, too. It is noteworthy that the best quality of the correlation can be obtained by the two-parameter equation:

$$\lg k_i = \lg k_{i,0} + \alpha N^+ \quad (5)$$

where α is a value dependent on the nature of electrophile.

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**XIII. ALKYL AND ALKENYL ESTERS OF SULFONIC ACIDS.
ALCOHOLYSIS AND ALKALINE HYDROLYSIS OF ALKYL
AND ALKENYL ESTERS OF P-TOLUENESULFONIC ACID.**

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The alcoholysis kinetics of 1-methylallyl, 1-methylpropyl, 3-methylallyl, 3-methylpropyl and alkaline hydrolysis of allyl ester of p-toluenesulfonic acid in acetone-water system at the temperature range 0-70°C has been investigated. Reactivity of esters is shown to obey the Taft equation. By the analysis of dependences in coordinates $\lg k_{T_2} - \lg k_{T_1}$ it was found that the studied series was isokinetic. The effect of hydroxyl ion additions on the rate constant has been investigated. The mechanism of alcoholysis and hydrolysis is discussed from the viewpoint of the ion pair conception.

Continuing to investigate the reactivity of alkyl and alkenyl esters of aromatic sulfonic acids, we studied the alcoholysis kinetics of 1-methylallyl (1-MATS), 1-methylpropyl (1-MPTS), 3-methylallyl (3-MATS), 3-methylpropyl (3-MPTS) and alkaline hydrolysis of allyl ester of p-toluenesulfonic acid (ATS).

Esters were obtained acc. to Ref.1, alcohols were rectified acc. to Ref.2. The purity of esters was checked chromatographically and by titration of p-toluenesulfonic acid resulting from complete alcoholysis or hydrolysis. The alcoholysis kinetics was measured titrimetrically, conductometrically, and spectrophotometrically³ under pseudomonomolecular conditions at the ratio of ester:alcohol (0.01-0.001) : (1.0-2.5) mol/l. The working wavelength for 1-MATS and 1-MPTS was 225 nm, for

* The author for communications

3-MATS and 3-MPTS-261 nm . The reaction rate constants were calculated by first-order equations (1), (2) or (3) depending on the used method of study where

$$k_1 = \frac{2.303}{t} \lg \frac{b}{b-x} \quad (1)$$

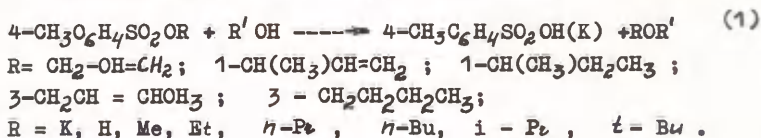
$$k_1 = \frac{2.303}{t} \lg \frac{\kappa_0 - \kappa_t}{\kappa_\infty - \kappa_t} \quad (2) \quad k_1 = \frac{2.303}{t} \lg \frac{D_0 - D_\infty}{D_t - D_\infty} \quad (3)$$

($b - x$) are changes in the ester concentration in time t ; $\kappa_0, \kappa_t, \kappa_\infty$ and D_0, D_t, D_∞ are, respectively, values of electroconductivities or optical density at the beginning of the reaction, in time t , and after the end of the reaction; t is time in sec.

The rate constant of alkaline hydrolysis was studied by titrimetric method. The rate constants were calculated by equation of second order (4), where ($a - x$) are changes in the alkali concentration in time t .

$$k_2 = \frac{2.303}{(a-b)t} \lg \frac{b(a-x)}{a(b-x)} \quad (4)$$

The reactions were controlled up to 80-90% of ester transformation. The rate constants of Tables 1-3 were calculated as arithmetical mean from 3-5 parallel measurements. The accuracy of estimation of the obtained results, the calculation of thermodynamic parameters and other calculations were carried out by the least squares method on a "Minsk-22" computer with reliability of 0.95. The reaction of esters with water, alcohols and KOH in aqueous acetone proceeds quantitatively and irreversibly according to the scheme (1):



Special tests have shown that alcoholysis of esters has the first order in ester. The order in alcohol was not checked since the kinetic study was carried out at constant al-

cohol concentrations (1 or 2.5 mol/l, depending on method), which considerably exceeded initial ester concentrations (0.01 - 0.001 M). Alkaline hydrolysis in acetone-water system obeys regularities of the second order reaction and is of the first order in ester and alkali. This is confirmed by the linearity of anamorphosis of Eqns. (2),(4) (Fig.1,2).

Irrespective of the methyl group location in α - or β -position in esters 1-MATS or 3-MATS the increase in the alcoholysis rate constant is essentially the same as against ATS⁴. In this case the same effect of R' in alcohols on the rate constants of both esters is observed. In passing from water to tert.-butyl alcohol the rate constant of 1-MATS decreases by the factor of 1786 at 50°C, the one of 3-MATS by the factor of 1700 (Tables 1-2). Thus, the methyl group in α or β position increases the resonance stability of the transition state in 1-MATS or 3-MATS as a result of α carbon atom P orbital overlapping with π electron pair of binary bond (bimolecular reaction) or increases the stabilization of a carbon ion owing to an interaction of vacant P orbital with π bond (monomolecular reaction) which leads to increase in 1-MATS reactivity over ATS. On the other hand, essentially the same influence of α or β methyl group on the rate constant increase indicates that methyl group in α - and β -position equally stabilizes both the transition state and the carbon ion⁵.

The reactivity of 1-MPTS and 3-MPTS depends markedly on the methyl group location. The methyl group in β -position does not practically influence the rate constant of 3-MPTS in comparison with propyl ester of p-toluenesulfonic acid (PTS)⁴. The methyl α -group increases considerably the reactivity of 1-MPTS in comparison with PTS and depends on R'-structure in alcohols. The rate constant of 1-MPTS in methanol is higher by 1471 times (40°C) and the one of tert.-butanol by 220 times than that of PTS. It is also observed that influence of R' in alcohols on the reactivity of 1-MPTS and 3-MPTS is different. The rate constant of 1-MPTS

T A B L E 1

Alcoholysis of 1-MATS and 1-MPTS in Alcohols R'OH

N°	$k_1 \cdot 10^4, 1/\text{sec}$			
	Alcoholysis of 1 - MATS			
	R'	30°	40	50°
1.	H	447 \pm 9	1380 \pm 32	4169 \pm 77
2.	Me	11.6 \pm 0.3	36.7 \pm 0.6	101 \pm 2
3.	Et	6.94 \pm 0.08	21.9 \pm 0.5	60.3 \pm 0.9
4.	n-Pr	3.89 \pm 0.85	12.3 \pm 0.2	33.9 \pm 0.6
5.	n-Bu	3.73 \pm 0.04	11.6 \pm 0.4	31.6 \pm 0.6
6.	i-Pr	2.18 \pm 0.03	6.90 \pm 0.1	19.0 \pm 0.4
7.	t-Bu	0.372 \pm 0.006	1.01 \pm 0.02	2.44 \pm 0.05
Alcoholysis of 1-MPTS				
N°	R'	40°	50°	60°
1.	H	968 \pm 29	2876 \pm 49	8110 \pm 120
2.	Me	12.8 \pm 0.4	38.0 \pm 0.5	103 \pm 2
3.	Et	5.54 \pm 0.08	16.6 \pm 0.3	45.0 \pm 0.6
4.	n-Pr	2.49 \pm 0.05	7.40 \pm 0.09	20.1 \pm 0.4
5.	n-Bu	2.23 \pm 0.05	6.61 \pm 0.09	18.1 \pm 0.3
6.	i-Pr	1.03 \pm 0.03	3.02 \pm 0.04	8.13 \pm 0.06
7.	t-Bu	0.132 \pm 0.002	0.331 \pm 0.005	0.772 \pm 0.010

TABLE 2

Alcoholysis of 3-MATS and 3-MPTS in Alcohols R'OH

N°	$k_1 \cdot 10^4, \text{sec}^{-1}$				
	Alcoholysis of 3-MATS				
	R'	20°	30°	40°	50°
1.	H	188 \pm 5	631 \pm 18	1950 \pm 62	5620 \pm 112
2.	Me	3.90 \pm 0.08	12.6 \pm 0.3	38.0 \pm 0.7	106 \pm 3
3.	Et	2.75 \pm 0.05	8.39 \pm 0.09	24.2 \pm 0.5	64.5 \pm 1.2
4.	Pr	1.67 \pm 0.03	5.10 \pm 0.08	15.1 \pm 0.4	41.3 \pm 0.8
5.	Bu	1.62 \pm 0.03	5.05 \pm 0.07	14.5 \pm 0.5	38.0 \pm 0.6
6.	i-Pr	1.26 \pm 0.04	3.68 \pm 0.07	10.1 \pm 0.2	25.9 \pm 0.4
7.	t-Bu	0.174 \pm 0.03	0.492 \pm 0.012	1.33 \pm 0.04	3.31 \pm 0.07
Alcoholysis of 3-MPTS					
N°	R'	$k_1 \cdot 10^6, \text{sec}^{-1}$			
		40°	50°	60°	70°
1.	H	31.2 \pm 0.08	92.3 \pm 1.2	242 \pm 4	591 \pm 10
2.	Me	1.05 \pm 0.02	3.04 \pm 0.08	8.16 \pm 0.09	20.6 \pm 0.4
3.	Et	0.720 \pm 0.010	2.04 \pm 0.06	5.38 \pm 0.07	13.5 \pm 0.4
4.	Pr	0.486 \pm 0.012	1.32 \pm 0.03	3.43 \pm 0.06	8.24 \pm 0.18
5.	Bu	0.477 \pm 0.009	1.29 \pm 0.02	3.23 \pm 0.07	7.53 \pm 0.20
6.	i-Pr	0.274 \pm 0.006	0.721 \pm 0.012	1.76 \pm 0.05	4.05 \pm 0.09
7.	t-Bu	0.0648 \pm 0.004	0.164 \pm 0.004	0.390 \pm 0.008	0.890 \pm 0.017

T A B L E 3

Bimolecular Rate Constants of Alkaline Hydrolysis of Allyl -p- Toluenesulfonate in
Aceton - Water System. $[\text{Ester}] = 0.01N$; $[\text{KOH}] = 0.02N$.

No	acetone -water (%)	$k_2 \cdot 10^3, \text{l. mol}^{-1} \cdot \text{sec}^{-1}$				
		10°	20°	30°	40°	50°
1.	100*	0.101	0.351	1.01	3.02	8.13
2.	90	0.123 ± 0.002	0.388 ± 0.009	1.16 ± 0.02	3.16 ± 0.08	8.30 ± 0.15
3.	80	0.145 ± 0.003	0.453 ± 0.008	1.35 ± 0.02	3.66 ± 0.07	9.55 ± 0.27
4.	70	0.156 ± 0.002	0.485 ± 0.008	1.47 ± 0.03	3.95 ± 0.12	10.6 ± 0.2
5.	60	0.243 ± 0.05	0.802 ± 0.012	2.51 ± 0.04	7.15 ± 0.21	19.4 ± 0.3
6.	50	0.459 ± 0.010	1.43 ± 0.03	4.42 ± 0.08	11.9 ± 0.2	32.4 ± 0.7
7.	40	0.823 ± 0.012	2.71 ± 0.04	8.51 ± 0.16	24.0 ± 0.6	65.3 ± 0.3
8.	30	1.89 ± 0.03	5.80 ± 0.10	17.6 ± 0.4	46.8 ± 0.9	125 ± 2
9.	20	3.15 ± 0.08	10.2 ± 0.2	30.6 ± 0.7	83.6 ± 1.8	216 ± 4
10.	10	4.23 ± 0.08	13.5 ± 0.3	43.2 ± 0.9	118 ± 5	333 ± 9
11.	0*	7.61	24.1	63.1	174	405

* Constants were obtained by extrapolation

in passing from water to tert.-butanol decreases at 50°C by the factor of 8690 and that of 3-MPTS by the factor of 236 only.

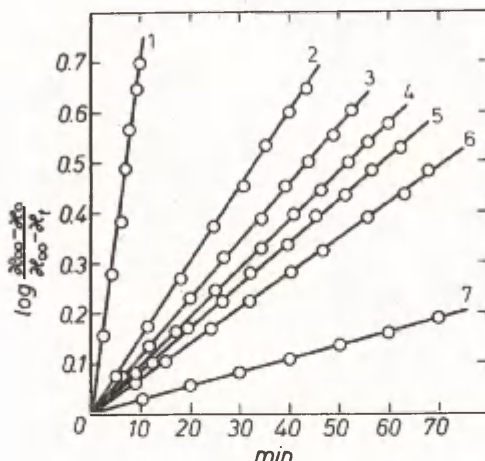


Fig.1. Plot of function $\lg \frac{H_{\infty} - H_t}{H_{\infty} - H_0}$ vs. time of alcoholysis of 3-MATS, 40°C. For numbers of lines see Table 2.

In order to determine the effect of electron-donating properties of alcohol nature on the alcoholysis rate the relationship $\lg k, -\sigma^*$ was studied by the Taft equation (5).

$$\lg k = \lg k_0 + \rho^* \sigma^* \quad (5)$$

The determination accuracy of ρ^* value characterizing the inductive effect of R' in alcohols for 3-MATS and 3-MPTS proved to be low (Fig.3), but we haven't succeed in finding some regularity for 1-MATS and 1-MPTS, since the sum of steric factors of R and R' does not effect the reaction rate. Therefore, the correlation by the expanded Taft equa-

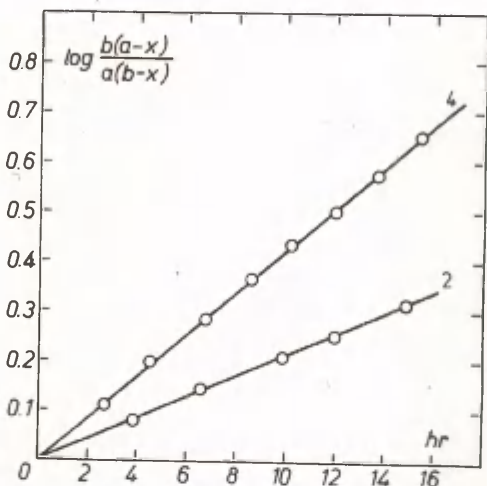


Fig.2. Plot of $\lg \frac{b(a-x)}{a(b-x)}$ vs. time for alkaline hydrolysis of ATS in acetone water system, at 30°C. For numbers of lines see Table 3.

tion which takes into account inductive and steric substituent effects (6) was carried out:

$$\lg k = \lg k_0 + \rho^* \sigma^* + \delta E_s^{\circ} \quad (6)$$

The satisfactory correlation by equation (6) (Fig. 4, 5) has been obtained, but the comparison of ρ^* and δ values indicates that the radical R' inductive effect prevails in alcohols with 3-MATS and 3-MPTS alcoholysis. The ρ^* value exceeds the value of δ more than by 7 times. The positive sign of ρ^* constant indicates the reaction rate decrease with increase in electron-donating characteristics

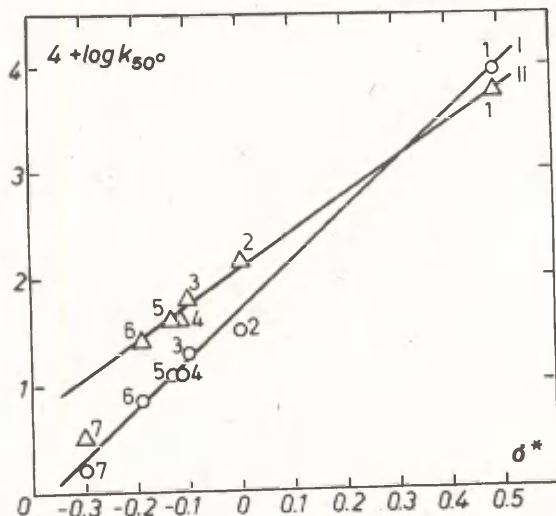


Fig.3. The dependence $\lg k_1 - \sigma^*$ of 3-MATS (I)
and 3-MPTS (II) alcoholysis
I - $\gamma 0.975$; $\beta^* 4.759$; $S_0 0.123$
II- $\gamma 0.953$; $\beta^* 4.014$; $S_0 0.285$
For numbers of lines see Table 2.

of R radical in alcohol molecule, i.e. the reaction rate constant decreases with increase in electronegative charge of hydrogen atom in the alcohol molecule and increases with positive charge increase in hydrogen atom. Therefore, in the alcoholysis reaction of alkyl and alkenyl esters on sulfonic acids alcohol behaves as an electrophilic reagent.

The rate constant temperature dependences of alcoholysis and alkaline hydrolysis over the studied temperature range fit the Arrhenius and Eyring equations ($\gamma 0.998 - 0.999$, $S_0 0.021 - 0.043$). The activation parameter values of the

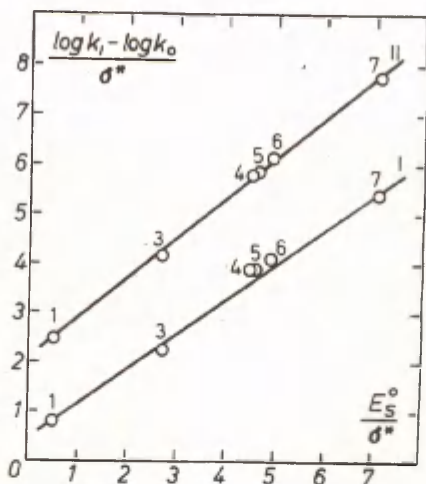


Fig.4. The dependence $\frac{\lg k_1 - \lg k_0}{\delta^{\ddagger}} - \frac{E_s^0}{\delta^{\ddagger}}$ of

1-MATS (I) and 1-MPTS (II) alcoholysis

I - δ 0.875; r 0.993; S_0 0.066

II - δ 1.001; r 0.958; S_0 0.231

Numbers of lines see in Table 1.

studied reactions are given in Tables 4 and 5. The analysis of isokinetic dependence was carried out in the Palm-Exner coordinates by Eq. (7)^{6,7}

$$\lg k_{T_2} = a + n \lg k_{T_1}; T_2 > T_1 \quad (7)$$

High correlation coefficients (r 0.99) of equation (7) indicate that alcoholysis and hydrolysis proceed by a similar mechanism (Fig.6).

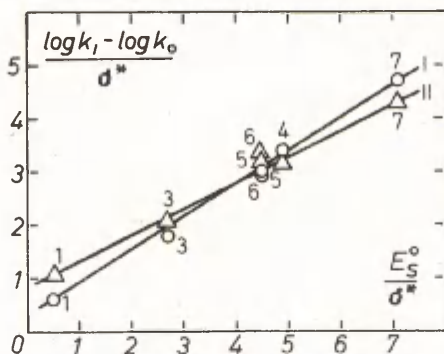


Fig.5. The dependence $\frac{\lg k_1 - \lg k_0}{\delta^*} - \frac{E_s^0}{\delta^*}$

of 3-MASS (I) and 3-MPTS (II)

I - δ 0.646; γ 0.997; S_0 0.014

II- δ 0.556; γ 0.980; S_0 0.032

For the numbers see Table 2.

TABLE 4
THERMODYNAMICAL PARAMETERS OF 1-MATS, 1-MPTS,
3-MATS, 3-MPTS ALCOHOLYSIS*

N°	E	$\Delta F^\#$	$\Delta H^\#$	$-\Delta S^\#$	$\lg A$
1	2	3	4	5	6
Alcoholysis of 1-MATS					
1.	22.25	21.56	21.46	0.32	14.63
2.	21.43	21.91	20.75	3.59	12.47
3.	21.32	22.21	20.66	4.89	12.19
4.	21.47	22.60	20.74	5.77	12.00

Table 4 (continued)

1	2	3	4	5	6
5.	21.23	22.66	20.55	6.55	11.84
6.	21.45	22.98	20.83	6.65	11.71
7.	18.64	24.29	18.00	19.48	9.00
Alcoholysis of 1-MPTS					
1.	21.92	24.40	21.16	10.06	12.78
2.	21.56	25.49	20.82	14.45	10.10
3.	21.75	26.02	21.03	15.44	9.88
4.	21.52	26.53	20.87	17.54	9.42
5.	21.63	26.61	20.99	17.40	9.45
6.	21.36	27.10	20.69	19.82	8.91
7.	18.34	28.53	17.63	33.75	5.88
Alcoholysis of 3-MATS					
1.	21.25	21.90	20.61	3.98	14.13
2.	20.67	21.87	20.03	5.71	12.01
3.	19.83	22.23	19.19	9.30	11.23
4.	20.32	22.48	19.68	8.67	11.36
5.	19.47	22.53	18.83	11.47	10.75
6.	18.95	22.78	18.31	13.85	10.24
7.	18.53	24.10	17.89	19.23	9.06
Alcoholysis of 3-MPTS					
1.	20.50	24.92	20.86	17.66	9.84
2.	21.23	27.11	20.59	20.18	8.85
3.	20.82	27.36	20.18	22.25	8.40
4.	20.23	27.64	19.59	24.94	7.81
5.	19.79	27.66	19.15	26.35	7.50

Table 4 (continued)

1	2	3	4	5	6
6.	19.25	28.03	18.61	29.18	6.88
7.	18.66	28.98	18.02	33.94	5.84

^{a)}The calculation errors of E , ΔF^\ddagger , ΔH^\ddagger , ΔS^\ddagger , $\lg A$ average 0.5 kcal/mol; 0.25 kcal/mol; 0.30 kcal/mol; 0.75 e.u. and 0.351 I/sec, respectively.

