

TARTU STATE UNIVERSITY



ORGANIC REACTIVITY

English Edition
of

Реакционная способность
органических соединений

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June 1974

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AMIDES AND HYDRAZIDES OF OXALIC ACID. XXXI
IONIZATION CONSTANTS OF SOME DERIVATIVES OF ARYLSULF-
AMIDES IN MIXED DIOXANE-WATER SOLVENT

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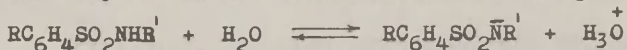
By the method of potentiometric titration in 60% aqueous dioxane at 25°C ionization constants of phenylamides of arylsulfonic acids and substituted amides of aryl sulfonyloxamine acids have been determined. The pK_a values for compounds studied were correlated with Hammett's σ -constants. Transmission factors of electronic effects on NH and NHCOCO

groups have been calculated by the " ρ - ρ " method.

Earlier [1] we studied influence of substituents on dissociation of the sulfohydrazide group in the substituted amides of arylsulfohydrazides of oxalic acid, which allowed to calculate the transmission factors of electronic effects of the oxamide group.

To obtain information about transmission factor of the oxamoyl group and also to study the influence of substituents of the arylsulfonyl and amide parts of the sulfamide molecule, ionization constants of phenylamides of arylsulfonic acids and those of substituted amides of arylsulfonyloxamine acids have been measured. Synthesis of the above mentioned compounds is effected according to the known methods [2,3]. Individuality of synthesized compounds was corroborated by the data of elementary analysis, IR and UV spectroscopy.

The process of acidic dissociation of the studied compounds may be described with the following equation:



Experimental

Phenylamides of arylsulfonic acids have been obtained by heating arylsulfochlorides with aromatic amines in pyridine [2], and the substituted amides of the arylsulfonyloxamine acids - by means of acylation of sodium salts of arylsulfamides with oxamine acid ethers [3].

Properties and the results of analysis of the compounds obtained are shown in Tables 1 and 2.

The ionization constants have been determined by means of potentiometric titration by the known method [4] in 60% aqueous dioxane at 25°C.

The determined transmission factors are averages of 2-3 experiments, including 7-9 measurements each; the pKa values have been processed statistically [5], the errors being calculated at the confidence level of 0.95.

Discussion

From Table 2 it is seen that substituents both in the arylsulfonyl and the amide parts of the sulfamide molecule materially influence the ionization constant value. Substitution of phenyl radical in sulfamide (series A) by phenyloxamoyl one (series B) results in considerable increase in the compound acidity ($\Delta \text{pKa} \approx 5$ units). This may be explained by different acceptor ability of the radicals mentioned above: the oxamoyl residue as compared with the phenyl one increases the shift of the unshared electron pair from the nitrogen atom of the sulfamide group thus to increase the acidity of compounds.

For quantitative evaluation of the influence, the substituents exert upon the dissociation of compounds in the

Table I. PHENYLAMIDES OF ARYLSULFONIC ACIDS AND ARYLSULFONYLOXAMIDES $RC_6H_4SO_2NHR'$

Nos.	R	R'	M.p. °C	Found, %		Formula	Calculated, %	
				N	S		N	S
I	m-NH ₂	C ₆ H ₅	124-125° [6]	-	-	C ₁₂ H ₁₂ NO ₂ S	-	-
2	p-OCH ₃		95-96	5.38	12.31	C ₁₃ H ₁₃ NO ₃ S	5.32	12.17
3	p-CH ₃		102-103 [7]	-	-	C ₁₃ H ₁₃ NO ₂ S	-	-
4	H		109-110 [8]	-	-	C ₁₂ H ₁₁ NO ₂ S	-	-
5	p-Br		119-120 [2]	-	-	C ₁₂ H ₁₀ BrNO ₂ S	-	-
6	p-NO ₂		138-139 [9]	-	-	C ₁₂ H ₁₀ N ₂ O ₄ S	-	-
7	p-NH ₂	COCONHC ₆ H ₅	228-229	13.39	10.16	C ₁₄ H ₁₃ N ₃ O ₄ S	13.16	10.04
8	p-OCH ₃		216-217	8.41	9.67	C ₁₅ H ₁₄ N ₂ O ₅ S	8.38	9.59
9	p-CH ₃		218-219	8.89	10.30	C ₁₅ H ₁₄ N ₂ O ₄ S	8.79	10.07
10	H		221-222	9.28	10.69	C ₁₄ H ₁₂ N ₂ O ₄ S	9.21	10.54
11	p-Cl		245-246	8.54	9.59	C ₁₄ H ₁₁ ClN ₂ O ₄ S	8.27	9.46
12	p-NO ₂		252-254	12.21	9.36	C ₁₄ H ₁₁ N ₃ O ₆ S	12.02	9.18
13	H	COCONHC ₆ H ₄ OCH ₃ -p	218-220	8.50	9.63	C ₁₅ H ₁₄ N ₂ O ₅ S	8.38	9.59
14		COCONHC ₆ H ₄ CH ₃ -p	229-230	8.89	10.17	C ₁₅ H ₁₄ N ₂ O ₄ S	8.79	10.07
15		COCONHC ₆ H ₄ Cl-p	269-270	8.35	9.61	C ₁₄ H ₁₁ ClN ₂ O ₄ S	8.27	9.46
16		COCONHC ₆ H ₄ Br-p	270-271	7.38	8.41	C ₁₄ H ₁₁ BrN ₂ O ₄ S	7.31	8.37
17		COCONHC ₆ H ₄ NO ₂ -p	245-246	12.21	9.31	C ₁₄ H ₁₁ N ₃ O ₆ S	12.08	9.17

* Compounds Nos. 1-7, 9 are crystallized from aqueous ethanol, and the rest of them - from aqueous dimethylformamide.

sulfamide group, Hammett's equation was used. The parameters of linear regressions of pK_a of the compounds studied vs. Hammett's σ -constants are given in Table 3.

Comparing the values of reaction constants of series A ($\rho = -1.862$) and series B ($\rho = -1.374$), one may conclude that the substituents with different acceptor ability at the amide nitrogen affect the sensitivity of the sulfamide group to the structural changes in the arylsulfonyl part of the molecule.

Table 2.

IONIZATION CONSTANTS OF PHENYLAMIDES OF ARYLSULFONIC
ACIDS AND SULFONYLOXAMIDES
 $RC_6H_4SO_2NHR'$

Compound	R	R'	pKa in 60% aqueous dioxane *
I	m-NH ₂	C ₆ H ₅	10.67
2	P-OCH ₃		10.70
3	P-CH ₃		10.65
4	H		10.36
5	P-Br		9.87
6	P-NO ₂		9.00
7	P-NH ₂	COCONHC ₆ H ₅	5.57
8	P-OCH ₃		4.95
9	P-CH ₃		4.83
10	H		4.56
11	P-Cl		4.23
12	P-NO ₂		3.60
13	H		COCONHC ₆ H ₄ OCH ₃ -P
14		COCONHC ₆ H ₄ CH ₃ -P	4.61
15		COCONHC ₆ H ₄ Cl-P	4.46
16		COCONHC ₆ H ₄ Br-P	4.45
17		COCONHC ₆ H ₄ NO ₂ -P	3.98

* Average values of pKa deviations make $\pm(0.01 \div 0.03)$.

Comparison of reaction constants of series B ($\rho = -0.772$) and those of the series of N-substituted arylbenzenesulfamides ($\rho = -2.876$ [1]) makes possible to evaluate the electronic transmission factor of the NHCOCO group, which may be calculated using the " $\rho - \rho$ " method [10], in accordance with which:

$$\rho_{\text{NHCOCO}} = \frac{\rho}{\rho_{\text{st}}}, \text{ where:}$$

ρ - the series constant, containing the oxamoyl group,

ρ_{st} - constant of the series of N-substituted arylbenzenesulfamides [1].

Table 3

CORRELATION PARAMETERS FOR DEPENDENCE OF pK_a
FOR PHENYLAMIDES OF ARYLSULFONIC ACIDS AND ARYLSULFONYLOXAMIDES UPON HAMMETT'S σ - CONSTANT

Series and No. of compounds pK_a of which are involved in regression analysis	Correlation equation	r^*	s	n
A (1-6)	$\text{pK}_a = (10.33 \pm 0.12) - (1.862 \pm 0.040) \cdot \sigma$	0.998	0.13	9
(7-12)	$\text{pK}_a = (4.58 \pm 0.07) - (1.374 \pm 0.037) \cdot \sigma$	0.996	0.05	8
B (10, 13-17)	$\text{pK}_a = (4.54 \pm 0.12) - (0.772 \pm 0.041) \cdot \sigma$	0.996	0.16	7

* The values of reaction constants (ρ), correlation coefficients (r), and standard deviation (s) were calculated by the least squares method.

Using the values of reaction constants for the substituted amides studied earlier, the electronic transmission

factor of the oxamoyl group was calculated as equal to 0.55

On the basis of the reaction constants of the substituted amides of the aryl sulfohydrazides of oxalic acid ($\rho = -0.563$ [1]) and substituted benzenesulfonyloxamides ($\rho = -0.772$, series B), using the " ρ - ρ " method, the transmission factor for the NH-group was calculated:

$$Z_{\text{NH}} = 0.73.$$

This value is close to that ($Z_{\text{NH}} = 0.81$) obtained from kinetic data of acylation of sodium salts of aryl sulfohydrazides ($\rho = -0.525$) and arenesulfamides ($\rho = -0.651$) [11] with the ethers of oxamine acids.

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AMIDES AND HYDRAZIDES OF OXALIC ACID. XXXII.
IONIZATION CONSTANTS FOR BISARYLSULFOHYDRAZIDES OF
OXALIC ACID

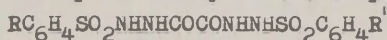
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Bisarylsulfohydrazides of oxalic acid have been obtained synthetically, for which in 60% aqueous dioxan at 25°C, using the potentiometric titration, the ionization constants have been determined. Influence of substituents of miscellaneous electronic nature upon pK_{a1} and pK_{a2} of the compounds obtained was studied.

Proceeding with studying the reactivity of oxalic acid derivatives [1-3], the authors effected synthesis of bisarylsulfohydrazides of oxalic acid with the purpose of determining the influence of substituents with miscellaneous electronic nature upon acidity of the compounds obtained



Bisarylsulfohydrazides of oxalic acid have been obtained by condensation of hydrazides of oxalic acid arylsulfohydrazides with arylsulfochlorides in pyridine or by interaction of oxalic acid dihydrazide with two equivalents of arylsulfochloride. The first way gives possibility of obtaining reaction products with miscellaneous substituents in the arylsulfonyl parts of the molecule, the second way may be effected only with similar substituents.

The constants for the compounds obtained synthetically

Bisarylsulfohydrazides of oxalic acid

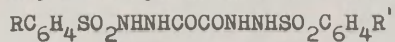


Table I

Nos.	R	R'	Yield, %	M.p. °C	Neutralization equivalent		Actual- ly, % N	Formula	Calcu- lated, % N
					Actual- ly	Calcu- lated			
I	p-NH ₂	H	64	218-219	208.1	413.4	17.12	C ₁₄ H ₁₅ N ₅ O ₆ S ₂	16.94
2	p-OCH ₃		73	227-228	217.3	428.4	13.21	C ₁₅ H ₁₆ N ₄ O ₇ S ₂	13.07
3	p-CH ₃		81	254-255	209.1	412.4	13.69	C ₁₅ H ₁₆ N ₄ O ₆ S ₂	13.58
4	m-CH ₃		70	241-242	208.0	412.4	14.22	C ₁₅ H ₁₆ N ₄ O ₆ S ₂	14.06
5	H		82	256-257	200.7	398.4	14.19	C ₁₄ H ₁₄ N ₄ O ₆ S ₂	14.06
6	p-Cl		80	237-238	217.0	432.9	13.07	C ₁₄ H ₁₃ ClN ₄ O ₆ S ₂	12.95
7	p-Br		63	252-253	239.9	477.3	11.81	C ₁₄ H ₁₃ BrN ₄ O ₆ S ₂	11.73
8	p-NO ₂		54	247-248	223.4	433.5	17.90	C ₁₄ H ₁₃ N ₅ O ₈ S ₂	15.79
9	p-OCH ₃	p-OCH ₃	68	232-233	231.1	458.6	12.50	C ₁₆ H ₁₈ N ₄ O ₈ S ₂	12.22
10	p-CH ₃	p-CH ₃	71	265-266	219.3	426.5	13.28	C ₁₆ H ₁₈ N ₄ O ₆ S ₂	13.14
II	p-Br	p-Br	59	289-290	280.5	556.2	10.14	C ₁₄ H ₁₂ Br ₂ N ₄ O ₆ S ₂	10.07
12	p-NO ₂	p-NO ₂	63	260-261	248.1	488.4	17.31	C ₁₄ H ₁₂ N ₆ O ₁₀ S ₂	17.20

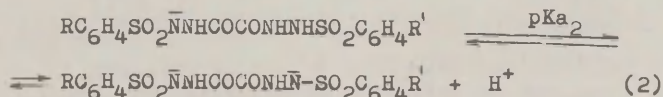
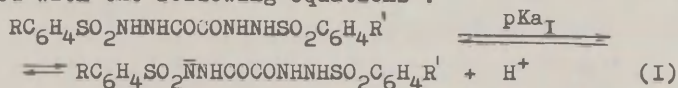
and the results of elementary analysis are shown in Table I.

Identification of bisarylsulfohydrazides was carried out by means of IR and UV spectroscopy.

The IR spectra of bisarylsulfohydrazides of oxalic acid contain characteristic bands of valence vibrations of NH, CO and SO₂ groups. Two absorption bands in the region of 3320-3060 cm⁻¹ characterise the valence vibrations of the NH group. Double character of the carbonyl bands (1720-1690 cm⁻¹) is indicative of symmetric valence vibrations in carbonyl groups of the compounds studied, which may be connected with their arrangement [4]. The valence oscillations of the SO₂ group are represented by two bands in the region of 1350 (ν as SO₂) and 1175 cm⁻¹ (ν^s SO₂). The presence of SO₂, NH, and CO groups in arylsulfohydrazides provides favourable conditions for formation of inter- and intramolecular H-bonds. This interference is corroborated by the low values of valence vibrations of the above-mentioned groups.

In UV spectra of bisarylsulfohydrazides maximum is seen in the region of 230-250 nm, characteristic of the benzene absorption.

Bisarylsulfohydrazides of oxalic acid have two ionization constants pK_{a1} and pK_{a2} which characterize acidity of the sulfohydrazide groups (Table 2). The process of acidic ionization of the studied compounds may be described with the following equations:



From Table 2 it is seen that the donor substituents (D) influence pK_{a2} and practically exert no influence upon pK_{a1} (R=D, R-H - series A); introduction of acceptor

substituents (A) vice versa results in pK_{a1} change, pK_{a2} remaining constant ($R=A$, $R'=H$ - series B).

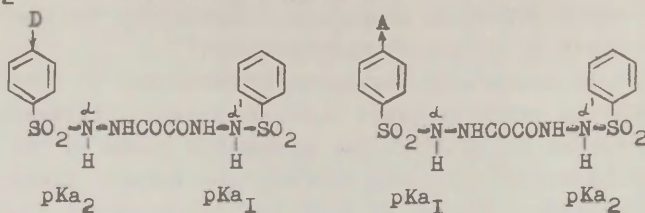


Table 2

IONIZATION CONSTANTS FOR BISARYLSULFOHYDRAZIDES
OF OXALIC ACID, $RC_6H_4SO_2NHNHCOCONHNHSC_6H_4R'$

Nos. *	R	R'	pK_{a1}^{**}	pK_{a2}
I	p-NH ₂	H	8.30	10.11
2	p-OCH ₃		8.29	9.63
3	p-CH ₃		8.29	9.43
4	m-CH ₃		8.28	9.32
5	H		8.29	9.28
6	p-Cl		8.02	9.19
7	p-Br		7.99	9.18
8	p-NO ₂	p-OCH ₃	7.43	9.22
9	p-OCH ₃		8.57	9.96
10	p-CH ₃		8.52	9.84
11	p-Br		7.92	9.31
12	p-NO ₂		7.15	8.44

* Number of the compound corresponds to that in Table I.

** Average deviations of the pK_a values equals $\pm (0.01 \div 0.03)$.

Absence of influence of substituents upon ionization of the second sulfohydrazide group (SO_2NHNH) in the series A and B may be ascribed to considerably dis-

tant position of substituents from the reaction center. Ionization of bisarylsulfohydrazides of oxalic acid depends on changes in electronic density at the nitrogen atom of sulfohydrazone group. Donor substituents increase electronic density, the acceptor ones decreasing it to create conditions for preferable detachment of hydrogen for the sulfohydrazone group, having greater deficit of electrons in the atom of nitrogen.

The pK_{a1} and pK_{a2} for hydrazides in the series C regularly change, substituents of different nature being introduced in the benzene nucleus.

For quantitative estimation of the influence of substituents upon the bisarylsulfohydrazone pK_{a1} and pK_{a2} Hammett's equation was used. Values for the induction constants were taken from literature [7]. The correlation parameters of pK_a dependence upon Hammett's σ - constant are dated in Table 3.

Table 3

CORRELATION PARAMETERS OF THE DEPENDENCE
OF pK_{a1} AND pK_{a2} FOR OXALIC ACID BISARYLSULFO-
HYDRAZIDES UPON HAMMETT'S σ -CONSTANT

Series and Nos of compounds, pK_a of which was involved in regression analysis	Correlation equation	r	s	n
A (1-5)	$pK_{a2} = (9.26 \pm 0.06) - (1.166 \pm 0.040) \cdot \sigma$	0.991	0.11	8
B (5-8)	$pK_{a1} = (8.26 \pm 0.10) - (1.027 \pm 0.034) \cdot \sigma$	0.998	0.07	9
C (5, 9-12)	$pK_{a1} = (8.26 \pm 0.10) - (1.296 \pm 0.020) \cdot \sigma$	0.999	0.04	8
	$pK_{a2} = (9.57 \pm 0.14) - (1.449 \pm 0.019) \cdot \sigma$	0.998	0.15	9

Values of the reaction constants for series A,B and C ($\rho_A=1.116$, $\rho_B=1.027$, $\rho_C=1.296$) inconsiderably differ from the ρ of the substituted amides of arylsulfohydrazides of oxalic acid studied earlier ($\rho=1.181$) [3] and also from those of the hydrazides of arylsulfohydrazides of oxalic acid ($\rho=1.232$), which is indicative of approximately equal influence of substituents on ionization of the sulfohydrazide group.

Experimental

Bisbenzenesulfohydrazide of oxalic acid. To 2.58 g of the hydrazide of benzoisulfohydrazide of oxalic acid in 20 ml of pyridine 1.77 g of benzenesulfochloride is added, heating being provided for 3 hours; the mixture is diluted with 5-fold quantity of water and acidified with hydrochloric acid to obtain acidic reaction. The residue is filtered off, washed with water and dried up. Yield of the substance is equal to 3.26 g.

The IR spectra were obtained using a UR-20 spectrometer in KBr (concentration of 0.5%), the UV spectra being obtained with an G Φ -4A instrument in ethanol ($c=2 \cdot 10^{-3}$ - $2 \cdot 10^{-5} M$).

The ionization constants are determined by means of the potentiometric titration method [8] in 60% aqueous dioxan at 25°C. The ionization constants found are mean average of 2-3 tests including 8-9 measurements each; values of pKa were processed statistically [9], the errors being calculated at the confidence level of 0.95. Values of reaction constants (ρ), correlation coefficients (r), and standard deviations (s) were calculated by the least squares method [10].

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KINETICS of The HYDROLYSIS of SUBSTITUTED
BENZYL SULPHONYL CHLORIDES

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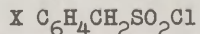
The kinetics of non-catalyzed hydrolysis of substituted benzylsulphonyl chlorides in a 70% solution of dioxane has been studied. The rate constants and activation parameters of the reaction have been determined. Benzyl sulphonyl chlorides are shown to be more sensitive to structural variation in the molecule, ρ_{30}° equals 1.39 than benzyl sulphonyl chlorides. ρ_{30}° equals 0.94. Possible reasons for this phenomenon have been discussed.

In an effort to further investigation on the influence of structural factors upon the reactivity of sulphonyl chlorides, it was of interest to study the kinetics of the non-catalyzed hydrolysis of substituted benzyl sulphonyl chlorides. The data on the kinetics of the hydrolysis are given in Table 2. The parameters characterizing the correlation relation are listed in Table 1.

Table 1. Parameters of the Hammet-Taft equation for the hydrolysis reaction of benzylsulphonyl chlorides.

T°C	$-\lg k_0$	ρ°	r	s
30	4.62 ± 0.01	1.39 ± 0.03	0.998	0.035
40	4.24 ± 0.01	1.33 ± 0.05	0.997	0.036
50	3.88 ± 0.02	1.28 ± 0.05	0.997	0.036

Table 2. Non-catalyzed hydrolysis of substitutedbenzyl sulphonyl chlorides



N	X	$k \cdot 10^5 \text{ sec}^{-1}$				E	lgA	-ΔS [#]
		20°	30°	40°	50°			
1	p-CH ₃		2.37±0.06	6.90±0.20	19.2±0.5	20.3±0.5	10.1±0.40	14.7±1.7
2	m-CH ₃	-	2.09±0.03	5.05±0.06	11.6±0.1	16.7±0.1	7.34±0.10	27.0±0.5
3	H	-	2.36±0.02	5.65±0.13	13.0±0.3	16.6±0.4	7.34±0.27	27.0±1.2
4	p-Cl	-	4.97±0.06	11.6±0.20	25.2±0.6	15.8±0.5	7.08±0.35	28.2±1.6
5	p-Br	-	5.69±0.05	13.2±0.20	28.8±0.6	15.8±0.2	7.13±0.17	28.0±0.8
6	m-Cl	-	7.81±0.06	17.7±0.20	38.5±1.0	15.5±0.2	7.08±0.15	28.2±0.7
7	m-NO ₂	14.7±0.2	34.0±0.40	73.6±0.80	153*	14.7±0.3	7.10±0.22	28.0±0.9
8	p-NO ₂	120 ±1.0	264*	553*	1050*	13.9±0.4	7.47±0.27	26.2±1.2
By the conductometric method								
	H	-	2.54±0.09	6.18±0.17	13.9±0.4	16.6±0.5	7.34±0.37	27.0±1.6
	p-Cl	-	5.46±0.13	12.5±0.20	27.9±0.4	15.9±0.6	7.18±0.45	27.8±2.1
	p-NO ₂	123±4.0	262 ±6.00	-	-	13.3	7.05	28.3

* The constants are calculated by extrapolation from the Arrhenius equation.

For p-NO₂: $k_{00} = (20.8 \pm 0.1) \cdot 10^{-5}$; $k_{100} = (52.0 \pm 0.6) \cdot 10^{-5}$.

$p\text{-CH}_3$ and $p\text{-NO}_2$ -benzylsulphonyl chlorides (Fig. 1) do not follow the particular correlation relation and they were not taken into account when these relations were calculated.

Some increase in the hydrolysis rate constants in the case of $p\text{-CH}_3$ -benzylsulphonyl chloride as compared with that of unsubstituted benzyl sulphonyl chloride appears to be associated with the thermal instability and decomposition of the substance under the experimental conditions similar to those for tertiary sulphonyl chloride [6].

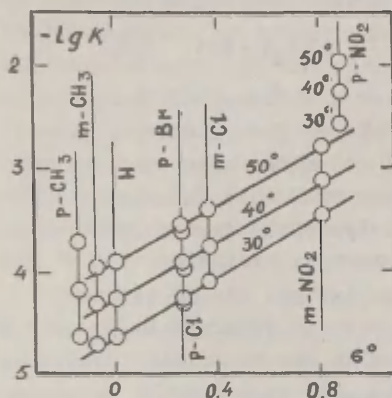
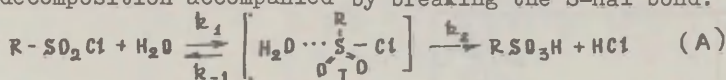


Fig. 1. Plots of $\lg k$ vs. σ° for the noncatalysed hydrolysis of benzyl sulphonyl chlorides *.

It is of interest that the reaction constants for the hydrolysis of benzylsulphonyl chlorides are greater than those for the corresponding benzenesulphonyl chlorides. For instance, for benzylsulphonyl chlorides $\rho_{30^\circ}^\circ$ equals 1.39 and for benzenesulphonyl chlorides $\rho_{30^\circ}^\circ$ equals 0.94 [1,2]. It is difficult to imagine in this particular case that an increase in ρ° for benzylsulphonyl chlorides is related to the increased electronic transmission factor system. It is obvious that the influence of the reaction mechanism features takes place here.