As it follows from Fig.6 three straight parallel lines depending on ester structure were obtained. Hence, all the systems studied by us have the same isokinetic temperature. The mean value of isokinetic temperature, β , calculated by equation (8)⁸ where $T = T_2/T_1$ for 1-MATS alcoholysis is (114 \pm 14),

$$\beta = T_2 \frac{1-x}{1-Tx} \quad (8)$$

TABLE 5
Activation Parameters for Alkaline Hydrolysis
of Allyl-p-Toluenesulfonate in Acetone-Water System⁸

Acetone-water (%)	E kcal/mol	ΔF^\ddagger kcal/mol	ΔH^\ddagger kcal/mol	$-\Delta S^\ddagger$ cal/mol grad	$\lg A$ l/mol·sec
100	19.87	21.79	19.29	8.52	11.35
90	19.12	21.71	18.54	10.81	10.86
80	19.02	21.61	18.44	10.85	10.85
70	19.16	21.57	18.57	10.25	10.98
60	19.90	21.28	19.32	6.81	11.75
50	19.33	20.94	18.75	7.48	11.58
40	19.86	20.57	19.28	4.41	12.25
30	19.04	20.12	18.46	5.70	11.97
20	19.19	19.81	18.60	4.31	12.32
10	18.82	19.79	19.24	1.89	13.93
0	18.02	19.33	19.44	1.40	12.82

*) Errors of estimation average 0.40 kcal/mol, 0.25 kcal/mol, 0.40 kcal/mol, 0.85 e.u. and 0.25 l/mol^{·sec}, respectively.

for 1-MPTS (105^{±8}), 3-MATS (120^{±5}), 3-MPTS (120^{±15}), and for alkaline hydrolysis of ATS (123^{±8})°K. It is noteworthy that the reagent nucleophilicity does not affect the dependence in coordinates $\lg k_T - \lg k_{T_1}$ whether the reagents be alcohol, water or hydroxyl ion.¹

Without going into details in discussing the abnormal, at the first glance, dependence (Fig.6) we want only to note that it indicates the common character of transition states in alcoholysis and hydrolysis reactions of each pair: ester-alcohol, ester-water, and ester-hydroxyl ion.

Hence, observance of the Taft equation, similar values of thermodynamic activation parameters, and the presence of the isokinetic correlation allow to conclude that alcoholysis and alkaline hydrolysis of esters proceed by the same mechanism. The alcoholysis of esters when reactivity changes are reached by varying structure of a nucleophilic reagent belongs to the third type of Hinshelwood classification⁹ with parallel enthalpy-entropy control of the reactivity with prevailing entropy component. The alkaline ATS hydrolysis where the reactivity is reached due to composition changes in acetone-water mixture belongs, according to Palm-Erner classification, to the isoenthalpy type with entropy control of the reactivity. One of the main reasons of changes in thermodynamic parameters both in alcoholysis and hydrolysis are solvation changes in initial ester and transition state influenced by radical R' electron effects in alcohols or composition of acetone-water mixture.

Analysis of the experimental data (Tables 1-3) indicates that there is much common in the nature of both alcohol polarity influence and acetone-water mixture composition on kinetic parameters of alcoholysis and hydrolysis. The transition from tert-butanol to water, or from acetone to water leads to an increase in the rate constant, but the rate constant dependence on a dielectric constant or molar fraction of one of components is non-linear. Deviations from the elec-

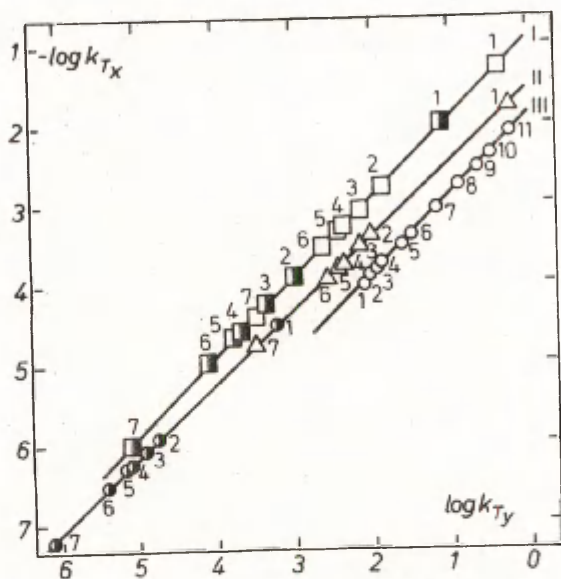
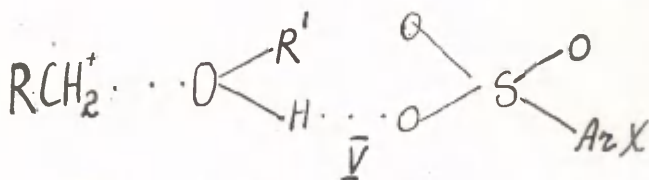
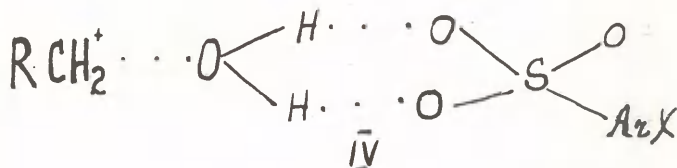
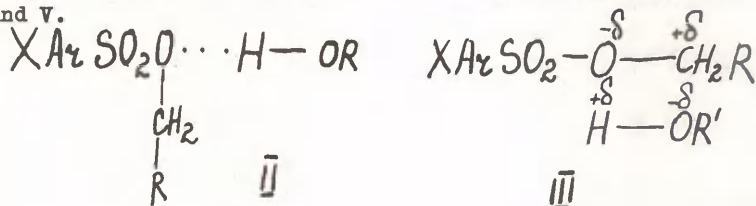


Fig.6. Plot of $\lg k_{T_x}$ vs. $\lg k_{T_y}$

I - 1-MATS - \square , 30-50° and
 1-MPTS - \blacksquare , 40-60° (Table 1);
 II - 3-MATS - \triangle , 20-50° and 3-MPTS - \bullet , 40-70°,
 (Table 2); III - ATS - \circ , 10-50° (Table 3).

trostatic theory in the reactions studied are due to specific solvent effect and result mainly from a hydrogen bond formation. It is supposed, for example, that from a total variety of effects exerted by a solvent on a reaction mechanism its ability to form hydrogen bonds with reagents or activated complex may be of decisive importance⁶. The specific solvation by water or alcohols may exert effect due to the presence of a hydrogen bond, resulting in the formation of structures II or III or, acc. to Harris¹⁰, structures IV and V.



As known¹¹ the value of the angular coefficient, n , in the Tommila equation identified with a number of water molecules, by which hydrated shells of the transition state differ from initial reagents is proposed to be a criterion to differ the reaction proceeding by S_N2 ($n \sim 2$) or S_N1 mechanism ($n \sim 6-7$). The number of water molecules was calculated by Eq. (9)

$$\lg k_2 = n \lg [\text{H}_2\text{O}] + \text{const} \quad (9)$$

It was found that the n value for 90-70% acetone is close to zero which agrees with a very high rate constant sensitivity to hydroxyl ion additions (Fig. 7, Table 6). For

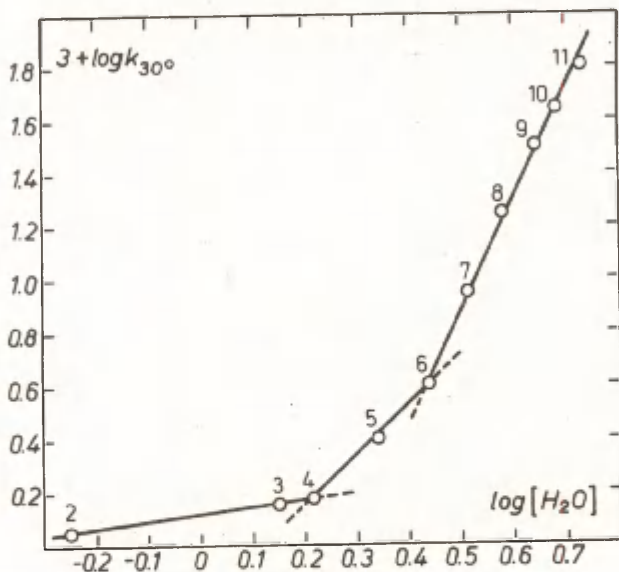


Fig. 7. Plot of $\lg k_2$ vs. $\lg [H_2O]$ for alkaline hydrolysis of ATS, $30^\circ C$
For numbers see Table 3.

70-50% solutions n is equal to 2, and for 50-0% to 4. The value of $n \approx 4$ indicates apparently that in solutions high in water ATS changes the reaction mechanism from bimolecular

to monomolecular. Solvent effects on the activation parameters are given in Tables 4 and 5.

T A B L E 6

Comparison of Rate Constants for Catalyzed and Neutral Hydrolysis of Allyl-p-Toluenesulfonate in Acetone-Water System, at 30°C.

Acetone- water v/v	* $k_1' \cdot 10^5$ sec ⁻¹	** $k_1 \cdot 10^5$ sec ⁻¹ [12]	k_1' / k_1
100	2.02	0.0182	111
90	2.32 ± 0.04	0.116 ± 0.02	20
80	2.70 ± 0.03	0.430 ± 0.09	6.3
70	2.94 ± 0.05	1.11 ± 0.03	2.7
60	5.02 ± 0.08	2.79 ± 0.07	1.8
50	8.84 ± 0.06	5.26 ± 0.22	1.7
40	17.0 ± 0.2	9.96 ± 0.19	1.7
30	35.2 ± 0.4	22.5 ± 0.4	1.6
20	60.0 ± 0.7	43.9 ± 0.8	1.4
10	86.4 ± 0.9	70.3 ± 2.2	1.2
0	123 ± 7	125 ± 23	1

*) k_1' is the first order rate constant calculated in the presence of 0.02 M KOH ($k_1' = k_1 + k_{OH^-}$).

**) k_1 is a rate constant of neutral hydrolysis

In all esters the polarity decrease in alcohol results in marked decrease in the rate constant and changes in thermodynamical parameters of alcoholysis (Table 4). The nature of activating parameters changes and their numerical meaning does not depend essentially on ester structure. In alkaline hydrolysis (Table 5), in contrast to alcoholysis, solvent does not affect essentially E , ΔF^\ddagger , and ΔH^\ddagger , but considerable changes in entropy of activation take place. According

to the data of Ref.8 this should be just expected in the presence of strong interactions of solute and solvent. The marked difference between activation entropy values depending on alcohol polarities and composition of acetone-water mixture may be assigned to the fact that different transition states correspond to them. The n value in the Tommila equation favors this assumption. To confirm this suggestion we have studied the influence of potassium hydroxide addition on the rate constant value.

As one can see from Tables 6 and 7 the reaction rate depends markedly on the reagent nucleophilicity and increases with an increase in the medium polarity. In water the rate constant for all esters (except 3-MPTS) does not depend on the presence of hydroxyl ions and indicates that the rate determining step is not connected with a nucleophile attack on an ester molecule. Thus the reaction mechanism is monomolecular. In *n*-propanol and *tert*-butanol rate constants increase with an increase in alkali concentration indicating the bimolecular reaction mechanism.

The rate constant of ATS alkali hydrolysis in aqueous acetone in the presence of 0.02 M KOH increases with an increase in medium polarity. However, the rate constant increase depends considerably on temperature and changes within rather narrow limits. The ratio $k_{H_2O}/k_{(CH_3)_2CO}$ at 10, 20, 30, 40, and 50°C equals 75, 69, 62, 58, and 50, respectively, whereas in neutral hydrolysis the ratio $k_{H_2O}/k_{(CH_3)_2CO}$ at 30°C is 6868¹². The marked difference between the values of $k_{H_2O}/k_{(CH_3)_2CO}$ for neutral and alkaline ATS hydrolysis in aqueous acetone indicates great influence of alkali on the rate constant in the solutions high in acetone and its insignificant influence in media with high water content (Table 6).

Since the basicity of OH^- anion depends directly on its solvation degree, it may be supposed that its influence on the rate constant is connected with the degree of its

TABLE 7

Influence of Alkali Addition on Rate Constants of
1-MATS, 1-MPTS, 3-MATS and 3-MPTS Alcoholysis. $[\text{Ester}] = 1.0 \cdot 10^{-3}$ mol/l.

Ester	T°C	KOH,	k', sec^{-1}		
			HOH	n-PrOH	t-BuOH
1-MATS*	30	- xxx	447 ± 9	3.89 ± 0.04	0.372 ± 0.006
	30	0.002	438 ± 7	26.8 ± 0.4	3.76 ± 0.05
	30	0.004	445 ± 8	58.4 ± 0.9	7.63 ± 0.12
1-MPTS**	40	- xxx	968 ± 29	2.49 ± 0.05	0.132 ± 0.002
	40	0.002	972 ± 28	19.2 ± 0.3	1.30 ± 0.02
	40	0.004	962 ± 17	41.8 ± 0.8	3.42 ± 0.04
3-MATS*	30	- xxx	631 ± 18	5.10 ± 0.08	0.492 ± 0.009
	30	0.002	633 ± 15	39.4 ± 0.3	4.52 ± 0.04
	30	0.004	628 ± 12	84.7 ± 0.9	8.63 ± 0.08
3-MPTS**	50	- xxx	92.3 ± 1.2	1.32 ± 0.03	0.164 ± 0.002
	50	0.002	114 ± 2	18.5 ± 0.2	3.20 ± 0.06
	50	0.004	133 ± 2	32.4 ± 0.6	5.23 ± 0.10

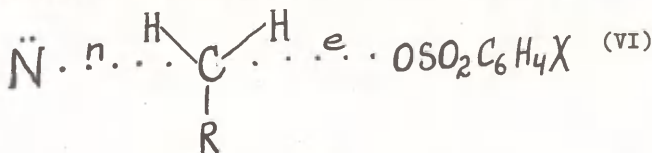
*) $k' \cdot 10^4$;

**) $k' \cdot 10^6$; ~~xxx~~ k'

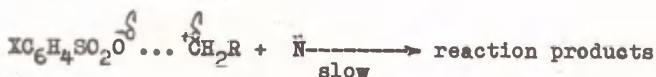
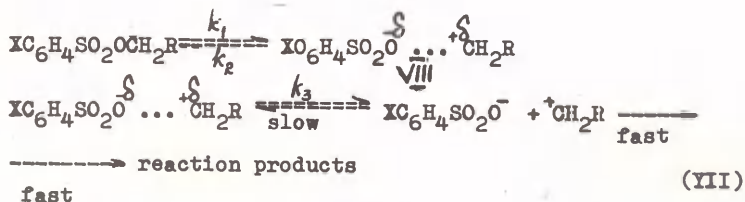
solvation. However, it follows from Tables 6 and 7 that potassium hydroxide effect on the rate constant depends not only on the medium polarity but also on the ester structure. Therefore, an increase or decrease in the reaction rate in the presence of potassium hydroxide is associated mainly with changes in the reaction mechanism, i.e. in the solva-

tion energy of reagents and an intermediate, but not with changes in the reagent nucleophilicity depending on the medium polarity. Hence, depending on the medium polarity and reagent nucleophilicity, for the same ester characteristic features both of mono and bimolecular mechanisms are observed. The mechanism of these reactions may be more complicated than a classical one of S_N1 or S_N2 .

Recently the idea of an intermediate mechanism has gained recognition. It may be successfully applied to the cases under consideration too, and we may assume the studied alcoholysis reaction to occur together with the formation of intermediate (VI) in which, depending on ester structure, medium polarity, and reagent nucleophilicity, the degree of covalent C-O (e) bond-breaking or the degree of bond formation (n) with a reagent (\ddot{N}) are predominant, i.e. the α carbon atom of sulfoester in the intermediate is always more positively charged than in the initial compound:



In the alcoholysis and hydrolysis of sulfoesters in low polar media changes in the bond formation order Δn_{N-C} (process n) are larger than changes in the bond breaking order Δn_{C-O} (process e). Changes in the ratio $\Delta n_{N-C} / \Delta n_{C-O}$ depend on the ester structure and mainly on the medium polarity. Different effects of potassium hydroxide on the reactivity of esters depending on the medium polarity may be accounted for by preequilibrium formation of a polarized ester molecule as an active intermediate with further slow step of its interaction with a nucleophile. This may be represented by the following scheme (VII):



where $\ddot{\text{N}} = \text{H}_2\text{O}$, ROH or OH. The effective reaction rate constant whose intermediate step is a dissociation of bond (VIII) into ions or an interaction with nucleophile is determined by equation (10):

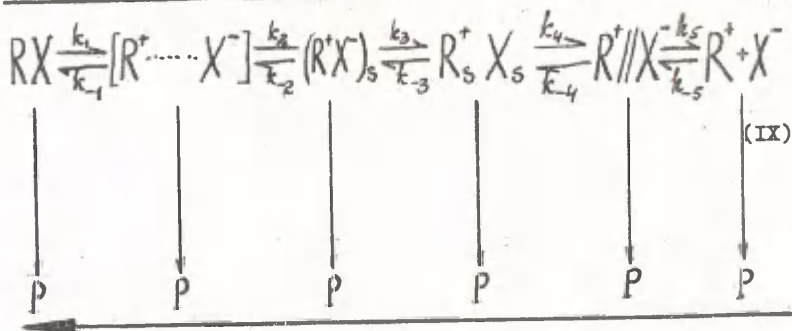
$$k_{\text{obs}} = \frac{k_1 \cdot k_3}{k_2} = K \cdot k_3 \tag{10}$$

Hence, the kinetic study of alcoholysis and alkaline hydrolysis of alkyl and alkenyl-p-toluenesulfonates allows to conclude that depending on the reaction conditions they proceed via mono or bimolecular mechanism. However, a nucleophilic attack by H_2O , ROH or OH ion which results in a covalent bond formation is preceded by a certain level of a charge distribution (VIII). Intermediate (VIII) with a distributed charge is stabilized by molecules of a solvating medium. The degree of charge distribution in an intermediate is a function of medium and a factor determining a relative mechanism position within the limits of boundary cases of mono and bimolecular mechanisms. In the limiting case the ester polarization occurs before the interaction with nucleophile which corresponds to monomolecular mechanism and occurs in hydrolysis of esters in water, since the rate constant does not depend on the alkali concentration.

According to Winstein intermediate (VIII) is equivalent to an ion pair¹³. Hence, different effects of potassium hydroxide on the rate constant depending both on the ester

structure and medium polarity are associated with the formation of compounds (VIII) different in their structure (ion pairs) (scheme IX). In so doing not the formation of these ion pairs, but their further transformation is a limiting phase of the process (p-reaction products).

An increase in the medium polarity and process e (VI)



A decrease in the medium polarity and increase in process n (VI).

Features observed for the same reactions and characteristic both of mono and bimolar reactions indicate that a nucleophile attack on ion pairs with different structure is a more favorable process than their further ionization or dissociation. Proceeding from ion-pair conception one can account for the fact that the points for tert-butanol and water or acetone and water in coordinates $\lg k_{T_2} - \lg k_{T_1}$ fall to the same straight line. It becomes also clear why the experimentally observed dependence of the bimolecular process on the solvent effect (bimolecular rate constant increases with an increase in the solvent polarity (Table 3)) is in contradiction with the classical theory of S_N2 mechanism according to which the rate of a charged nucleophile with a neutral substrate must change insignificantly and even somewhat decrease with increase in the medium polarity.

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Acid-Catalytic Solvolysis of Alkyl Fluorides in Sulfuric Acid Solutions

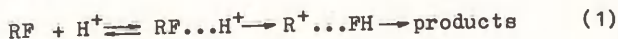
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Solvolysis rates of *t*-BuF, *i*-PrF, EtF, and MeF in sulfuric acid solutions are measured at 25°C. For the acid-catalytic reaction the larger range of changes in the reactivity than for hydrolysis of RF is characteristic of. The ratio of rates in the sequence *t*-BuF > *i*-PrF > EtF is $10^8:10^5:1$. The increase in selectivity may result either from the increase in the S_N1 character of the limiting step in the catalytic solvolysis of primary and secondary RF, or from the decrease in the catalytic action of an acid in passing from tertiary to secondary and primary RF.

Hydrolysis of alkyl fluorides (RF) in water proceeds slowly, differences in the reactivity of compounds with primary and tertiary C-F bonds being not large in this system (at 25°C rate constants are $3 \cdot 10^{-7}$ and $0.8 \cdot 10^{-9} \text{ sec}^{-1}$ for *t*-BuF and MeF, respectively¹). Increase in the acidity leads to increase in the reactivity. The data are available on the acid-catalytic solvolysis of *t*-BuF in nitric and perchloric acid solutions², of BzF in sulfuric, perchloric³, and nitric⁴ acid solutions.

In the present work the solvolysis rates of Me-, Et-, *i*-Pr-, and *t*-BuF (including the C-F bond heterolysis) are measured in sulfuric acid solutions:



Passing from hydrolysis to acid-catalytic solvolysis of alkyl fluorides is found to lead to sharp increase in the selectivity: in the sequence $\text{MeF} < \text{EtF} < \text{i-PrF} < \text{t-BuF}$ the rate increases by about 7-8 orders of magnitude.

The kinetics was studied by the GLC method^{5,6} by the consumption of alkyl fluorides* by sulfuric acid solutions from the gas phase. Values of the true rate constants in the absence of the gas phase were calculated by the equation:

$$k = k_H(1 + \alpha\lambda) \text{ where } k_H = \frac{1}{[\text{RF}]^g} \frac{d[\text{RF}]^g}{d\tau} ;$$

$\alpha = [\text{RF}]^g / [\text{RF}]^s$ is a distribution coefficient of RF between gas and solution; λ is a ratio of gas and liquid volumes in the flask. The α values were determined either from a series of kinetic runs at various λ (see Refs 5,6), or estimated by determining the ratio of concentrations of RF^{11} in the gas and solution. From the data obtained (Table 1) one can see that the α values depend weakly on the sulfuric acid concentration at $[\text{H}_2\text{SO}_4] \leq 30$ mass per cent, increase in the region of 50-70% H_2SO_4 and decrease in the concentrated sulfuric acid. The α values of alkanes¹¹ and molecular hydrogen¹² change analogously with increase in the sulfuric acid concentration.

* Alkyl fluorides were synthesized by the known procedures 7,8,9,10. The individuality of RF was established using GLC, NMR, and mass-spectrometry.

Table 1.
Solvolysis Rate Constants of Alkyl Fluorides in
Sulfuric Acid Solutions and Distribution Coeffi-
cients of RF between Gas and Solution, 25°C,
 k in sec^{-1} .

RF	H ₂ SO ₄ , %	-H ₂ O	lg $k + 5$	α
1	2	3	4	5
t-BuF	13.2	0.64	1.77	1.4
	16.8	0.85	2.13	1.9
	21.6	1.15	2.33	1.4
	25.5	1.50	2.53	1.3
	30.5	1.85	2.93	1.8
i-PrF	53.2	3.70	1.3	2 ^a
	57.1	4.15	1.5	3 ^a
	62.1	4.82	2.4	5 ^a
	66.8	5.48	3.3	II ^a
	72.1	6.23	3.9	17 ^a
EtF	85.0	8.29	0.02 ^b	0.4 ^a
	90.0	9.03	0.54	0.2
	94.1	9.50	0.91	0.2
	96.0	9.88	1.02	0.1
				0.1 ^a
	98.3	10.35	1.40	0.1 ^a
MeF	99.9	11.43	0.73 ^b	-

^a Estimated by the method of Ref. 11

^b Calculated by the equation $k = 1.67 \cdot 10^{11} e^{-\frac{22100}{RT}}$
from a series of kinetic runs at 59.2°, 70°, and 79°C.

^c The value of k_H at $\lambda = 1.24$ ($\alpha \leq 0.1$).

Increase in the sulfuric acid concentration leads to the exponential growth of the rate. In the case of MeF the reaction proceeds with the marked rate in 100% H₂SO₄

only ($H_0 = -11.94$). The data for *t*-BuF, *i*-PrF, and EtF fit the equation:

$$\lg k = -a_1 H_0 + b_1 \quad (2)$$

The values of parameters a_1 and b_1 for these systems together with the values for the solvolysis of *t*-BuF in perchloric and nitric acids obtained elsewhere ² are listed in Table 2.

The reaction rates of *t*-BuF and *i*-PrF, *i*-PrF and EtF in the solutions of H_2SO_4 with close concentrations differ by some orders of magnitude (see the Fig.), and the values of parameters b_1 allow to estimate the change range of the reactivity in the series of RF. In the middle of the range of H_0 ($H_0 = -5$):

$$t\text{-BuF} : i\text{-PrF} : EtF \approx 10^8 : 10^5 : 1$$

Table 2

Parameters of Eq. (2) for EtF, *i*-PrF, and *t*-BuF.

RF	Acid and the range of conc., a ₁ w/w		b ₁	Refs.	
EtF	H ₂ SO ₄	85-90	0.65	-10.4	this work
i-PrF		50-70	1.1	- 8	this work
t-BuF		10-30	0.86	- 3.7	this work
t-BuF	HNO ₃	3-37	1.06	- 3.7	[2]
t-BuF	HClO ₄	5-40	1.14	- 3.6	[2]

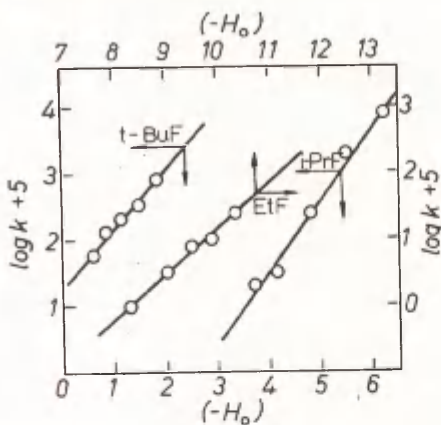


Fig. Plot of $\lg k$ (k in sec^{-1}) vs. H_0 for solvolysis of RF in sulfuric acid solutions, 25°C .

The role of H^+ in the acid-catalytic solvolysis is in electrophilic contribution to the C-F bond heterolysis. Analogously, ions of metals, M^+ , forming stable complexes, MX^{13} , accelerate the hydrolysis of RX and increase the selectivity. It should be noted further that increase in the selectivity in the solvolysis of RX results from

decrease in the medium nucleophilicity (see Ref. 14), accompanied, evidently, by decrease in the solvating power of a solvent relative to carbocations.

Both these effects - decrease in the medium nucleophilicity and electrophilic contribution into the carbon-halogen bond fission contribute, probably, into the observed selectivity of the RF solvolysis in the sulfuric acid solutions. The selectivity of the solvolysis reflects the stability of possible intermediates (carbonium ions or ion pairs) to the greater extent than the selectivity of the hydrolysis of these substrates. Formally, this indicates the increase in the degree of the S_N1 -character of the solvolysis limiting step of primary and secondary alkyl fluorides. However, the increase in the selectivity can also occur due to the decrease (within the framework of the same mechanism) in the efficiency of an acid catalytic action in passing from

tertiary to primary C-F bonds. These problems need further investigations.

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CATALYTIC PROPERTIES OF TRIALKYLAMINES IN THE MEZYLATION REACTION OF p-CHLOROPHENOL

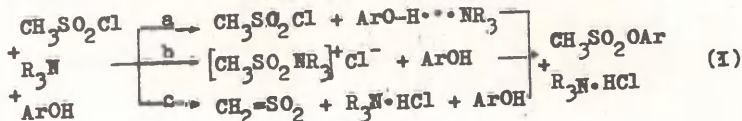
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The mezylation kinetics of p-chlorophenol in the presence of nine trialkylamines in benzene has been studied at 30°C. The reaction proceeds by two competing mechanisms, namely by the sulphene mechanism and by the preassociative general base catalysis. For the first time, separation of the above pathways has been made from the kinetic data. The influence of the trialkylamine structures on the competing mechanism rates is described by the Brønsted equation and by the modified Taft equation. The reaction parameters obtained have been used to substantiate the influence of the catalyst structure on the ratio of the competing pathways.

Proceeding from the literature data on catalysis of ether formation reactions by tertiary amines three reaction mechanisms can be assumed for mezylation of phenols in the presence of trialkylamines



where Ia is a general-base catalysis mechanism, Ib is a nucleophilic catalysis mechanism, Ic is an elimination-addition or the so called "sulfene" mechanism.

Earlier, on the basis of the studies of reaction kinetics⁴ and the results of isotope studies⁵, we showed that mesylation of phenol in the presence of triethyl amine proceeded according to scheme Ic. Thus the reaction order in phenol and, hence, the reaction sensitivity to the phenol structure are equal to zero. The use of deuterophenol practically results in 100% formation of α -monodeuterated ether $\text{CH}_2\text{DSO}_2\text{OC}_6\text{H}_5$.

In passing to dimethyl benzyl amine and tribenzyl amine⁵ the reaction proceeds by the sulfene mechanism side by side with the general-base catalysis (scheme Ia) as evidenced by the decrease in the formation of α -monodeuterated ethers up to 50-80%.

In order to investigate in detail the influence of the trialkylamine structure on the rate and mechanism of alkylsulfonate formation, the mesylation kinetics of p-chlorophenol in the presence of tributyl- (I), tripropyl- (II), triethyl- (III), diethylmethyl- (IV), dimethyl cyclohexyl- (V), diethylbenzyl- (VI), dimethylbenzyl- (VII), tribenzylamine (IX) and triethylene diamine (VIII) in benzene has been studied at 30°C.

Experimental.

Methane sulfonyl chloride, phenol, and p-chlorophenol were purified by redistillation under vacuum; physical constants are consistent with the literature ones.

Benzene was purified according to⁶. "Chemically pure" I, II, III, IV, V, VII were boiled over p-toluene sulphonyl chloride, dried over melted potassium hydroxide, distilled over metallic sodium; middle fractions were collected. The physical constants agreed with the literature ones.

VI was synthesized by the procedure described in⁷ using benzyl chloride and diethylamine. The purification was performed as described above. VIII was purified by

sublimation under vacuum. IX was purified by repeated recrystallization from methanol. The physical constants were in agreement with the literature ones.

The kinetics of methylation of p-chlorophenol in the presence of trialkylamines was investigated with two methods, namely with potentiometric determination of chloride ions formed in the reaction, and with gas chromatographic determination of the end product phenyl methane sulphonate (LHM-8MD #5 chromatograph with 10% silicon SE-30 on chromosorb, gas-carrier was helium) with an internal standard.

The kinetic studies were carried out at the following reagent concentrations: (a) methane sulphonyl chloride 0.003 mole/l; (b) ArOH 0.02 - 0.06 mole/l; (m) trialkylamine 0.06 - 0.006 mole/l.

The acylation reaction was performed according to the following technique. The reagents were placed into a bulb equipped with a ground stopper and two appendices - 5 ml of methane sulphonyl chloride was placed into one appendix, and 5 ml of a tertiary amine solution and 5 ml of a phenol solution into the other. The solutions were mixed after being thermostated for 10 minutes. The moment of mixing was considered as the beginning of the reaction. The reaction was stopped by binding the unreacted tertiary amine with an excess of nitric acid (1:5 aqueous solution) with vigorous stirring. The mixture was quantitatively transported into the cell to be titrated and the amount of chloride ion was determined. For the GLC analysis, 1-10 mcl of benzene solution (sulfonates are insoluble in water) was collected after stopping the reaction before titration. Since chloride ions were in the water layer, collection of such a small quantity of the benzene solution does not affect the results of titration as shown by check experiments. The kinetic measurements were repeated twice, the results obtained coinciding.

The reaction rate constants obtained under the pseudo-first order were calculated according to the formula

$$k_1 = 1/t \cdot \ln a/(a-x) \quad (2)$$

The reaction rate constants were calculated either by dividing k_1 by m (with $m \gg a$) or (with $m \approx a$) using the formula

$$k_2 = 1/t \cdot 1/(m-a) \cdot \ln a(m-x)/m(a-x) \quad (3)$$

The accuracy of the obtained data was characterized by a confidence interval with the probability of 0.95. The kinetic and correlation parameters were computed by the least-square method⁸ using the "Promin-2" computer.

Results and Discussion.

The kinetic data on mezylation of phenol in the presence of triethylamine (Table 1) obtained by both methods are close (potentiometric titration, GLC), but the yield of chloride ion is observed to exceed that of sulfonate. The check runs (without phenol) performed using benzene sulfonyl chloride which is more reactive than methane sulfonyl chloride in nucleophilic substitution reactions and for which the realization of the sulphene mechanism is impossible showed that hydrolysis did not occur under the experimental conditions. The higher yield of chloride ion seems to be caused by side reactions (the yield of phenol methane sulfonate equals 90-80%), on the one hand, and, on the other hand, by hydrolysis at the moment of the reaction stop due to the presence of reactive sulfene.

Table 1. Data on the Kinetics of Mezylation of Phenol in the Presence of Triethyl Amine in Benzene at 30°C, a 0.003, b 0.01, m 0.02 mole/l

Method	$k_1 \cdot 10^3, s^{-1}$	$k_2 \cdot 10^2, l/mole \cdot s$
GLC	1.04 ± 0.04	5.2 ± 0.2
Potentiometric titration	1.66 ± 0.05	8.3 ± 0.3
Potentiometric titration (without phenol)	1.50 ± 0.04	7.5 ± 0.2

Check runs with methane sulphonyl chloride show (Table I) that the chloride ion is formed as fast as in the presence of phenol. Together with the fact that the GLC results and those of potentiometric titration are close, this confirms that sulfene is formed (scheme Ib) in the rate limiting step. The reactive sulfene formed reacts quickly with phenol to form sulfonate and in the absence of phenol is oligomerized undergoing a number of conversions⁹.

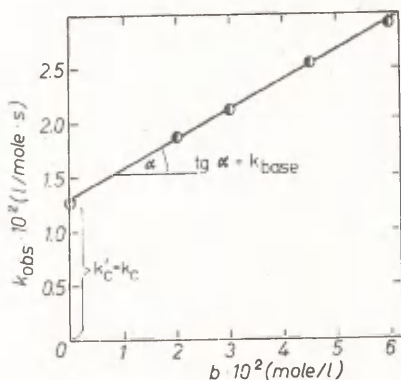


Fig.1. The influence of the initial concentration of p-chlorophenol on the mezylation kinetics in the presence of tributyl amine in benzene at 30°C (k_{obs}). (● - the GLC method; ○ - the potentiometric titration method).

constans k_g which coincide numerically with the k'_g -values (Table 2). As the formation of sulphene is the limiting step of the reaction, k'_g derived by calculations (Table 2) from the results of the kinetics of ether formation (GLC) and k_g obtained experimentally from the chloride ion yield coincide.

With tributyl-, tripropyl-, diethylbenzyl-, dimethylbenzyl- and tribenzylamine (GLC) when the p-chlorophenol concentration is increased the observed second-order rate constant k_{obs} increases linearly (Fig.1, Table 2), the straight line cutting off an intercept on the axis of ordinates rather than pass the origin. When studying the interaction between methane sulphonyl chloride and the corresponding trialkylamines on the basis of chloride ion yield (potentiometric titration) we obtained second-order rate

Table 2.

The Influence of the Trialkylamine Structure on the p-Chlorophenol
Methylation Kinetics in Benzene at 30°C, a 0.003, m 0.02 mole/l

R ₃ N	$\Sigma G \cdot 10$	$\frac{M}{21.11}$	pK_a^{13}	$k_g \cdot 10^4$ 1/mole·s	$k_{obs} \cdot 10^4$ (1/mole·s) for b(mole/l)				$k'_g \cdot 10^4$ 1/mole·s	$k_b \cdot 10^3$ 1 ² /mole ² ·s	r
					0.02	0.03	0.045	0.06			
I	-0.390	4.50	9.93	127 \pm 3	187 \pm 6	211 \pm 3	255 \pm 5	290 \pm 1	130 \pm 3	272 \pm 3	0.99
II	-0.345	4.10	10.65	67 \pm 3	95 \pm 4	131 \pm 3	164 \pm 4	204 \pm 8	60 \pm 3	230 \pm 10	0.99
III	-0.300	3.80	10.78	750 \pm 20	-	520 \pm 10	-	500 \pm 10	-	-	-
IV	-0.200	3.00	10.43	5900 \pm 290	-	1800 \pm 90	-	1200 \pm 100	-	-	-
V	-0.150	2.97	10.43	1920 \pm 80	1060 \pm 50	800 \pm 40	740 \pm 30	-	-	-	-
VI	0.015	4.10	9.44	7.0 \pm 0.3	15.5 \pm 0.5	17.0 \pm 0.8	22.5 \pm 0.5	26.5 \pm 1.0	7.8 \pm 0.3	32 \pm 2	0.99
VII	0.215	2.23	8.91	8.0 \pm 0.4	11.5 \pm 0.5	14.7 \pm 0.7	15.5 \pm 0.5	20.4 \pm 0.8	7.9 \pm 0.3	20 \pm 1	0.98
VIII	0.400	1.30	11.79	3310 \pm 100	1410 \pm 50	1080 \pm 30	-	-	-	-	-
IX	0.645	4.15	6.90	0.009	-	-	-	0.05	0.009	0.7	-

As shown elsewhere⁴ the reaction order in sulfonyl chloride and tertiary amine is equal to 1. Thus, together with the sulfene mechanism having general second order (zero order in phenol) the reaction mechanism with general third order is realized. The third order rate constants (k_b) were determined as the slope of $k_{obs.}$ vs. b (Fig.1, Table 2). Processing of the obtained rate constants, k_b , according to the Brönsted equation results in correlation equation 4.

$$\lg k_b = (-8.1 \pm 0.9) + (0.72 \pm 0.09) pK_a^{R_3N}; S_0 = 0.28; r = 0.97 \quad (4)$$

As is seen from Fig.2, the k_b -value for tributylamine falls out. If this value is ignored, then good correlation according to the Brönsted equation is observed. $\lg k_b = (-7.7 \pm 0.3) + (0.67 \pm 0.03) pK_a^{R_3N}; S_0 = 0.08; r = 0.99 \quad (5)$

More complete consideration of both induction parameters and steric parameters of trialkyl amines is given by the modified Taft equation proposed originally by Bogatkov-Popov-Litvinenko^{II} where the steric characteristic of aliphatic amines (B_N) is given on the basis of the isostericity principle. For the k_b -values (I, II, VI, VIII, IX) we have obtained a good correlation from this equation (Fig.3).

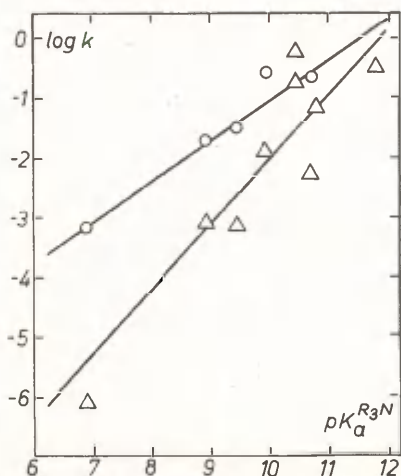


Fig.2. Dependence of the reaction rate on the trialkyl amine basicity (Δ - for the sulfene mechanism k_s , \circ - for the general-base catalysis mechanism k_b).

$$\lg k_b = (-0.76 \pm 0.07) + (-2.55 \pm 0.04) \Sigma \sigma^+ + (0.18 \pm 0.02) E_N; \\ S_0 = 0.03; \quad r = 0.999 \quad (6)$$

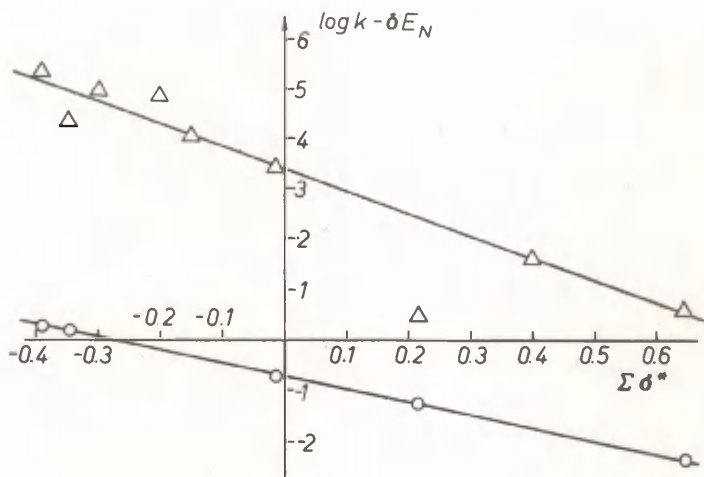


Fig.3. Dependence of the reaction rate on the inductive ($\Sigma \sigma^+$) and steric (E_N) characteristics of substituents in trialkylamine (Δ - for the sulphene mechanism k_B , \odot - for the general-base catalysis mechanism k_b).