*The refined value σ° obtained from hydrolysis of phenyl-tosylates [10] was used for $X = m\text{-NO}_2$

When the kinetics of the interaction between p-CH₃-benzenesulphonyl halides and diethylamine in benzen [4] and as well as in 70% aqueous isopropanol [5] was studied, the reactivity of the substances specified was found to be appreciably dependent on the nature of halide. The latter phenomenon indicates that the reaction of nucleophilic interaction of benzylsulphonyl halides in the media of various polarity is conducted be stages through the rapid equilibrium stage of formation of type I complex (scheme A) and through the slow stage of the complex decomposition accompanied by breaking the S-Hal bond.



One should not probably expect a substantial change in the reaction mechanism as one passes from benzenesulphonyl chlorides to benzyl sulphonyl chlorides when one proceeds from the data presented in the work of Tonnet and Hambly [8] in which the kinetics of the hydrolysis and deuterolysis of methanesulphonyl chloride in dioxan-water solution of a various water percentage was investigated, and an evidence was obtained that the process rate is governed by the easiness of breaking the S-Cl bond in the transition state.

The effective rate constant (k_{eff}), according to the steady state method [7] for processes of similar kind, is determined as $k_{eff} = \frac{k_1 \cdot k_2}{k_{-1} + k_2}$, since $k_{-1} \gg k_2$, $k_{eff} = K_1 \cdot k_2$, where K_1 is the equilibrium constant for the first reaction stage. In this particular case the parameter φ^* is an additive value [9] which consists of φ_1 characterizing the stage of transition complex formation and φ_2 characterizing the stage of complex decomposition.

Since the process of transition complex formation is to be accelerated, and the process of breaking the S-Cl bond is to be decelerated for the reaction of hydrolysis

in passing from sulphonyl chlorides with electron-donating substituents to sulphonyl chlorides with electron-attracting substituents, the value should, in this case be determined by the difference between ρ_1 and ρ_2 values. Hence, one can write the following equations for the particular reaction series

$$\begin{aligned}\rho^{\circ}(\text{benzenesulphonyl chlorides}) &= \rho_1 - \rho_2 \\ \rho^{\circ}(\text{benzyl sulphonyl chlorides}) &= \rho_1' - \rho_2'\end{aligned}$$

The methylene bridge must naturally weaken the influence of benzene ring substituents on the reaction centre (sulphur atom). In consequence, ρ_1 and ρ_2 must be greater for benzenesulphonyl chlorides than ρ_1' and ρ_2' for benzyl sulphonyl chlorides.³⁸ The $-\text{CH}_2-$ bridge in the molecule of benzyl sulphonyl chloride apparently acts in such a way that certain decrease in the ρ_1' value in respect of ρ_1 involves a considerable decrease in ρ_2 , which, in principle, may result in a considerable increase in the effective values of the reaction constants for chlorides in question.³⁹

The analysis of the activation parameters both for benzenesulphonyl chlorides [1] and for benzylsulphonyl chlorides (Table 1) is rather in favour of an isoentropic course of the process. An increase in the reactivity of sulphonyl chlorides having electron-attracting substituents seems to take place at the expense of the activation energy.

³⁸ The absolute values of ρ_1 and ρ_2' are meant.

³⁹ The final proof for the above arguments is possible if the values of k_1 and k_2 are determined separately which involves considerable difficulties.

Experimental

Benzyl sulphonyl chlorides 2-,5,7,8 (Table 3) were prepared by the reaction between sodium salts of benzylsulphonic acids and PCl_5 [11], while p-Br-benzylsulphonyl chloride was obtained by the reaction of corresponding sodium salt with PCl_5 in the presence of POCl_3 . p- CH_3 -Benzylsulphonyl chloride, because of its thermal instability, was synthesized through magnesium derivative similar to propanesulphonyl chloride [12]. The sodium salts of benzyl sulphonic acids were prepared by reactions of the corresponding benzyl bromides with sodium sulfite [11]. Sulphonyl chlorides 3,4,6-8 (Table 3) were purified to the constant melting point by repeated crystallization from a mixture of benzene and light petroleum (1:3), while sulphonyl chlorides 1,2,5 from light petroleum only. The characteristics of sulphonyl chlorides are given in Table 3.

Table 3. Constants of benzyl sulphonyl chlorides
X $\text{C}_6\text{H}_4\text{CH}_2\text{SO}_2\text{Cl}$

Number	X	M.p. °C	Analysis for S,%	
			Found	Calculated
1	p- CH_3	80-81	15.36	15.67
2	m- CH_3	49.5-51	15.78	15.67
3	H	93-94*	17.01	16.82
4	p-Cl	96-97**	14.31	14.24
5	m-Cl	73-74***	14.40	14.24
6	p-Br	117-119	11.63	11.90
7	m- NO_2	101-102	13.90	13.61
8	p- NO_2	91-92****	13.83	13.61

* 94-95 [14], ** 95 [14], *** 72-73 [15], **** 91.5-92.5 [11].

The hydrolysis of benzyl sulphonyl chlorides was carried out in a 70% (by vol.) solution of dioxane and water.

(the procedure is similar to that of Vizgert [3]) using the argentometric titration method [12]. When studying the kinetics of the hydrolysis by the conductometric method [13] the rate constants and activation parameters are close to those obtained by the argentometric titration method (Table 1). In the argentometric titration method 0.05N solutions of silver nitrate and of ammonium rhodanate were used, the indicator was ferric sulphate. The concentration of sulphonyl chloride was 0.02 mol/l, and in the case of the conductometric method it was 0.002 mol/l. Dioxane was purified by an ordinary method [16]. The hydrolysis rate constants were calculated from the first order equation and were determined as average from 12 to 16 measurements. The activation parameters were calculated graphically and from the Arrhenius equation. The accuracy of the kinetic measurements was evaluated using methods of mathematical statistics [17] at the confidence level of 0.95. The correlation parameters were computed by the least-squares method using the electronic computer "Promin-2".

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BASE STRENGTHS OF BENZOATES OF SOME 1-AMINO-3-
-ALKOXY-(ALKYLTHIO)-2-PROPANOLS

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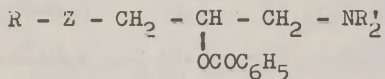
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By potentiometric titration method the base strengths of benzoates of some 1-amino-3-alkoxy-(alkylthio)-2-propanols in absolute ethanol were determined. It has been established that the nature of alkoxymethyl and alkylthiomethyl radicals does not affect the base strength. The pK_a values of most aminoethers give a good correlation with the Taft σ^* values.

As a part of the study, devoted to the relationship between structure and properties of aminoethers¹⁻³, base strength of some benzoylcholine analogs of the type












was measured in absolute ethanol solution.

Though the base strength of aminoethers is well described in literature¹⁻⁸, the effect of alkoxymethyl and alkylthiomethyl substituents on base strength has not been studied as yet.

Discussion

It can be seen from the Table that the base strength of aminoethers is greatly influenced by changes in nitrogen-containing residue of aminoether molecule. For example, substitution of the piperidine group for diethylamine and hexamethyleneimine groups slightly affects the base strength. In passing from the piperidine substituent to morpholine, however, the base strength is decreased by 2 units of pK_a . The difference between the basicities of the dibutylamine and diethylamine analogs is negligible. Dibutyl radical is known⁹ to possess more pronounced electron-donating properties than diethyl. The steric effect is probably the determining factor in this case as has been shown earlier⁶.

Table
Base Strength of Aminoethers $R-Z-OH_2-CH(OCOC_6H_5)-CH_2-NR_2^+$
in Ethanol Solution

N	R	Z	$-NR_2^+$	Points number	Δv^*	pK_a
1	2	3	4	5	6	7
I	CH_3	O	$-N$ 	18	0.65	6.18 ± 0.01
II	C_2H_5	O	$-N$ 	17	0.94	6.11 ± 0.03
III	C_3H_7	O	$-N$ 	16	0.35	6.00 ± 0.02
IV	C_4H_9	O	$-N$ 	17	0.30	5.97 ± 0.02
V	C_4H_9	O	$-N$ 	16	1.20	5.78 ± 0.02
VI	C_4H_9	O	$-N$ 	16	1.31	3.85 ± 0.02
VII	C_4H_9	O	$-N(C_2H_5)_2$	17	1.01	6.09 ± 0.02
VIII	C_4H_9	O	$-N(C_4H_9)_2$	17	0.51	6.01 ± 0.03
IX	C_4H_9	S	$-N$ 	16	0.70	5.98 ± 0.02
X	C_4H_9	S	$-N$ 	18	0.42	5.88 ± 0.02
XI	C_4H_9	S	$-N$ 	17	0.72	3.98 ± 0.02
XII	C_4H_9	S	$-N(C_2H_5)_2$	16	0.70	6.04 ± 0.01

1	2	3	4	5	6	7
XIII	C ₄ H ₉	S	-N(C ₄ H ₉) ₂	17	1.21	6.33 \pm 0.02
XIV	C ₅ H ₁₁	S	-N \bigcirc	16	0.54	5.85 \pm 0.04
XV	C ₆ H ₁₃	S	-N \bigcirc	17	0.31	5.89 \pm 0.02
XVI	C ₇ H ₁₅	S	-N \bigcirc	18	0.92	5.83 \pm 0.02

* - an average error of volume percentage.

The data of the Table indicate that the increase of alkoxyethyl (I-IV) and alkylthiomethyl (IX, XIV-XVI) radicals does not affect the base strength.

This is probably due to the fact that as alkoxyethyl groups are sufficiently removed from the reaction centre (nitrogen), their induction effect is fully extinguished while transferring through the carbon chain.

On the other hand, there was no appreciable change in base strength when alkylthiomethyl (IX) was substituted for alkoxyethyl radical (IV). It coincides with the data of Tamellini⁷ who studied aminoethers of saturated carboxylic acids.

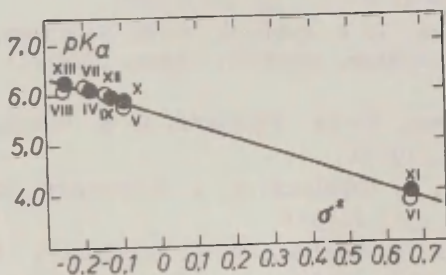


Fig. pK_a vs. σ^*

The above data made it possible to consider the $R-Z-CH_2-\underset{\substack{| \\ OCOC_6H_5}}{CH}-CH_2-$ group as a constant substituent.

In such a case the compounds under study can be expected to follow the Taft equation¹⁰⁻¹³.

The treatment of the data obtained using least-squares method has given: $r=0.993$, $\rho^*=-2.481$, and $s=0.11$. This is a proof of a good correlation between pK_a and ρ^* of the substituent at the nitrogen atom (see Fig.).

Experimental

The base strength of the compounds under study was measured by potentiometric titration method using pH-meter pH-340 with glass electrode of ESL-10-05 type and silver chloride electrode of EVL-IM3 type filled with saturated KCl solution in ethanol. The electrodes were calibrated by solutions of 0.05 M potassium biphthalate ($pH=4.01$) and 0.05 M sodium tetraborate ($pH=9.16$). Titration method and calculation of pK_a are described elsewhere¹.

Due to the less stability of aminoether bases, we used their hydrochlorides synthesized by us earlier¹⁴. The purity of the compounds was controlled by melting point, elementary analysis and thin-layer chromatography.

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MEDIUM AND SUBSTITUENT EFFECT IN THE OXIDATION
OF TRIPHENYL VERDAZYLs WITH TETRANITROMETHANE

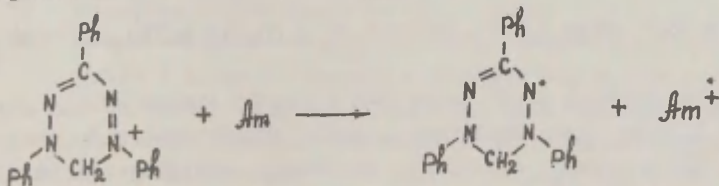
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The kinetics of para-C-phenyl-substituted triphenyl verdazyls ($X-RN^+$, $X = H, Cl, CH_3, CH_3O, NO_2$) oxidation with tetranitromethane in C_6H_{12} , C_6H_5Cl , C_6H_6 , THF, $C_6H_5NO_2$, $C_6H_5OCH_3$, CH_3CN , and propylene carbonate (PC) ($v = k[X-RN^+] \cdot [C(NO_2)_4]$) is studied spectroscopically by the stopped-flow method. The reaction rate increases with the increasing dielectric constant of the medium, and in C_6H_{12} and THF it shows a good correlation with Hammett σ -constants and $E_{1/2}$ in oxidation of $X-RN^+$ in CH_3CN . It was concluded that at the rate-determining step an electron transfer from $X-RN^+$ to $C(NO_2)_4$ takes place giving anion-radical pair $[X-RN^+, \dot{C}(NO_2)_3, NO_2^-]$.

In case the charge separation occurs at the rate-determining step, the rate of an electron-transfer reaction must be greatly dependent on the medium polarity¹. We have found, however, that the rate of amine oxidation with triphenyl verdazyls involving electron transfer only slightly depends on the medium polarity².



This is, probably, due to the fact that for the reaction in question the polarity of the transition state has but little difference from that of the initial state.

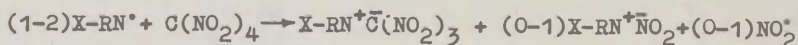
The oxidation of triphenyl verdazyl radicals ($X\text{-RN}^\bullet$) into corresponding cations ($X\text{-RN}^+$) appears to be a convenient model for studying medium effects on the rates of chemical processes involving electron transfer. $X\text{-RN}^\bullet$ oxidation with benzoyl peroxide (BP) shows³ that the rate of this reaction is unaffected by the medium polarity since the electron transfer from $X\text{-RN}^\bullet$ to BP takes place after the rate-determining step⁴. In our further study using a stronger electron acceptor (tetranitromethane) for $X\text{-RN}^\bullet$ oxidation we found that in this case the reaction rate greatly depended upon the nature of a solvent.

Experimental

Triphenyl verdazyl ($H\text{-RN}^\bullet$) and para-C-phenyl-substituted verdazyls ($X\text{-RN}^\bullet$, $X = \text{CH}_3$, Cl , CH_3C , NO_2) were obtained and purified as described elsewhere⁵. Tetranitromethane was stripped under argon. Kinetic studies were conducted by the stopped-flow method with spectrophotometric recording⁶. The reaction course was followed by the change in absorption of the solutions at λ_{max} $X\text{-RN}^+$ over the range 550 to 575 nm. $X\text{-RN}^\bullet$ and $\text{C}(\text{NO}_2)_4$ concentrations varied within the ranges $(0.5 - 3.0) \cdot 10^{-4}$ and $(0.3 - 20) \cdot 10^{-4}$ mol/l, respectively.

Results and Discussion

$X\text{-RN}^\bullet$ reacts with $\text{C}(\text{NO}_2)_4$ as follows⁷:



Experiments with $X\text{-RN}^\bullet$ taken 2-3 times in excess over $\text{C}(\text{NO}_2)_4$ have shown that the reaction stoichiometry depends upon the nature of a solvent. In hexane, cyclohexane, benzene, chlorobenzene, anisole and THF one molecule of $X\text{-RN}^\bullet$ is consumed per one molecule of $\text{C}(\text{NO}_2)_4$, the reaction pro-

ducts being $X-RN^+\bar{C}(NO_2)_3$ and NO_2^\bullet . In nitrobenzene, acetonitrile and propylene carbonate this ratio is 1.3:1, 1.6:1, and 2:1, respectively. The reaction products in the latter solvent are $X-RN^+\bar{C}(NO_2)_3$ and $X-RN^+\bar{NO}_2$. Similar solvent induced changes in the reaction stoichiometry were also observed during the oxidation of triphenyl methyl radical⁸ and $X-RN^{\bullet 9}$ with benzoyl peroxide. In all cases regardless of the reaction stoichiometry the radical oxidation rate is described by a bimolecular kinetic equation, i.e. for our reaction

$$\frac{d(X-RN^+)}{dt} = k[X-RN^\bullet][C(NO_2)_4].$$

This proves that $X-RN^+\bar{NO}_2$ is formed after the rate-determining step.

Table I
Solvent Effect upon the Rate of NO_2-RN^\bullet Oxidation
with Tetranitromethane at 20°C

Solvent	ϵ	$k \cdot 10^{-3}$, 1/mol·sec
Cyclohexane	2.0	0.74 ± 0.1
Chlorobenzene	5.6	30 ± 7
Benzene	2.3	38 ± 8
Tetrahydrofuran	7.4	46 ± 10
Nitrobenzene	34.8	110 ± 30
Anisole	4.3	190 ± 50
Acetonitrile	37.5	620 ± 200
Propylene carbonate	69.0	>1000

Table I gives a comparison between the k (20°) values for the oxidation reaction of NO_2-RN^\bullet with tetranitromethane in different solvents and dielectric constants of the solvents. A considerable increase of NO_2-RN^\bullet oxidation rate

* $X-RN^+\bar{NO}_2$ readily oxidates in air into $X-RN^+\bar{NO}_3$ ⁷.

with ϵ is observed in cyclohexane, nitrobenzene, chlorobenzene, THF, acetonitrile and propylene carbonate. In the above series of solvents $\lg k$ values show a satisfactory correlation with the values of $1/\epsilon$ and $(\epsilon-1)/(2\epsilon+1)$ (in both cases $r = 0.97$). This suggests that an increase in the reaction rate with the medium polarity in the studied series of solvents is due to the effect of a nonspecific solvation.

An increase of the reaction rate in the series $C_6H_5Cl < C_6H_6 < C_6H_5OCH_3$ may be ascribed to the easiness of complex formation between $C(NO_2)_4$ and unsaturated compounds, in which a strong polarization of C-N bond occurs¹⁰. (Dipole moment of $C(NO_2)_4$ increases from 0 to about 5 D, Ref. 11). Association constants for these complexes are very small (for complexes with benzene in heptane $K_{ass} = 0.003$ l/mol at 20°C); their values fall greatly with the decrease of electron-donating properties of an unsaturated compound.¹¹ Bearing in mind the correlation between the reaction rate and ϵ values in chlorobenzene, this solvent may be regarded as actually forming no complex with $C(NO_2)_4$. This suggests, therefore, that an increase in the reaction rate in passing from C_6H_{12} to C_6H_5Cl is basically due to the effects of a nonspecific solvation, whereas that observed when passing from C_6H_6 to $C_6H_5OCH_3$ is caused by the specific solvation effects.

It should be noted that triphenyl verdazyl solvation with aromatic solvent molecules leads to a decrease in their activity during the oxidation with BP¹². This effect, however, is not very pronounced (oxidation rate of $H-RN^*$ with BP in benzene is approximately half as great as that in hexane). That is why in our case the change in the reaction rate is mainly determined by $C(NO_2)_4$ specific solvation effects.

Table II shows that the reactions of NO_2-RN^* oxidation with tetranitromethane have low values of activation energy and relatively high negative values of entropy of activation. Both parameters show a comparatively small depen-

dence from the solvent nature. The reaction rate is about 10^3 times lower for the oxidation of $\text{NO}_2\text{-RN}^\bullet$ with BP in benzene than for the oxidation with tetranitromethane; which fact is due to approximately twice as large activation energy.

Table III shows the substituent effect in triphenyl verdazyl on the radical oxidation rate in cyclohexane and THF. In both solvents the rate constants show excellent correlation with Hammett σ -constants and good correlation with X-RN^\bullet polarographic oxidation potentials in acetonitrile¹³.

$$\begin{aligned} \lg k/k_0 &= -2.176, & r &= 0.999, S_0 = 0.020 \\ \lg k/k_0 &= -20.8 \Delta E_{1/2}, & r &= 0.981, S_0 = 0.069 \quad \text{Cyclohexane} \\ \lg k/k_0 &= -1.136, & r &= 0.994, S_0 = 0.018 \\ \lg k/k_0 &= -10.0 \Delta E_{1/2}, & r &= 0.985, S_0 = 0.033 \quad \text{THF} \end{aligned}$$

Table II

Kinetic Parameters of the Reaction of $\text{NO}_2\text{-RN}^\bullet$ with Tetranitromethane in Cyclohexane, Benzene and THF

Solvent	$k \cdot 10^{-3}$, l/mol·sec		E kcal/mol	$-\Delta S^\ddagger$ e.u.
	30°	40°		
C_6H_{12}	0.9 ± 0.1	1.1 ± 0.1	3.7	35
C_6H_6	48 ± 10	57 ± 10	4.1	26
THF	60 ± 10	78 ± 15	4.9	22

Table III

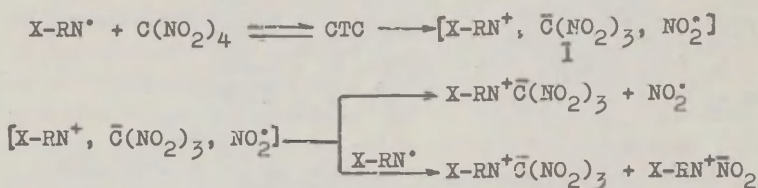
Substituent Effect in Triphenyl Verdazyl on Oxidation Rate in Cyclohexane and THF at 20°C

Substituent	NO_2	Cl	H	CH_3	CH_3O
C_6H_{12} $k \cdot 10^{-3}$, l/mol·sec	0.74 ± 0.1	14 ± 2	$36 \pm 2^*$	100 ± 20	130 ± 25
THF $k \cdot 10^{-3}$, l/mol·sec	46 ± 10	160 ± 40	300 ± 50	480 ± 100	770 ± 230

* In hexane at 20°C $k = (34 \pm 2) \cdot 10^{-3}$ l/mol·sec

It is interesting to note that the reaction of $X-RN^{\bullet}$ oxidation with tetranitromethane is much more sensitive to the electron effect of a substituent than that of $X-RN^{\bullet}$ oxidation with benzoyl peroxide (in C_6H_6 $\rho = -0.55$ at $20^{\circ}C$ ³) or that of $X-RN^+$ with aromatic amines (for aniline in CH_3CN $\rho = 0.44$ at $20^{\circ}C$ ¹⁴).

The results of the present study of the kinetics of triphenyl verdazyl oxidation with $C(NO_2)_4$ suggest that the reaction proceeds via an intermediate charge-transfer complex (CTC) with an electron transfer from $X-RN^{\bullet}$ to $C(NO_2)_4$ at the rate-determining step followed by the tetranitromethane C-N bond rupture.



Ion-radical pair I formed at the rate-determining step of the reaction splits into the salt $X-RN^+ \bar{C}(NO_2)_3$ and the radical NO_2^{\bullet} (radical escape from the cage) in low polarity solvents. It is more stable in polar solvents and hence has time to react partially (nitrobenzene, acetonitrile) or completely with $X-RN^{\bullet}$ within the cage.

Tetranitromethane is known to form readily charge transfer complexes^{10,11}. These have a heteropolar structure ($C_6H_6 \rightarrow NO_2 \cdots \bar{C}(NO_2)_3$) and the C-N bond rupture which follows the charge transfer is a stabilizing process¹⁵.

Studies of the kinetics of alkoxides¹⁶ and phenoxides¹⁷ oxidation with tetranitromethane have shown that in the first case the C-N bond rupture occurs simultaneously with the electron transfer, whereas in the second it follows the transfer. The difference is due to the relatively stable phenoxy radicals being formed by phenoxides

during the electron transfer. In connection with this it should be emphasized that in our case an electron transfer results in the formation of stable cations $X-RN^+$.

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THE KINETICS OF REACTION OF ortho- AND para-DERIVATIVES OF BENZYL AMINES WITH ELECTROPHILIC AGENTS

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The kinetics of reaction of benzyl amine and its o- and p-derivatives ($R = \text{OCH}_3$, C_2H_5 , Br and NO_2) with 2,4-dinitrochlorobenzene and p-toluenesulfochloride in tetrahydrofuran and ethanol were investigated. From the correlation of $\lg k$ for p-derivatives of the benzyl amines with the values of σ for the C_2H_5 group and o-derivatives have been calculated. It was found that o- NO_2 -group in 2,4-dinitrochlorobenzene molecule does not hinder sterically its reaction with o-derivatives of the benzylamine and even produces a little accelerating effect. The positive effect of o- OCH_3 -group depends on the solvent nature. The activation parameters of the reaction of benzylamines with 2,4-dinitrochlorobenzene in tetrahydrofuran are close for different derivatives, and the activation energy for the reaction with p-toluenesulfochloride is zero.

Many reactions of ortho-substituted aromatic and some arylaliphatic compounds such as esterification of acids¹⁻³, hydrolysis and solvolysis of esters^{2,4,5,6} etc as well as ionization of acids⁷, infrared spectra⁴ and chemical shifts of protons measured by nmr^{8,9} have been investigated to elucidate the nature of the ortho-effect. The complicated interaction between the ortho-substituent and the reaction center causes a great variation in σ_o values in different reaction series and contradictions in various authors' conclusions on the nature of the ortho-effect. E.g., Chapman^{1,10} evaluates the steric substitu-

ent constants F_s while Charton considers that steric ortho-substituent effects are either absent^{2,11} or take place very rarely⁸ and the reason is the difference between the ortho- and para-electronic effects which are erroneously considered as equal in the literature.⁷ But from this point of view it is impossible, for example, to explain the fact that σ_o values obtained from the correlation of data for meta- and para-substituted compounds form another straight line when the solvent or temperature are changed¹². In this case the interaction between the ortho-substituent and the reaction center is likely to take place outside of benzene ring via solvent molecules. The latter effect probably plays important part in the biochemical processes.

Thus, additional experimental data are needed for the examination of the ortho-substituent influence in a different type of reactions.

In this paper the reaction kinetics of benzylamine and its ortho- and para-derivatives with electrophilic agents have been investigated. Such arylaliphatic system seems to be attractive since the interaction between the substituent and the reaction center in the system through the aromatic ring is weakened while that outside of the ring with the participation of the solvent molecules is not ruled out. The choice of the substituents is motivated by both their various electronic effects on the reaction center and the relative similarity of their effective volumes. p-Toluenesulfochloride (TS) and 2,4-dinitrochlorobenzene (DNB) have been used as electrophilic agents and thus it was possible to compare agents with various sterical effects. The reaction kinetics have been studied in ethanol at 20° and in tetrahydrofuran at 15-35° for DNB and at 0-40° for TS.

EXPERIMENTAL

Benzyl amine (of the chemically pure grade) was distilled in a vacuum.

ortho- And para-brom, and o- and p-methoxybenzyl amines

were prepared by conversion of corresponding bromoanilines and anisidines into nitriles¹³ which were reduced then.¹⁴

o- and p-Ethylbenzylamines were prepared by nitration of ethylbenzene followed by separation of the isomeric mixture in a vacuum distillation column of no less than 12 theoretical plates (≈ 3 torr). In this case low and high fractions were chromatographically pure o- and p-ethylbenzenes. Ethylanilines prepared by reduction of ethylnitrobenzenes¹⁷ were converted into nitriles¹³ and then into benzylamines¹⁴.

o- and p-Nitrobenzylamines were prepared from nitrobenzylbromides by condensation with potassium phthalimide in dimethyl formamide¹⁸ with subsequent hydrolysis of condensation products and isolation of amines.¹⁹ o-Nitrobenzylbromide was prepared in bromination of o-nitrotoluene by bromosuccinimide²⁰ and p-nitrobenzylbromide in bromination of p-nitrotoluene by bromine²¹. Freshly distilled nitrobenzylamines were used in kinetic experiments. Analysis of benzyl amines for nitrogen gave the calculated values within the experimental error.

p-Toluenesulfochloride and 2,4-dinitrochlorobenzene were crystallized from ether, their m.p. being 68-69° and 51-52° respectively.

Tetrahydrofuran (THF) was additionally purified.²²

Ethanol was distilled and was used as 96% C_2H_5OH .

Kinetic Procedure and Data Processing

The

rate of the reaction under investigation was measured by chlorine-ion concentration change titrimetrically. The reaction of amines with DNB was stopped by 1n HNO_3 , and in the case of TS - by trifluoroacetic acid with the subsequent addition of water before titration. The reaction kinetics agrees well with the second order equation. The evaluation of constants was performed according to reaction stoichiometry²³. The activation and correlation parameters and errors were calculated according to generally accepted formulae.

Table 1
Second-order rate constants ($\text{l.mol}^{-1}.\text{sec}^{-1}$) * and activation parameters for the
reaction of benzyl amines with 2,4-dinitrochlorobenzene and p-toluenesul-
fochloride in THF

Substi- tuent	TS	DNB					
	$k_2 \cdot 10^3, 0-40^\circ$	$k_2 \cdot 10^3, 15^\circ$	$k_2 \cdot 10^3, 25^\circ$	$k_2 \cdot 10^3, 35^\circ$	$E \frac{\text{kcal}}{\text{mol}}$	$-\Delta S^\ddagger$	$\lg A$
H	253±6	1.75±0.03	2.97±0.03	5.10±0.08	9.5	40.2	4.44
p-OCH ₃	609±10	2.72±0.03	4.62±0.06	7.58±0.07	9.0	41.0	4.27
p-C ₂ H ₅	440±8	2.25±0.02	3.86±0.06	6.46±0.07	9.3	40.4	4.41
p-Br	103±3	0.752±0.008	1.29±0.02	2.16±0.03	9.3	42.5	3.93
p-NO ₂	22.0±0.6	0.238±0.003	0.410±0.011	0.704±0.006	9.5	44.1	3.58
o-OCH ₃	797±16	5.11±0.09	9.12±0.12	15.7±0.4	9.9	36.6	5.22
o-C ₂ H ₅	341±10	1.43±0.02	2.58±0.04	4.25±0.08	9.5	40.5	4.38
o-Br	39±1	0.411±0.008	0.73±0.01	1.30±0.01	10.2	40.6	4.35
o-NO ₂	19.2±0.6	0.217±0.003	0.398±0.006	0.693±0.005	10.2	41.8	4.08

* The arithmetic means of 2-3 individual measurements are given with their standard deviations.

RESULTS AND DISCUSSION

Table 1 gives the second-order rate constants for the reaction of benzyl amine with DNB and TS in THF. Investigation of the reaction kinetics of benzyl amines with TS over the temperature range of 0-40° revealed zero activation energy, therefore the average values of rate constants for this range are given in the Table.

The second-order rate constants for the reaction of benzyl amines with DNB in ethanol at 20° are given in Table 2. To use TS under these conditions proved to be impossible because of its interaction with the solvent.

Table 2

Second-order rate constants ($\text{l.mol}^{-1}.\text{sec}^{-1}$) for the reaction of benzyl amines with 2,4-dinitrochlorobenzene in ethanol, 20°.

Substituent	$k_2 \cdot 10^3$	Substituent	$k_2 \cdot 10^3$
o-OCH ₃	1.05±0.02	p-OCH ₃	0.433±0.007
o-C ₂ H ₅	0.283±0.007	p-C ₂ H ₅	0.371±0.005
o-Br	0.177±0.005	p-Br	0.204±0.004
o-NO ₂	0.87±0.02	p-NO ₂	0.842±0.007
H	0.329±0.006		

The logarithms of the rate constants of p-substituted benzylamines reactions with DNB and TS in THF and alcohol correlate well by the Hammett equation with application of Taft σ^* constants (those reported by Mareš and Palm⁵ were used in the diagram of the correlation dependences in alcohol, and those obtained for the solvents without hydroxy groups²⁴ for THF°. The lower value of correlation coefficient for the reaction with TS (Table 3)

Table 3

Correlation parameters for the reaction of benzyl amines with
2,4-dinitrochlorobenzene and p-toluenesulfochloride^{x)}

Agent	Solvent	t°	lg k _o	ρ	r	s
TS	THF	0-40°	-0.537	-1.58±0.11	0.995	0.075
DNB	- "-	15°	-2.769	-1.195±0.053	0.998	0.036
- "-	- "-	25°	-2.538	-1.187±0.051	0.998	0.035
- "-	- "-	35°	-2.314	-1.173±0.057	0.998	0.039
- "-	Ethanol	20°	-3.480	-0.736±0.025	0.999	0.019

x) n=4

Table 4

σ^o Values obtained from the correlation equation $\lg k = \lg k_o + \rho\sigma_p^o$

Substituent	T e t r a h y d r o f u r a n					Ethanol
	DNB				TS	
	15°	25°	35°	6° average	0-40°	DNB, 20°
p-C ₂ H ₅	-0.10	-0.11	-0.11	-0.11	-0.11	-0.066
o-OCH ₃	-0.40	-0.42	-0.43	-0.42	-0.28	-0.68
o-C ₂ H ₅	0.064	0.042	0.049	0.052	-0.044	0.092
o-Br	0.52	0.51	0.49	0.51	0.55	0.37
o-NO ₂	0.75	0.73	0.72	0.73	0.75	0.78

can be explained by greater errors in k_2 determination because of high rates of this reaction.

σ° Values for $p\text{-C}_2\text{H}_5$ -group and o -substituents being investigated were calculated on the basis of the obtained correlation parameters which made it possible to compare sterically hindered and sterically unhindered electrophilic agents action and also the influence of medium on the σ° value of ortho-substituents.

While analysing the obtained data it is interesting to note that σ° for o - and $p\text{-NO}_2$ -groups in both reaction series in THF turned out to be virtually the same (σ° for $p\text{-NO}_2$ is 0.73, for $o\text{-NO}_2$ average σ° value is also 0.73) and very close to each other in alcohol ($\sigma^\circ_p = 0.82$; $\sigma^\circ_o = 0.78$). At the same time σ° for the reaction of nitrophenyl ester of p -toluene sulphonic acid alkaline hydrolysis in water-alcohol medium is 0.995, and for $p\text{-NO}_2$ σ° is 0.88 (see Ref.6). The absence of the difference in our case is probably due to the influence of the closely situated $o\text{-NO}_2$ -group on the reactive aminogroup (possibly via H-bond). Thus, the expected effect of o -benzylamine reaction rate decrease as compared with that of p -isomer does not take place. Activation parameters for benzylamines reaction with DNB in THF are similar for various substituents.

Small differences in σ° values for o -substituents obtained in the reaction of benzylamines with two electrophilic agents are probably due to the influence of electrophilic agent $o\text{-NO}_2$ -group which is particularly pronounced in the case of methoxybenzylamine.

σ° Value for $o\text{-OCH}_3$ -group in alcohol obtained in our work is very much different from that found by other authors for hydrolysis of phenyl esters of p -toluene sulfonic acid in alcohol-water media (-0.68 as compared with -0.067 after Maremã^b). This phenomenon is probable due to the possibility of weak H-bond formation between $o\text{-OCH}_3$ and NH_2 -groups of amine in contrast to substituted phenyl esters of p -toluene sulfonic acid and also to the nature of the solvent. The higher p -

sitive ortho-effect observed when substituting THF for alcohol in the reaction with DNB (that can be seen from a mere comparison of k_o/k_p ratios which are 1.97 for THF and 2.42 for alcohol) signifies that the effect of $o\text{-OCH}_3$ -substituent on the reaction center outside the benzene ring via the solvent becomes more pronounced.

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THE KINETICS OF INTERREACTION OF BENZOTHAZOLYL-2-SULPHENYLAMIDE WITH ALDEHYDES

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The kinetics of interreaction of benzothiazolyl-2-sulphenylamide with aldehydes in the mixture of dioxan with water has been studied. It has been shown that there is a linear dependence between the reaction rate constants and electrophilic characteristics of aldehydes. In the case of aromatic aldehydes the rate constant is correlated with σ by Hammett. The activation parameters E and $\lg A$ are calculated and validity of the isokinetic dependence verified. On the basis of the data obtained a reaction mechanism is suggested.

Lately N-alkylidensulphenylamides were widely used as accelerators in manufacturing of laminated articles (1). In this connection a great deal of examples have appeared in literature on synthesis of a number of derivatives of N-alkylidene- and N-arylidene benzothiazolyl-2-sulphenylamides (2). In spite of the practical importance of this reaction its kinetics has not been studied yet.

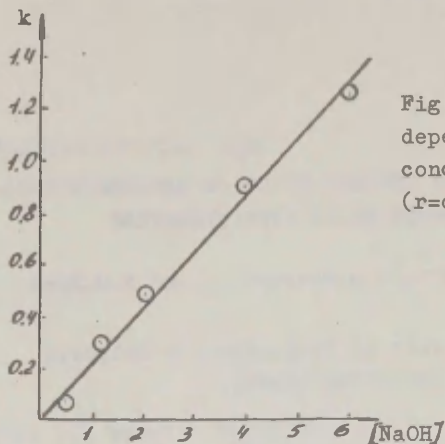


Fig.I. Rate constant dependence on NaOH concentration.

($r=0.9975$, $S_0=0.65$)

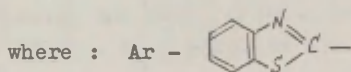
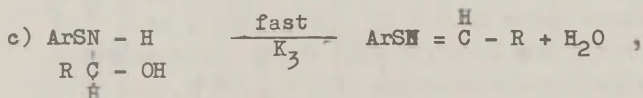
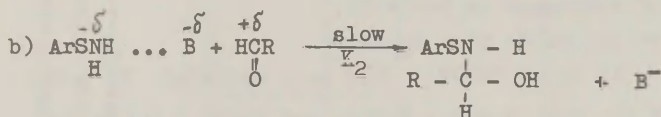
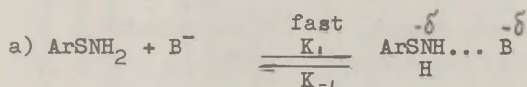
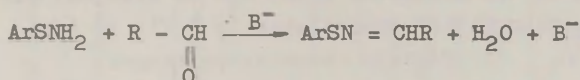
It is known from literature that reaction of amines and amides with aldehydes and ketones is catalysed both by acids and bases (3,4). From the data previously reported (5) it is obvious that acids cannot catalyse reaction of benzothiazolyl-2-sulphenylamide with aldehydes as interreact themselves with sulphenylamides generating by-products (5).

We have shown that reaction of benzothiazolyl-2-sulphenylamide with aldehydes proceeds in the presence of base and its rate depends to a great extent on the base strength. In the presence of weak bases or without them the reaction proceeds very slowly. Thus, rate constant of reaction of furfural with benzothiazolyl-2-sulphenylamide at 25° in the mixture of dioxan with water without catalyst is 0.0016 l/mol.sec, in pyridine it is 0.0032 l/mol.sec, and if sodium hydroxide is present it is 40.62 l/mol.sec, i.e., in the presence of strong base it increases by four powers of ten.

As the examination of reaction in the mixture of dioxan with water (28% H_2O) showed the reaction-kinetical order is 2.

We have studied how the amount of base (NaOH) influences the reaction rate constant. As it is seen from Fig.1 the amount of sodium hydroxide introduced into reaction mixture influences linearly on the rate constant value. It was found by extrapolation that K_{25} at $C_{NaOH}=0$ is 0.0013 l/mol.sec, that correlates well with the experimental data obtained ($K = 0.0016$ l/mol.sec). This shows bases to be catalysts of the reaction.

The data obtained allow us to suggest the following mechanism for the reaction of benzothiazolyl-2-sulphenylamide with aldehydes:



The same mechanism is supposed for reaction of amides of carboxylic acids with aldehydes (3).

It was found on studying the kinetics of reaction of benzthiazolyl-2-sulphenylamide and aldehydes that reaction rate constants depend on electrophilic properties of the latter (Table I).

A linear dependence is observed between reaction rate constants and aldehyde electrophilic properties for which pK_A of corresponding acids were taken (Fig.2). A linear dependence is also observed between the reaction rate constants and σ by Hammet (Fig.3). The introduction of electron-donating substituents into the benzene ring decreases reaction rate constants while electron-attracting substituents increase them.

The analysis of temperature dependence of reaction rate constants shows that in the temperature range studied (10.5 - 35°) the values of the rate constants are described well by the Arrhenius equation. We examined the isokinetic relationship in coordinates $\lg K, 1/T$; $\lg A, E$; and $\lg K_{T_2}, \lg K_{T_1}$ for various temperature ranges.

for various temperature ranges. In all coordinates (Figs. 4, 5, 6) linear dependences were found.

(In all plots the point numbers correspond to the numbers of compounds in Table I).

The values of \mathcal{K} from equation

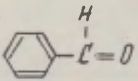
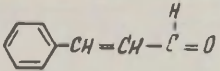
$\lg K_{T_2} = \text{const} + \mathcal{K} \lg K_{T_1}$, provided $T_2 > T_1$ are 0.889 ± 0.037 ; 0.923 ± 0.042 ; and 0.898 ± 0.035 for the temperature pairs 10.5 , 35 ; 10.5 , 25 ; 18.0 , 35 ; the ratios T_1/T_2 are 0.920; 0.951; 0.945 , respectively.

Isokinetic temperatures are 1017°K, 774°K, and 637°K being on interval $T_2 < \beta < +\infty$. From the linear dependence in coordinates $\lg A, E$ we found $\beta = 719^\circ\text{K}$ and from $\lg K, 1/T$ $\beta = 641^\circ\text{K}$.

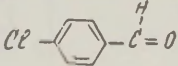
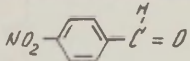
Thus, by three independent methods the value $\beta = 757.6^\circ\text{K}$ was found.

Table I

The Kinetics of reaction of benzothiazolyl-2-sulphenylamide with aldehydes in a dioxan-water mixture (water 28%) (Concentration ratio benzothiazolyl-2-sulphenylamide/NaOH/aldehyde is 1:1:2).

No.:	Aldehyde	Sulphenyl- amide concentra- tion, mol/l	pK _A	Hammett σ	Reac- tion temp. °C	Rate constant kcal/mol	Activation energy ccal/m	Preexpo- nential factor
I	2	3	4	5	6	7	8	9
57 I.		4.10 ⁻² 2.10 ⁻² "- "-	4.18	0	10.5 18.0 25.0 35.0	17.06 ± 0.80 23.12 ± 1.56 30.22 ± 0.74 43.12 ± 2.78	6.61 ± 0.35	14.57 ± 0.59
	Benzaldehyde							
2.		4.10 ⁻² 2.10 ⁻² "- "-	4.44	-	10.5 18.0 25.0 35.0	6.27 ± 0.50 9.25 ± 1.17 12.61 ± 0.70 19.52 ± 1.17	8.02 ± 0.58	16.09 ± 0.99
	Cinnamic aldehyde							

I	2	3	4	5	6	7	8	9
3.	$\text{CH}_3\text{O}-\text{C}_6\text{H}_4-\overset{\text{H}}{\underset{ }{\text{C}}}=\text{O}$	4.10^{-2}			10.5	1.99 ± 0.05	$8.51 \pm$	$15.79 \pm$
	p-Methoxybenzaldehyde	"	4.49	-0.268	18.0	2.85 ± 0.10	0.41	0.71
		2.10^{-2}			25.0	4.03 ± 0.29		
		"			35.0	6.62 ± 0.49		
4.	$\text{CH}_3-\text{N}(\text{CH}_3)-\text{C}_6\text{H}_4-\overset{\text{H}}{\underset{ }{\text{C}}}=\text{O}$	0.15	5.026		10.5	0.07 ± 0.001	$11.33 \pm$	$17.44 \pm$
	p-Dimethylaminobenzaldehyde	"	-0.83		18.0	0.10 ± 0.08	0.88	1.50
		"			25.0	0.20 ± 0.01		
		"			35.0	0.34 ± 0.02		
5.	$\text{HC}=\text{CH}-\overset{\text{H}}{\underset{ }{\text{C}}}=\text{O}$	2.10^{-2}			10.5	23.54 ± 1.40	$5.93 \pm$	$13.72 \pm$
	Furfurol	"	3.15	-	18.0	31.92 ± 0.53	0.001	0.55
		"			25.0	40.62 ± 0.77		
		"			35.0	56.1 ± 0.46		

I	2	3	4	5	6	7	8	9
6.	 p-Chloraldehyde	1.10^{-2} -"- -"- -"-	3.99	+0.227	10.5 18.0 25.0 35.0	20.00 \pm 1.31 26.06 \pm 1.73 37.50 \pm 2.83 51.65 \pm 2.92	6.93 \pm 6.17	15.29 \pm 0.29
7.	 p-Nitrobenzaldehyde	2.10^{-3}	3.44	+0.778	25.0	1320 \pm 29.5		

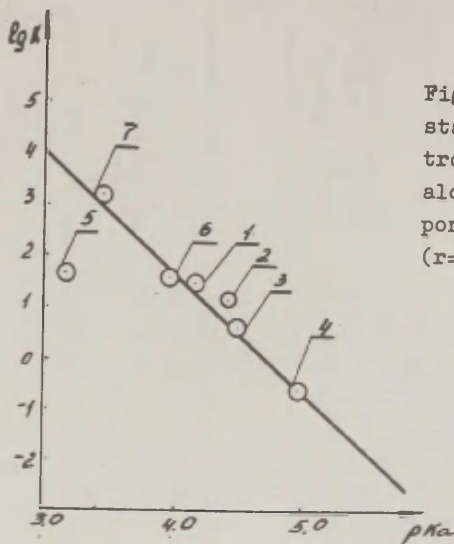
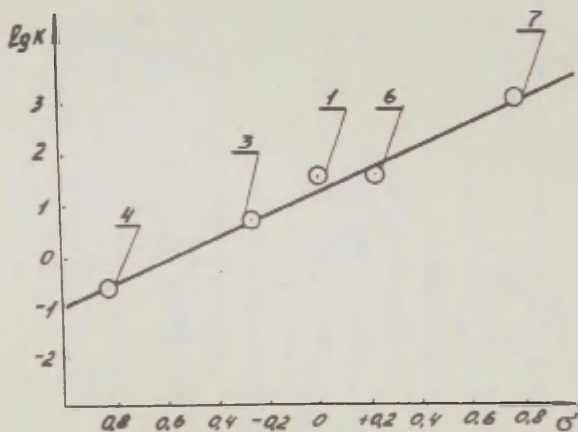


Fig.2. Reaction rate constant dependence on electrophilic properties of aldehydes (pK_A of corresponding acids) at 25°C ($r=0.987$, $S_o=0.167$).

Fig.3. Reaction rate constant dependence on σ at 25°C ($r=0.994$, $S_o=0.045$).



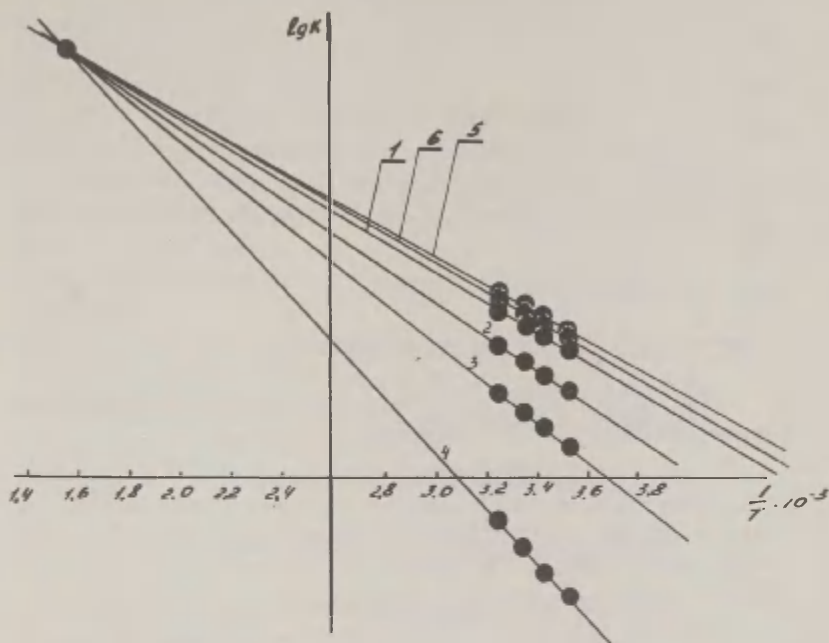


Fig.4. Dependence of $\lg K$ on $1/T$

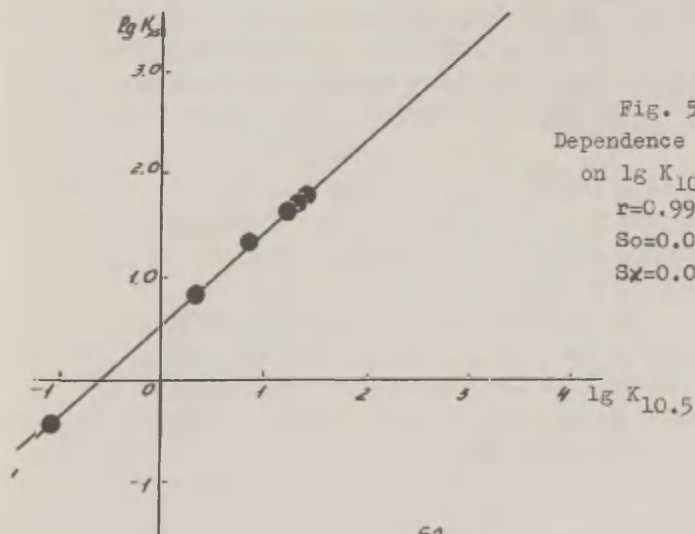


Fig. 5
Dependence of $\lg K_{35}$
on $\lg K_{10.5}$
 $r=0.999$
 $S_0=0.0191$
 $S_x=0.0081$

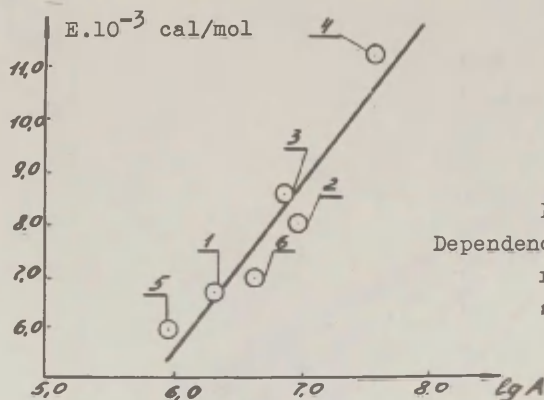


Fig. 6
Dependence of E on lg A
 $r = 0.952$
 $s = 0.483$

The experimental data obtained allow to consider this reaction series to be isoentropic.