An analysis of the obtained ρ_b and δ_b values shows that the influence of the steric parameters of the catalyst is rather weak, especially if they are compared with the influence of the induction characteristics ($\rho_b/\delta_b = 14$). It is obvious that it is for this reason that a satisfactory correlation is observed by the Brønsted equation which is not very characteristic of alkyl amines. Since the steric influence of the substituents in R_3N is insignificant for the given reaction, using pK_a values as structural characteristics of tertiary amines which reflect, in the first place, the induction influence of the substituents on the reaction center, to describe the reaction

rate dependence on the catalyst structure also gives satisfactory results.

The insignificant influence of the steric characteristics of the reaction center and the significant influence of the induction ones on the catalysis by tertiary amines of alkanesulphonation reaction of phenols are in favor of the general-base catalysis mechanism (scheme 1a) and testify against the alternative nucleophilic mechanism (scheme 1b) for the steric environment of the catalytic center¹⁴ is most important and its basicity is of less importance.

Thus, alkanesulphonylation of phenols in the presence of tertiary amines is described by the equation

$$dx/dt = k_g(a-x)(m-x) + k_b(a-x)(b-x)(m-x) \quad (7)$$

In the case of the reaction proceeding by the general-base catalysis mechanism the formation of hydrogen-bonded amine-phenol complexes is the first reaction step (scheme 1a), the strength of the bond increasing with increasing basicity (acidity) and steric accessibility of amines (phenols). The reaction mechanism is defined in this case as the preassociative general-base catalysis mechanism². This mechanism is confirmed by the kinetic data obtained when catalyzing the reaction by triethyl-, diethylmethyl-, dimethylcyclohexylamine and triethylenediamine. As seen from Table 2 a decrease is observed in k_{obs} when these catalysts are used, and b is increased. This may be associated with a decrease in the trialkylamine active concentration as a result of its complexation with phenol. At the same time, whereas formation of such complexes results in realizing the preassociative general-base mechanism (scheme 1a) for I, II, VI, VII, IX, the above mechanism fails because of the high rate of the sulphene pathway (scheme 1c) for III, IV, V, VIII. With $k_g \gg k_b(m-x)$ reaction rate equation 7 is reduced to 8.

$$dx/dt = k_g(a-x)(m-x) \quad (8)$$

Indeed, as Table 2 shows k_g is much higher for III, IV, V and VIII than for I, II, VI, VII, IX. In this case, the above phenomenon seems to be brought about by an increase in the

steric accessibility when passing from I,II to III-Y and from VI,VII to VIII, which leads to a considerable increase in k_g resulting in the suppression of the pathway of the general-base catalysis. However, an increase in the steric accessibility also leads to formation of stronger complexes with p-chlorophenol resulting in a decrease in the effective concentration of the catalyst, the higher being b the more being the decrease. A decrease in the effective concentration of the catalyst entails decrease in the observed rate constant (k_{oba}). Therefore we use the k_g values obtained with $b=0$ from the potentiometric titration method as a measure of the rate of the sulphene pathway for III,IV,Y,VIII. In the case of the remaining trialkylamines, as was stated above, coincidence of k_g and k'_g is observed. The processing of the k_g values according to the Brønsted equation for all trialkylamines used gives the correlation equation

$$\lg k_g = (-12 \pm 1) + (1.0 \pm 0.2) \text{p}K_{\text{a}}^{\text{RN}}; S_0 = 0.72; r = 0.93 \quad (9)$$

If the most deviating values of k_g for IV,Y are excluded, then the correlation equation will have the form (Fig.2)

$$\lg k_g = (-13 \pm 1) + (1.1 \pm 0.1) \text{p}K_{\text{a}}^{\text{RN}}; S_0 = 0.45; r = 0.97 \quad (10)$$

It is possible that the deviation of the k_g -values for IV,Y is associated with the great steric accessibility of the catalytic center of the trialkylamines in point (Table 2). Thus, the Brønsted equation can describe satisfactorily the influence of the trialkylamine structures on their catalytic properties in the methylation reaction of phenols.

The processing of the obtained rate constants k_g according to the modified Taft equation for all trialkylamines used gives the following correlation equation

$$\lg k_g = (2.5 \pm 0.9) + (-4.6 \pm 0.8) \Sigma \sigma^{\text{X}} + (1.4 \pm 0.3) E_{\text{N}}; \\ S_0 = 0.8; r = 0.93 \quad (11)$$

After excluding the most deviating constant (for dimethyl benzyl amine) the following correlation (Fig.3) is obtained:

$$\lg k_g = (3.4 \pm 0.3) + (-4.4 \pm 0.3) \Sigma \sigma^{\text{X}} + (1.6 \pm 0.1) E_{\text{N}};$$

$$S_o = 0.3; \quad r = 0.99 \quad (12)$$

A comparison of ρ_s^* - and δ_s -values indicates a greater sensitivity of the mechanism to the inductive influence of the substituents in trialkylamine than to the steric one, which supports the realization of the sulphene mechanism and is at variance with the alternative nucleophilic mechanism (scheme 1b).

An analysis of the obtained parameters β, ρ^*, δ for the mechanism of preassociative general-base catalysis and for the sulphene mechanism shows that the latter has higher sensitivity to the basicity and steric accessibility of the catalyst, tertiary amine. The obtained data imply that an increase in the basicity (III, IV) leads to a greater rise in the k_s -value than in the k_b ($\rho_s^*/\rho_b^* = 1.7$; $\beta_s/\beta_b = 1.6$), and the pathway of the general-base catalysis is suppressed. An increase in the steric accessibility of the trialkylamine nitrogen atom (IV, V) results in a still more considerable increase in k_s as compared with k_b ($\delta_s/\delta_b = 9$) leading to the complete predominance of the sulfene mechanism.

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EQUIVALENCE OF THE BASICITY SCALES

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The analysis of the literature sources shows that the description of solvent effects on physico-chemical behavior (kinetic and spectral phenomena, enthalpies of mixing and complex formation) of solute by means of the basicity factors only is inadequate. The two-parameter equations of Pawcett-Krygowski, Drago, Kamlet-Taft also do not give accurate enough results of calculations as these do not take into consideration non-specific solvation of solute and the medium auto-association. Satisfactory results can be obtained only with the use of five-parameter linear equation of free energies which takes into account various aspects of interaction in solutions:

$$\gamma = a_0 + a_1(n^2 - 1)/(n^2 + 2) + a_2(\epsilon - 1)/(2\epsilon + 1) +$$

$a_3\delta^2 + a_4B + a_5E$. The applicability of the above cited equation is illustrated on the examples of description of the influence of solvent on various physico-chemical phenomena in the binary CHCl_3 - donors systems.

We have compared different scales of basicity given in the literature (Koppel-Palm, Gutmann, Drago, Johansen, Terentyev, Kamlet-Taft) and shown the possibility of their mutual evaluating by means of linear poly-parameter equations. The B_{PhOH} scale is the most practi-

cally suitable one.

Electron-donating power (basicity) is one of the most important characteristics of organic compounds. This value is widely used to evaluate solvent effects on kinetic and spectral properties of solutes and to characterize the ability of solutes to complex formations and mixing enthalpies with acceptors. Many correlation dependences exist. To connect substance properties with complex formation enthalpies or some spectral characteristics Gutmann ¹ has proposed one-parameter correlation between the above values and donor numbers DN, i.e. enthalpies of mixing of donors with SbCl_5 . But this one-parameter dependence is considerably simplified and is suitable only in some particular cases. Many other one-parameter dependences proposed in literature, e.g., the correlation between substance properties and changes in OD-band in MeOD solutions ² or mixing enthalpies with CHCl_3 ³ have only limited validity. Therefore the equations are proposed which take into account a greater number of solvent parameters (properties). Fawcett and Krygowsky ⁴ give the two-parameter equation in which the donor number DN determines the nucleophilicity and the Reichardt "polarity" parameter E_T ⁵ determines the electrophilicity of solvents:

$$y = a_0 + a_1 \text{DN} + a_2 E_T$$

In the recently published work ⁶ for the purpose of more accurate description of kinetics in different solvents the authors propose to supplement the one-parameter Grunwald-Winstein equation with a second term which takes into account the basicity of solvents. The latter is based on the rate of triethyloxonium ion hydrolysis in these solvents.

The most complete description of various solvation effects on kinetics or spectral characteristics is given by V.A. Palm and coworkers ⁷. They have proposed a four-parameter equation of free energies:

$$Y = a_0 + a_1 \frac{n^2 - 1}{n^2 + 2} + a_2 \frac{g - 1}{2g + 1} + a_3 B + a_4 E$$

which takes into account separately different effects of both specific and non-specific solvation. Recently we have shown that the same equation supplemented with a fifth term, the cohesion energy density, δ^2 , is suitable for the characteristics of solvent effects on pure thermodynamic processes of distribution of substances between two phases, gas absorptions and on mixing enthalpy values of substances and complex formation enthalpies as well ⁸. The sense of δ^2 parameter which characterizes according to Hildebrand ⁹ the interaction of solvent molecules consists in the evaluation of energy loss on the intrusion of a foreign substance into the liquid structure - the molecule of soluted gas, forming complex a.o.

Since linear poly-parameter free-energy equations are so widely applied in many fields of solvent chemistry, it is natural that there appears a problem of some unification of considered parameters. Whereas the polarizability, polarity, and cohesion energy density parameter concepts have a theoretical base and are used by many authors in the identical sense, factors which characterize the specific solvation are empirical values and different authors use frequently different scales which hampers the equivalent interpretation of literature data.

Ref. ¹⁰ gives the compendium of ca. 200 values of basicities "B", i.e. shifts of phenol OH-band in its IR-spectrum under the effect of studied substances with phenol in CCl_4 solution which rules out the possibility of non-specific solvation. The corresponding data exist in the literature for several hundreds of less common substances. The authors of Ref. ¹⁰ have shown that the scale of "B" values is proportional to some other well known basicity scales with a high correlation coefficient ($R=0.97+0.99$), i.e. spectral band shifts OH or OD of MeOH, MeOD, t-BuOH, p-Fluorophenole, -Si-OH or shifts XH of HCl, pyrrole ¹¹, diphenylamine, HClNO. Thus, the authors of Ref. ¹⁰ propose a universal dependence:

$$\Delta \bar{\nu}_{\text{HX}}^{\text{CCl}_4} = a + b \Delta \bar{\nu}_{\text{PhOH}}^{\text{CCl}_4} = a + bB$$

Ref. ¹² establishes also the presence of a linear relationship between shifts of -OH (OD) IR-bands of different hydroxyl containing compounds when forming hydrogen bond with bases.

We have shown elsewhere ¹³ that purely thermodynamic scale of donor numbers, DN, correlates satisfactorily with the spectral B-scale by means of a two-parameter equation which takes into account solvent polarizability factors:

$$\text{DN} = 8.200 + 0.0876B - 35.734 \frac{n^2 - 1}{n^2 + 2}; \quad R = 0.973; s = 3.32$$

As the basicity scale "B" is at present the most representative and to obtain data of the OH-band shifts of the IR spectrum is experimentally easier, we consider it expedient to compare some other literature basicity scales with the "B" scale.

The authors of Ref ¹⁰ have shown that the scales based on shifts of IR-bands of hydrogen bond are equivalent. The verification of the data on shifts of H-N bond in HCNS ¹⁴ or OD in MeOD (new data in Ref. ¹⁵) confirms this conclusion.

The following equation was obtained for H-N band spectral shifts for 18 substances ¹⁴ (HCNS in CCl₄ in the presence of bases:

$$\Delta \bar{\nu}_{\text{HN}} = (71.2 \pm 7.2) + (1.908 \pm 0.035)B; \quad R = 0.997; s = 14.5$$

where $\Delta \bar{\nu} = \bar{\nu}_{\text{gas}} - \bar{\nu}_{\text{sol}}$. Replacement of a one-parameter equation by a five-parameter one increases the R-value to 0.998.

In Ref. ¹⁰ for the solvent influenced OD-band shift the following relationship was obtained for 54 points

$$\Delta \bar{\nu}_{\text{OD}} = (30 \pm 2) + (0.382 \pm 0.09)B; \quad R = 0.987$$

The authors of Ref. ¹⁵ verified and refined these data. After mathematical treatment of these data the following dependence for 47 solvents was obtained:

$$\Delta V_{OD} = (27.2 \pm 3.2) + (0.42 \pm 0.01)B; R=0.981; s=15.0$$

The use of five-parameter equation increases the R-value to 0.984. However, since polarity, polarizability, and electrophilicity parameters are negligible, the same result may be obtained by using only two-parameter equation which uses the basicity and cohesion energy density of solvents as correlated parameters:

$$\Delta V_{OD} = 12.33 + 159.93\delta^2 + 0.420B; R=0.984; s=14.0$$

However, for weaker H-bonds which are formed by chloroform one-parameter dependence on "B" is not suitable any more although the basicity remains the most significant parameter in that case too. In a series of articles by Seearlee, Tamress and coworkers an attempt was made to use mixing heats of substances with CHCl_3 at 1:1 ratio as a scale of their basicity. But the data obtained give no single dependence on ΔV_{OD} (the authors established the presence of three different linear correlations for various groups of substances - for ethers³, amines¹⁶ and aromatic hydrocarbons¹⁷; for a number of substances numerous deviations from linearity were observed¹⁸).

We have shown recently that the dependence of heats of mixing of CHCl_3 on the second component properties may be satisfactorily described by linear polyparameter equations providing that the data are divided into two groups: unassociated and associated (alcohols, amines, acids) liquids.¹⁹ While for 45 substances R is equal to 0.693 only, for separate groups the following equations with a satisfactory correlation were obtained:

a) non-associated compounds (see Fig. 1a)

$$-\Delta H = 95.53 - 1157.6\delta^2 + 2.43B; R=0.974 (r_{OB}=0.964)$$

a) associated compounds (see Fig. 1b)

$$-\Delta H = 0.558 - 2478.6 \frac{n-1}{n+2} + 2.462B; R=0.973 (r_{OB}=0.93).$$

*Such a subdivision into two groups of associated and unassociated substances is necessary for the description of

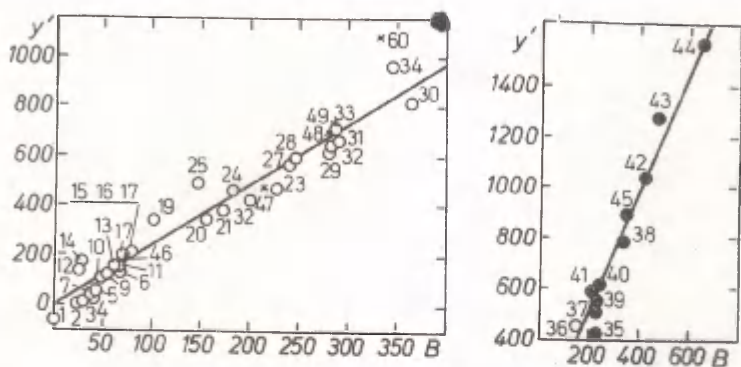


Fig.1. Relationship between functions a) $y' = -\Delta H_{CHCl_3}$ 1157.6 for unassociated solvents or b) $y' = -\Delta H_{CHCl_3} + 2478.6f(n)$ for associated compounds and solvent basicity "B". The solvents: 1- CCl_4 ; 2- CH_2Cl_2 ; 3- o-dichlorobenzene; 4- dichloroethane; 5-bromobenzene; 6-nitromethane; 7- α -chloronaphthalene; 8- chlorobenzene; 9-benzoylchloride; 10-benzene; 11-nitrobenzene; 12- $SOCl_2$; 13-toluene; 14- SO_2Cl_2 ; 15- m-xylene; 16- o-xylene; 17- p-xylene; 18- mesitylene; 19-acetic anhydride; 20-benzonitrile; 21-methylacetate; 22-methylpropionate; 23-acetone; 24-ethylacetate; 25- $POCl_3$; 26-diethylcarbonate; 27-dioxane; 29- Et_2O ; 30- $DMSO$; 31-THF; 32- i- Pr_2O ; 33- Bu_2O ; 34- $MeCONMe_2$; 35- i-BuOH; 36-acetic acid; 37- i-AmOH; 38- $PhNH_2$; 39-n-PrOH; 40-EtOH; 41-MeOH; 42- $PhNMe_2$; 43-Pyr; 44- Et_3N ; 45-pyrrole; 46-diethylsulfate; 47- γ -butyrolactone; 48-tetrahydropyran; 49-trimethylene oxide; 50- $(EtO)_3PO$. According to Ref.19

Table 1

PMR CHEMICAL SHIFTS OF CHCl_3 IN SOLVENTS
AND THEIR PARAMETERS

N°	Solvent	ppm	$\frac{n^2-1}{n^2+2}$	$\frac{\epsilon-1}{2\epsilon+1}$	δ^2	B	E
1	Cyclohexane	0	0.2563	0.203	0.068	0	0
2	CCl_4	0.128	0.2742	0.225	0.076	0	0
3	CHCl_3	0.178	0.2563	0.359	0.088	14	3.3
4	Bu_2O	0.538	0.2421	0.289	0.061	285	0
5	Dioxane	0.578	0.2543	0.223	0.110	237	4.2
6	Et_2O	0.680	0.2167	0.344	0.057	280	0
7	Ethylacetate	0.714	0.2275	0.374	0.082	181	1.6
8	i- Pr_2O	0.716	0.2256	0.329	0.052	293	0
9	Methylacetate	0.723	0.2218	0.395	0.091	170	3.6
10	THF	0.765	0.2451	0.404	0.076	287	0
11	Cyclohexanone	0.914	0.2699	0.461	0.104	242	0.5
12	MeCOEt	0.922	0.2309	0.461	0.085	209	2.0
13	Et_3N	1.158	0.2430	0.243	0.051	650	0
14	Piperidine	1.608	0.2703	0.381	0.075	706	0

the second component effect on shifts of deformation frequencies of C-H bond of CHCl_3 $\bar{\nu}=1210 \text{ cm}^{-1}$ in solvents (our data) or valent frequencies C-D of CDCl_3 $\bar{\nu}=2252 \text{ cm}^{-1}$. The latter value is proposed in Ref. 20, 21 as a measure of substance basicity, but our calculations show that it may be matched with "B" or "OD" scales only by means of poly-parameter equations. For data of Ref. 20 (8 points):

$$\Delta\nu_{\text{CD}} = 42.44 - 96.26 \frac{n^2-1}{n^2+2} - 0.104B; R=0.992; s=2.01$$

The H-bond formation between CHCl_3 and organic donors is studied by the PMR-method too²². However, PMR changes do not correlate satisfactorily with the basicity "B" due to perturbing influence on non-specific solvation. After treating mathematically the most complete list for 14 solvents from Ref. 23 (Table 1) the following relationships were obtained:

$$\Delta = (0.229 \pm 0.080) + (0.00181 \pm 0.00025)B; R=0.904; s=0.186$$

$$\Delta = -0.105 + 2.279 \frac{n^2-1}{n^2+2} + 1.340 \frac{\delta-1}{2\delta+1} + 6.015\delta^2 + 0.00185B - 0.0262E; R=0.987; s=0.040 \quad \text{or}$$

$$\Delta = -0.545 + 1.597 \frac{\delta-1}{2\delta+1} + 3.068 + 0.00182B; R=0.986; s=0.081 \text{ (Fig.2).}$$

Although the basicity of solvents remains the most significant parameter and determines the value of chemical shift of CHCl_3 protons in ppm, a satisfactory correlation between these factors can be realized only with taking into account perturbing effects caused by auto-association of a solvent determined by its cohesion energy density and its polarity. Excluding the δ^2 parameter from calculations decreases the correlation coefficient R to 0.979 and excluding the polarity parameter reduces this value to 0.937. Thus, for weaker H-bonds one-parameter correlation between the bond characteristics and the basicity parameter "B" is

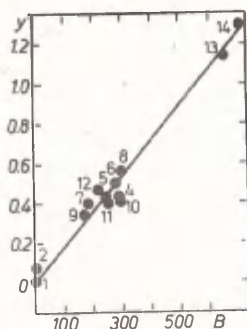


Fig. 2. Plot of $y' = \Delta - 1.598f(\delta) - 3.068\delta^2$ vs. basicity B for PMR shifts of CHCl_3 .

linear dependence on two parameters of solvents - the basicity DN according to Ref. ¹ and the electrophilicity (polarity) E_T according to Ref. ⁵. Krygowski has shown convincingly that solvent effects on the chemical kinetics, equilibrium and spectral phenomena cannot be satisfactorily described by physical models of solvation only. But one cannot agree with the proposed model, as it takes into account specific solvation phenomena only:

$$Q = Q_0 + \alpha E_T + \text{BDN}$$

Though the proposed model is applicable both for kinetic and spectral and some thermodynamic data (ion activity coefficients, ion solvation enthalpies, solution enthalpies), a satisfactory correlation ($R \geq 0.95$) is obtained only in 55% of all studied cases ²⁴. In 35% of cases the authors consider the correlation as reasonable ($0.9 > R > 0.95$) but according to Ref. ⁷ such a value of R should be considered as unsatisfactory. In 10% of cases the value of R is less than 0.9. Thus in every second case a two-parameter equation gives an unsatisfactory correlation or gives no corre-

impossible.