EXPERIMENTAL PART

Benzothiasolyl-2-sulphenylamide was obtained by method of Kharach (6) with following repeated recrystallization from toluene. Aldehydes and dioxan of analytically pure grade were purified according to an ordinary method(7).

The concentration of reagents was measured by formation of corresponding N-alkylidenesulphenylamides which was determined spectrophotometrically with spectrophotometre CF-4A at $\lambda_{\max} = 330 - 365 \text{ nm}$.

The reaction order was determined by integration (8).

The catalytic reaction rate constant was calculated by the second-order kinetical law:

$$K = \frac{I}{t(a-b)[\text{NaOH}]} \cdot \ln \frac{(a-x)b}{(b-x)a}$$

where a, b are the initial concentrations of reagents,
x is the amount of reacted matter in the unit of volume at an instant t,
and $[\text{NaOH}]$ is the initial concentration of catalyst.

The activation energy was estimated by the least-squares method (9) and the exactness of calculated constants evaluated statistically. The isokinetic temperature was estimated after Palm (11).

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EFFECT OF SOLVENTS ON GRIGNARD REACTION

XI. Anisole

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The kinetics of the reaction of n-propylmagnesium bromide with pinacolone in anisole has been investigated. From the dependence of pseudo-first-order reaction rate constant on the concentration of Grignard reagent it has been concluded that anisole solvates propylmagnesium bromide weakly. The data of earlier experiments have been involved into the discussion and it has been shown that the effect of the medium on the rate of the reaction is determined by polarity, basicity, and steric effect of the solvent.

The influence of medium on the reactivity of Grignard reagent toward ketones has been investigated in our laboratory making use of the reaction of n-propylmagnesium bromide with pinacolone as a model¹⁻⁶. The obtained experimental facts permitted to classify the investigated solvents on the bases of the behavior of alkylmagnesium bromides in the media⁶. It was possible to distinguish two groups of solvents. To the first one belong the weakly solvating media like ethyl ether. In the solvents of this group the association of Grignard reagent is significant, and the dependence of the pseudo-first-order reaction rate constant on the concentration of Grignard reagent of an excess can be approximately described by a second-order reaction law. The other

group consists of THF type, i.e., of strongly solvating solvents in which Grignard reagent is in monomeric form and the kinetics of the reaction in these media resembles that of a third-order reaction.

In order to extend our knowledge of the effect of the medium on the reactions of organomagnesium compounds we have investigated the kinetics of our model reaction, i.e. of the reaction of n-propylmagnesium bromide with pinacolone in anisole. At present nothing is known of the association of Grignard reagent and of the position of Schlenck equilibrium in anisole.

The plot of pseudo-first-order reaction rate constant vs. the concentration of Grignard reagent (Fig. 1) resembles the same for solvents of ethyl ether type⁴. Consequently, Grignard reagent is noticeably associated in anisole and the latter is related to the class of solvents weakly solvating organomagnesium compounds, at least n-propylmagnesium bromide. This is in agreement with the conclusions drawn from other experimental facts^{7,8}.

As to the rates of the reaction of n-propylmagnesium bromide with pinacolone in investigated media, anisole stands between ethers and tertiary amines (Table 1). Because of the differences in reaction order and also in the association degree in the media, particularly at higher concentrations, the pseudo-first-order reaction rate constants related to 0.1 N Grignard reagent solutions have been compared with each other. The initial data are taken from the other papers 3-5.

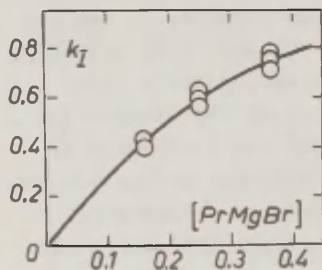


Fig. 1

The plot of the pseudo-first-order rate constant of the reaction of n-propylmagnesium bromide with pinacolone vs. concentration of Grignard reagent in anisole at 20°C.

Table 1

Pseudo-first-order rate constants of the reaction of 0.1N n-propylmagnesium bromide with pinacolone in various media at 20°C and the characteristics of solvents.

Solvent	$k_1(\text{sec}^{-1})$	γ^a	B^b	$E_S^{o'0}$
Et_3N	1.6^d	0.243	290	- 4.4
Me_2NPh	0.8^e	0.364	200	- 2.0
PhOMe	0.28^f	0.345	78	- 1.7
Bu_2O	0.19^e	0.296	129	- 2.8
Et_2O	0.017^e	0.345	129	- 2.4
THF	0.003^f	0.404	142	- 0.9

^a Kirkwood function of the dielectric constant, $(D-1)/(2D+1)$.

^b measure of the basicity; IR shift, $\Delta\nu_{\text{OD}}$, at the complex-formation with the base in MeOD; the quoted⁹ values for B are made use of.

^c isosteric constants of solvent molecules (see Ref.⁹), magnesium atom as reaction center (cf. Ref.¹⁰)

^d extrapolated to the temperature of 20°C

^e interpolated data

^f extrapolated according to the experimental plot of k_1 vs. concentration of Grignard reagent.

The relationships between reaction rate and properties of the solvent were difficult to find out because of the multitude of solvent-solute interaction mechanisms. Thus, for instance, we have emphasized⁴ already, that the action of specific solvation of organomagnesium compound consists of the changes in electrophilicity of magnesium atom, nucleophilicity of the organic part, and the position of the Schlenck equilibrium. In addition, there is a relatively strong influence of the medium polarity^{11,12}, the magnitude

of which, in its turn, depends on the specific solvation^{11,13}.

For the reaction of dipropylmagnesium with pinacolone it was found that, the contribution of the medium polarity being subtracted, the effect of specific solvation on the reaction rate can be quantitatively described, at least within the range of used solvents, by means of the isosteric constants of solvents¹³. That, of course, does not exclude the existence of more complicated relationships (that of a multitude of interaction mechanisms) total effect of which in the case of given set of solvents may be correlated, e.g. with the constants E_S^0 . In the latter case, however, the steric effect of the solvent molecule seems to play the crucial role.

In the case of the reaction of n-propylmagnesium bromide the reaction center is less encombrated and therefore one can expect also the appearance of other solvent effects besides the steric one.

It turns out that within our set of data (Table 1) the magnitude and character of the steric effect of the solvent are not obvious. In fact, the reaction rate constants for triethyl amine, butyl and ethyl ether and THF decrease with decreasing values of the E_S^0 constants, as it can be expected according to the earlier results¹³, but the logarithms of the same rate constants correlate with the values of Kirkwood function for the media even better, also showing the expected sign of the regression parameter (cf. Ref.¹²). Moreover, the points for dimethylaniline (DMA) and anisole fall out.

In connection with the specific solvation the comparison of data is admissible only for DMA, anisole, and ethyl ether, i.e. for the solvents with close values of dielectric constant. According to the present ideas about the steric effect of solvents DMA should stand between anisole and ethyl ether. Actually the reaction in DMA proceeds faster than in anisole. This likely shows the predominating influence of the solvent basicity, the more so as the reaction rate increases with increasing basicity. So it seems to be possible that

nucleophilicity of carbanionic center of organomagnesium compound is controlling the reaction rate rather than electrophilicity of magnesium atom. It should be mentioned that the latter conclusion does not coincide with our earlier ideas about the mechanism of the specific solvation effect².

If there was a simple dependence of the reactivity on solvent basicity, the latter being expressed in scale of B constants (see Table 1 and respective footnote), ethyl ether should take the place between DMA and anisole. As a matter of fact, the reaction in ethyl ether proceeds considerably slower than in both other solvents. From the comparison of E_S^0 values for the solvents it follows that steric effect of the solvent apparently reduces the reaction rate. One can suppose that the steric effect hinders the coordination of solvent with substrate and so reduces the effective basicity of the solvent.

However, one should take into consideration that the effective basicity of the solvent and, probably, also the immediate steric effect of the latter determine not only the reactivities of both organomagnesium halide and diorganomagnesium compound, but also the ratio of their concentrations through a shift in the Schlenck equilibrium. Thus, the quantitative relationships between the reaction rate and solvent properties evidently are of extremely complicated form and the qualitative conclusions, inferred above, particularly on the physical meaning on the rate dependences on various constants, may appear to be somewhat erraneous. With much more confidence one can conclude that the medium effect to the rate of the investigated reaction is determined by polarity, basicity and steric effect of the solvent.

Experimental

Anisole was treated with solid potassium hydroxide and distilled over the sodium wire in argon gas atmosphere. The fraction of b.p. 48°C at 10 mm Hg was used.

Grignard reagent was prepared in a usual manner, filtered through sintered glass and diluted as desired. All the operations on reagents and Grignards were carried out under pure dry argon gas.

Kinetics of the reaction was followed by noting the heat development during the reaction as described earlier³. The results of the measurements are listed in Table 2.

Table 2
Results of kinetic measurements

Conc. of n.PrMgBr, N	$k_1 \text{ sec}^{-1}$	Conc. of n.PrMgBr, N	$k_1 \text{ sec}^{-1}$
0.161	0.429	0.362	0.771
	0.397		0.758
0.248	0.632		0.713
	0.586	0.540	0.789
	0.575		

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EFFECT OF SOLVENTS ON GRIGNARD REACTION

XII. The Reaction of Diphenylmagnesium with Benzophenone

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The kinetics of the reaction of diphenylmagnesium with benzophenone has been investigated in dibutyl ether, diethyl ether, anisole, tetrahydrofuran, and in their mixtures with n-heptane. It has been found that the logarithm of the reaction rate constant linearly depends on the Kirkwood function of the medium. It has been shown that the slope of the line presents the sensitivity of the reaction to changes in the polarity of the medium. The dependence of the sensitivity on the nature of the solvating agent demonstrates the nonadditivity of specific and nonspecific effects of the medium. The magnitude of the sensitivity is apparently determined by the effective basicity of the solvent.

At present the quantitative consideration of solvent effects is one of the topical problems in physical organic chemistry. There is a great deal of attempts made to express the influence of the solvent on the reaction rates or physical properties of organic compounds by means of various correlation equations (a review in Ref.¹). Recently Koppel and Palm¹ suggested a general equation, based on the

idea of the solvent-solute interaction via the nonspecific solvation (the effects of polarity and polarizability of the solvent) and specific (electrophilic or nucleophilic) solvation. In some cases also the steric effect of the solvent may appear. It is assumed that all the interaction mechanisms noted above are additive and therefore the contribution of each of them can be separately and quantitatively taken into account with the corresponding term in the equation. Making use of their equation the authors were able to describe satisfactorily the influence of the medium on a great deal of different chemical and physical processes¹.

However, it should be emphasized that in the cases of sufficiently strong solvent-solute interaction the complexes formed from solvent and substrate molecules should rather be considered as different chemical compounds of different physical properties and, consequently, of different sensitivity towards the influence of nonspecific solvation. In other words, when the specific solvation is strong enough, one hardly can expect the persistence of the additivity of different solvent effects. Koppel and Palm claimed that the additive approach could satisfactorily be applied when hydrogen-bonded solvent-solute complexes were formed. However, the range of the conclusion is not quite clear.

J. Koppel and Tuulmets^{2,3} found that the logarithm of the rate constant of the reaction of dipropylmagnesium with pinacolone in the mixtures of n-heptane with solvating solvents (ethyl ether, tetrahydrofuran, etc.) linearly depends on the Kirkwood function of the dielectric constant of the medium. At the same time the slope of the line (sensitivity to the changes in medium polarity) largely varies depending on the solvating agent. It has been concluded from that that the effects of specific and nonspecific solvation are not additive for the considered reaction. Since such a conclusion is of principal significance, it is necessary to examine it in some other cases. Moreover, a correlation analysis of the kinetic data for the reaction

of dipropylmagnesium with pinacolone in various media showed that the most significant specific solvent effect, controlling the reactivity in the reaction, evidently was the steric effect of the solvent³. Naturally, in the case of sterically less encombrated reagents one can expect the appearance of other solvent effects in addition to the steric one.

According to these considerations we have carried out a kinetic investigation on the reaction of diphenylmagnesium with benzophenone in some basic solvents and in their mixtures with n-heptane.

The set of solvents applicable to the investigation on the organomagnesium reactions is limited because of low solubility of reagents, extreme reaction rate or insufficient inertness of the solvent. For instance, in course of this work it appeared that diphenylmagnesium is insufficiently soluble in triethylamine, pyridine, and in the mixtures of dimethylaniline with n-heptane.

Experimental

Purified solvents and solutions of organomagnesium compounds were operated only under dry pure argon gas.

Solutions of diphenylmagnesium. Phenylmagnesium bromide in dibutyl or diethyl ether was prepared by conventional method; solutions were filtered through sintered glass. Under vigorous stirring dioxane was slowly added in a slight excess (less than 10%). After the precipitate had fallen out the clear solution was removed and stored. For replacing diethyl ether by anisole or tetrahydrofurane, ether was distilled, a small amount of corresponding solvent was added and redistilled under reduced pressure, then the dry residue was dissolved in the solvent. The completeness of the replacement (up to the traces) was checked by means of glpc analysis of samples decomposed by water. Solutions in the n-heptane mixtures were prepared by weighing samples as described earlier². Immediately before kinetic

measurements the solutions were analysed to the content of basic magnesium.

Solvents. Diethyl ether was dried over heated calcium chloride and distilled from Grignard reagent. Tetrahydrofuran, dibutyl ether and anisole were treated with potassium hydroxide, then distilled from sodium metal under reduced pressure. n-Heptane was distilled twice from sodium metal.

Kinetics of the reaction was followed by the evaluation of the heat as described earlier⁴. Benzophenone was dissolved in the corresponding solvent before the use. All the kinetic measurements were carried out at 20°C under pseudo-first-order conditions: the excess of diphenylmagnesium was not less than 25 mole to one mole of ketone. Second-order rate constants k_{II} were obtained dividing the pseudo-first-order constants by molar concentration of diphenylmagnesium. The constants are listed in Table 1.

Table 1
Rate constants of the reaction of diphenylmagnesium with benzophenone in various media

Solvent- agent	Content of n-heptane in vol. %	Cone. of Ph ₂ Mg M	N ^o of runs	k_I, sec^{-1}	$k_{II},$ $\frac{1}{\text{mol. sec}}$
Bu ₂ O	-	0,060	3	0,553 \pm 0,021	9,23
Et ₂ O	-	0,142	3	0,623 \pm 0,051	4,38
	15	0,109	5	0,609 \pm 0,019	5,58
	29	0,104	3	0,809 \pm 0,026	7,78
	36	0,101	4	0,972 \pm 0,014	9,62
PhOMe	-	0,157	6	0,695 \pm 0,061	5,42
	25	0,142	7	0,861 \pm 0,027	6,06
	45	0,138	7	1,01 \pm 0,04	7,35
THF	-	0,166	4	0,0228 \pm 0,0007	0,138
	12	0,157	2	0,0266 \pm 0,0010	0,170
	21	0,154	2	0,0415 \pm 0,0010	0,270

D i s c u s s i o n

For the reactions of dipolar molecules, specific solvent effects being constant or negligible, one usually can observe a linear relationship between the logarithm of the rate constant and the Kirkwood function of dielectric constant of the medium, $(D-1)/(2D+1)$. In general case a dependence on the polarizability of the medium, expressed as a function of the refractive index, $(n^2-1)/(2n^2+1)$, is also possible.⁵

The logarithms of rate constants for the reaction in mixtures of ethers with n-heptane were plotted against the Kirkwood function and against the function of the refractive index of the medium as well. Dielectric constants and refractive indexes of the mixtures were calculated assuming their linear dependence on volume fractions of components. The published constants for pure solvents were used⁶.

It appeared that, like at the reaction of dipropylmagnesium with pinacolone^{2,3}, the solvating component of the mixture being the same, the logarithm of the rate constant of the reaction linearly depends on the polarity of the medium. The slope of the line (denoted by α , Table 2) considerably varies for different solvating agents. In Fig. 1 the dependence of rate constants on Kirkwood function is represented. However, analogous result was obtained by plotting the logarithms of the same constants against the polarizability of the medium, therefore these data do not permit to distinguish the effects of medium polarity and polarizability. Nevertheless, some additional facts, given below, enable us to consider the influence of polarity to predominate the latter.

It is of great importance to learn that the addition of inert solvent does not cause any shift in solvating equilibria. In other words, one must ascertain whether the changes in reaction rate are not caused by, say, the changes in association degree of the reagent.

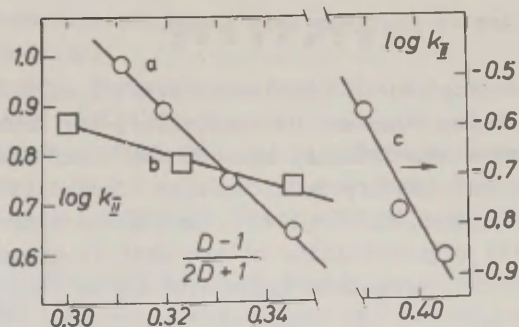


Fig. 1

The dependence of $\log k_{II}$ on medium polarity for the reaction between diphenylmagnesium and benzophenone in binary mixtures of n-heptane with: diethyl ether (a), anisole (b), and tetrahydrofuran (c).

Ducom⁷ investigated the equilibrium

$(Et_2Mg.S)_2 + 2S \rightleftharpoons 2Et_2Mg.2S$, where S is Et_2O or THF, in benzene. The equilibrium constants found by him permit to conclude that in the 0.2M solution of diethylmagnesium in binary mixture, diethyl ether - 90 vol.% of n-heptane, 85% of the reagent is still in monomeric form (95% in the case of tetrahydrofuran). This result is not in agreement with the findings of Ashby⁸ about the considerable increase of the association degree of organomagnesium compounds, diethylmagnesium included, with increasing concentration of them in diethyl ether. However, there is no reason to assume that the increase in the degree of association in the latter case is caused by the decrease in the ether concentration only.

On the other hand, if the increase in the rate constant is caused by a change in the association degree of the reagent or by a shift in some other solvating equilib-

rium, the same effect should be observed after addition of any inert solvent. It has been found in our laboratory⁹ that addition of dichloromethane to the solution of ethylmagnesium bromide in diethyl ether results in a decreasing rate of the reaction with pinacolone. The slope of the linear relationship between the logarithm of the rate constant and the Kirkwood function of the medium within the error of the determination coincides with that found for the ether-heptane system.

The same data permit also to judge, which of the mechanisms of nonspecific solvation is predominating. If the changes in the reaction rate were caused by changes in polarizability of the medium, the rate constant should have changed in the same direction after the addition of both n-heptane and dichloromethane, which was not the case.

Consequently, the increase in the reaction rate after the addition of n-heptane is caused, above all, by the decrease in the dielectric constant of the medium, the slope of the linear relationship can be considered as a measure of the sensitivity of the reaction towards changes in the polarity of the medium, and the dependence of the sensibility factor (α , Table 2) on the nature of solvating agent actually demonstrates the nonadditivity of specific and nonspecific medium effects for organomagnesium compounds.

The rate constants for the reaction in pure solvents (Table 1) do not reveal any obvious dependence on the properties of medium.

Table 2

Sensitivity of the reaction to changes in the medium polarity (α) and the characteristics of solvents

Solvating agent	α	B^a	$E_S^{a,b}$
Anisole	-3	78	-1.7
Diethyl ether	-10	129	-2.4
Tetrahydrofuran	-20	142	-0.9

- ^a measure of the basicity: IR shift, $\Delta\nu_{OD}$, at the complex-formation with the base in MeOD; the quoted¹ values for B.
^b isosteric constants of solvent molecules¹, magnesium atom regarded as reaction centre.

The absolute values of α in Table 2 vary in accordance with the changes in solvent basicity, however the influence of the steric effect seems to be suppressing. Therefore, one can assume that the sensitivity of the reaction towards changes in medium polarity is determined, above all, by the effective basicity of the solvent, and the sensitivity is the higher the greater is the effective basicity. This conclusion is in good agreement with the idea about a cyclic structure of the transition state of the reaction¹⁰ (see also review¹¹ and the refs. there in). Indeed, if the transition state of the reaction, because of its cyclic structure and of being less solvated, is of low polarity, the difference in polarities of initial and transition states, and accordingly also the sensitivity of the reaction to changes in medium polarity, are the higher the more polar is the initial state.

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EFFECT OF SOLVENTS ON GRIGNARD REACTION

XIII. A Quantitative Treatment of the Medium Effects

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The intrinsic nature of the inadditivity of the medium effects in the case of the reactions of organo-magnesium compounds has been discussed. An equation for quantitative description of the influence of the solvent upon the reaction kinetics has been deduced. A formulation of the effective basicity of the solvent has been suggested. The notion "index of effective acidity" has been introduced.

1. I n t r o d u c t i o n

A number of papers, dealing with systematic investigations on the influence of the solvent upon the reactivity¹⁻¹⁵ or physico-chemical properties¹⁶⁻¹⁹ of organomagnesium compounds, have been published during the last decade. Some immediate investigations on the equilibria of solvent replacement have also been carried out²⁰⁻²¹.

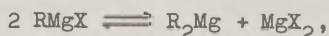
In the works cited above qualitative sequences of the solvents have been suggested. In some cases they partly coincide, but sometimes have considerable differences in the order of the solvents. The meaning of relative solvating

power or relative basicity of the solvents has been attributed to such sequences^{1-6,10-12,16,18,20,21}.

The fact that the orders of the solvents, suggested in the literature, markedly depend upon the substrate and on the process, from which they have been determined, shows that no absolute sequence of the solvents, even only for organomagnesium compounds, can be in question. Thus, for instance, it has been noticed long ago²² that the concept of the basicity and that of the solvating power of the solvent do not coincide. In addition, it has been shown^{12,13,20,21,23} that the steric effect of the solvent considerably controls the solvating power of the latter, or, at least, its influence upon the reactivity or on the structure of organomagnesium compound. In this connection it is clear that the order of the solvents is greatly determined by the steric effect and other properties of the substrate.

On the other hand, it has been shown^{13,24,25} that non-specific solvation exerts a strong influence on the reactivity of organomagnesium compounds, at least, in their reactions with ketones. In connection with this it has to be taken into account that the orders of relative solvating power of solvents, determined from the reactivity, reflect in addition to the effects of specific solvation, also a considerable contribution of medium polarity.

Evidently, when organomagnesium halide is the substrate, the dependence of the reactivity on the solvent is most complicated, since the solvent has, besides its direct effects, also a remarkable influence on the position of the Schlenck equilibrium^{26,27}



controlling in this way the ratio of the concentrations of the species of different reactivity.

From the discussion above it is obvious that qualitative treatment of such a complicated set of phenomena cannot lead to unambiguous results. Therefore a quantitative approach, accompanied by an exact separation of different

solvent effects, is indispensable.

A great deal of attempts have been made to express the influence of the solvent on the reaction rate or physical properties of organic compounds by means of various correlation equations (for a review see Ref. 28). Recently Koppel and Palm²⁸ suggested a general equation, based on the idea of the solvent-solute interaction via the nonspecific solvation (the effects of polarity and polarizability of the solvent) and specific (electrophilic and nucleophilic) solvation. In some cases also the steric effect of the solvent may appear. It is assumed that all the interaction mechanisms noted above are additive and therefore the contribution of each of them can be separately and quantitatively taken into account with the corresponding term in the equation. For a general case the Koppel-Palm equation is represented as follows

$$A = A_0 + \gamma Y + pP + eE + bB + \delta E_S, \quad (1)$$

where A and A_0 denote the reactivities or physico-chemical properties in given and reference solvent, respectively, and other terms express the contributions of polarity, polarizability, electrophilic solvation, nucleophilic solvation, and the steric effect of the solvent, respectively. Making use of their equation the authors succeeded in describing satisfactorily the influence of the medium on a great deal of different chemical and physical processes²⁸.