Since one-parameter correlations of some physico-chemical properties with separate properties (characteristics) of solvents are satisfactory only for some particular cases, many authors propose the use of two-parameter equations.

Here first of all we should refer to the above mentioned model by Fawcett and Krygowski ⁴ which is based on a

lation at all, whereas the use of a four-parameter equation which takes into account both the non-specific and specific solvation produces much better results as shown in Ref. ⁷ and other later articles. However, more perfect picture of solvent effects may be obtained if using a five-parameter equation which includes the factor of cohesion energy density of solvent i.e. its "resistance" against the influence of external factors. Though the E_T parameter includes partially the factors of non-specific solvation (as shown in Ref. ²⁵), they are rigidly connected with the electrophilicity parameter E and are not differentiated depending on the character of process or solute nature. Therefore the E_T parameter does not describe correctly the influence of non-specific solvation.

Hence, other one- or two-parameter equations based on the use of the data on complex formation enthalpies do not give a satisfactory description of solvent effect on processes in the solvents. This concerns in particular the multiplicative rule of V.A. Terentyev ²⁶ proposed for characteristics of H-bonds. According to this rule the H-bond formation enthalpies,

ΔH , the logarithms of complex formation equilibrium constants, $\lg K$, and the corresponding shifts of spectral band of X-H groups in the IR spectra may be described by the following equation:

$$J = A \times D$$

where "A" and "D" are characteristics of donor and acceptor powers of interacting components. The appropriate values of "A" and "D" were obtained on the basis of averaged data for many H-bond formation reactions; the reaction between pyridine and phenol was assumed as an initial one. But such a rule is observed not in all cases or frequently with unsatisfactory accuracy only. This will be clear, if to take into account the technique of evaluating ΔH and K values which is realized always in the presence of some excess of a second component ²⁷, i.e. under conditions when non-specific solvation is possible to a certain degree. The relative

value of deviations called by this effect depends on the strength of the H-bond. It is clear also that the multiplicative rule gives the best results for the values of spectral shifts, $\Delta\nu$, for which experiments are possible in the inert solvent medium with only insignificant excess of a second component. Indeed, as we have shown previously for strong H-bonds, in most cases a satisfactory linear interdependence may be observed, though introduction of additional terms into the equation may slightly improve correlation in many cases.

Besides, the inapplicability of the multiplicative rule towards the equilibrium constants was demonstrated recently in Ref.²⁸ on the theoretical grounds.

The same reasonings should be applied towards the one-parameter "rule of base-acid function multiplications" of A.V. Yohansen and the two-parameter B-C scale of Drago. The first scale²⁹ uses the formula: $\Delta X = \Delta X_{A_1} P_1 E_j$ for the description of H-bond formation enthalpies, IR spectra intensities or band changes.

Here " ΔX " are changes in the studied properties under standard conditions. The author proposed the interaction of phenol with diethyl ether as a standard reaction. P_1 and E_j parameters characterize the acidic (electrono-accepting) ability of A_1H molecule and basic (electrono-donating) ability of molecule B_j in the H-bonds. The values $E=0$ for CCl_4 and $E=1.0$ for Et_2O were used as standard electrono-donating parameters (E-factors).

Thus, the scale from Ref.²⁹ does not differ essentially from the scale of Ref.²⁶ and for it the same reproofs are to the point. Really, the picture cited by the author of Ref.²⁹ illustrates the interdependence of different H-bond energies vs. the bond energy with phenol, but at the same time in the figure one may see a significant dispersion of experimental points.

We made an attempt to realize a correlation between "E"-factors and corresponding values of Koppel-Palm basicities "B" (i.e. $\Delta\nu_{PhOH} = \Delta\nu_{MeOD}$) for 27 points (Table 2), but the

Table 2
"E-FACTORS" OF SOLVENT BASICITIES ACCORDING TO
YOHANSEN Ref.²⁹ AND THE SOLVENT PARAMETERS

N°	Solvent	"E"	B	$\frac{n^2-1}{n^2+2}$	$\frac{\epsilon-1}{2\epsilon+1}$	δ^2	E Palm
1	CCl ₄	0	0	0.2742	0.225	0.076	0
2	Et ₂ O	1.0	280	0.2167	0.344	0.057	0
3	THF	1.04	287	0.2451	0.404	0.076	0
4	Dioxane	0.94	237	0.2543	0.223	0.110	4.2
5	PhOEt	0.62	158	0.2979	0.341	0.100	0.8
6	Ph ₂ O	0.42	123	0.3340	0.321	0.068	0
7	DMF	1.17	291	0.2584	0.488	0.198	2.6
8	Me ₂ CO	0.90	224	0.2201	0.465	0.095	2.1
9	Ethylacetate	0.88	181	0.2275	0.374	0.082	1.6
10	(BuO) ₃ PO	1.24	283	0.2555	0.397	0.040	6.3
11	DMSO	1.27	362	0.2826	0.485	0.225	3.2
12	Sulfolane	0.92	157	0.2849	0.483	0.133	2.3
13	Methylnitrate	0.55	65	0.2327	0.480	0.170	5.1
14	Et ₃ N	1.70	650	0.2430	0.243	0.051	0
15	PhNMe ₂	0.70	422	0.3225	0.362	0.095	0
16	Pyridine	1.53 or	1.30 472	0.2989	0.441	0.104	0
17	MeCN	0.75	160	0.2106	0.480	0.140	5.2
18	PhCN	0.68	155	0.3084	0.471	0.123	0
19	Benzene	0.27	48	0.2947	0.231	0.085	2.1
20	Et-O-t-Bu	1.22	298	The values of "E-Palm" are absent in the literature and the corresponding data are not included into the calculations by means of five-parameter equation.			
21	(t-Bu) ₂ O	1.38	321				
22	Propylene oxide	0.82	282				
23	Furane	0.35	103				
24	Bu ₂ S	0.80	252				
25	Ph ₂ CO	0.85	192				
26	Dimethylsulfate	0.68	75				
27	Me ₃ NO	1.47	467				

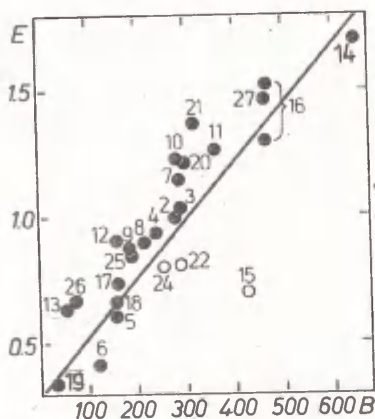


Fig. 3. Plot of "E-Factor" of Yohansen ²⁹ vs. basicity B.

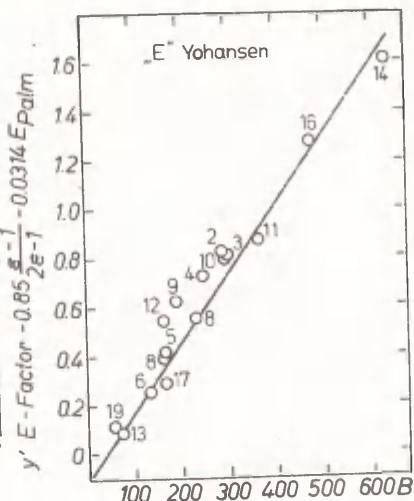


Fig. 4. Plot of the function $y' = \text{"E-Factor"} - 0.830 f(\delta) - 0.0314 E_{\text{Palm}}$ vs. basicity B.

obtained results were unsatisfactory (Fig.3).

The use of a five-parameter equation for 19 points for which all the necessary parameters were present improves the correlation markedly ($R=0.937$) and after excluding from calculations the "worst" point N°15 (dimethyl-aniline) one obtains an excellent correlation ($R=0.982$). It is quite possible that the initial data for dimethylaniline are incorrect, as this point is the most deviating also in the case of one-parameter dependence between the "E-Factor" and "B". When excluding this point, R increases immediately up to 0.924!

For 18 points the following equation was obtained:

$$\begin{aligned} \text{"E-Factor"} = & 0.107 + 0.011 \frac{n^2-1}{n^2+2} + 1.009 \frac{\delta-1}{2\delta+1} - \\ & - 0.621 \delta^2 + 0.0026B + 0.034 E_{\text{Palm}}; R=0.982; s=0.092; \end{aligned}$$

$$r_{01}=0.234; r_{02}=0.278; r_{03}=0.062; r_{04}=0.939; r_{05}=0.048$$

The exclusion of unimportant factors allows to simplify the following equations:

$$\text{"E-Factor"} = -0.100 + 0.830 \frac{g-1}{2g+1} + 0.00262B + 0.0314 E_{\text{Palm}} ;$$

$$R=0.9801 \quad s=0.093 \text{ (Fig.4), or some worse:}$$

$$\text{"E-Factor"} = -0.097 + 1.030 \frac{g-1}{2g+1} + 0.00255B; R=0.970; \\ s=0.115.$$

Thus the "E-Factor" scale is reduced to the same "B" scale based on H-bond, but the former values are subject to perturbing effect of non-specific solvation (caused by polarity of solvent) and somewhat less to electrophilic solvation.

Analogous considerations are valuable for the E-C scale of Drago³⁰. This author states that proportionality between the enthalpies of complex formation of different acceptors with the same donors and their donor numbers DN suggested by Gutmann is not observed in many cases. With the purpose to correct these disagreements he proposed the following two-parameter equation founded on the theory of "soft" and "hard" bases and acids:

$$\Delta H = E_A E_B + C_A C_B$$

where A and B are indices referring to reagents (Lewis acid and base) and E and C are the corresponding characteristics obtained by statistical data handling of many reaction series. However, the author himself shows that when treating the literature data with the purpose to obtain E and C values, one obtains significant standard errors in many cases. The physical sense of the proposed parameters is also not quite clear (electrostatic and covalent contributions). However, when performing calculations by the formula from Ref.³⁰, significant disagreements with the experimental values are found in many cases. With a view to eliminate the influence of these discrepancies Drago in posterior letters refused from the spectrophotometric determination

Table 3

COVALENT C_B AND ELECTROSTATIC E_B CHARACTERISTICS
OF SOLVENTS ACCORDING TO DRAGO³⁰ AND CORRESPONDING
BASICITIES "B"

N ^o	Solvent	C_B	E_B	B
1	Pyridine	6.40	1.17	472
2	NH ₃	3.46	1.36	473
3	EtNH ₂	6.02	1.37	667
4	Et ₂ NH	8.83	0.866	637
5	Et ₃ N	11.09	0.991	650
6	MeCN	1.34	0.886	160
7	DMFA	2.48	1.23	291
8	MeCONMe ₂	2.58	1.32	343
9	Ethylacetate	1.74	0.975	181
10	Methylacetate	1.61	0.903	170
11	Me ₂ CO	2.33	0.987	170
12	Et ₂ O	3.25	0.963	280
13	i-Pr ₂ O	3.19	1.11	279
14	Bu ₂ O	3.30	1.06	285
15	Dioxane	2.38	1.09	237
16	THF	4.27	0.978	287
17	DMSO	2.85	1.34	362
18	Sulfolane	3.16	1.38	157
19	Me ₂ NCONMe ₂	3.10	1.20	336
20	Benzene	0.681	0.525	48
21	p-Xylene	1.78	0.416	68
22	Mesitylene	2.19	0.574	77
23	(Me ₂ N) ₃ PO	3.55	1.52	471
24	Piperidine	9.32	1.01	706

of ΔH values and proposes to use only calorimetric results. However, as a matter of fact, Drago's formula suffers from the same intrinsic sin as other one- or two-parameter dependences where the non-specific interaction is not taken into account.

When verifying the dependence between the characteristic of basicity C_B according to Drago and the basicity "B" for 24 compounds (see Table 3) for which all the necessary characteristics are present, only a low correlation coefficient was obtained $R=0.872$.

$$C_B = -(0.0789 \pm 0.5353) + (0.0119 \pm 0.0014)B; R=0.872$$

The use of a five-parameter equation slightly improves the correlation ($R=0.933$) and after excluding the most deviating points $N^{\circ}N^{\circ}3,5,24$ ($EtNH_2$, Et_3N , piperidine) from considerations one obtains for 21 points an equation with satisfactory correlation coefficient:

$$C_B = -3.049 + 15.345 \frac{n^2-1}{n^2+2} + 3.988 \frac{g-1}{2g+1} - 25.484 \delta^2 + 0.0123B - 0.0386E; R=0.969; s=0.6381; r_{01}=0.029; r_{02}=0.064; r_{03}=0.176; r_{04}=0.894; r_{05}=0.557$$

Since the polarity and electrophilicity parameters are negligible,

$$C_B = -0.867 + 9.277 \frac{n^2-1}{n^2+2} - 15.393 \frac{g-1}{2g+1} + 0.124B; R=0.964; s=0.645$$

The excluding of $f(n)$ or δ^2 parameters decreases the correlation more considerably - the R value falls to 0.951 or 0.898, respectively.

It is of interest that the dependence between the thermodynamic characteristic C_B and spectral one B is markedly affected by the polarizability and cohesion energy density parameters. The first parameter is, as shown above, of importance for the correlation of the thermodynamic scale of donor numbers with the spectral "B"-scale and the δ^2 parameter improves this dependence too, though is less important¹⁹. The role of the cohesion energy density factor,

i.e. the energy of autoassociation of solvent molecules becomes clear, if assuming that a cavity in an associated structure of liquid ³¹ is necessary in order to introduce a soluting gaz molecule ^{8,32}, for passing of a solute from one phase into another or the complex formation. The stronger is the interaction between the solvent molecules the more is the energy loss required to form the cavity; the coefficient at the cohesion energy density term correlates with the sign "minus". The scale of Drago is constructed on the base of complex formation enthalpies. We have shown the same role of δ^2 parameter when considering solvent effects on the enthalpies of complex formation with iodine ³³.

Unlike the C_B scale, the scale for electrostatic contributions E_B (for bases) proposed by Drago does not correlate neither with the considered parameters nor with their combinations. The most closely this parameter is, probably, connected with the solvent polarity. For 24 points from Table 3 the following relationship is obtained by a five-parameter equation:

$$E_B = -0.147 + 0.129 \frac{n^2-1}{n^2+2} + 1.631 \frac{\delta-1}{2\delta+1} + 0.515 \delta^2 + 0.00057B + 0.0068E; R=0.811; s=0.184; r_{01}=0.014; r_{02}=0.705; r_{03}=0.502; r_{04}=0.483; r_{05}=0.276$$

To achieve a satisfactory correlation ($R=0.970$) 6 points should be excluded from the consideration, i.e. 25% of total quantity which is unlikely correct. The pair correlation coefficient with the polarity term increases to 0.925. As the parameters of polarizability and basicity are negligible, we may suppose with a considerable probability that the E_B factor is mainly associated with a non-specific solvation of considered in Ref. ³⁰ complexes caused by the polarity of the second compound.

We have also to consider the " β " scale of basicities of Kamlet and Taft based on shifts of UV spectra of p-nitroaniline in different solvents. To characterize the H-bonds, ("the influence of solvent polarity") these authors

Table 4

The β -Scale of H-Bond Acceptor Ability according to Ref. 34.
Corresponding Solvent Parameters

N ^o	Solvent	B	$\frac{n^2-1}{n^2+2}$	$\frac{\epsilon-1}{2\epsilon+1}$	δ^2	B	E
1	PhOCH ₃	0.247	0.3030	0.345	0.097	155	1.4
2	Dioxane	0.386	0.2543	0.223	0.110	237	4.2
3	PhNO ₂	0.393	0.3215	0.479	0.113	67	0
4	PhCN	0.409	0.3084	0.470	0.123	155	0
5	Methylacetate	0.456	0.2218	0.395	0.091	170	1.6
6	Ethylacetate	0.481	0.2275	0.385	0.082	181	1.6
7	Et ₂ O	0.488	0.2167	0.344	0.057	280	0
8	Bu ₂ O	0.490	0.2421	0.289	0.061	285	0
9	Me ₂ CO	0.499	0.2201	0.465	0.105	224	2.1
10	MeCOEt	0.504	0.2309	0.461	0.084	209	2.0
11	Tetrahydropyran	0.512	0.2531	0.440	0.081	290	(0)
12	THF	0.523	0.2465	0.405	0.076	287	0
13	Cyclohexanone	0.534	0.2699	0.460	0.104	242	0.5
14	Pyridine	0.661	0.2989	0.441	0.104	472	0
15	Et ₃ N	0.686	0.2430	0.243	0.051	650	0
16	DMFA	0.710	0.2584	0.488	0.198	291	2.6
17	MeCONMe ₂	0.749	0.2627	0.480	0.199	343	2.4
18	N-methylpyrrolidone	0.754	0.2773	0.488	0.121	319	1.3
19	DMSO	0.752	0.2826	0.485	0.225	362	3.2
20	(Me ₂ N) ₃ PO	0.990	0.2730	0.475	0.096	471	0
21	t-BuOH	0.950	0.2343	0.434	0.110	247	5.2
22	i-PrOH	0.920	0.2302	0.460	0.131	236	8.7
23	n-BuOH	0.850	0.2421	0.467	0.112	231	10.8
24	EtOH	0.770	0.2214	0.469	0.167	235	11.6
25	MeOH	0.620	0.2034	0.478	0.201	218	14.9
26	PhCH ₂ OH	0.560	0.3139	0.445	0.169	208	10.9
27	Ethylenglycole	0.510	0.2593	0.481	0.388	224	15.0
28	H ₂ O	0.140	0.2051	0.491	0.592	156	21.8
29	Ethylbenzoate	0.431	0.2966	0.385	0.064	142	?
30	CH ₂ ClCOOEt	0.363	0.2545	0.463	0.096	125	?

proposed first a two-parameter α - β scale of donor-accepting power of H-bonds which was later supplemented with the third π -parameter which should characterize the non-specific solvation term. We shall not consider in details this scale proposed in Ref.³⁴ but just point out some of its defects, namely: 1) the scale is valid for a small number of solvents only (ca.30); 2) shifts of absorption maxima in UV spectrum are usually registered with less precision than in IR spectra and the proposed in Ref.³⁴ scale is based on the difference of frequency shifts of two compounds: p-nitroaniline and N,N-p-nitrodiethylaniline; 3) the common parameter of non-specific solvation π does not differ separate and in most cases different influence of polarity and polarizability of medium on physico-chemical processes; 4) in a number of cases, as shown by the same authors³⁴, it is necessary to separate the β -scale into 2 scales: for alcohols and non-associated solvents.

The β -scale may be connected with the basicity "B"-scale by means of a polyparameter equation. If considering all 28 points listed in Table 4, the total correlation coefficient is very low (only 0.817). But if considering separately non-associated solvents N°N° 1-20 and alcohols N°N° 21-28, the correlation is much better. For the first class of solvents $R=0.915$ and when excluding the most deviating points N°18 (N-methylpyrrolidone) and N°20 (HMPA) R value grows up to 0.966:

$$\beta = 0.267 - 1.267 \frac{n^2-1}{n^2+2} + 0.585 \frac{\delta-1}{28+1} + 1.23 \delta^2 +$$

$$+ 0.000818B - 0.0018E; \quad R=0.960; \quad s=0.043; \quad r_{01}=0.121; \\ r_{02}=0.306; \quad r_{03}=0.526; \quad r_{04}=0.715; \quad r_{05}=0.103.$$

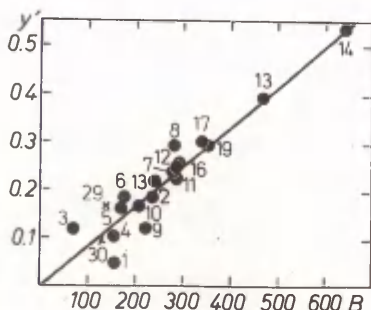


Fig. 5. Plot of function $y' = B + 1.243f(n) - 0.593f(\delta) + 1.192\delta^2$ vs. the basicity B for non-associated solvents. N°N° refer to points as listed in Table 4.

If excluding in turn separate parameters, the R value decreases, respectively, to 0.929; 0.926; 0.918; 0.658; and 0.965.

Thus the electrophilicity parameter turns out to be negligible. The most valuable one is the basicity parameter but introduction of non-specific solvation and cohesion energy density terms into calculations improves the correlation considerably:

$$\beta = 0.257 - 1.243 \frac{n^2 - 1}{n^2 + 2} +$$

$$+ 0.593 \frac{\delta - 1}{2\delta + 1} + 1.192\delta^2 + 0.00081B; R=0.9651; s=0.041.$$

The reliability of the proposed regression equation is confirmed by the fact that the data for p.p. 29 and 30 not taken into account in the initial calculations because of unknown electrophilicity parameter "E" coincide excellently with the equation.

For alcohols (points N°N° 21-28) the following equation was obtained:

$$\beta = -0.697 - 1.131 \frac{n^2 - 1}{n^2 + 2} + 5.226 \frac{\delta - 1}{2\delta + 1} - 0.521\delta^2 - 0.055E;$$

$R=0.988$; $s=0.063$ (the basicity term is negligible) or a little worse:

$$B = 2.058 + 7.740 \frac{\delta - 1}{2\delta + 1} - 0.521\delta^2 - 0.061E; R=0.981; s=0.063$$

The exclusion of polarity parameter lowers the R value to 0.952, when excluding δ^2 $R=0.970$ and when excluding E $R=0.920$. Thus the β -scale for alcohols approaches more

likely the Reichardt's "polarity" scale.

Hence, for the description of solvent effects on phenomena which occur in solutions, in general case it is necessary to use a five-parameter equation which takes into account both the specific and non-specific solvation and the cohesion energy density as well. The basicity scales proposed by different authors are equivalent and their reciprocal evaluating is possible.

To our mind the use of the scale of donor numbers (DN) or basicities (B) is the most expedient. Both these scales are subject to perturbing effect of non-specific solvation only insignificantly. The former scale is practically insensitive to small perturbing effects of non-specific solvation as it is based on the considerably higher values of thermal mixing effects of substances with SbCl_5 which are of the order of many units or dozens of kcal/mole. However, the DN values are cited for only ca. 70 compounds and to obtain them precious calorimetric measurements are necessary. On the contrary, the basicity "B" values are listed for many hundreds of compounds, corresponding spectral values may be obtained easily and with great precision and the conditions of spectral measurements which are carried in dilute solution of CCl_4 with relatively small excess of donor towards phenol provide almost complete suppression of non-specific solvation process. Both scales supplement each other. One cannot obtain the "B" values for acid chloroanhydrides, inorganic chlorides, and many other similar substances due to chemical reactions which take place. In its turn the listed values of DN, i.e. the mixing heats with SbCl_5 for water and alcohols are hardly precise as these compounds decompose SbCl_5 . But since both scales are readily convertible¹³ the needed values in one scale may be easily obtained on the basis of corresponding values in the other scale.

The general shortcoming of DN and B scales, as of any other among the above considered scales, is their empiricity. They have no direct connection with the structure of molecules and no theoretical base. Some objections may arise

as to the solvent used: the donor numbers are measured in dichloroethane solution but we know that in the CCl_4 medium the heats of mixing of donors with SbCl_5 are different^{35,36}. On the other hand, CCl_4 used as a solvent for spectral determination of "B" values is itself a weak acceptor, i.e. can compete with phenol or other electron acceptors for a donor molecule. Probably the most correct from the methodical point of view should be a scale based on the values of free energies of electron solvation³⁷ but to obtain these data experimentally is rather difficult. At present they are available for water, methanol, and DMF only. Therefore now one should be recommended to use the B_{PhOH} scale to calculate solvent effects on the behavior of solutes by means of polyparameter equations, as this scale is the most representative and precise one.

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ALKYL AND ALKENYL ESTERS OF SULFONIC ACIDS
XXV. CORRELATION OF HAMMETT-TAFT SUBSTITUENT
CONSTANTS WITH SOME PARAMETERS OF PMR, NQR, IR,
AND UV SPECTRA AND DIPOLE MOMENTS OF SULFOESTERS
AND OTHER SULFOCOMPOUNDS.

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PMR spectra of substituted propargylbenzenesulfonates were studied. Linear correlations are established between proton chemical shifts in benzene ring or Δ -methylene group of propargylbenzenesulfonate, which is a reaction center, and substituent constants in benzenesulfoacid. Influence of structural factors X and Y in $X-SO_2-Y$ compounds on the correlation between physical parameters of molecules and σ -constants of the Hammett-Taft equation is compared on the basis of PMR, NQR, IR, and UV spectral data and dipole moments.

Much attention is paid to studies of correlations between the values of physical parameters of sulfo compounds and Hammett σ -constants based on changes in NQR spectrum frequencies¹⁻³, changes in IR spectrum frequencies and intensities⁴⁻¹², on displacements of electronic absorption band maxima in UV spectra¹³⁻¹⁸, and on changes in dipole moment values¹⁹⁻²².

Recently we have shown^{14,21} that there exists a quantitative dependence between changes in dipole moment values and σ -constants of the Hammett equation and that a satisfactory linear dependence exists between the displacements of symmetric (ν_s) and asymmetric (ν_{as}) bands of SO_2 group valent oscillations in sulfoesters and the electronic substituent effects⁶. The position of frequencies and the inten-

sity of ν_s and ν_{as} bands of S-O bond in XSO_2Y compounds depends considerably on the character of X and Y substituents and on the aggregate state. Correspondingly there exists a correlation between the Hammett σ constants and the ν_s or ν_{as} frequencies. One may observe the splitting or redistribution of absorption band intensities in the region of ν_s and ν_{as} too.

It is interesting to investigate the reasons of breaking of correlations, of band splittings and of redistribution of its intensities. Therefore we have studied the PMR spectra of substituted propargylbenzenesulfonates and compared the dependencies of physical parameters of molecules on the Hammett constants for many compounds including the SO_2 group and consider the reasons which have lead to those phenomena,

EXPERIMENTAL

The esters were obtained according to Ref 23. The purity of esters was verified chromatographically. The PMR spectra were obtained on Varian T-60 spectrometer with frequency 60 MHz in CCl_4 solutions. Tetramethylsilane (TMS at $30 \pm 1^\circ C$) was used as an internal standard. The proton chemical shifts are determined in δ scale relatively to TMS.

RESULTS AND DISCUSSION

The investigation of esters by means of PMR method permits to obtain valuable information about the electron density distribution in their molecules. The values of chemical shift in PMR spectra depend markedly on the sulfur atom status in C-S and S-O ester bonds, on the state of 2p orbitals of an oxygen atom and on the influence of X-substituents in benzene ring.

The data from Table 1 show that with an increase in the electron-accepting power of X the chemical shift of protons in the aromatic ring and α -methylene group increases too which indicates their electron deshielding in the studied series of esters. The aromatic protons are the most sensitive to substituent effects, since the transmission of electronic influence of substituent "X" is realized immediately.

Table 1
 PROTON CHEMICAL SHIFTS OF SUBSTITUTED PROPARGYL-
 BENZENE SULFOESTERS AND RATE CONSTANTS OF THEIR
 ETHANOLYSIS. $4\text{-XC}_6\text{H}_4\text{SO}_2\text{OCH}_2\text{C}\equiv\text{CH}$.

N°	X	$\delta_{\text{H}_{\text{Ar}}}$	$\delta_{\text{-CH}_2\text{-}}$	$\delta_{\text{-CH}}$	$k \cdot 10^6, 1/\text{sec}, 50^\circ$
1.	MeO-	7.36	4.61	2.56	3.72
2.	PrO-	7.38	4.61	2.56	3.80
3.	Me-	7.50	4.62	2.56	4.19
4.	n-Bu-	7.49	4.62	2.56	4.20
5.	Et-	7.49	4.62	2.56	4.20
6.	H-	7.60	4.65	2.57	7.16
7.	Cl-	7.70	4.68	2.57	18.6
8.	Br-	7.71	4.68	2.57	19.0
9.	CN-	8.10	4.74	2.58	63.2
10.	NO ₂ -	8.20	4.76	2.58	93.3

In the series of p-substituted propargylbenzene sulfoesters a linear correlation between the values of aromatic proton chemical shifts and the σ values of substituents "X" (see Fig. 1) is observed. This dependence may be described by equation (1):

$$(1) \quad \delta_{\text{H}_{\text{Ar}}} = 7.60 + (0.794 \pm 0.078)\sigma; r=0.984$$

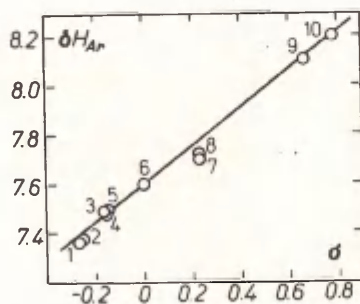


Fig. 1. Plot of PMR chemical shifts of benzene ring protons vs. σ values. Numbers refer to points as listed in Table 1.

Values of chemical shifts of the propargyl group protons indicate that the transmission of the substituent "X" effects through the $-\text{SO}_2-$ group and the ester oxygen atom takes place only on the α -methylene group of alcoholic component which presents a reaction center in the nucleophilic substitution reactions ^{24,25}. The correlations of $-\text{CH}_2-$ group δ with σ or σ° constants of the Hammett equation are linear and the following equations are obtained:

$$\delta_{-\text{CH}_2-} = 4.64 + (0.155 \pm 0.096)\sigma^\circ ; r=0.985 \quad (2)$$

$$\delta_{-\text{CH}_2-} = 4.65 + (0.143 \pm 0.082)\sigma ; r=0.982 \quad (3)$$

The influence of the substituents "X" on the aromatic protons is five times stronger than on the α -methylene group protons of the alcoholic component. The noted substituent effects on the ester reaction center - the α -carbon atom of alcoholic component - manifest themselves also in their reactivity which is illustrated by the comparison of the ethanolysis rate constants in Table 1.

Thus, the correlation between chemical shifts of aromatic protons and the σ constants indicates the presence of a conjugation effect. The correlation $\delta_{\text{HAX}}-\sigma$ is at least much better ($r=0.984$) than the correlation $\delta_{\text{HAR}}-\sigma^\circ$ ($r=0.954$). There exists a correlation between chemical shifts of the α -methylene group protons and both the σ and σ° constants of substituents "X", the correlation coefficient for σ and σ° being essentially the same. This phenomenon is caused first of all by steric peculiarity of sulfoester structures; alkyl- and arylsulfoesters exist in a conformation with the gauche location of alkyl and aryl radicals. On the basis of the dipole moment investigations we have established that the alcoholic component of sulfoesters is taken out from the C-O-S plane on angle of $40-60^\circ$ in the direction of the oxygen atom of SO_2 group ^{14,26,27} and, as a result, the conjugation between two fragments of the molecule, $\text{Xalk}(\text{C}_6\text{H}_4)\text{SO}_2$ and $\text{Oalk}(\text{C}_6\text{H}_5)$, is interrupted. The same conclusion was made by the authors of Ref. ²⁸ on the basis of studies of the Kerr effect for arylmethanesulfonates.

Table 2
CORRELATION BETWEEN PHYSICAL PARAMETERS
OF SULFOESTER MOLECULES AND CONSTANTS OF THE HAMMETT-
-TAFT EQUATION

Compound	Method	Correlated parameters	Nature of correlation	Ref.
1	2	3	4	5
$\text{AlkSO}_2\text{Cl}^{35}$	NQR	$\nu_m - \sigma$	linear	1
$\text{XC}_6\text{H}_4\text{SO}_2\text{Cl}^{35}$	NQR	$\nu_m - \sigma$	linear	1
$\text{X}_1\text{X}_2\text{X}_3\text{X}_4\text{C}_6\text{HSO}_2\text{Cl}$	NQR	$\nu_m - \sigma$	linear	2
$\text{X}_1\text{X}_2\text{X}_3\text{X}_4\text{C}_6\text{HSO}_2\text{F}$	NQR	$\nu_m - \sigma$	linear	2
RSO_2Cl	NQR	$\nu_m - \sigma^+$	linear	3
$\text{XC}_6\text{H}_4\text{SO}_2\text{CF}_3$	IR	$\nu_s - \sigma$	linear	4
$\text{XC}_6\text{H}_4\text{SO}_2\text{CF}_3$	IR	$\nu_{as} - \sigma$	linear	4
$\text{XC}_6\text{H}_4\text{SO}_2\text{F}$	IR	$\nu_s - \sigma$	no linear	5
"	IR	$\nu_{as} - \sigma$	linear	5
$\text{XC}_6\text{H}_4\text{SO}_2\text{CH}_2\text{CH}_2\text{CH}_3$	IR	$\nu_s - \sigma$	no linear	6
"	IR	$\nu_{as} - \sigma$	linear	6
$\text{XC}_6\text{H}_4\text{SO}_2\text{CH}_2\text{CH}=\text{CH}_2$	IR	$\nu_s - \sigma$	no linear	6
"	IR	$\nu_{as} - \sigma$	linear	6
$\text{XC}_6\text{H}_4\text{SO}_2\text{CH}_2\text{C}=\text{CH}$	IR	$\nu_s - \sigma$	no linear	6
"	IR	$\nu_{as} - \sigma$	linear	6
$\text{AlkSO}_2\text{NHC}_6\text{H}_5$	IR	$\nu_s - \sigma^*$	linear	7
"	IR	$\nu_{as} - \sigma^*$	linear	7
$\text{C}_2\text{H}_5\text{SO}_2\text{NHC}_6\text{H}_4\text{X}$	IR	$\nu_s - \sigma$	no linear	7
"	IR	$\nu_{as} - \sigma$	no linear	7
$\text{XC}_6\text{H}_4\text{SO}_2\text{C}_6\text{H}_4\text{Y}$	IR	$\nu_s - \Sigma\sigma^+$	linear	8
"	IR	$\nu_{as} - \Sigma\sigma^+$	linear	8
$\text{X}-2-\text{ClC}_6\text{H}_3\text{SO}_2\text{C}_6\text{H}_4\text{OH}-4$	IR	$\nu_s - \sigma$	no linear	9
"	IR	$\nu_{as} - \sigma$	linear	9
$\text{XC}_6\text{H}_4\text{SO}_2\text{Cl}$	IR	$\nu_s - \sigma, \sigma^+$	no linear	10
"	IR	$\nu_{as} - \sigma, \sigma^+$	no linear	10
$\text{Alk(Ar)SO}_2\text{Alk(Ar)}$	IR	$\nu_s - \Sigma\sigma^*$	linear	11
"	IR	$\nu_{as} - \Sigma\sigma^+$	linear	11
$\text{XC}_6\text{H}_4\text{SO}_2\text{NH}_2$	IR	$\frac{\nu_s + \nu_{as}}{2} - \sigma$	linear	12

Table 2 (continued)

1	2	3	4	5
$\text{XC}_6\text{H}_4\text{SO}_2\text{F}$	UV	$\lambda - \sigma_c^+$	linear	13
$\text{XC}_6\text{H}_4\text{SO}_2\text{CH}_2\text{C}\equiv\text{CH}$	UV	$\lambda - \sigma_c^+$	non-linear	14
$\text{XC}_6\text{H}_4\text{SO}_2\text{Cl}$	UV	$\lambda - \sigma_c^+$	linear	15
$\text{HC}_6\text{H}_4\text{SO}_2\text{Br}$	UV	$\lambda - \sigma_c^+$	linear	16
$\text{XC}_6\text{H}_4\text{SO}_2\text{NH}_2$	UV	$\lambda - \sigma_c^+$	linear	17
$\text{XC}_6\text{H}_4\text{SO}_2\text{NHNH}_2$	UV	$\lambda - \sigma_c^+$	linear	18
$\text{XC}_6\text{H}_4\text{SO}_2\text{NHC}_6\text{H}_5$	UV	$\lambda - \sigma_c^+$	non-linear	19
$\text{XC}_6\text{H}_4\text{SO}_2\text{OC}_6\text{H}_5$	UV	$\lambda - \sigma_c^+$	non-linear	19
$\text{XC}_6\text{H}_4\text{C}_6\text{H}_4\text{SO}_2\text{Cl}$	UV	$\lambda - \sigma_c^+$	non-linear	19
$\text{XC}_6\text{H}_4\text{SO}_2\text{Cl}$	UV	$\lambda - \sigma_c^+$	non-linear	19
$\text{XC}_6\text{H}_4\text{SO}_2\text{F}$	Dip.mom.	$\int \sigma_c^+$	linear	20
$\text{XC}_6\text{H}_4\text{SO}_2\text{OCH}_2\text{CH}=\text{CH}_2$	Dip.mom.	$\int \sigma_c^+$	linear	21
$\text{XC}_6\text{H}_4\text{SO}_2\text{NHC}_6\text{H}_5$	Dip.mom.	$\int \sigma_c^+$	linear	22
$\text{C}_6\text{H}_5\text{SO}_2\text{NHC}_6\text{H}_4\text{X}$	Dip.mom.	$\int \sigma_c^+$	linear	22
$\text{XC}_6\text{H}_4\text{SO}_2\text{OCH}_2\text{C}\equiv\text{CH}$	Dip.mom.	$\int \sigma_c^+$	linear	14

They have shown that the polarity and polarizability of ester molecules correspond to the perpendicularity of aromatic ring and C-O-S group planes ($\varphi = 90^\circ$) and to the predominance of gauche-conformation of C-S-O-C chain.

Many investigations were carried out dealing with the influence of substituents in the aromatic ring on changes in physical parameters with the purpose to determine the ability to transfer the electronic effect. Table 2 lists some correlations of sulfocompounds, XSO_2Y , where effects of substituents X and Y are studied. As one can see from Table 2 correlations are absent for IR^{5-7,9,10} and UV^{14,19} spectra. But it is surprising that for one and the same substance under the same conditions of studying spectra one observes the absence of correlation for one of the bands only, mainly for ν_s . This does not agree with observation of Bel-

lany²⁹ that for sulfo compounds $X-SO_2-Y$ there exists, analogously to carbonyl compounds³⁰, a correlation between symmetric and asymmetric valent frequencies of SO_2 group. Later Robinson³¹ has established that other sulfo compounds also obey this regularity. The correlation $\nu_s = f(\nu_{as})$ proved to be very useful and then it was found possible to operate with the position of one band only or with the halfsum of the bands $\frac{1}{2}(\nu_s + \nu_{as})$ ^{12,31-33}.

A disturbance in the correlation when studying IR spectra may be accounted for by some causes:

1. The bands of symmetric vibration of SO_2 group are placed in the spectrum region $1200-1160\text{ cm}^{-1}$. In the same region the absorption bands of many other groups (e.g. C-H, C-Cl) are placed. Hence, the interpretation of spectra in this region is difficult^{6,9,34}.

2. One may observe the splitting of ν_s and ν_{as} bands of sulfo compounds in suspension or solid state and the same bands are very wide and flat on their peaks. The conclusion can be drawn that such a form of the band is formed by superposition of two or more neighbouring bands. In solutions the progression of narrow bands is observed⁶.

3. Changes in molecule coplanarity are possible which results in disturbing the electron effect transmission⁸ or in the existence of compounds in the form of two rotatory isomers³⁵.