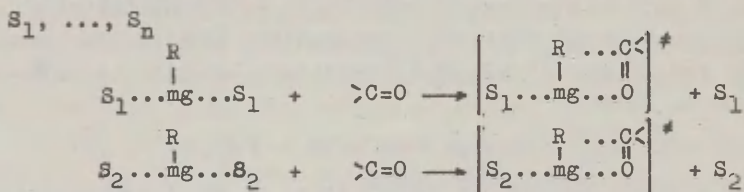
It follows from the additivity, taken as a principle for the equation (1), that the sensitivity of the process towards the nonspecific effects of the medium must be constant, i.e. independent of the intensity of specific solvation. However, the results of the kinetic investigations on the reactions of diorganomagnesiums with ketones in mixtures of basic solvent and *n*-heptane, at which the changes in dielectric constant of the medium at constant specific solvation were obtained by variation the amount of added *n*-heptane, demonstrate^{24,29} that the sensitivity of the reaction towards changes in medium polarity strictly de-

depends on the nature of solvating agent. Thus, it has been shown that in this case the mechanisms of solvent-solute interactions are not additive. The kinetic data for the reaction of dipropylmagnesium with pinacolone could be well correlated by means of the following nonlinear equation

$$\lg k = \lg k_0 + \gamma Y + \delta E_S^{\sigma} + aYE_S^{\sigma}, \quad (2)$$

in which $Y = (D - 1)/(2D + 1)$, and E_S^{σ} is the isosteric constant of the solvent.

The cause of the inadditivity of medium effects can be revealed by a detailed consideration of a reaction of organo-magnesium compounds with ketone in a set of solvents



As it is necessary to compare only the initial and transition states, for the sake of clarity the equilibrium of recoordination in the reaction scheme is omitted.

In so far as the molecule of the solvent remaining at the magnesium atom during the activation can be considered as a variable substituent, the molecule of the solvent which is replaced by ketone must be considered as a electro-negative leaving group. It follows that, in fact, the considered process in any solvent S_1 is an entirely different chemical reaction.

As a general conclusion, one can infer that the application of an additive correlation equation for a set of solvents is admissible only when the specific solvation remains constant during the process, or, in the opposite case, can be used only formally and roughly when the specific solvent effects are weak enough.

One can also see from the reaction scheme given above that the difference between the polarities of initial and

transition states is determined by the solvating agent. This reveals itself in the reaction kinetics as a dependence of the sensitivity of the reaction rate towards the changes in medium polarity upon the nature of the electrondonating component of the binary mixture, or, more generally, as an additivity between specific and nonspecific medium effects.

In order to consider the reaction in the solvents S_1, \dots, S_n as a common reaction series, one must withdraw the requirement for additivity in terms of Koppel-Palm equation and introduce another supposition about the additivity, i.e., one must assume that the contributions of the molecules S_i to the total free energy of the complex are additive. In other words, one should assume that there are no direct or indirect (e.g., via B-strain) interactions between the molecules of the solvent in the complex, or the interactions are negligible. Then it is possible, e.g. in the case discussed above, to consider the influence of one molecule S_i as that of the substituent and the effect of the other molecule S_j as a result of changes in specific solvation simultaneously, separately and additively.

Of course, such an assumption is valid only within certain limits since in the case of sufficiently bulky molecules of the complexing solvent it is hardly possible to ignore their steric interactions.

2. I n a d d i t i v i t y e q u a t i o n

A nonlinear equation can formally be derived from the Koppel-Palm equation by addition of the all possible cross-terms. Doing so, when the terms of electrophilic solvation and also that of polarizability^{*} are omitted, we obtain

$$\lg k = \lg k_0 + yY + bB + \delta E_S + a_1 YB + a_2 YE_S + \\ + a_3 BE_S + a_4 YBE_S.$$

^{*} In the case of organomagnesium reactions among the non-specific medium effects only that of polarity seems to be of importance²⁹.

However, even if not to mention the inelegance of the equation, the physical meaning of the constants a_1, \dots, a_4 remains obscure.

In order to obtain a less formal nonlinear equation we proceed from the same physical models of solvent-solute interaction as the Koppel-Palm equation is based on, and from the assumption of lack of interactions between the solvating molecules of the solvent.

In first approximation one can neglect also the immediate steric effect of the solvent. Indeed (see the reaction scheme), steric interactions between the solvent molecule not leaving during the activation and the group R in initial and transition states seem to differ only little. If it is so, we may put

$$\lg k = \lg k_0 + \alpha Y + \beta B^{\#}, \quad (3)$$

where the effective basicity $B^{\#} = f_1(B, E_S)$, sensitivity of the reaction towards medium polarity $\alpha = f_2(B^{\#})$, and the measure of the medium polarity, Y , can be expressed, e.g., by means of the Kirkwood function $(D - 1)/(2D + 1)$ (see Ref. 28).

Making use of the measure of electron-donating properties of the base, B , and of the scale of isosteric constants of solvents, E_S^{σ} (see Ref. 28) we took for the effective basicity following expression

$$B = \varphi_0 + \varphi_1 B + \varphi_2 BE_S^{\sigma} \quad (4)$$

The expression (4) meets the natural requirements (i) the scales $B^{\#}$ and B must be linearly dependent on each other when steric effects are absent, and (ii) when electron-donating properties approach to zero, the $B^{\#}$ value must approach to zero or a constant independently of the extent of steric effects. The term φ_0 may be equal to zero or a constant in accordance with the scale chosen.

Let us then assume that the sensitivity of the reaction rate to changes in medium polarity, α (the denotation has been used already^{24,13,29}), is linearly dependent

on the effective basicity of the solvent

$$\alpha = Y_0 + \theta B^{\#} \quad (5)$$

In Eq. (5) Y_0 and θ are characteristic of the reaction. From Eq. (3), (4), and (5) we obtain

$$\lg k = A_0 + jY + bB + c_1 YB + c_2 BE_S^{O'} + c_3 YBE_S^{O'}, \quad (6)$$

where

$$\begin{aligned} A_0 &= \lg k_0 + \beta \varphi_0 & c_1 &= \theta \varphi_1 \\ Y &= Y_0 + \theta \varphi_0 & c_2 &= \beta \varphi_2 \\ b &= \beta \varphi_1 & c_3 &= \theta \varphi_2 \end{aligned} \quad (7)$$

From the equalities (7) one can see that if the Eq.(6) holds, following relationships between the experimental values should be valid

$$\frac{b}{c_1} = \frac{c_2}{c_3} = \frac{\beta}{\theta} \quad (8a)$$

$$\frac{b}{c_2} = \frac{c_1}{c_3} = \frac{\varphi_1}{\varphi_2} = \varphi^{\#}, \quad (8b)$$

and, consequently,

$$b = \frac{c_1 c_2}{c_3} \quad (8c)$$

The ratio β / θ is characteristic of the reaction, and $\varphi^{\#}$ is that of the substrate. The latter determines the scale of effective basicity of the solvents in respect of the substrate (see Eq. (4)). Let $\varphi^{\#}$ be called the index of effective acidity (IEA).

3. Reactions with ketones

The use of equation (6) in the case of the reactions of organomagnesium compounds is connected with certain difficulties. In the first place, the possible set of appli-

cable solvents is relatively limited because of low solubility of reagents, extreme reaction rate or insufficient inertness of the solvent. In the next place, the correlation with the aid of a six-parameter equation needs highly exact and numerous experimental data almost lacking at present. It should be added that in the case of the solvents frequent for organomagnesium compounds (ethers, some amines etc.), good internal correlations between various sets of constants (of products of constants), can be observed, which in its turn may lead to false results.

For reasons discussed above only two sets of experimental data from the results of kinetic investigations on the reactions of dipropylmagnesium with pinacolone^{12,13,24} and diphenylmagnesium with benzophenone²⁹ could be used for to checking Eq.(6). The measurements of rate constants in pure solvents were accompanied with independent experimental determination of the sensitivity constants, α (see Eq. (3) and (5)), calculated from the relationship

$$\lg k = \lg k_0 + \alpha (Y - Y_0), \quad (9)$$

where k_0 and Y_0 are related to pure solvent, and k and Y to the mixtures of the donating solvent with *n*-heptane.

Because of lack of data and other reasons we had to work almost without statistical degrees of freedom and to carry out the provisory verification of Eq. (6) on the basis of relationships (8), on that of rationality of signes and values of parameters, and, as far as possible, of comparision of calculated and independent experimental data.

As a measure of electron-donating properties of the solvents (B) the IR-shift of phenol, $\Delta \nu_{OH}$, obtained from complexing with corresponding base in carbon tetrachloride³⁰ has been used. The scale of $\Delta \nu_{PhOH}$ is practically linearly connected with wellknown scale of $\Delta \nu_{CH_3OD}$ but is more exact and complete.

As characteristics of the steric effect of solvent molecules the $B_S^{0'}$ constants have been used. The latters are

equal to E_S^O constants for isosteric substituents in which heteroatom is modeled by methylene or methyne group. E_S^O are constants, purified of the contribution of "hyperconjugation" and related to Taft's E_S constants in the following way³¹

$$E_S^O = E_S - 0.33(3 - n_H) + 0.13 n_C.$$

The values of B, E_S^O , and dielectric constants, used in calculations, are given in Appendix (Table 5).

Let us consider first the reaction of diphenylmagnesium with benzophenone. The initial data from a previous work²⁹ are reproduced in Table 1.

Making use of the data for diethyl ether, tetrahydrofuran and anisole, and solving the set of equations

$$\alpha_1 = y + c_1 B_e + c_2 (BE_S^O)_i \quad (10)$$

we found y , c_1 and c_2 . Then we solved the set of equations (11) with the data for the same solvents

$$\lg k_{ei} = \lg k_{eo} + b_e B_i + c_{3e} (BE_S^O)_i, \quad (11)$$

where $\lg k_{eo} = A_0 - yY_e$, $b_e = b - c_1 Y_e$, $c_{3e} = c_2 - c_3 Y_e$, and subscript e denotes the medium with a dielectric constant equal to that for diethyl ether. The values of $\lg k_{ei}$ were calculated from experimental values of $\lg k_1$ according to the relationship (9) making use of experimentally determined values of α .

In consequence we obtained Eq. (12) for expression the dependence of the rate of the reaction of diphenylmagnesium with benzophenone (at 20°C) upon the effects of medium:

$$\lg k = -2.76 + 11.0 Y + 0.041 B - 0.128 YB + 0.0068 BE_S^O - 0.022 YBE_S^O \quad (12)$$

The agreement between calculated from this equation and experimentally obtained values for dibutyl ether (Table 1) can be considered as quite satisfactory if to take into account that the experimental rate constant is probably diminished because of the association of diphenylmagnesium which is associated in dibutyl ether to a considerably

higher extent than in other solvents (Ref. 23).

Table 1

The reaction of diphenylmagnesium with benzophenone

Solvent	$A_{\text{O}} + Y$	$bB + c_2 BE_{\text{S}}$	$c_1 YB + c_3 YBE_{\text{S}}$	$\lg k_{\text{calc}}$	$\lg k_{\text{exp}}$	α_{exp}
Bu ₂ O	0.44	6.26	-5.52	1.17	0.96	...
PhOMe	1.02	4.56	-4.85	(0.73)	0.73	-3
Et ₂ O	1.02	6.91	-7.26	(0.66)	0.64	-10
THF	1.68	10.01	-12.55	(-0.86)	-0.86	-20

Since the relationship (8c) fits fairly:

$$b = 0.041 \text{ and } c_1 c_2 / c_3 = 0.040,$$

it demonstrates that equation (12) holds. At the same time for diphenylmagnesium $\varphi^{\text{K}} = 5.9$ and for the reaction $\beta / \theta = -0.32$. By virtue of the sign of α ($\alpha < 0$) one can expect that $\theta < 0$. Then it follows that $\beta > 0$. The latter signifies that in this case the rate enhancing effect of the solvent basicity acting on the nucleophilic center of the substrate, exceeds its rate hindering effect which consists in suppressing the activity of the electrophilic center at magnesium atom. This result coincides with the observations on the influence of the solvent upon such reactions as alkyl exchange at the metal atom, metallation etc.^{2,32}.

One can see from Table 1 that the effects of the solvent as a substituent (3-d column), and also the effects of changes in specific solvation during the activation (4-th column) are considerable, but they extinguish each other to a large extent. Apparently, this should be the explanation of relatively weak medium effects observed in the reactions of organomagnesium compounds with ketones, nitriles⁵, and alkynes^{3,4}.

For the reaction of dipropylmagnesium with pinacolone the set of the solvents is somewhat larger (the data from

earlier papers^{12,13,24} in Table 2) but a considerable part of the solvent constants are in correlation with each other. For the same reason an earlier correlation¹³ according to Eq. (2) may be false (correlation coefficient for the pair $B_S^{O'} - YB_S^{O'}$, $r = 0.987$).

The value of sensitivity constant, α , was known for diethyl ether, tetrahydrofuran and dimethoxymethane, but, when the data for the latter were included, the calculations lead to the results deprived of meaning. Therefore the set of equations (10) was solved only for diethyl ether and tetrahydrofuran, and the searched values were expressed relative to y . The system (11) was solved for diethyl ether, tetrahydrofuran, and anisole. Then, from the comparison of $\lg k_{\text{calc}}$, expressed as multiples of y , with the corresponding experimental values it was estimated that $y \approx 1.0$.

Table 2

The reaction of dipropylmagnesium with pinacolone

Solvent	$A_0 + yY$	$bB +$ $+ c_2 BE_S^{O'}$	$c_1 YB +$ $+ c_3 YBE_S^{O'}$	$\lg k_{\text{calc}}$	$\lg k_{\text{exp}}$	α_{exp}	α_{calc}
iPr ₂ O	0.89	-1.71	3.05	2.23	2.37	...	-10
Bu ₂ O	0.85	1.85	-1.09	1.61	1.85	...	
Et ₂ O	0.91	2.74	-2.41	(1.24)	1.22	-6	(-6)
PhOMe	0.91	2.40	-2.45	(0.86)	0.86	...	
PhNMe ₂	0.93	5.51	-5.68	0.76	0.92	...	
THF	0.98	6.34	-8.08	(-0.76)	-0.81	-19	(-19)
(MeO) ₂ CH ₂				1.04 ^a	0.22	-15 ^a -9 ^b	-9

^a $D = 2.7$

^b $D = 5$

Thus, Eq. (13) was found for the dependence of the rate of the reaction of dipropylmagnesium with pinacolone (at 20°C) upon medium effects

$$\lg k = 0.56 + 1.0 Y + 0.027 B - 0.096 YB + 0.0082 BE_S^{O'} - 0.030 YBE_S^{O'} \quad (13)$$

The accordance between the calculated and experimental rate constants (Table 2) is only satisfactory, that is apparently caused by great inaccuracy in determination of parameters in Eq. (13).

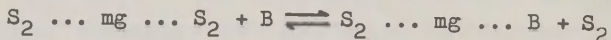
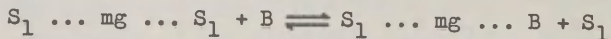
The great discrepancy between calculated and experimental data for dimethoxymethane can be explained by an inexact value of $D = 2.7$ in literature²⁸. Indeed, if in calculation of constant α from experimental data (Eq. (9)) $D=5$ is used, estimated from experimental $\lg k$ by means of Eq. (13), the calculated (according to Eq. (10)) and experimental values of α coincide (Table 2).

Validity of relationship (8c) confirms that Eq. (13) holds: $b = 0.027$ and $c_1 c_2 / c_3 = 0.026$. For dipropylmagnesium $\varphi^* = 3.3$, and for its reaction with pinacolone $\beta / \theta = -0.28$. The same consequences as in the case of the reaction of diphenylmagnesium with benzophenone follow.

When passing to diisopropyl ether, the value of α , calculated according to Eq. (10), changes its signe (Table 2). It is impossible to decide now, whether it occurs actually, or is an apparent result of invalidity of Eq. (13) for particularly bulky solvents. Experimental determination of α for the reaction in diisopropyl ether is made difficult by a high rate of the process.

4. Non kinetic examples and the effective basicity of solvents

Treating the recoordination equilibrium in the solvents S_1, S_2, \dots, S_n

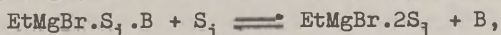


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one can meet the same problem of inadditivity between the mechanisms of the influence of the solvent as in the case of the reaction kinetics (1). However, in most cases the difference in polarities of the complexes $S_1 \dots mg \dots S_1$

and S_1 ... mg ... B apparently is insignificant, and when the assumption of negligibility of the interactions between the ligands S_1 in the complex is valid, the molecule of the solvent may be considered as a substituent.

Thus, e.g., the constants of the equilibrium²⁰



where B denotes (+)(S)-1-ethoxy-2-methylbutane, can be correlated well according to the equation

$$\lg K = A_0 + bB + cBE_S^{\sigma'}, \quad (14)$$

where, from Eq. (3), (4), (6) and (7), $A_0 = \lg K_0 + \beta \varphi_0$, $b = \beta \varphi_1$ and $c = \beta \varphi_2$.

The results of the correlation according to Eq. (14) are as follows:

Solvents: Et_3N , THF, BuOMe, Et_2O , Bu_2O

$$A_0 = -3.40 \pm 0.19 \quad r = 0.999$$

$$b = (21.06 \pm 0.98) \cdot 10^{-3} \quad s = \pm 0.066 (\pm 3.7\%)$$

$$c = (3.28 \pm 0.16) \cdot 10^{-3}$$

Hence, for ethylmagnesium bromide $\varphi^* = b/c = 6.4$ and for 2-methyltetrahydrofuran one can estimate (from the equilibrium constant²⁰) $E_S^{\sigma'} = -1.1$ (cf. the same for THF, $E_S^{\sigma'} = -0.9$).

In the case of processes in which specific solvation does not change, the problem of inadditivity does not appear. Chemical shift of α -hydrogens in diethylmagnesium¹⁹ can be correlated with the characteristics of the solvents according to following equation:

$$\delta = A_0 + \gamma Y + bB + cBE_S^{\sigma'} \quad (15)$$

The results of the correlation are as follows:

Solvents: dioxane, THF, Et_2O , Bu_2O , $i\text{Pr}_2\text{O}$, $i\text{PrOEt}$,

Et_3N , Pr_3N ,

$$A_0 = 36.3 \pm 7.6^*$$

$$\gamma = -45 \pm 18 \quad r = 0.998$$

$$b = 0.125 \pm 0.022 \quad s = \pm 2.6 (\pm 10\%)$$

$$c = 0.028 \pm 0.004$$

* δ_{CH_2} (Hz) are read¹⁹ from the frequency of TMS.

Hence, for diethylmagnesium $\psi^{3\#} = b/c = 4.5$. Eq. (15) and experimental data¹⁹ permit us to estimate the isosteric constant for HMPT: $E_S^{O'} = -1.3$

The signes of the parameters y , b , and c are in accordance with the fact that increasing shielding, i.e. an increase in ligand basicity in this case, shifts the signal upfields, and the polar medium effects result in a shift towards lower field³³. The correlation of the same data according to an equation of type (1) gave^{28,34} $y > 0$ and $b > 0$ which are hardly explicable from the physical point of view.

If the index of effective acidity is available one can estimate a qualitative scale of the solvent basicity relative to the substrate. By virtue of Eq. (4) it may be written

$$\frac{B^{3\#}}{\psi_2} - \frac{\psi_0}{\psi_2} = \psi^{3\#}B + BE_S^{O'} = B' \quad (16)$$

where B' is expressed in relative units.

Thus, e.g., making use of the $\psi^{3\#}$ value found before for diethylmagnesium, one can calculate a sequence of solvent basicity (Table 3) exactly reproducing, except the insignificant shift of tetrahydropyrane, the order of the solvents determined by the investigation on the equilibria of solvent replacement at diethylmagnesium in benzene²¹. Of course, only monodental solvents, for which the values B and $E_S^{O'}$ were available, could be considered.

Table 3

Comparision of basicities of the solvents relative to diethylmagnesium

Solvent	B'	Solvent	B'
iPr ₂ O	60	THP	960
Et ₃ N	70	2-Me-THF	970
Bu ₂ O	480	THF	1030
Et ₂ O	590	HMPT	1510
Dioxane	780		

The fact that the knowledge of an experimental value enables us to predict precisely the behaviour of another set of the bases in an entirely different process, is a sufficient evidence for principal validity of the quantitative treatment of the effective basicity in form of Eq. (4).

The indexes of effective acidity of organomagnesium compounds, arranged in Table 4 in order of decreasing IEA, deserve particular attention. The last four IEA values have been calculated in this work. Phenyl- and methylmagnesium bromides are placed according to the considerations discussed below. It follows from the comparison of the data in Table 4, that, as expected, the IEA is the greater the higher are the electron-accepting properties of the compound and the lower are the steric hindrances for the coordination with donors. Though the following correlation is rather formal, it is of certain interest to notice that

$$\varphi'' = 10.1 + 2.4 E_S^{O'} + 0.6 \sum \sigma'', r = 0.995, s = \pm 0.6$$

Table 4

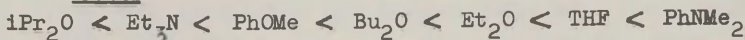
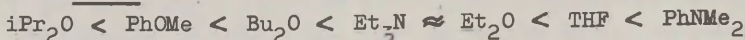
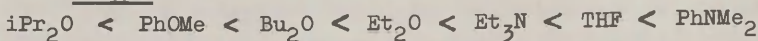
Indexes of effective acidity and some characteristics of organomagnesium compounds

Compound	φ''	$E_S^{O'}$ ^a	$\sum \sigma''$ ^b
PhMgBr	7	...	3.6
MeMgBr	2.8
EtMgBr	6.4	-2.1	2.7
Ph ₂ Mg	5.9	-2.4	1.2
Et ₂ Mg	4.5	-2.4	-0.20
Pr ₂ Mg	3.3	-2.6	-0.23

^a isosteric constants; magnesium atom is modeled by the methyne group, the heteroatom of the donor regarded as reaction centre

^b the sum of inductive constants for the substituents at magnesium atom

The influence of the effective acidity of the substrate upon the effective basicity of donors can be directly demonstrated by following orders, formed from a selected set of bases:



From these orders and IEA values the controlling rôle of steric hindrances in acid-base interactions is evident. Thus, e.g., the strongest of these bases in respect of proton, triethylamine, proves to be rather a weak base relative to organomagnesium compounds, and according to how the steric requirements of the substrate diminish, the base gradually shifts to the right along the basicity order.

The veracity of the considerations above and of the calculated orders is also shown by independent experimental facts.

Eq. (12) permits us to predict that triethylamine complex of diphenylmagnesium must react with benzophenone in diethyl ether by 3 to 4 times faster than corresponding ether complex, and the same complex in tetrahydrofuran by about 35 times faster than corresponding tetrahydrofuran complex. It is found³⁵ that the addition of triethylamine in molar ratios of 1:1 and 2:1 to diphenylmagnesium in diethyl ether and tetrahydrofuran causes practically no change in reaction rate constants. Subsequently, the solvent replacement equilibria in these systems are not shifted towards the formation of triethylamine complex, which is in agreement with the calculated basicity order for these solvents.

Addition of triethylamine in a molar ratio of 1:1 to ethylmagnesium bromide in diethyl ether accelerates the reaction with hexyne-1 as much as 8.4 times³⁶, and an identical admixture to methylmagnesium bromide solution increases the reaction³⁶ rate by a factor of 136. It follows that, on the one hand, triethylamine solvates these substrates stronger than diethyl ether, and, on the other hand, the effective acidity of methylmagnesium bromide is greater than that of ethylmagnesium bromide. At the same time triethylamine does not accelerate the reaction of hexyne-1 with diethylmagnesium in diethyl ether³⁶. Addition of triethylamine (1:10) to phenylmagnesium bromide in diethyl ether enhances the rate of absorption of acetylene in the mixture by 1620 times³⁷. At the same time the effect of addition of triethylamine to tetrahydrofuran solution is negligible³⁵. The sequence inferred from these facts: $\text{Et}_2\text{O} \ll \text{Et}_3\text{N} < \text{THF}$ permits us to estimate for phenylmagnesium bromide $\varphi^* \leq 7$.

5. A p p e n d i x

Table 5

The constants for the solvents used in calculations

Solvent	D	B	$E_S^{\text{O'}}$
Anisole	4.33	155	-1.7
Dibutyl ether	3.06	285	-2.8
Diethyl ether	4.335	280	-2.4
Diisopropyl ether	3.88	293	-4.3
Dimethoxymethane	2.7	223	-1.8
Dimethylaniline	5.02	422	-2.0
Dioxane	2.21	237	-1.2
Ethyl isopropyl ether	4.05	277	-3.3
Hexamethylphosphorotriamide	29.6	471	(-1.3) ^a
Methyl butyl ether	...	263	-2.0
2-methyltetrahydrofuran	...	285	(-1.1) ^a

Solvent	D	B	E _S ^α
Tetrahydrofuran	7.39	287	-0.9
Tetrahydropyran	...	290	-1.2
Triethylamine	2.42	650	-4.4
Tripropylamine	2.56	650	-4.7

^a estimated in present work

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COMMON SCALE OF INDUCTIVE CONSTANTS σ^*
FOR NEUTRAL AND CHARGED SUBSTITUENTS *

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On the basis of aqueous pK_a values of carboxylic acids (25°) a common scale of σ^* constants for neutral and charged substituents is derived. An electrostatic correction is introduced for charged substituents. Several applications of the new scale are considered.

As a rule, in the most of model reactions used for the deriving of substituents σ^* constants the reaction center carries ionic charge either in initial or final (transition) states. Hence, certain complications for the building of general scale of inductive constants both for neutral and charged substituents arise.

In a recent work² this problem has been solved by introducing into gross rate or equilibrium constants of reactions, including reagents with charged substituents, corrections for the intramolecular electrostatic interaction of the latter with charged reaction center.

Starting with these principles a brief description of constructing a new general scale of inductive σ^* constants was given¹). However, so far as the main emphasis of Ref. 1 lays in the demonstration of the existence of universal constant of inductive interaction (ρ^*), more thorough outline

*The main results of this work were briefly outlined in Ref. 1.

of some other aspects of the work¹, particularly the treatment of data, will be given now.

Primary treatment of experimental equilibrium data for the compounds $X(CH_2)_nY$ (X and Y denote the variable substituent and reaction center, respectively) was performed according to the following equation³:

$$\log K_{n+1} = (\log K_{n+1}^0 - Z_{CH_2}^{\#} \log K_n) + Z_{CH_2}^{\#} \log K_n$$

where K_{n+1} and K_n denote equilibrium or rate constants for the compounds with $n+1$ and n methylene groups between X and Y; K_{n+1}^0 and K_n^0 are the same for the reference X.

This procedure eliminates the necessity of using any previous set of inductive constants and subjects a test for checking up, within a given reaction series, the constancy of the inductive attenuation factor of carbon atom $Z_{CH_2}^{\#}$. On condition that the electrostatic correction² for the ²intra-molecular ion-ion interaction has been introduced for the charged substituents the treatment^{*} of data from Tables 1 and 2 for the series of dissociation of carboxylic acids and substituted ammonium ions in H_2O at 25° (see also Fig. 1-3) evidences that the pK_a values for compounds with uncharged as well as with charged substituents obey the same single relationship^{***} in terms of Eq.(1)

*Correlation statistics was presented in Ref. 1.

*** It is worth mentioning that the attenuation factor $Z_{CH_2}^{\#} = 0.350 \pm 0.012$ for the series of carboxylic acids is quite close to the literature values of 0.36^8 and 0.388^3 . The corresponding values¹ (0.47-0.55) for the series of dissociation of substituted ammonium ions differ from it considerably. Nevertheless the agreement with previous literature^{3,9,10} values is rather good.

Table 1A

Experimental pK_a Values⁴ for Dissociation of Carboxylic Acids $X(CH_2)_nCOOH$ in Water at 25° (Uncharged Substituents)

	X	n	pK_a		X	n	pK_a
1.	H	1	4.75	13.	OH	1	3.83
		2	4.87			2	4.51
2.	Me	0	4.75			3	4.72
		1	4.87	14.	OMe	1	3.57
3.	CH=CH ₂	1	4.35			2	4.46
4.	C≡CH	2	3.32			3	4.68
		3	4.21	15.	OEt	1	3.60
		4	4.60			2	4.40
5.	Ph	1	4.31	16.	OPh	1	3.17
		2	4.66			2	4.32
		3	4.76	17.	COOH ^b	0	1.57
6.	F	1	2.7			1	3.15
7.	Cl	1	2.85			2	4.17
		2	4.08	17a.	COOH ^b	1	3.69 ^e
		3	4.52	18.	COOMe(Et)	1	3.35
		4	4.70	19.	CN	1	2.47
8.	Br	1	2.90			2	3.99
		2	4.01			3	4.44
		3	4.64	20.	NO ₂	1	1.65
		4	4.77			2	3.79
9.	J ⁻	1	3.16	21.	ONO ₂	1	2.26
		2	4.09	22.	SH	1	3.68
		3	4.64			2	4.34
		4	4.77	23.	SCN	1	2.58
10.	CHCl ₂	0	1.29	24.	SO ₂ CF ₃	1	2.06
11.	CF ₃	0	-0.3 ^a	25.	SO ₂ Ph	1	2.44
		1	3.03	26.	SO ₂ CF ₃	1	1.88
12.	CCl ₃	0	-0.89	27.	SiMe ₃	1	5.29
						2	4.91

^a pK_a value, calculated according to the additive scheme is -1.40.

^b Statistical correction included.

^c Corrected (+0.52) for the intramolecular H-bond in the monoanion of malonic acid (see text).

T a b l e 1B

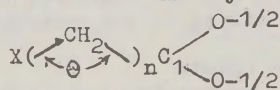
Experimental pK_a -Values⁴ for Dissociation of Carboxylic Acids $X(CH_2)_nCOOH$ in Water at 25° (Charged Substituents), Distances r between Ionic Substituent X and Reaction Center, Electrostatic Corrections^{a, b} $\Delta pK_{a,es}$, and Intrinsic Inductive Terms $\Delta pK_a^{ind} = pK_a - \Delta pK_{a,es}$ in the Gross Values of pK_a .

X	n	pK_a	$r^c(\text{\AA})$	$-\Delta pK_{a,es}$	ΔpK_a^{ind}
28. COO^-	0	3.98	3.0	-1.00	2.98
	1	5.40	3.8	-0.79	4.61
28a. COO^- e	1				4.09
29. NH_3^+	1	2.35	3.4	0.88	3.23
	2	3.55	4.4	0.68	4.23
	3	4.03	5.6	0.54	4.57
30. $NMeH_2^+$	1	2.35	3.4	0.88	3.23
31. NMe_2H^+	1	1.95	3.4	0.88	2.83
32. NMe_3^+	1	1.83	3.4	0.88	2.71
33. PBu_3^+	1	2.34	3.4	0.88	3.22
34. PPh_3^+	1	1.77	3.4	0.88	2.65
35. SO_3^-	1	4.05	5.5	-0.55	3.50

$$^a \Delta pK_{a,es} = \frac{Ne^2 Z_X}{2,3 RT \epsilon} \left(\frac{Z_Y}{r_{XY}'} - \frac{Z_Y}{r_{XY}} \right), \text{ where for the equilibrium}$$

$X(CH_2)_n Y \xrightleftharpoons{K_n} X(CH_2)_n Y'$ Z_X , Z_Y and $Z_{Y'}$ denote respectively the charges on the substituent X and reaction center in the initial and final states; r_{XY} and r_{XY}' - distances between point charges on the substituent and reaction center in initial and final states; ϵ - macroscopic dielectric constant of solvent.

^b Following model of the carboxylate-anion was accepted:



The charge of the COO^- group is located at 0.72 Å from C_1 ; $\theta = 109^\circ 28'$

^cInteratomic distances were taken from Ref. 5. Trans-configuration of the polymethylene chain is assumed.

^dStatistical correction is included.

^eCorrected (-0.52) for the intramolecular H-bond in the monoanion of malonic acid (see text).

T a b l e 2A

pK_a for Dissociation of Substituted Ammonium Ions
 $\text{X}(\text{CH}_2)_n\text{NH}_3^+$, $\text{X}(\text{CH}_2)_n\text{NMe}_2\text{H}^+$, and $\text{X}(\text{CH}_2)_n\text{NEt}_2\text{H}^+$ in Water
 at 25° (Neutral Substituents)^a

	X	n	pK_a		X	n	pK_a
	<u>$\text{X}(\text{CH}_2)_n\text{NH}_3^+$</u>			8.	SiMe_3	2 3	10.97 10.73
1.	H	0 1 2	9.15 10.62 10.63		<u>$\text{X}(\text{CH}_2)_n\text{NMe}_2\text{H}^+$</u>		
2.	Ph	1 2 3 4	9.34 9.83 10.20 10.39	9.	Me	0	9.80
				10.	C=CH	1 2 3 4	6.97 8.25 8.80 9.16
3.	OH	0 2 3	6.05 9.51 9.96	11.	Cl	0	0.46
				12.	OH	0	5.20
4.	OMe	0 1 2	4.60 9.50 9.92	13.	OMe	0 2 3	3.46 8.96 9.36
5.	COOMe(Et)	1 2 3	7.66 9.13 9.71	14.	NMe_2^b	1 2	8.70 9.50
				15.	CN	1 2	4.1 7.0
6.	NH_2^b	0 2 3 4	7.81 9.79 10.32 10.50		<u>$\text{X}(\text{CH}_2)_2\text{NEt}_2\text{H}^+$</u>		
				16.	NEt_2^b	1 2	9.22 9.88
7.	CN	0 1 2	1.1 5.34 7.7	17.	CN	0 1 2 3 4 5	-2.0 4.55 7.65 9.29 10.08 10.46

^aData are taken from compilations.^{6,7}

^bStatistical correction included.

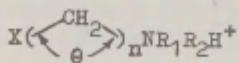
Table 2B

Experimental pK_a Values^{6,7} for Dissociation of Substituted Ammonium Ions $X(CH_2)_nNH_3^+$, $X(CH_2)_nNMe_2H^+$, and $X(CH_2)_nNMe_2H^+$ in Water at 25°C (Charged Substituents), Distances r between Ionic Substituent X and Reaction Center, Electrostatic Corrections^{a,b} $\Delta pK_{a,es}$, and Intrinsic Inductive Terms $\Delta pK_a^{ind} = pK_a - \Delta pK_{a,es}$ in Gross Values of pK_a

X	n	pK_a	r^c	$\Delta pK_{a,es}$	ΔpK_a^{ind}
<u>$X(CH_2)_nNH_3^+$</u>					
18. COO^-	1	9.78	3.4	0.88	8.90
	2	10.36	4.4	0.68	9.58
	3	10.56	5.6	0.54	10.02
19. NH_3^+	0	-0.58	1.47	2.04	1.46
	2	6.85	3.7	0.81	7.66
	3	8.29	4.9	0.61	8.90
	4	9.20	6.1	0.49	9.69
	5	9.74	7.2	0.42	10.16
<u>$X(CH_2)_nNMe_2H^+$</u>					
20. NMe_2H^+	2	6.00	3.7	0.81	6.81
	3	8.00	4.9	0.61	8.61
21. S^-	2	10.70	3.5	0.86	11.56
22. Net_2H^+	1	3.41	2.14	1.40	4.81
	2	7.00	3.7	0.81	7.81
	3	8.70	4.9	0.61	9.31

^a See footnote^a to the Table 1B

^b The following model of substituted ammonium ion was accepted:



Point charges are centered on X and N , $\theta = 109^\circ 28'$

^c Interatomic distances were taken from Ref.5.

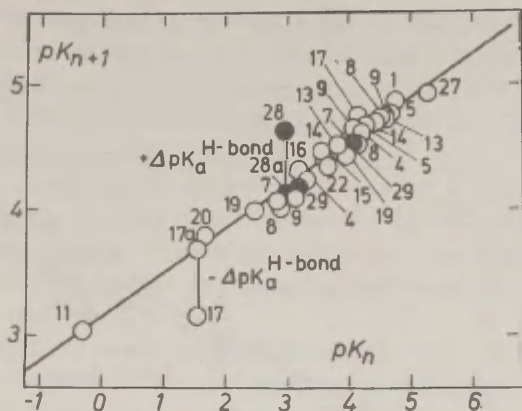


Fig. 1. Dependence of $\log K_{n+1}$ on $\log K_n$ values for dissociation of carboxylic acids in H_2O at 25° . Numbering of points corresponds to Table 1. Filled circles denote charged substituents

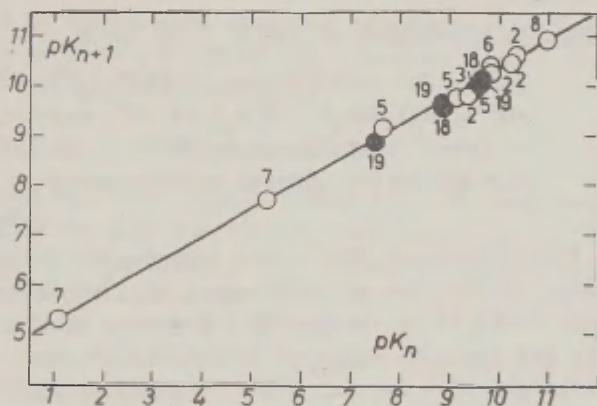


Fig. 2. Dependence of $\log K_{n+1}$ on $\log K_n$ values for dissociation of ammonium ions $X(CH_2)_nNH_3^+$ in H_2O at 25° . Numbering of points corresponds to Table 2. Filled circles denote charged substituents

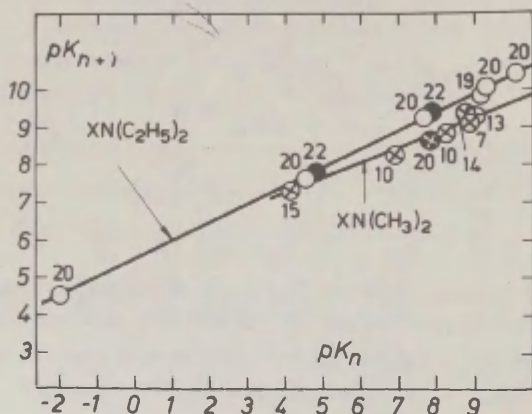
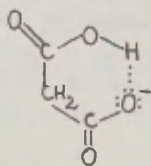


Fig. 3. Dependence of $\log K_{n+1}$ on $\log K_n$ values for dissociation of $X(CH_2)_nNMe_2H^+$ and $X(CH_2)_nNEt_2H^+$ in H_2O at 25° . Numbering of points corresponds to Table 2. Filled circles denote charged substituents.

At a first glance in Fig. 1 the behavior of the points corresponding to the 1st and 2nd steps of dissociation of malonic acid seems to be exceptional. However, equal absolute values and opposite signs of deviations of these points from the straight line for all other compounds evidence convincingly the presence of intramolecular H-bond in the monanion of malonic acid:



The latter seems to account

for the strengthening of this acid in the first step and weakening it in the second step of dissociation. Therefore, after introducing the corresponding corrections for this H-bond, COOH and COO⁻ groups behave like all other "normal" electronegative substituents.

The homogeneity of the influence of a full set of substituents in various model processes as demonstrated by the observance of Eq.(1) is a prerequisite for making use of these reaction series for constructing new set(s) of σ^* -constants.

Formally, every homogenous series can serve for this purpose. However, from the practical viewpoint, preference should be given to the process for which as many as possible data are available. This condition is better of all fulfilled for the series of dissociation of carboxylic acids in water.

It should be noted that, in principle, Eq.(1) excludes³ the necessity of introducing an arbitrary reference substituent. Indeed, the observance of this Eq. assumes the existence of the natural absolute reference point which corresponds to the equality of the numerical values of abscissa $\log K$ and ordinate $\log K_{n+1}^*$:

$$\log K_{n+1}^0 = \log K_n^0 = \log K^0 \quad (2)$$

It was shown earlier¹ that for all cases considered, $\log K^0$ values are practically indistinguishable from the $\log K$ values for the methylgroup. Hence, the latter as an arbitrary reference⁸ simultaneously also plays the role of the natural origin of the σ^* scale.

Taking into account condition (2) one can define σ^* as follows:

$$\sigma^* = (\log K - \log K^0) / \rho^* \quad (3)$$

Holding the Taft's⁸ scaling of σ^* -constants, we corre-

³Strictly speaking, such a situation should hold for the compound for which $n \rightarrow \infty$.

lated the pK_a values of substituted acetic acids XCH_2COOH (H_2O , 25°) with $\sigma_{CH_2X}^\#$ -constants for XCH_2 groups calculated by the original Taft⁸ procedure from data on the rate constants of basic (k_B) and acid (k_A) hydrolysis of esters XCH_2COOEt :

$$\sigma_{CH_2X}^\# = \frac{1}{2.48} \left(\log \frac{k_B}{k_B^0} - \log \frac{k_A}{k_A^0} \right) \quad (4)$$

Most of the $\sigma_{CH_2X}^\#$ -values were taken from Ref.8; the corresponding values for $CHCl_2$ and CCl_3 groups were calculated on the basis of more recent data¹¹.

T a b l e 3

Correlation of the pK_a -Values for the Dissociation of Substituted Acetic Acids XCH_2COOH (H_2O , 25°) with

$\sigma_{CH_2X}^\#$ -values calculated according to Eq.(4) for the

"Normal" Substituents

	X	pK_a	$\sigma_{CH_2X}^\#$
1	Cl	2.85	1.05
2	Ph	4.31	0.215
3	OPh	3.17	0.850
4	CN	2.47	1.30
5	OMe	3.57	0.52
6	Me	4.85	-0.1
7	SiMe ₃	5.22	-0.26
8	$CHCl_2$	1.29	1.94 ^a)
9	CCl_3	-0.89	3.06 ^a)

^a Calculated in this work using data from Ref.¹¹ for ethyl esters of di- and trichloroacetic acids.

Least-squares treatment of data from Table 3 leads to the following results (see also Fig. 4):

$$pK_a^{CH_2X} = (4.74 \pm 0.05)^+ - (1.820 \pm 0.037) \sigma_{CH_2X}^\# \quad (5)$$

$$R=0.999; \quad s=0.11; \quad s\%=1.8$$

where $s\% = s/\Delta pK_a^{\max}$; s = standard deviation, ΔpK_a^{\max} = maximum change of pK_a .

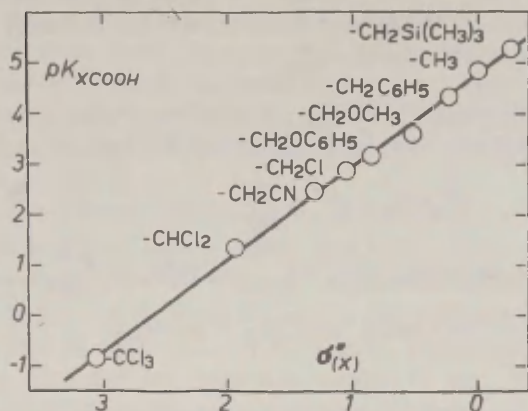


Fig. 4. pK_a of dissociation of acetic acids $XCOOH$ vs. $\sigma^*(X)$ -constants

The above treatment of data eliminates the use of the attenuation factor $Z_{CH_2}^*$ on condition that this quantity is equal both for the ester hydrolysis and dissociation of carboxylic acids.

Taking into account Eq.(5), one can rewrite Eq.3 in the following form:

$$\sigma^*(X) = (pK_a - 4.74) / 1.82 \pm 0.08 \quad (6)$$

If necessary, σ^* -values for various lengths of polymethylene chain can be calculated using the attenuation factor $Z_{CH_2}^* = 0.350$:

$$\sigma_n^* = (Z_{CH_2}^*)^n \sigma_X^* \quad (7)$$

The set of σ^* -values for several electroneutral and charged substituents, calculated according to formulae (6) and (7) was presented in Ref. 1.

An attempt to construct the set of σ^* -constants on the basis of aqueous dissociation of substituted ions of ammonium $X(\text{CH}_2)_n\text{NH}_3^+$ and $X(\text{CH}_2)_n\text{NMe}_2\text{H}^+$ is, in principle, not less founded. Certain advantage of these series is due to some data for $n=0$ which excludes direct or indirect inclusion of attenuation factor $Z_{\text{CH}_2}^*$.

Least-squares treatment of data from Table 2 according to Eq.(8) leads to the following results (see also Fig. 5):

$$\text{pK}_a = \text{pK}_a^0 + \rho^* \sigma_{(X)}^* \quad (8)$$

$$\text{i. } \text{XNH}_3^+ : \text{pK}_a = (10.79 \pm 0.74) - (3.77 \pm 0.70) \sigma_{(X)}^* \quad (9)$$

$$R=0.983; \quad s=0.88; \quad s\%=14.7$$

$$\text{ii. } \text{XNMe}_2\text{H}^+ : \text{pK}_a = (9.56 \pm 0.40) - (3.20 \pm 0.27) \sigma_{(X)}^* \quad (10)$$

$$R=0.989; \quad s=0.77; \quad s\%=8$$

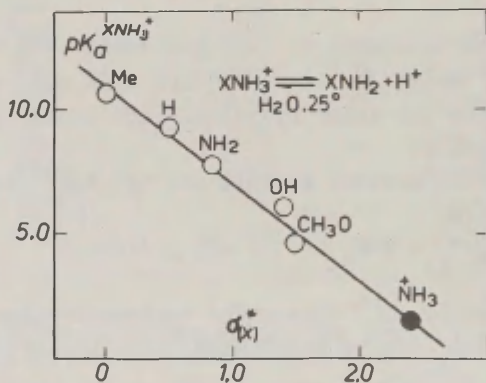


Fig. 5. Variation of pK_a with $\sigma_{(X)}^*$ for ammonium ions XNH_3^+ in water, 25°.

σ^{\ddagger} -constants, calculated from these or some other secondary model processes were also presented in Ref.1.

The σ^{\ddagger} -values, reported there for electroneutral electronegative substituents are very close to the literature ^{3,8} values. However, because the latter were calculated from gross experimental data without taking into account the electrostatic correction term, they considerably exceed our values for substituents carrying the net positive charge (e.g. NH_3^+), and are much lower for anionic substituents (e.g. COO^-).

Table 4 points out that σ^{\ddagger} -constants calculated from different reaction series agree satisfactorily. Coincidence of σ^{\ddagger} -constants for COO^- group calculated from the series of dissociation of carboxylic acids and dehydration of hydrated forms of ketenes (vide infra) seems especially instructive because the reaction center of the latter process carries the unit net charge neither in the initial nor in the final states of reaction. Hence, the introduction of the electrostatic correction term into the gross experimental data is not necessary.

T a b l e 4

The σ^{\ddagger} -Constants of COO^- and NH_3^+ Groups Calculated from Various Reaction Series

	Dissociation of XCOOH	Dissociation of XCH_2COOH	Dissociation of XNH_3^+	Dehydration of XCMe(OH)_2
1. COO^-	0.96	1.00	-	0.84
2. NH_3^+	-	2.35	2.32	-

Analysis of Data for Other Reaction Series

The least-squares structure-reactivity analysis of aqueous pK_a -values for dissociation of alcohols, XOH , and thiols, XSH , pK_a -values of carboxylic acids in DMSO and DMF, and $\log K_D$ values of dehydration of hydrates of ke-

tones was performed in terms of Eq.(8) for verification of the applicability of a new set of σ^{π} -constants.

Results of this analysis are included in Table 5 and presented in Figs. 6-9 (filled circles denote charged substituents).

Table 5

Structure-Reactivity Analysis in Terms of Eq.(8)^a
of $\log K_a$ Values of Dissociation of some Brönsted
Acids and Dehydration of Hydrated Forms of Ketenes

Reaction	$\log K_o$ $\pm \log K_o$	σ^{π} $\pm \sigma^{\pi}$	R	S	S%	References
1. Dissociation of XOH ^{b,c} , H ₂ O, 25°	-15.54 \pm 0.15	2.72 \pm 0.10	0.984	0.56	4.5	4
2. Dissociation of XSH, H ₂ O, 25°	-10.30 \pm 0.09	3.98 \pm 0.15	0.991	0.27	3.5	12-16
3. Dissociation of XCOOH, DMSO, 25°	-12.52 \pm 0.08	3.49 \pm 0.08	0.999	0.11	3.0	4
4. Dissociation of XCOOH, DMF, 25°	-13.19 \pm 0.09	3.06 \pm 0.08	0.999	0.11	2.0	4
5. Dehydration of XCMc(CH) ₂ , H ₂ O, 25°	2.70 \pm 0.17	-1.67 \pm 0.11	0.984	0.21	5.6	17
6. Dissociation of XCH ₂ CH ₂ NH ₃ ⁺ , H ₂ O, 25°	-10.73 \pm 0.15	3.28 \pm 0.28	0.982	0.22	7.5	6,7

^a Attenuation factor $Z_{CH_2}^{\pi} = 0.350$ was always used.