4. An error in determining the SO_2 group valent vibration frequencies ($2-4\text{ cm}^{-1}$) and the relatively insignificant interval of changes under the influence of substituents also leads to disturbance in the correlation, e.g. the absence of correlation between the ν_s values and the G -constants adduced in Refs^{5,6,9} may be explained by errors in frequency determinations.

The electron absorption spectra of sulfo compounds with the general formula $XO_6H_4SO_2R$ ($R=Cl, Br, F, NH_2, NHNH_2, OR, OC_6H_5, NH_2CH_2, NHC_6H_5$) have two absorption bands of unlike intensity:

a short wave intensive band (K-band) and a long wave band with the small intensity (B-band). The K-band proved out to be shifted bathochromically in the correlation with the G_c^+ constants of substituents. This displacement is accompanied by an increase in the K-band intensity with an increase in G_c^+ values. The small intensive B-band is almost independent of the substituent nature in the benzene ring.

The breaking of the linear dependence between the benzene ring absorption band and substituent effects may be associated with the often observed overlapping of K and B bands which can lead to errors in the band identification and, as a result, to the correlation breaking as one observes in Ref. ¹⁴. Another reason of the disturbance of the correlation between $\Delta\lambda$ values and the influence of substituents in the benzene and biphenyl sulfochlorides, arylsulfoesters, and arylsulfoanilides ¹⁹ may be in significant errors when determining the position of absorption maxima for these compounds. As shown in Ref. ¹⁵ a satisfactory linear correlation is observed between the G_c^+ values and the bathochromic shifts of K-bands for benzenesulfochlorides with the growth of +M effect of p-substituents "X".

Thus, on the basis of the analysis of NQR, PMR, IR, and UV spectra or dipole moments of compounds with SO_2 group the conclusion can be made that the disturbance of the correlation for some XSO_2Y compounds is caused by the violation of molecules coplanarity, the presence of rotational isomers or errors in determining frequencies.

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Note of the Editor.

Application of the correct procedure of multilinear regression analysis to the values from Table 1 leads to the following results.

The equation used is

$$Y \approx Y_0 + \rho \delta^0 + \rho_R^+ \delta_R^+ + \rho_R^- \delta_R^-$$

Point samples are 1, 3, 6 + 10

Y	Y_0	ρ	ρ_R^+	ρ_R^-	s	n
$\delta_{H_{Ar}}$	7.607 ± 0.016	0.486 ± 0.029	0.246 ± 0.025	0.456 ± 0.053	0.012	7
δ_{-CH_2-}	4.645 ± 0.004	0.135 ± 0.024	0.024 ± 0.007	—*	0.0034	7
$lgk+6$	0.83 ± 0.04	1.41 ± 0.04	—*	—*	0.04	7

*The parameter is excluded in the course of data handling as statistically insignificant on the confidence level of 0.95.

Solvent Effects on the Reaction Kinetics of Dialkylmagnesium with Epoxides

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The reaction kinetics of diethylmagnesium with 3-phenyl-1,2-epoxypropane is studied in ethyl ether and its mixtures with tetrahydrofuran, *n*-heptane, benzene, and chlorobenzene. The reaction mechanism is verified. Dialkylmagnesium dimers are more reactive than monomers. The reaction rate is not sensitive to changes in the medium polarity and polarizability. Additions of non-solvating solvents accelerate the reaction via shifting the association equilibrium position.

I. Introduction.

One of the most interesting problems in the field of organomagnesium compounds is a relationship between their reactivity and medium. In this laboratory solvent effects in the reactions of organomagnesium compounds with ketones and acetylenic compounds are studied quantitatively ¹⁻³. In some cases a quantitative separation of specific and non-specific solvation effects was reached. Then reactions with epoxides were subject to studies.

The reaction between organomagnesium compounds and epoxides is of interest as a general method of obtaining alcohols. Therefore a lot of works (Refs. 4,5) are devoted to preparative aspects of this reaction. However, few kinetic studies

have been carried out. Little is known about solvent effects on this reaction. This is accentuated for by the fact that the reaction between Grignard reagent and epoxides is rather complicated. Only with symmetric organomagnesium compounds the reaction leads practically to one or two products.

The group of French scientists⁶ has studied the reaction kinetics of diethylmagnesium with 3-phenyl-1,2-epoxypropane in ethyl ether. Having determined the reaction initial rates under equimolecular or close conditions the authors have come to the conclusion that the total trimolecular reaction has the second order in organomagnesium compound. The same work shows that in stronger solvating solutions than ethyl ether the reaction is very slow or does not occur at all.

Our goal was to elucidate separately the role of specific and non-specific solvations in the reaction of diorganomagnesium compounds with epoxides. As a model process we used the reaction of diethylmagnesium with 3-phenyl-1,2-epoxypropane which leads practically to 1-phenyl-3-pentanol only and is studied partially by the French scientists. The kinetic measurements were carried out under pseudomonomolecular conditions at high excess of diethylmagnesium. This minimises reaction product effects and, if varying the concentration of a reagent in excess, gives more pieces of information on the reaction mechanism. Ethyl ether, mixtures of ethyl ether with tetrahydrofuran; and mixtures of ethyl ether with various polarity non-solvating solvents (heptane, benzene, and chlorobenzene) were used as reaction media. Kinetic measurements were carried out by the method of samples. Further analysis was done with the use of GLC.

2. Experimental Technique. Reagents and Solvents.

All operations with purified substances and solutions of organomagnesium compounds were carried out in the atmosphere of pure dry argon.

3-Phenyl-1,2-epoxypropane was synthesized by oxidizing allylbenzene with benzoylhydroperoxide⁷. The product was distilled in the argon current, the fraction 92-93.5°C (14 mm Hg) was collected, $d_4^{20} = 1.0181$; $n_D^{20} = 1.5229$.

Diethylmagnesium was obtained in the form of ethereal solution from the solution of ethylmagnesium bromide prepared as usually. Magnesium bromide was settled by adding slowly 1.5 mole of dioxane per a mole of ethylmagnesium bromide.

Diethylmagnesium solutions were prepared by adding weighed portions of corresponding solvents to an appropriate amount of the ethereal solution of dialkylmagnesium. Solution concentrations in basic magnesium were determined by titration.

Solvents (ethyl ether, tetrahydrofuran, benzene, chlorobenzene, heptane) were purified, if necessary, from peroxides, dried, and before use were distilled in the argon current over metallic sodium or calcium hydride.

Kinetic Measurements

The reaction between diethylmagnesium and 3-phenyl-1,2-epoxypropane was carried out under pseudomonomolecular conditions. The excess of diethylmagnesium averaged 20 moles per a mole of epoxide. Measurements were done at $30 \pm 0.2^\circ\text{C}$.

The reaction flask placed into the thermostat was closed with a teflon stopper with holes to let argon and reagents in and to take samples. The holes were closed with silicone rubber stoppers. Hypodermic syringes were used for transfer of solutions.

The reaction kinetics was followed using the method of samples. At appropriate moments of time from the reaction mixture samples (2 ml) were collected and hydralized by 2 ml of 20% aqueous solution of NH_4Cl . The ethereal layer was separated and dried by anhydrous magnesium sulfate. The samples were analyzed by the GLC method.

The analysis was done on a "Voruchrom" chromatograph with flame-ionization detector. Stationary phase-5% silicone oil "XE-60" on chromatone N-AW 0.20-0.25 mm. Gas-carrier is nitrogen. Temperature of the column is 165°C . Heptadecane

and acenaphthene were used as an internal standard. The reaction course may be monitored both by the consumption of epoxide and the formation of alcohol (1-phenyl-3-pentanol). However, more reproducible results were obtained by the first method. The first order rate constants, k , were calculated by the least squares method from the linear relationship:

$$\ln \varphi = \ln (\varphi_0 - \varphi_0) - kt$$

where φ is a ratio of peak heights of epoxide and the internal standard on the chromatogram.

Fig. 1 illustrates an example of such a relationship. Accuracy of determining the rate constant averages $\pm 10\%$.

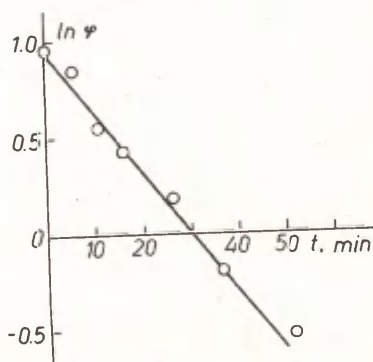


Fig. 1. Semilogarithmic plots of the reaction of diethylmagnesium (0.35 mol/l) with 3-phenyl-1,2-epoxypropane. φ is a ratio of peak heights of epoxide and the internal standard on the chromatogram.

3. Ethyl Ether. The Reaction Mechanism .

The reaction kinetics of diethylmagnesium with 3-phenyl-1,2-epoxypropane in ethyl ether was studied under pseudo-monomolecular conditions over the concentration region of diethylmagnesium from 0.06 to 0.56 mol/l. Table 1 lists the first order rate constants obtained. The dependence of the latter on the diethylmagnesium concentration is illustrated in Fig. 2.

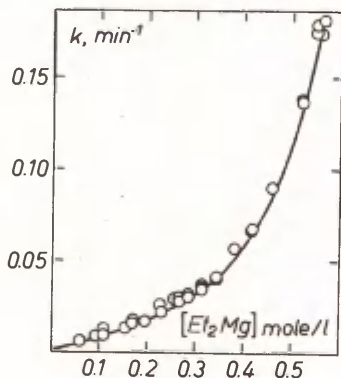


Fig. 2. Plot of first order reaction rate constants of 3-phenyl-1,2-epoxypropane with diethylmagnesium vs. molar concentration of the latter in ethyl ether.

The shape of the curve in Fig. 2. indicates that the reaction mechanism is complicated. The French scientists⁶ have studied the same process under equimolecular conditions by the reaction initial rates at diethylmagnesium concentration 0.145 and 0.336 mol/l. At these concentrations diethylmagnesium was assumed to be essentially in the monomer form. Comparing their results with various reaction schemes, the authors have suggested the following mechanism involving the monomeric form only:

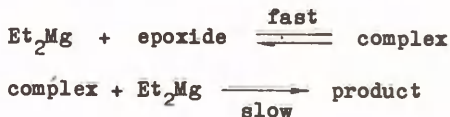


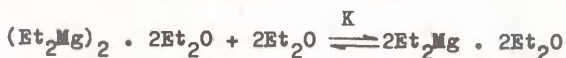
Table 1

Pseudomonomolecular Reaction Rate Constants
of Diethylmagnesium with 3-Phenyl-1,2-Epoxy-
propane in Ethyl Ether at 30°C

Concentration (mol/l)			k_{\min}^{-1}
diethylmagnesium	monomer	dimer	
0.06	0.05	0.005	0.006 0.006
0.09	0.07	0.009	0.007 0.008 0.010
0.11	0.09	0.013	0.010 0.010 0.013
0.15	0.11	0.020	0.012 0.012
0.17	0.12	0.025	0.016 0.017 0.018
0.20	0.14	0.031	0.016
0.23	0.15	0.038	0.021 0.026
0.26	0.17	0.044	0.029
0.27	0.18	0.047	0.028 0.030 0.031
0.28	0.18	0.053	0.031
0.32	0.20	0.058	0.035 0.037
0.32	0.20	0.060	0.038 0.038 0.038
0.34	0.21	0.065	0.039 0.040
0.38	0.23	0.077	0.058
0.42	0.24	0.090	0.067 0.070
0.46	0.23	0.115	0.091
0.52	0.26	0.132	0.138 0.139
0.55	0.25	0.150	0.175 0.180
0.56	0.25	0.155	0.175 0.183

To our mind, at diethylmagnesium concentration of 0.3 mol/l, dimers cannot be neglected and with higher concentrations the suggested mechanism does not account for the dependence of the first order constants on the diethylmagnesium concentration found by us. Therefore an attempt has been made to take into account the association of diethylmagnesium in the ethereal solution.

Data on the association of diethylmagnesium are scanty and contradictory. For the equilibrium



Westera et al. have found the value of $K=3.3 \cdot 10^{-3} \text{ l.mol}^{-1}$ in benzene and $K \sim 8 \cdot 10^{-4} \text{ l.mol}^{-1}$ in cyclohexane. Unlike this, Ducom⁹ has obtained the value of $K=6.3 \text{ l.mol}^{-1}$ in benzene. Ashby and coworkers¹⁰ have published the dependence of the apparent degree of the diethylmagnesium association on the molal concentration of the latter in ethyl ether determined ebullioscopically.

To convert these data into the molarity scale we have determined experimentally the dependence of the density of diethylmagnesium ethereal solution on its concentration and then assuming values to the association equilibrium constant, K, calculated dependences of the association degree on the concentration. The best agreement of the calculated curve with the experimental one was obtained at $K=6.60 \cdot 10^{-3} \text{ l.mol}^{-1}$. To our mind the agreement of this value with the data of Westera is reasonable. Further it is not difficult to obtain monomer and dimer concentrations with any titrated concentration of diethylmagnesium (Fig.3, Table 1). Realizing that these data are of rather approximate character, we assume, nevertheless, that they characterize, qualitatively at least, the diethylmagnesium state in ethyl ether.

To compare our experimental data with those of the French group we have used the titrimetrical concentrations of diethylmagnesium which were equated by the French scientists to the monomer concentration. Calculation with the assumption of the reaction being trimolecular by the formula

$$C = \frac{k^o c^2}{k_{obs}} - \frac{1}{K}$$

has proved to be possible only within the concentration range from 0.06 to 0.3 mol/l. The values of $k^o = 0.265 \pm 0.017$ $\text{l.mol}^{-1} \text{min}^{-1}$

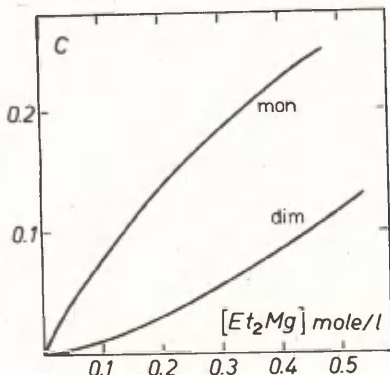
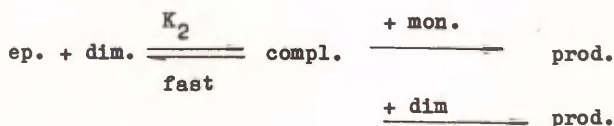


Fig. 3. Plot of diethylmagnesium monomer and dimer concentrations vs. titrimetrical diethylmagnesium concentrations in ethyl ether.

and $K = 12 \pm 2.1$ l.mol^{-1} have been obtained. This result is close enough to that obtained elsewhere by the French group: $k = 0.275 \pm 0.005$ and $K = 6.2 \pm 0.6$.

Substitution of monomer or dimer concentrations for the total concentration of diethylmagnesium has produced no reasonable results. However the observed first order reaction rate constant has been found to depend essentially linearly on the square of dimer concentrations beginning with the total diethylmagnesium concentration of 0.15 mol/l (Fig.4). On this basis the following reaction mechanism may be suggested:



$$k_{\text{obs.}} = \frac{k_{11}K_1/\text{mon.}^2 + (k_{12}K_1 + k_{21}K_2)/\text{mon.}/\text{dim.} + k_{22}K_2/\text{dim.}^2}{1 + K_1/\text{mon.} + K_2/\text{dim.}}$$

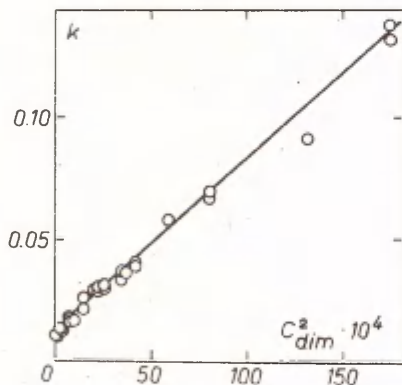


Fig. 4. Plot of the reaction rate constant observed vs. dimer concentrations in diethylmagnesium solutions.

In this case, evidently, equilibria of coordination complex formations between diethylmagnesium and epoxide are strongly shifted to the left, i.e. $(K_1/\text{mon.} + K_2/\text{dim.}) \ll 1$, and reactivity of dimers exceeds markedly that of monomers ($k_{12}, k_{22} \gg k_{11}, k_{21}$). The last conclusion is, to our mind, of especial interest. Quite possible that with the other reactions involving organomagnesium compound this fact

should be also taken into account.

It should be emphasized that above the reaction rate constant was assumed to be independent of the medium polarity. Dielectric constant of diethylmagnesium ethereal solutions is known ¹¹ to increase significantly with the solution concentration. We have established (see section 4) that the reaction rate constant is not sensitive to the solvent polarity (dielectric constant).

4. Mixtures of Ethyl Ether with Tetrahydrofuran.

In strongly solvating solvents the reaction of diethylmagnesium with epoxide proceeds very slowly. Thus, e.g., according to Ref. 6 the reaction yield with 3-phenyl-1,2-epoxypropane (1:1) at 35°C for 24 hours is 95% in ethyl ether, 2% in tetrahydrofuran, and 0% in hexamethapoll. These solvent effects are accounted for by specific solvation and the necessity of coordination of epoxide with a magnesium atom. However, the question about non-specific solvent effects on the reaction remained open.

With reactions of organomagnesium compounds with ketones we used ¹ adding non-solvating solvents, e.g. heptane, varying thus the reaction mixture dielectric constant with specific solvation being constant. This method allowed to find out medium polarity effect on the reaction studied.

In the given case this method, however, cannot answer unequivocally to the question about the role of non-specific solvation, since additions of inert solvents can shift markedly the position of the association equilibrium, and the reaction rate with epoxide (as shown in section 3) is sensitive enough to the ratio of monomer and dimer concentrations.

We have studied the reaction kinetics in various mixtures of ethyl ether with tetrahydrofuran at constant concentration of diethylmagnesium (0.35 mol/l). On the one hand, diethylmagnesium in tetrahydrofuran is known ¹⁰ to be always monomeric. On the other hand, we found elsewhere ¹² that with

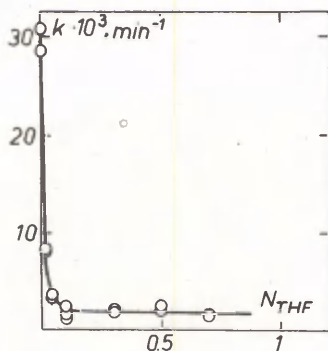


Fig. 5. Plot of pseudo-monomolecular reaction rate constants of diethylmagnesium (0.35 mol/l) with 3-phenyl-1,2-epoxypropane vs. tetrahydrofuran content in ethereal solution.

Table 2

Pseudomonomolecular Reaction Rate Constants of Diethylmagnesium (0.35 mol/l) with 3-Phenyl-1,2-Epoxypropane in Mixtures of Ethyl Ether with Tetrahydrofuran

Molar fraction THF	k, min^{-1}	$\frac{D-1}{2D+1}^*$
0	0.040**	0.345
0.01	0.0083 0.0082	0.346
0.04	0.0036 0.0032	0.349
0.10	0.0025 0.0016 0.0012	0.353
0.30	0.0022 0.0020	0.369
0.50	0.0025 0.0022	0.382
0.70	0.0016 0.0015	0.392

* Kirkwood function of the medium dielectric constant calculated proceeding from the assumption about

** additivity of component molar fractions from section 3.

propylmagnesium bromide beginning with the amount of tetrahydrofuran of 20 mol% the resolution equilibrium was completely shifted to tetrahydrofuran as a stronger base. We proceeded from the assumption that with diethylmagnesium an analogous picture should be observed. Table 2 lists the results of our kinetic measurements. Fig. 5 illustrates the dependence of pseudomonomolecular rate constants.

Small additions of tetrahydrofuran turned out to strongly slow down the reaction. However, beginning with the fraction of tetrahydrofuran of 10 mol% the reaction rate constant is independent of the tetrahydrofuran content in the mixture and, hence, independent also of the medium polarity measured in terms of Kirkwood function (see Table 2). On this basis the conclusion can be made that a solvent influences the reaction studied via specific solvation and the medium polarity effect may be neglected. Simultaneously the pseudofirst order rate constant for 0.35 molar solution of diethylmagnesium in tetrahydrofuran can be estimated : $0.0019 \pm 0.0004 \text{ min}^{-1}$

5. Mixtures of Ethyl Ether with Non-Solvating Solvents

As established elsewhere^{13,14}, additions of n-heptane to dipropyl- and diphenylmagnesium solutions in different donor solvents accelerate markedly the reaction with ketones. Logarithm of the reaction rate constant depends linearly on the reaction mixture Kirkwood function up to relatively high content of heptane. This indicates that the solvent polarity influences the reaction rate.