^b Additive value $\sigma_{CF_3}^{\pi} = 3.33^1$ for the inductive constant of CF₃ group was used.

^c σ^{π} -constants for some substituents of unpaired spin were calculated using the aqueous $pK_a^{7,18}$ for free radicals -

hydroxylic acids of general formula XOH :

$\sigma_{(\text{CH}_2)}^{\text{H}} = 1.77$; $\sigma_{(\text{C} \cdot \text{HMe})}^{\text{H}} = 1.48$; $\sigma_{(\text{C} \cdot \text{Me}_2)}^{\text{H}} = 1.26$; $\sigma_{\text{C}^{\cdot}(\text{CF}_3)_2}^{\text{H}} = 5.1$; $\sigma_{(\text{O}^{\cdot})}^{\text{H}} = 4.1$, and, formally, for the unpaired electron $\sigma^{\text{H}} = 1.35$ (from pK_a for $\cdot\text{OH}$ radical; X - is absent).

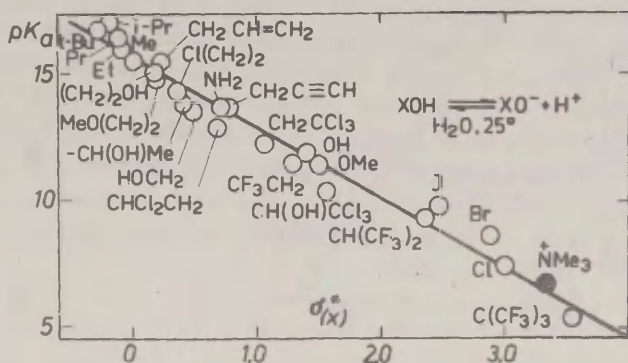


Fig. 6. Dependence of pK_a for dissociation of alcohols XOH in H_2O at 25° on $\sigma_{(\text{X})}^{\text{H}}$ -constants.

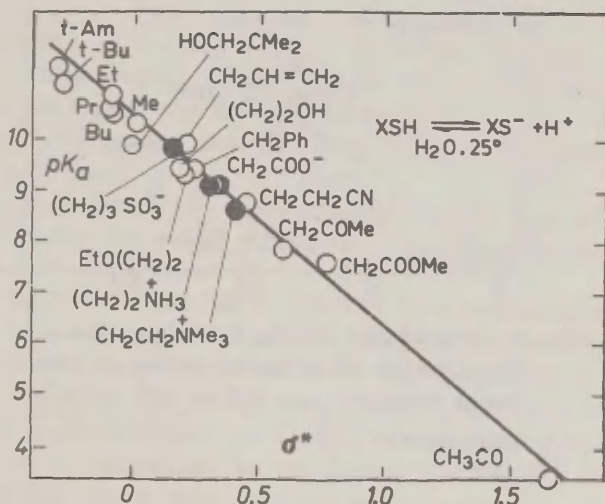


Fig. 7. Dependence of pK_a for dissociation of thiols XSH in H_2O at 25° on $\sigma_{(\text{X})}^{\text{H}}$ -constants.

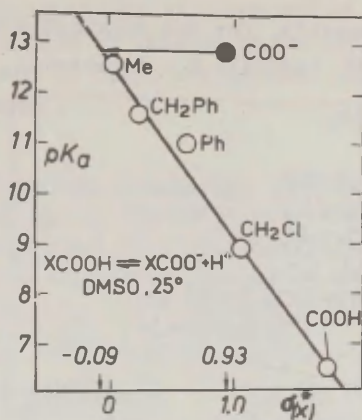


Fig. 8. Dependence of pK_a for dissociation of carboxylic acids $XCOOH$ in DMSO at 25° on $\sigma(X)$ -constants.

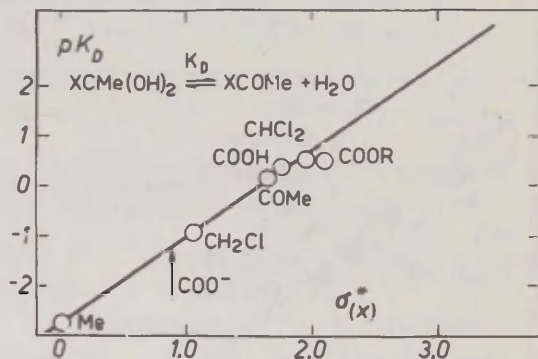
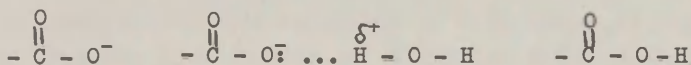


Fig. 9. Dependence of $\log K_D$ values for dehydration of hydrated forms of ketones $XCOMe(OH)_2$ in H_2O at 25° on $\sigma(X)$ -constants.

With the only exception[‡] of dissociation of carboxylic acids XCOOH in DMSO the neutral and charged substituents behave in the same, homogenous way. For the pK_a of carboxylic acids in DMSO, however, σ^{\ddagger} -value +0.92 for the COO^- group is not applicable^{‡‡}. It is probably due to the change in nature and intensity of solvation of this substituent by solvent molecules when going from hydroxylic solvent (H_2O) to aprotic medium. Indeed, when in DMSO the COO^- group is not practically solvated electrophilically then in H_2O , due to the latter type of solvation, carboxylate group behaves like something between electrophilically unsolvated form and its protonized form (i.e. COOH group):



DMSO, the lack of electrophilic solvation; $\sigma^{\ddagger} = -0.09$

H_2O ; H-bonding
 $\sigma^{\ddagger} = 0.92$

Protonization; carboxyl-group
 $\sigma^{\ddagger} = 1.72$

Therefore it is necessary to introduce for this group a new σ^{\ddagger} -value, equal to -0.09, i.e. if electrophilic solvation is excluded, the moderately electronegative COO^- group (in H_2O) changes into slightly electropositive (in DMSO) substituent.

Data from Ref.^{19,20} and Table 5 evidence that the only condensed media for which ρ^{\ddagger} -values for dissociation of

[‡]Quite a large absolute value ($s=0.6$) of standard deviation for the dissociation of alcohols ($s\%=5$) does not allow to draw an unambiguous conclusion about the deviation of the point for water ($\Delta pK_a=1.3$) from the straight line for other alcohols. However, on condition that this deviation is real it is equivalent to the demand use the σ^{\ddagger} -constant, approximately equal zero, for hydrogen as substituent.

^{‡‡}COOH-group behaves "normally".

carboxylic acids are considerably different from the values in aqueous solution, are DUSO and DMF. However, in any other solvent (pure or mixed) which is able to form H-bonds (alcohols, HCONH_2 , etc.), $\rho_{\text{medium}}^* \approx \rho_{\text{H}_2\text{O}}^*$, and, consequently, also, $\sigma_{\text{COO}^-}^*(\text{medium}) \approx \sigma_{\text{COO}^-}^*(\text{H}_2\text{O})^*$.

The results of the present paper and Ref. 1 once more confirm the wide applicability of the principle which interprets the inductive interaction as a unique (homogenous) formal type of interaction.

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Parameters of General Basicity of Solvents

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A new set of parameters of general (Lewis) basicity of solvents has been built up on the basis of the acid-base hydrogen-bond formation induced shifts of the stretching frequencies of the OH-group of phenol in the CCl_4 medium.

Recently^{1,2}, a scale of solvent basicity parameters (B) has been suggested on the basis of the solvent shifts of the stretching frequencies of the OD-group of deuterio-methanol in the media of pure bases:

$$B = \Delta \nu_{\text{OD}} = \nu_{\text{MeOD}}^{\circ} - \nu_{\text{MeOD} \dots B} \quad (\text{cm}^{-1}) \quad (1)$$

where $\nu_{\text{MeOD}}^{\circ}$ and $\nu_{\text{MeOD} \dots B}$ refer to the gas phase and pure base B, respectively.

The applicability of this scale has been demonstrated on various examples². Nevertheless, certain problems of principle as well as practical nature arise.

Indeed, one should take into account that no attempt to introduce possible corrections on the nonspecific and electrophilic solvent-solute interactions into the gross $\Delta \nu_{\text{OD}}$ -basicity parameters has been made. In general, because of the lack of any a priori grounds for neglecting those interactions in the wide range of solvents, there are

no guarantees (see, however, Ref. 3, 4) that the B-parameters of Eq.(1) do really reflect only the Lewis' basicity of the respective bases.

On the other hand, from the practical viewpoint, one should remind the frequent impossibility to measure the OD-stretching frequencies of MeOD (or the X-H band of the other proton donor X-H) in the medium of the pure base B because of the overlap of the OD-bands of free and bonded (monomeric) methanol and absorption bands of the solvent. Primarily, such a situation holds for various hydroxylic solvents (alcohols, phenols, carboxylic acids) which because of the strong autoassociation are optically opaque in the respective spectral region. Therefore, the necessity of referring the scale of general basicity to the unique reference state in some inert media, either by measuring the respective parameters in the medium of the latter or by introducing the corrections on the solvent-solute interactions into the gross parameters like $\Delta\sqrt{\nu_{OD}}$, suggests itself. First alternative seems to be more simple. Since most of all the literature data²² refer to the hydrogen bonding complex formation of phenol with various bases in the CCl_4 , it seems expedient to use this process for building up a new scale of general (Lewis') basicity of the solvents as follows:

$$B = \Delta\sqrt{\nu_{PhOH}^{CCl_4}} = \sqrt{\nu_{PhOH}^{CCl_4}} - \sqrt{\nu_{PhOH...B}^{CCl_4}} \quad (2)$$

where $\sqrt{\nu_{PhOH}^{CCl_4}}$ and $\sqrt{\nu_{PhOH...B}^{CCl_4}}$ refer to the stretching frequencies of the free and hydrogen-bonded phenolic OH-group in the media²² of CCl_4 , respectively.

As a matter of fact, representation of the solvent basicity parameters by Eq.(2) is equivalent to the introduction of the postulate that base-induced shifts of

²² As far as we know, there are literature data on the shifts of the phenolic OH-group for more than 700 bases in this media.

^{22a} In the following the superscript CCl_4 is omitted.

Table 1

Solvent General (Lewis¹) Basicity Parameters B^{a,b} as Derived from Eq.(2).

1	2	3	1	2	3
Base	B(cm ⁻¹)	References	Base	B(cm ⁻¹)	References
A.			13. Me ₆ C ₆	102(2)	10, 19
1. Gas phase	0 ^c	-	14. PhC≡CH	80	15
B.			15. PhCH=CH ₂	43(3)	12
2. Saturated			16. Naphthalene	48	6, 10
Aliphatic			D.		
Hydrocarbons	0 ^c	-	Halogenated		
C. Unsaturated or			Hydrocarbons		
Aromatic			<u>Fluorides</u>		
Hydrocarbons ^d			17. BuF	40	20
3. Cyclohexene	97(1)	10, 14, 15	18. c-HexF	53	21
4. PhH	48(0.6)	7, 10, 16, 17, 18	19. PhF	38	13
5. PhMe	58(1)	6, 7, 10, 18	<u>Chlorides</u>		
6. PhEt	58(1)	10, 12	20. BuCl	59(1)	22
7. Ph(i-Pr)	56(1)	10, 14	21. t-BuCl	64 ^e	-
8. Ph(t-Bu)	60	10	22. c-HexCl	67(1)	7, 21
9. 1,2-Me ₂ C ₆ H ₄	68	10	23. CH ₂ Cl ₂	23 ^f	-
10. 1,3-Me ₂ C ₆ H ₄	68	10	24. CHCl ₃	14 ^f	-
11. 1,4-Me ₂ C ₆ H ₄	68(1)	10	25. CCl ₄	0 ^c	-
12. 1,3,5-Me ₃ C ₆ H ₃	77(1)	7, 10	26. ClCH ₂ CH ₂ Cl	40 ^g	-
			27. PhCl	38(3)	6, 13, 18

1	2	3	1	2	3
28. 1,2-Cl ₂ C ₆ H ₄	28 ^h	-	47. MeOCH ₂ OMe	223(3)	6, 26, 29
29. 1,3-Cl ₂ C ₆ H ₄	17 ^h	-	48. MeOCH ₂ Cl	150	26
30. PhCH ₂ Cl	40	25	49. MeOCH ₂ CH ₂ Cl	208	26
31. 1-Cl-C ₁₀ H ₇	37	13	50. MeOCH ₂ CH ₂ OMe	238(3)	6, 29
<u>Bromides</u>			51. MeO(CH ₂) ₄ OMe	263	29
32. BuBr	68(1)	8,9	52. Et ₂ O	280(3)	See Ref. 27 for additional references
33. c-HexBr	86(3)	7,21	53. EtOPr	272	26
34. PhBr	40(2)	6, 13, 18	54. EtO(i-Pr)	277	26
<u>Iodides</u>			55. EtOBu	277	26
35. BuI	74(2)	9, 20, 22	56. EtO(t-Bu)	298(1)	26, 28
36. i-PrI	85	20	57. EtOAm	275	26
37. c-HexI	91	7, 21	58. EtOCH ₂ Cl	169(6)	27
38. PhJ	38	13	59. EtOCH ₂ CH ₂ Cl	227	26
E. Ethers ⁱ			60. EtOCH ₂ CH=CH ₂	256	26
39. Me ₂ O	246	26	61. EtOCH ₂ Ph	219	26
40. MeOPr	263	26	62. CHMe(OEt) ₂	241	26
41. MeOBu	263	26	63. CMe ₂ (OMe) ₂	257	28
42. MeO(i-Bu)	262	26	64. Pr ₂ O	279(3)	26, 30
43. MeO(t-Bu)	295	26	65. i-Pr ₂ O	293(8)	26, 30, 31
44. MeOAm	263	26	66. Bu ₂ O	285(2)	6, 8, 13, 22, 26, 29, 31
45. MeO(i-Am)	261	26	67. t-Bu ₂ O	321(4)	28, 31
46. MeOCH ₂ CH=CH ₂	248	26, 29			

1	2	3	1	2	3
68. Am_2O	275	26	85. MeCOOMe	170	30
69. $\text{O}(\text{CH}=\text{CH}_2)_2$	155	26	86. MeCOOEt	181(5)	6, 7, 17, 26, 30, 34, 38
70. $\text{O}(\text{CH}_2\text{CH}=\text{CH}_2)_2$	242(5)	26, 29	87. $\text{MeCOO}(\text{i-Am})$	194	38
71. $\text{O}(\text{CH}_2\text{Ph})_2$	233(2)	7, 13, 18, 21, 26, 30	88. MeCOOPh	121	37
72. $\text{O}(\text{CH}_2\text{CH}_2\text{Cl})_2$	178	26	89. $\text{MeCOOCH}=\text{CH}_2$	143	26
73. $\text{CH}_2(\text{CH}_2)_3\text{CH}_2\text{O}$	290	6, 32	90. EtCOOEt	174(1)	6, 30
74. $\text{CH}_2(\text{CH}_2)_2\text{CH}_2\text{O}$	287(3)	6, 7, 8, 13, 26, 30, 31, 33, 34	91. $\text{EtCOOCH}_2\text{CH}_2\text{Cl}$	146	37
75. $\text{O}(\text{CH}_2)_2\text{O}(\text{CH}_2)_2$	237(2)	6, 7, 8, 9, 26, 35	92. $\text{ClCH}_2\text{COOEt}$	125(7)	6, 9, 30
76. $\text{CH}_2(\text{CH}_2)_2\text{O}$	282	26	93. $\text{CHCl}_2\text{COOEt}$	119(12)	37
77. PhOMe	155(4)	6, 7, 13, 18, 26, 30	94. PhCOOMe	160	6
78. PhOEt	158(6)	13, 26, 30	95. PhCOOEt	142	30
79. Ph_2O	123(2)	6, 7, 13, 18, 26, 30, 36	96. PhCOOPh	157	30
80. $\text{Me}_3\text{SiO}(\text{t-Bu})$	261	28	97. $\text{CH}_2(\text{COOEt})_2$	190	38
81. Furan	103	30	98. $(\text{COOEt})_2$	86 ^h	-
82. Dioxolane	196	29	99. $\text{CH}_2=\text{CHCOOMe}$	163	26
83. $\text{C}(\text{OEt})_4$	156(7)	28, 29	100. $(\text{MeO})_2\text{CO}$	136	6
84. $(\text{CH}_3\text{CO})_2\text{O}$	100(5)		101. $(\text{EtO})_2\text{CO}$	145(4) ^h	-
F. Esters ^k			102. $1,2-(\text{COOBu})_2\text{C}_6\text{H}_4$	190	38
			G. Carboxylic Amides		
			103. HCONH_2	270(5) ^m	-
			104. HCONHMe	287(4) ^j	-

1	2	3	1	2	3
105. HCONMe_2	291(3)	7, 19, 39, 40	1. Nitriles ^p		
106. MeCONMe_2	343(1)	7, 34, 39, 40	123. HCN	140(5) ^q	
107. MeCONEt_2	335(5)	9, 40	124. MeCN	160(3)	6, 19, 36, 40, 43, 46-50
108. EtCONMe_2	325	40	125. EtCN	162(3)	46, 47, 48
109. $\text{P(O)(NMe}_2)_3$	471(4) ⁿ	-	126. PrCN	164(4)	46, 48
H. Aldehydes and Ketones ^o			127. i-PrCN	166	46
110. MeCHO	264 ^h	-	128. t-BuCN	166(3)	46
111. EtCHO	170	30	129. $\text{CH}_2=\text{CHCN}$	139(3)	12, 46, 48
112. PhCHO	180(6)	6, 30, 38	130. MeSCN	153	36, 51
113. Me_2CO	224(5)	6, 8, 30, 33, 34, 35, 40, 43, 44, 45	131. PhSCN	138	47
114. MeCOCH_2Cl	142(1) ^j	-	132. PhCN	155(3)	6, 46-49
115. MeCOEt	209(6)	12, 17, 30, 38	133. PhCH_2CN	155(4)	46, 48
116. MeCOBu	210	30	134. $\text{CH}_2=\text{CHCH}_2\text{CN}$	149(2)	46, 50, 52
117. $\text{t-Bu}_2\text{CO}$	195	30	J. Nitro compounds ^r		
118. Cyclohexanone	242(2)	6, 30, 38	135. MeNO_2	65(1)	53, 54
119. MeCOPh	202(9)	6, 30, 33, 43	136. EtNO_2	66	53
120. PhCOPh	192(5)	6, 8, 25, 30, 43	137. i-PrNO_2	68	53
121. MeCOCOMe	121	30	138. t-BuNO_2	73	53
122. MeCOCOEt	214	30	139. PhNO_2	67	53
			K. Hydroxylic compounds		
			140. H_2O	156(1)	27

1	2	3	1	2	3
<u>Alcohols</u> ^s			<u>Primary</u>		
141. MeOH	218(3)	27	159. NH ₃	473(2) ^j	-
142. EtOH	235(1)	27	160. EtNH ₂	667 ^h	-
143. i-PrOH	236(2)	27	161. PrNH ₂	661 ^h	-
144. BuOH	231	56	162. BuNH ₂	537 ^h	
145. i-BuOH	230(2)	27	163. PhNH ₂	346(6)	25, 58, 59
146. s-BuOH	240(3)	27	<u>Secondary</u>		
147. t-BuOH	247(4)	27	164. Et ₂ NH	637(15) ^v	-
148. t-AmOH	261(1)	27	165. i-Pr ₂ NH	597 ^h	-
149. CH ₂ =CHCH ₂ OH	204(1)	27	166. Bu ₂ NH	691 ^h	-
150. c-HexOH	242(3)	27	167. (PhCH ₂) ₂ NH	476 ^h	-
151. ClCH ₂ CH ₂ OH	183(1)	27	168. PhNHMe	452 ^h	-
152. HOCH ₂ CH ₂ OH	224(3)	27	169. Piperidine	706 ^w	-
153. MeOCH ₂ CH ₂ OH	238(4)	27	170. Pyrrole	343 ^h	-
154. PhCH ₂ OH	208(3)	27	<u>Tertiary</u> ^x		
155. PhOH	130(2)	57	171. Et ₃ N	650	35
156. HOOH	90 ^t	-	172. PhNMe ₂	422(5) ^j	-
<u>Carboxylic Acids</u>			173. Ph ₃ N	460	60
157. MeCOOH	131(9)	37	174. N-Me-piperidine	727 ^y	-
158. EtCOOH	139(2)	37	175. N-Me-pyrrole	114	10
L. Amines ^u			176. C ₅ H ₅ N	472(4)	See Ref. 27
			177. 2-Me-C ₅ H ₄ N	508(10)	58, 61

1	2	3
178. 4-Me-C ₅ H ₄ N	495(5)	7, 58, 61
179. 2,6-Me ₂ -C ₅ H ₃ N	535	61
180; 2,4,6-Me ₃ -C ₅ H ₂ N	531	61
181. 3,5-Cl ₂ -C ₅ H ₃ N	374	6
182. Quinoline	494(4)	7, 61
M. Sulphur compounds ^z		
183. Et ₂ S	251	8
184. Bu ₂ S	252(7)	21, 22, 26
185. Me ₂ SO	362(3)	See Ref. 27
186. Et ₂ SO	360	8
187. i-Pr ₂ SO	360	62
188. Ph ₂ SO	294	6
189. Sulpholane	157(1)	This work
190. 2,5-Dimethyl-sulpholane	181	6
191. Me ₂ SO ₄	75	63
N. Miscellaneous ^{aa}		
192. Ph ₃ NO	422(8)	6, 64
193. Me ₃ NO	467	40, 64
194. Et ₃ PO ₄	331	6
195. Ph ₃ PO ₄	232	6
196. Si(OEt) ₄	222(3)	6, 28, 29
197. MeSi(OEt) ₃	237	29
198. B(OBu) ₃	222	6

Footnotes: ^a As a rule, the B parameters presented in column 1 are the averaged values (arithmetic mean) of the best available literature values of ΔV_{PhOH} . In the parenthesis, the standard deviations of the latter are presented. ^b The ΔV_{PhOH} -values for a large number of bases, not presented in Table, can be found in Refs. 5-9 and in the references therein. See also footnotes to the separate classes of solvents. ^c By definition. ^d See also Refs. 10-13. ^e Calculated from the data of Ref. 23 using parameters of Eq.(3)

stretching frequencies of the X-H band of the proton donors in the infinite dilution in the inert media can also characterize the Lewis basicity of the corresponding pure bases as solvents. The general basicity scale of the most typical solvents, derived according to Eq.(2), is presented in Table 1.