For the reaction of diethylmagnesium with epoxide the reaction rate is found to be independent of the solvent polarity (section 4). Nevertheless, additions of n-heptane to the ethereal solution of diethylmagnesium influence markedly the reaction rate, the rate constant increasing with the heptane content in the reaction mixture.

The reaction rate constants were determined under pseudomonomolecular conditions at diethylmagnesium concentration 0.2 mol/l. Table 3 lists the results. Fig. 6 illustrates

the plot of rate constant vs. the reaction mixture composition. The reaction mixture composition is calculated taking into account that not less than a mole of ether is coordinated with a mole of diethylmagnesium.

Correlation of the rate constant logarithms with the Kirkwood function of the medium dielectric constant calculated proceeding from the assumption of additivity of component mole fractions has revealed no linear dependence, just as should be expected on account of the results from section 4. Hence, the role of heptane in this case is in decreasing ether concentration and shifting thus the association equilibrium position. As assumed in section 3 an increase in dimer contents in the reagent leads to increase in the reaction rate constant which can account for the above results.

Table 3

Pseudomonomolecular Reaction Rate Constants of Diethylmagnesium (0.2 mol/l) with 3-Phenyl-1,2-Epoxypropane
in Ethyl Ether - n-Heptane Mixtures

Mole fraction of heptane	k, min^{-1}	Conc., mol/l			$k \left(\frac{[\text{eth}]}{[\text{eth}]_0} \right)$	$k_0 \left(\frac{[\text{dim}]}{[\text{dim}]_0} \right)^2$
		ether	dim.	mon.		
0	0.017	9.3	0.032	0.14	0.017	0.017
0.08	0.040	8.6	0.039	0.12	0.037	0.025
0.20	0.064	7.5	0.047	0.11	0.051	0.037
0.42	0.098	5.4	0.060	0.080	0.057	0.060
0.55	(0.106) *	4.2	0.072	0.056	(0.048)	0.086

* Precipitation begins.

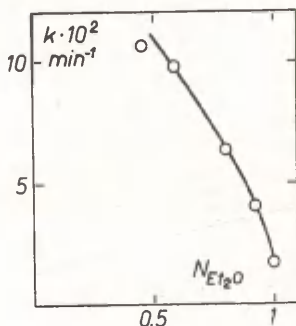


Fig.6. Plot of the reaction rate constant of diethylmagnesium (0.2 mol/l) with 3-phenyl-1,2-epoxypropane vs. ethyl ether-heptane mixture composition.

To verify this assumption we calculated concentrations of ether, dimer, and monomer in the reaction mixture with various additions of heptane. Calculations were done using the association equilibrium constant of diethylmagnesium in pure ethyl ether (determined from the data of Ashby (section 3)) and the constant for the system diethylmagnesium-ethyl ether in cyclohexane (from Ref. 8). Additivity of mole fractions of medium component effects on the association equilibrium was assumed. Table 3 lists the obtained concentrations of species.

Further we proceeded from the following assumptions.

If recoordination equilibria of ether for epoxide at magnesium atom are actually strongly shifted to the left (see scheme in section 3), i.e. $(K_1/\text{mon}/ + K_2/\text{dim}/) \ll 1$, then

$$k_{\text{obs}} = \frac{k_{11}K_1/\text{mon}/^2}{/\text{ether}/} + \frac{(k_{12}K_1 + k_{21}K_2)/\text{mon}/\text{dim}/}{/\text{ether}/} + \frac{k_{22}K_2/\text{dim}/^2}{/\text{ether}/}$$

Multiplying the observed rate constants by the ratio of ether concentrations for this mixture $/\text{ether}/$ and the solution in pure ether $/\text{ether}/_0$:

$$k' = k \frac{[\text{ether}]}{[\text{ether}]_0}$$

one finds specific rate constants depending only on the association equilibrium position in the solution (the last but one column in Table 3).

On the other hand, if the reaction rate constant is actually determined mainly by the square of dimer concentration (see section 3), the same specific constants should be approximately equal to the constant in pure ether multiplied by the square of the ratio of dimer concentrations in this mixture and in pure ether:

$$k' \approx k_0 \left(\frac{[\text{dim}]}{[\text{dim}]_0} \right)^2$$

Data in two last columns in Table 3 agree satisfactorily enough which confirms the probability of our assumptions and above explanation of influence of heptane additions on the reaction rate.

To verify finally whether medium polarity and polarizability effects on the reaction rate are absent, some measurements of rate constants in the mixtures of ethyl ether with benzene and chlorobenzene were done*. Since diethylmagnesium concentrations in these experiments were varied from 0.08 to 0.17 mol/l, the values obtained by dividing the first order rate constant by diethylmagnesium concentration are compared. This is associated with the fact that the plot of pseudomonomolecular rate constants vs. concentration in pure ether within this concentration range is essentially linear (section 3). The plot of these conventional rate constants vs. medium composition (Fig. 7) has the same character as with ethyl ether-heptane system (Fig. 6), i.e. an increase in the content of a non-solvating solvent leads always to an increase in the reaction rate. At the same time additions of heptane and benzene decrease and

* With the assistance of V. Alt.

those of chlorobenzene increase medium dielectric constant as compared with pure ether. As to the polarizability of ether medium, it increases with adding benzene and chlorobenzene but changes little with additions of heptane. Thus, the non-specific solvation effect on this reaction may be neglected.

It should be, however, noted that non-specific solvation exerts, apparently, certain effects on the association equilibrium constant of organomagnesium compound. This follows from different values of equilibrium constants determined in different inert media (see section 3). The same follows from different values of rate constants with equal additions of different solvents to ethyl ether (Fig. 7) which comes in the end to differences in association equilibrium constants in mixtures. The question about the role of solvent polarity and polarizability separately remains still open.

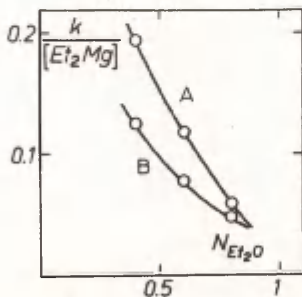


Fig. 7. Plot of reaction rate constant of diethylmagnesium with 3-phenyl-1,2-epoxypropane vs. content of:
A-chlorobenzene
B-benzene
in the mixture with ethyl ether.

6. Conclusion.

The carried out studies of the reaction kinetics of diethylmagnesium with 3-phenyl-1,2-epoxypropane in different media have extended and verified concepts about the reaction mechanism between symmetric organomagnesium compounds and epoxides.

In the first fast reaction step coordination of epoxide with organomagnesium compound and ejection of a solvent molecule occur. Equilibrium of a coordination complex formation is shifted to initial substances. The equilibrium position and thus the reaction rate depend significantly on the solvating ability of a solvent. In strong donor solvents the reaction rate falls essentially to zero.

In the second reaction step a complex of epoxide reacts with a second organomagnesium compound to form alcoholate.

Dialkylmagnesium dimers are more reactive over monomer species. Since an increase in the dialkylmagnesium concentration in the solution is accompanied by increase in the reagent association, at high concentrations of the latter an abnormal increase in the reaction rate is observed.

The reaction rate is not sensitive to changes in the medium polarity and polarizability. However, the latter influence the association equilibrium constant. Additions of non-solvating solvents to ethyl ether increase the reaction rate by shifting the association equilibrium to the formation of dimers.

Hence, for this reaction the dependence of reactivity on a solvent comes to specific solvation effect and association equilibrium position of dialkylmagnesium in a concrete medium.

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Reestimation of Differences Between pK_{BH}⁺ Values of Weak Bases Calculated by Marziano and Cox-Yates Methods

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The analysis ¹ of pK_{BH}⁺ values calculated by Marziano and Cox-Yates methods has been re-examined because of the erroneous use of H₂SO₄ molarities in Marziano treatment previously. ¹ It has been found that the use of [H⁺] values from Ref. 4 in the Marziano treatment did not lead to smaller differences between pK_{BH}⁺ values calculated by Marziano and Cox-Yates methods for very weak bases protonated in concentrated H₂SO₄ solutions. A conclusion has been drawn that at least one of the functions M_c and X needs to be corrected for the range 60-95% H₂SO₄ (wt/wt).

In our previous analysis ¹ the pK_{BH}⁺ values for weak bases calculated by the Marziano² and Cox-Yates³ methods have been compared. It has been shown that they are essentially the same, if H₂SO₄ % at half-protonation of the bases studied is < 60 (wt/wt). Very weak bases half protonated in > 60% H₂SO₄ (wt/wt) have been found to give remarkably different pK_{BH}⁺ values in Marziano and Cox-Yates treatments. But these conclusions have been drawn using in the Marziano equation ²

$$\log \frac{[B]}{[BH^+]} + \log [H^+] = n_B M_c - pK_{BH^+} \quad (1)$$

H_2SO_4 molar concentrations (c_{acid} ; mole/dm³) as estimates for $[\text{H}^+]$.¹ On the other hand, it has been overlooked¹ that the activity coefficient function, M_c , has been calculated² using the hydrated protons molar concentrations $[\text{H}^+]$ as given in Ref. 4. A comparison between $\log[\text{H}^+]$ ⁴ and $\log c_{\text{acid}}$ in aqueous sulfuric acid is shown in Fig. 1.

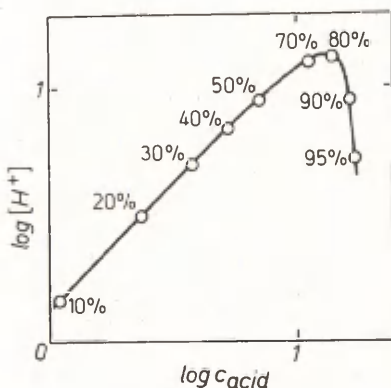


Fig. 1. Plot of $\log[\text{H}^+]$ ⁴ vs. $\log c_{\text{acid}}$ (mole/dm³) for aqueous sulfuric acid solutions. The points show the H_2SO_4 % (wt/wt).

The rupture of linearity $\log[\text{H}^+]$ vs. $\log c_{\text{acid}}$ in concentrated H_2SO_4 solutions causes some doubts about the claimed¹ large differences in pK_{BH^+} values in these solutions if the experimental data were processed according to Eq. 1 and

the excess acidity method ³

$$-\log \frac{[B]}{[BH^+]} - \log C_{H^+} = m^* X + pK_{BH^+} \quad (2)$$

In order to clear up this question we repeated all the calculations described in our previous paper ¹ with the only difference that now the $[H^+]$ values from Ref. 4 were used in Eq. 1. The pK_{BH^+} calculations were performed with the same set of 28 hypothetical bases as before ¹. The differences obtained

$$\Delta = pK_{BH^+}(\text{Eq. 1}) - pK_{BH^+}(\text{Eq. 2}) \quad (3)$$

are represented in Table 1. This Table shows that for bases not weak enough ($\log I=0$ in $\leq 60\%$ H_2SO_4 , wt/wt) the differences (Eq.3) are reasonably small. For weaker bases which are half-protonated in more concentrated H_2SO_4 solutions ($> 60\%$ H_2SO_4 , wt/wt) Eqs. 1 and 2 yield markedly different pK_{BH^+} values (one can find the respective $pK_{BH^+}(\text{Eq.2})$ values in Table 2 in Ref.1). Compared with the Δ values reported previously ¹ (see the Δ values in parentheses in Table 1) the use of $[H^+]$ values from Ref.4 in Eq.1 has lead to even larger discrepancies in pK_{BH^+} values. Surprised by this result we carried out the pK_{BH^+} calculations by Eqns.1 and 2 for following two real weak bases: 1-cyanoazulene (I) and 1,3-dihydroxy-2-methylbenzene (II). The indicator ratio values in aqueous sulfuric acid solutions for these bases were taken from Refs. 5 and 6, respectively. The $[H^+]$ values from Ref. 4 were used. For 1-cyanoazulene we obtained $pK_{BH^+} = -7.54 \pm 0.41$; $n_B = 13.54 \pm 0.87$ (Eq.1) and $pK_{BH^+} = -6.55 \pm 0.39$; $m^* = 1.41 \pm 0.10$ (Eq.2). A similar discrepancy in pK_{BH^+} values was found in the case of 1,3-dihydroxy-2-methylbenzene: $pK_{BH^+} = -8.37 \pm 0.33$; $n_B = 12.49 \pm 0.59$ (Eq.1) and $pK_{BH^+} = -6.68 \pm 0.24$; $m^* = 1.11 \pm 0.05$ (Eq.2). The errors are given at the confidence level $P=0.95$ and the half-protonation takes place at 66% H_2SO_4 (wt/wt) and 73.4% H_2SO_4 (wt/wt) for I and II, respectively. The differences in pK_{BH^+} values for bases

Table 1

The Differences Δ (Eq.3) Between
 pK_{BH^+} (Eq.1) and pK_{BH^+} (Eq.2) for
 the Bases Chosen ^{*})

m [*]	at H ₂ SO ₄ concentrations (wt/wt)			
	20%	40%	60%	80%
0,4	-0.06(0.06)	-0.06(0.08)	-0.08(0.08)	-0.62(-0.19)
0.6	-0.06(0.06)	-0.07(0.06)	-0.11(0.05)	-1.19(-0.79)
0.8	-0.07(0.05)	-0.08(0.06)	-0.15(0.02)	-1.66(-1,28)
1.0	-0.07(0.04)	-0.10(0.04)	-0.20(-0.03)	-2.10(-1.70)
1.2	-0.08(0.03)	-0.10(0.04)	-0.26(-0.10)	-2.53(-2.14)
1.4	-0.10(0.02)	-0.12(0.02)	-0.32(-0.15)	-2.96(-2.55)
1.6	-0.10(0.02)	-0.13(0.01)	-0.38(-0.21)	-3.39(-2.96)

* The values in parentheses are those from our previous paper ¹ where instead of $[H^+]$ ⁴ H₂SO₄ molar concentrations have been used in Marziano treatment ².

I and II are quite as large as one can anticipate using the Δ (Eq.3) estimates given in Table 1.

The results obtained in this paper with $[H^+]$ from Ref.4 in Eq. 1 can be summed up as follows. There seems to be no other way as to confirm the conclusion drawn in our previous paper ¹ about the differences in pK_{HH^+} values calculated by Eqns.1 and 2. If so, at least one of the functions involved (M_c ² and X ³) needs to be corrected in the range 60-95% H_2SO_4 (wt/wt).

Experimental

The same computer and software were used as in our previous paper ¹. The $[H^+]$ values from Ref. 4 used now instead of sulfuric acid molarities in Eq. 1 have been calculated by the equation

$$[H^+] = p/r$$

where

$$r = -1.6958 + 872.96/(93 + p) + 1.2453(0.01p)^4 + \\ + 30.879(0.01 p)^{20} + 5.816(0.01 p)^{28} + 0.022638 p$$

where p is the $H_2SO_4\%$ (wt/wt).

The author is grateful to Dr. R.A. Cox for turning our attention to the erroneous use of H_2SO_4 molarities in the Marziano equation in our previous paper ¹

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On the Interpretation of Experimental Data
on the Alkaline Hydrolysis Rate of Esters
in Aqueous - Ethanol Solutions

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The interpretation of the experimental data on the alkaline hydrolysis rate of a series of phenyl acetates in aqueous - ethanol solutions reported in the communication of Istomin et al¹ is discussed. The attention is paid to the fact that the experimental data used in this work involve "mixed" effective rate constants without a common content within the whole series studied.

In the work of B. I. Istomin and coworkers¹ hydrolysis rates of a series of phenyl acetates are measured. Kinetic measurements were carried out spectrophotometrically under pseudomonomolecular conditions. Bimolecular rate constants, k_2 , were calculated from the relationship $k_2 = k_1 : c_{\text{NaOH}}$. On the basis of the data obtained the authors have found non-additivity in structure and medium effects on the hydrolysis of phenyl acetates in aqueous - ethanol media which results in a reversal of the solvent effect with changes in the leaving group structure (realization of the isoparametricity phenomenon). The work considered suggests a trifactorial regression model which describes adequately the experimental data obtained.

However, the data published by other authors raise some doubts whether such an interpretation of the rate constants observed for this reaction is correct.

1. In aqueous - alcohol solutions concentration of

hydroxide ions is, on the whole, not equal to the concentration of the base added (c_{NaOH}) but is determined by the equilibrium:



i.e. this concentration is always lower. The degree of this disparity (concentration of alkoxide ions) depends on a concrete alcohol, on the concentration of this alcohol in the solution, and temperature^{2,3,4}. The works of Murto^{2,3,4} list the values of K_{ha} for aqueous - ethanol solutions (K_{he}). Since the value of the equilibrium constant, K_{he} , changes with temperature and alcohol mole fraction from 0.33 to 0.98, neglect of equilibrium (1) results in a significant error, especially at high alcohol concentrations. From the K_{he} values available³ it follows, e.g., that at temperature 25°C in 50 v/v ethanol the ratio

$c_{\text{EtO}^-} : c_{\text{OH}^-} = 0.12 (K_{\text{he}} \approx 0.40)$, and in 90% ethanol

$c_{\text{EtO}^-} : c_{\text{OH}^-} = 2.0 (K_{\text{he}} \approx 0.73)$. This means that in 90%

ethanol concentration of hydroxide ions is about three times lower than that of a base added. Thus, calculation of the second order rate constants by dividing first order rate constants by the concentration of sodium hydroxyl added (as it was done in Ref.1) should lead to erroneous results.

2. Since due to equilibrium (1) concentration of etoxide ions in ethanol solutions is high enough, the parallel reaction of ethanolysis (overetherification) is inevitable⁵. Only some quantitative data on the alkaline overetherification rate of phenyl acetates in aqueous - ethanol solutions are available. However, as known from the works of Bender⁶ and Jencks^{7,8,9,10} in aqueous solutions nucleophilicity of alkoxide ions relative to carbonyl carbon exceeds usually that of hydroxide ion. For example, the reaction of p-nitrophenyl acetate with etoxide ion proceeds 14.6 times faster than with hydroxide ion (according to the calculations of Koskikallio⁵ on the basis of experimental data of Murto⁴ and Jencks⁸). The overetherification rate constant

of phenyl acetate in ethanol at 25°C equals¹¹ $k_2 = 1.25 \pm 0.07 \text{ l/mol}^{-1} \text{ sec}^{-1}$ and is rather close to the rate constant for the reaction of the same ether in 90% aqueous ethanol determined in the work of Istomin et al¹. $k_2 = 1.370 \pm 0.034$. It seems to be much more probable that the latter rate constant characterizes solvolysis rather than hydrolysis rate or is, at least, a sum of hydrolysis and overetherification rates.

On the basis of the above the conclusion may be drawn that in the work of Istomin et al¹ only hydrolysis rate constants for pure water have simple physical sense; the other constants are complex. Surely on the basis of formal constants one can construct any formal models including multiparameter cross correlation equations as done in the work of Istomin et al¹. However, these models characterize complex processes as a whole, and on their basis one can say nothing about influence of different factors on the course of concrete hydrolysis and ethanolysis reactions. For example, originally described in Ref. 1 non-additivity in the effects of the medium and the leaving group structure, manifestation of isoparametricity in the structure and medium effects on the alkaline hydrolysis of esters with the experimentally observed reverse in the dependence of reactivity on medium when passing through the isoparametric value of a substituent effect measure could be due to differences in the leaving group effects for hydrolysis and ethanolysis reactions. In this case one should check whether the appearance of cross terms in the multiparameter correlation equations is caused by changes in the physical content of the rate constants within the series studied or by the presence of parallel processes possessing different sensitivity to changes in the reagent structures and reaction conditions.

Difficulties appearing in measuring alkaline hydrolysis rates of esters in aqueous-alcohol solutions have been known for a long time (see, e.g., the work of Tommila¹²).

With the equilibrium (1) constants known, K_{he} , one can easily determine the hydrolysis rate constants of ethyl ethers of acids in aqueous-ethanol solutions. In this case the overetherification reaction does not prevent from estimating the constants as the products are identical with the reagents. With ethers of other alcohols both the values of K_{ha} and relative concentrations of reaction products (ester and acid salt) are necessary. Spectrophotometric technique of kinetic measurements used in Ref. 1 does not allow to solve this problem, since the reaction is monitored by following changes in the solution optical density caused by the difference of extinction coefficients of a substituted phenolate ion on the one hand, and an initial ester, on the other hand. Since the former substance results both from the hydrolysis and alcoholysis reaction, just an overall reaction rate can be measured.

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