It is interesting to compare the $\Delta\nu_{\text{PhOH}}$ -parameters with the analogous $\Delta\nu_{\text{HX}}$ -values for the other standard

from Table 2 for the series 1. ^f Calculated from the data of Refs. 8, 24 using parameters of Eq.(3) from Table 2 for the series 7 and 11. ^g Calculated from the data of Ref. 8 using parameters of Eq.(3) from Table 2 for the series 7. ^h Calculated from the data of Ref. 24 using parameters of Eq.(3) from Table 2 for the series 11. ⁱ See also Refs. 13, 26-28. ^j Measured in the present work. For experimental details see Refs. 23, 37. ^k See also Refs. 6, 8, 30, 37. ^l See also Refs. 39 and 40. ^m Measured in the present work as described in Refs. 27, 37. The value given refers to the lower frequency (more intensive) maximum. $\Delta\nu_{\text{PhOH}}$ for the other maximum equals 208 ± 5 . ⁿ The average from values 467^{42} and 475^j is given. ^o See also Refs. 6, 30, 38. ^p See also Refs. 46, 47. ^q Calculated in this work using the correlation $\Delta\nu_{\text{PhOH}} = \Delta\nu^0 + \rho^{\text{X}} \sigma^{\text{X}}(\text{x}) + \rho_{\text{R}}^+ \sigma_{\text{R}}^+$ for substituted nitriles XON ($\rho^{\text{X}} = -24.81 \pm 1.00$; $\rho_{\text{R}}^+ = -58.87 \pm 2.43$; $\Delta\nu^0 = 151.8 \pm 1.4$; $R = 0.987$, $s = 5.8$; 31 statistical degrees of freedom). ^r See also Ref. 53. ^s See also Ref. 37. ^t Calculated on the basis of the linear relationship²⁷ between $\Delta\nu_{\text{PhOH}}$ values for ethers and alcohols and Taft σ^{X} -constants. ^u See also Ref. 58. ^v Calculated from Eq.(3) (Series 1 and 11 from Table 2) using data from Ref. 24 and measurements in this work ($\Delta\nu_{\text{MeOH}} = 386 \text{ cm}^{-1}$). ^w Calculated from Eq.(3) (Series 1 from Table 2) using the value $\Delta\nu_{\text{MeOH}} = 401(2) \text{ cm}^{-1}$ measured in this work. ^x See also Ref. 6 and 61. ^y Calculated from Eq.(3) (series 1 from Table 2) using the value $\Delta\nu_{\text{MeOH}} = 431(\text{cm}^{-1})^j$. ^z See also Ref. 62. ^{aa} See also Ref. 28 and 64.

proton donors HX in the same standard media (CCl_4) as well as in the media of the pure bases (as a rule, $\Delta\nu_{\text{HX}}^{\text{CCl}_4}$ -values were taken from Refs. 5-8, 13, 22-24, 33, 38, 65-72). On condition that all those frequency shift scales refer to the standard inert media and characterize the Lewis basicity of the corresponding bases it is evident that they must be equivalent to each other. Indeed, in all cases considered, data of Table 2 evidence that $\Delta\nu_{\text{HX}}^{\text{CCl}_4}$ and $\Delta\nu_{\text{PhOH}}^{\text{CCl}_4\text{-para}}$ parameters are connected by the linear relationship^m (see also Refs. 6, 67, 68, 71, 73, 74 in a form of Eq.(3):

Table 2
Parameters of Eq.(3) for Various Proton Donors HX

HX, Conditions	a^+s_a	b^+s_b	r	s%	Number of points
1. MeCH, CCl_4	-12 ± 2	0.611 ± 0.009	0,991	2.9	89
2. HCl; CCl_4	-10 ± 17	1.610 ± 0.094	0,990	5.3	8
3. t-BuOH, CCl_4	8 ± 3	0.446 ± 0.017	0,989	3.6	23
4. 4-FC ₆ H ₄ OH, CCl_4	5 ± 4	1.005 ± 0.015	0,998	2.2	27
5. Pyrrole, CCl_4	-10 ± 3	0.533 ± 0.012	0,984	4.4	69
6. HCl in pure base B	81 ± 14	1.265 ± 0.078	0,975	5.5	15
7. PhOH in pure base B	14 ± 10	1.031 ± 0.057	0,978	7.2	17
8. Ph ₂ NH, CCl_4	0.3 ± 2.3	0.314 ± 0.008	0,985	4.8	50
9. PhC≡CH, CCl_4	9 ± 3	0.207 ± 0.009	0,973	5.0	39
10. PhOD, CCl_4	9 ± 8	0.630 ± 0.031	0,985	4.5	15
11. MeOD in pure base B	30 ± 2	0.382 ± 0.009	0,987	3.2	54
12. HNCO, CCl_4	-3 ± 8	1.246 ± 0.039	0,994	4.7	15
13. >SiOH^a	47 ± 8	1.458 ± 0.031	0,995	2.2	28
14. PhOH, CCl_4	(1,0)	(0)	(1,0)	(0)	-
15. $\text{H}^+ + \text{B} \rightleftharpoons \text{BH}^+$	$38 \pm 4, 2$	58500 ± 1290	0.891	12	22

^a Surface silanol groups. Frequency shifts are due to the absorption of the base from vapor phase to the surface.

^b By definition.

$$\Delta \nu_{\text{HX}}^{\text{CCl}_4} = a + b \Delta \nu_{\text{PhOH}}^{\text{CCl}_4} \quad (3)^{34}$$

For some important bases for which the literature data for $\Delta \nu_{\text{PhOH}}$ were not available, Eq.(3) was used for predicting the latter values on the basis of $\Delta \nu_{\text{HX}}$ -parameters. The calculated values are also included in Table 1. If, however, $\Delta \nu_{\text{HX}}$ -values refer to the non-inert, non-reference media (e.g., to the pure base B), Eq.(3) should hold only on condition that the contributions of nonspecific and electrophilic solvent-solute interactions in the gross solvent shifts are negligible for the whole set of bases. Linear relationships in terms of Eq.(3) (N^o 6, 7, 11, 13, and 14 from Table 2) strongly suggest that this is the case.

One should pay attention to the approximate linear relationship between the $\Delta \nu_{\text{PhOH}}$ -parameters and the gas phase proton affinities (PA) for certain, not too extensive, set of bases. One may hope that additional more accurate data as for PA (weak bases) as well as for $\Delta \nu_{\text{PhOH}}$ (e.g., amines) make possible an unambiguous solution of the problem about the relationship between the IR-shift parameters and Brönsted basicity of bases (see Ref. 66 for literature and discussion).

Series N^o 13 from Table 2 is also quite instructive and suggests that the change from CCl_4 to the gas phase does not tell on the change of the relative basicity order of bases. As it is expected⁷³, the slopes b of Eq.(3) for various HX depend approximately-linearly on the pK_a -values of these hydrogen acids in water. It once again evidences the applicability of the rule of multiplying of the acidic and basic factors^{73,75} for donor-acceptor interactions.

From the practical viewpoint it is important that Eq. (3) holds approximately also for $\Delta \nu_{\text{OD}}$ (B-parameters of Refs. 1 and 2). Least squares treatment of the latter in terms of

* For the CCl_4 medium the ordinate a must equal zero.

general four-parameter equation^{1,2} for the solvent effects

$$A = A_0 + yY + pP + eE + bB \quad (4)$$

which includes a new general basicity scale $\Delta\sqrt{V}_{\text{PhOH}}$ instead of previous $\Delta\sqrt{V}_{\text{OD}}=B$ -parameters and takes $A=\Delta\sqrt{V}_{\text{OD}}$ (Solvents N° 1, 4, 5, 19, 25, 27, 34, 50, 52, 65, 66, 74, 75, 77, 78, 85, 86, 105, 106, 113, 115, 119, 124, 125, 132, 136, 139, 171, 172, 176, 177, 182, and 185 from Table 1 were included) results only in a slight improvement of correlation characteristics (cf. series N° 11 from Table 2):

$$\Delta\sqrt{V}_{\text{OD}} = (-0.3 \pm 7.1) + (11.4 \pm 7.2)Y + (71.2 \pm 26.8)P + (2.3 \pm 1.1)E + (0.395 \pm 0.010)\Delta\sqrt{V}_{\text{PhOH}} \quad (5)$$

$t = (E-1)/(E+2)$; $P = (n^2-1)/(n^2+2)$; for E-parameters see Ref. 78; $R=0.992$; $s\%=3.0$.

However statistically significant, first three terms in the right-hand side of Eq.(5) have rather a low relative weight. For example, for the maximum range of variation of the $\Delta\sqrt{V}_{\text{OD}}$ -parameter (289 cm⁻¹; transfer from gas phase to Et₃N) the contribution of the $b\Delta\Delta\sqrt{V}_{\text{PhOH}}$ term is 89 per cent, whereas the relative weight of the $p\Delta Y$ -term is ca. 1 per cent; the $p\Delta P$ -term ca 6%; the contribution of the $e\Delta E$ -term is negligible. Even for the hypothetical base for which all solvent parameters have their extreme values ($\Delta Y=0.96$; $\Delta P=0.35$; $\Delta E=21.8$ and $\Delta\Delta\sqrt{V}_{\text{PhOH}}=650$) the contribution of the $b\Delta\Delta\sqrt{V}_{\text{PhOH}}$ term is of 76 per cent. Therefore it is evident, that as a rule, however not always^{*}, the earlier^{1,2} used $B(\Delta\sqrt{V}_{\text{OD}})$ -parameters characterize in rather a satisfactory approximation the general basity of bases, as measured by $\Delta\sqrt{V}_{\text{PhOH}}$ -values (new B-parameters).

However, on the reasons given above the preference must be given to the latter parameters. Some applications of the new B-parameters of solvents for quantitative correlation of the solvent effects are given elsewhere⁷⁹.

^{*} It is possible to select certain pairs of bases (e.g., DMSO and aniline) for which the contributions of all four terms of Eq. 4, 5 are of comparable importance.

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Extended Scale of Solvent
Electrophilicity Parameters

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An extended scale of the solvent electrophilicity parameters has been suggested on the basis of recent literature data on the E_T -parameters of solvents.

Earlier, the solvent electrophilicity E-scale was derived for several individual solvents on the basis of the E_T parameters of Dimroth and Reichardt^{2,3}. Later on⁴, this scale has been expanded to the aqueous sulfuric and perchloric acids. In connection with the recent extension⁵ of the E_T -scale it is also expedient to extend the solvent electrophilicity scale (E) of pure media. By definition¹, the E-parameters are calculated as follows:

$$E = E_T - E_T^0 - yY - pP \quad (1)$$

where Y and P are the polarity and polarizability parameters of solvents; the respective susceptibility values y and p are estimated from the E_T -data for properly selected, only non-specifically interacting with N-phenolpyridinium betaines, solvents.

As compared with our earlier work¹ a slightly modified reference set of solvents for determination of the y and p-values was used. The following pure media were included: hexane, cyclohexane, 1,2-dichloromethane, 1-chloropropane,

chlorobenzene, diethyl ether, dibutyl ether, di-isopropyl ether, diphenyl ether, tetrahydrofuran, piperidine, N,N,N',N'-tetramethylguanidine, triethylamine, pyridine, quinoline, CCl₄, nitrobenzene, benzonitrile, N,N,N',N'-tetramethylurea, hexamethylphosphortriamide, fluorobenzene, 1,2-dimethoxyethane, iodobenzene, bromoethane, 1,2-dichlorobenzene, and 1,1,2,2-tetrachloroethane. The dependence of E_T-parameters of these solvents on the characteristics of nonspecific solvating power³ of the solvents can be described by the following equation:

$$E_T = (25.10 \pm 1.06) + (14.84 \pm 0.74)Y + (9.59 \pm 3.70)P \quad (2)$$

$$R = 0.974; s = 0.78; s\% = 7$$

Within their reliability intervals, the parameters of Eq. (2) are practically indistinguishable from those given in Ref. 1. Taking into account Eq.(2), Eq.(1) can be rewritten for the calculation of E-parameters in the more definite form:

$$E = E_T - 25.10 - 14.84Y - 9.59P \quad (3)$$

Since the present standard deviation s, s% of Eq.(2), and reliability intervals of E_T⁰, y, and p-parameters are somewhat lower, as compared with the earlier work¹ the E-values (see the Table) calculated by Eq. (3) are characterized by the lower uncertainty intervals.

Table

E Parameters^a of Pure Solvents as
Calculated from Eq.(3)

Solvent		E	Solvent		E
1.	Hexane	(0)	7.	EtBr	(0)
2.	Cyclohexane	(0)	8.	Et ₂ O	(0)
3.	PrCl	(0)	9.	i-Pr ₂ O	(0)
4.	CCl ₄	(0)	10.	Bu ₂ O	(0)
5.	CHCl ₂ CHCl ₂	(0)	11.	Ph ₂ O	(0)
6.	EtBr	(0)	12.	MeOCH ₂ CH ₂ OMe	(0)

³ $Y = (\xi - 1) / (\xi + 2)$; $P = (n^2 - 1) / (n^2 + 2)$.

Solvent	E	Solvent	E
13. THF	(0)	47. HCONH ₂	14.5
14. PhF	(0)	48. HCONHMe	11.9
15. PhCl	(0)	49. HCONMe ₂	2.6
16. PhBr	(0)	50. MeCONMe ₂	2.4
17. PhJ	(0)	51. MeCONHMe	9.9
18. PhCN	(0)	52. MeNO ₂	5.1
19. PhNO ₂	(0)	53. EtNO ₂	2.8
20. 1,2-Cl ₂ C ₆ H ₄	(0)	54. MeCN	5.2
21. Piperidine	(0)	55. EtCN	3.2
22. C ₅ H ₅ N	(0)	56. PhCH ₂ CN	2.2
23. Quinoline	(0)	57. H ₂ O	21.8
24. CO(NMe ₂) ₂	(0)	58. MeOH	14.9
25. NH(NMe ₂) ₂	(0)	59. EtOH	11.6
26. P(O)(NMe ₂) ₃	(0)	60. ProH	10.6
27. Et ₃ N	(0)	61. i-ProH	8.7
28. 2,6-Me ₂ C ₅ H ₃ N	(0)	62. BuOH	10.3
29. CCl ₃ Me	1.5	63. i-BuOH	7.4
30. CH ₂ Cl ₂	2.7	64. sec-BuOH	7.4
31. CHCl ₃	3.28	65. t-BuOH	5.2
32. CH ₂ ClCH ₂ Cl	3.0	66. MePrCHOH	7.1
33. Me ₂ CO	2.1	67. Et ₂ CHOH	6.2
34. MeCOEt	2.0	68. PhCH ₂ OH	10.9
35. MeCOPh	0.7	69. HOCH ₂ CH ₂ OH	15.0
36. Cyclohexanone	0.5	70. MeOCH ₂ CH ₂ OH	12.5
37. MeCOPr	-0.6	71. O(CH ₂ CH ₂ OH) ₂	12.8
38. MeCO(i-Bu)	0.1	72. H ₂ NCH ₂ CH ₂ OH	10.4
39. HCOOMe	3.1	73. PhOH	13.7 ^b
40. MeCOOEt	1.6	74. HCOOH	16.7
41. (MeCO) ₂ O	3.7	75. MeCOOH	14.6
42. N-Methylpyrrolid- -2-one	1.3	76. O(CH ₂ CH ₂ OEt) ₂	1.0
43. Et ₂ NH	1.2	77. 1,4-Dioxan	4.2
44. H ₂ NCH ₂ CH ₂ NH ₂	2.5	78. PhOMe	1.4
45. NH ₃	10.6 ^b	79. PhOEt	0.8
46. PhNH ₂	6.2	80. C ₆ H ₆	2.1
		81. PhMe	1.5

	Solvent	E		Solvent	E
82.	1,3,5-Me ₃ C ₆ H ₃	0.8	85.	Me ₂ SO	3.2
83.	Ph(t-Bu)	1.2	86.	Sulpholane	2.3
84.	2-Me-C ₅ H ₄ N	-0.7			

^aE-values for the reference set of solvents are given in parenthesis. ^bCalculated on the basis of the correlation of the rate constants of the solvolysis of t-BuCl in various solvents.

In addition to the E-values calculated from the first time, the Table includes also the E-parameters calculated over again from Eq.(3) for the solvents for which these values were reported earlier¹. As a rule, for the latter set of solvents, the E-values derived in the present work are practically indistinguishable from those reported¹.

Some examples of the application of the present set of E-values for the quantitative correlation of solvent effects are given elsewhere⁶.

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Kinetics and Mechanism of Reaction of HCl
with Methanol, Ethanol, and 1-Propanol and
Conductometry of Respective Solutions

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The more precise and complete experimental data on reaction rates of HCl with absolute methanol, ethanol, and 1-propanol and on conductivities of the solutions of HCl in these alcohols are reported. In relatively dilute solutions of HCl linear dependences of first order rate constants on equivalent conductivities of respective solutions were observed. These linearities are interpreted as confirmation of the mechanistic scheme with rate limiting decay of ion pairs. The positive deviations from this relationship for higher concentrations of HCl in methanol were observed.

In our preceding papers^{1,2} the results of the investigation of the kinetics of the reaction of HCl with absolute methanol and ethanol as well as the results of a conductometric study of respective solutions were reported. A correlation between kinetic and conductometric data has been observed. This relationship has been regarded as a proof that the observed rate is proportional to the concentration of ion pairs $\text{ROH}_2^+ \text{Cl}^-$.

This study is purposed to check the results and con-

clusions of those papers by using more precise apparatus for conductometric measurements.

Experimental

Methanol (chemically pure), ethanol (rectified up to 95.5 per cent), and 1-propanol (pure) were dried as described elsewhere.³ The solutions of HCl in alcohols investigated were prepared as described previously.¹ For conductometric measurements a device ERCP-60, constructed by Reeben⁴ was used at frequency of 1590 Hz. The conductometric cells with non-platinized or slightly platinized electrodes were used. Before each experiment the cell has been sealed. The cell constants were determined at different temperatures, and extrapolated to the temperatures needed in measurement. For calibration the data reported by Noyes and Melcher⁵ were used. The cells were thermostated by ultrathermostat U-8.

Below 70°C the thermostat was filled with water (accuracy $\pm 0.02^\circ\text{C}$ in the inner vessel), in the range of 70 to 95°C with glycerol ($\pm 0.05^\circ\text{C}$), and in that of above 95°C with oil ($\pm 0.15^\circ\text{C}$ with glycerol in the inner vessel).

In conductometric rate measurements at temperatures above 40°C the time-dependence of conductivity of the reaction mixture was recorded by potentiometer EZ-4. Reactance was compensated with help of a subdivided capacitor P-515. The output scale was calibrated by means of a resistor P-517 or P-517 M.

At lower temperatures (25 and 40°C) separate simultaneous compensations of reactance and real resistance were carried out during each measurement. Thus, real resistance, R_x , of the solution in cell was equalled to the reading at the resistor.

The effective conductivities, κ_{obs} ($\Omega^{-1} \text{ cm}^{-1}$), were calculated from the R_x values obtained.

The accuracy of measurements with respect to absolute values was of 0.5 to 1 per cent.

The initial fragment of the kinetic curve, conductivity vs. time, passes through a maximum, which reflects the dynamics of the temperature equalization between the reaction mixture and the heat-transfer agent.

Initial data for conductivity of the HCl solution in a given alcohol at a given temperature were found by graphical extrapolation as shown in Fig. 1.

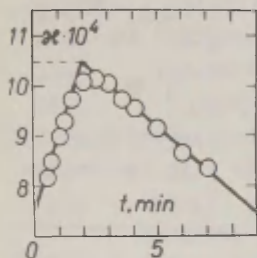


Fig. 1. An example of graphical extrapolation for obtaining the initial data for conductivity of HCl 0.0133 M in ethanol at 75°C. t denotes time in minutes.

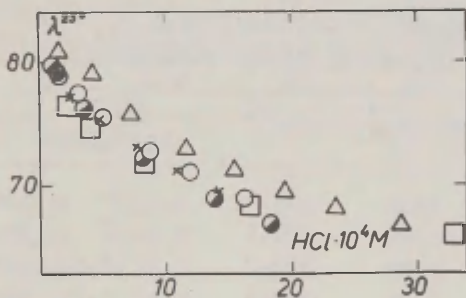


Fig. 2. The λ values for HCl solutions in ethanol at 25°C as reported by several authors.

- Murray-Kust and Hartley⁷
- × Ogston⁸
- △ Bezman and Verhock⁹
- El-Aggan et al.¹⁰
- present work

Using these results of conductometric measurements and taking into account the dependence of the conductivity on the concentration of HCl as obtained from initial conductivities, the effective rate constants k (sec^{-1}) were calculated putting them equal to the initial slopes of plots in coordinates of $\sqrt{[\text{HCl}]}$ and time (the method of initial rates).

The corrections resulting from the conductivity of pure alcohol, κ_{ROH} , were introduced: $\kappa = \kappa_{\text{obs}} - \kappa_{\text{ROH}}$.

The equivalent conductivities of solutions investigated were calculated according to the formula:

$$\Lambda = 1000 \kappa / \sqrt{[\text{HCl}]} \Omega^{-1} (\text{g-equiv})^{-1}$$

The comparison of the Λ values for solution of HCl in ethanol at 25°C obtained in this study with respective values from literature is represented in Fig. 2.

Rate constants at higher HCl concentrations ($[\text{HCl}] \geq 0.1 \text{ mol.l}^{-1}$) were measured using titrimetric techniques.²

The results of measurements are listed in Tables 1 through 5.

Table 1
Equivalent Conductivities Λ ($\Omega^{-1} (\text{g-equiv})^{-1}$)
for Solutions of HCl in Absolute Methanol at 25 and 80°C

$\sqrt{[\text{HCl}]}$ (mol/l) $\times 10^3$	Λ^{25°	Λ^{80°	$\sqrt{[\text{HCl}]}$ (mol/l) $\times 10^3$	Λ^{25°	Λ^{80°
2000	-	68.4	54	132.5	183.9
1360	-	86.3	27	143.6	211.4
849	-	101.0	13.5	154.4	225.2
750	-	104.0	6.7	164.8	247.2
493	82.3	113.5	3.3	171.4	265.9
214	-	145.8	1.6	181.1	279.5
108	119.3	164.2			

Table 2
Effective Rate Constants for the Reaction of HCl
with Absolute Methanol at 80°C

$\frac{[\text{HCl}]}{(\text{mol/l}) \times 10^3}$	$k \times 10^5 \text{ sec}^{-1}$	$\frac{[\text{HCl}]}{(\text{mol/l}) \times 10^3}$	$k \times 10^5 \text{ sec}^{-1}$	$\frac{[\text{HCl}]}{(\text{mol/l}) \times 10^3}$	$k \times 10^5 \text{ sec}^{-1}$
3660	34.3	754	16.2 [Ⓜ]	4.2	1.67 ^{ⓂⓂ}
2900	34.5	712	16.2	3.6	1.53 ^{ⓂⓂ}
2750	33.7	447	15.3	2.7	1.29 ^{ⓂⓂ}
1960	28.0	345	13.3 [Ⓜ]	1.9	0.91 ^{ⓂⓂ}
1400	23.1	144	10.8 [Ⓜ]	1.3	0.66 ^{ⓂⓂ}
1280	23.3	99	9.50 [Ⓜ]	0.9	0.43 ^{ⓂⓂ}
1070	21.3	55	7.85 [Ⓜ]		
920	18.5	21.6	4.76 [Ⓜ]		

[Ⓜ] Calculated from data reported by Hinshelwood.⁶

^{ⓂⓂ} From our earlier report².

Table 3
Equivalent Conductivities Λ ($\Omega^{-1}(\text{g-equiv})^{-1}$) for
Solutions of HCl in Absolute Ethanol at Several Temperatures

$\frac{[\text{HCl}]}{(\text{mol/l}) \times 10^3}$	25°	40°	60°	75°	100°
501	-	-	-	-	31.5
212	-	-	-	-	33.6
106	32.2	34.1	35.9	36.5	35.9
53	37.5	43.0	46.1	51.8	48.6
26.5	43.7	51.0	53.2	63.9	59.2
13.3	52.2	62.5	66.1	78.9	74.7
6.63	59.9	72.6	80.3	95.2	91.8
3.31	65.9	81.5	94.5	112.7	107.5
1.66	69.1	83.2	104.7	128.9	126.4
0.83	71.6	89.3	114.2	139.1	149.5
0.41	74.5	90.9	118.8	148.7	164.2
0.21	76.4	92.3	119.9	151.0	191.3

Table 4

Effective Rate Constants for the Reaction
of HCl with Absolute Ethanol at 75 and 100°C

$\overline{[HCl]}$ (mol/l) $\times 10^3$	75° $k \times 10^6$ sec ⁻¹	100° $k \times 10^4$ sec ⁻¹	$\overline{[HCl]}$ (mol/l) $\times 10^3$	75° $k \times 10^6$ sec ⁻¹	100° $k \times 10^4$ sec ⁻¹
501	-	1.7 [*]	3.31	5.1	1.1
106	-	1.6 [*]	1.66	3.8	0.81
53	9.9	1.5	0.83	2.9	0.72
26.5	8.8	1.4	0.41	-	0.51
13.3	7.9	1.3	0.21	-	0.38
6.63	6.3	1.2			

^{*} Titrimetric method

Table 5

Equivalent Conductivities λ ($\Omega^{-1}(\text{g-equiv})^{-1}$) for
Solutions of HCl in Absolute 1-Propanol and Effective Rate
Constants for the Reaction of HCl with Absolute 1-Propanol
at 110°C

$\overline{[HCl]}$ (mol/l) $\times 10^2$	λ	k sec ⁻¹	$\overline{[HCl]}$ (mol/l) $\times 10^2$	λ	k sec ⁻¹
41.8	-	4.4 [*]	1.11	20.0	3.7
18.0	12.6	4.2 [*]	0.56	25.5	-
9.0	12.4	4.1	0.28	35.6	3.1
4.5	13.5	4.0	0.14	47.7	2.7
2.25	16.5	-	0.07	62.0	-

^{*} Titrimetric method

Discussion

The results obtained confirm the conclusion^{1-3,6} that for the reaction between HCl and absolute alcohol the effective value of the first-order rate constant, k , is smaller at lower concentrations of HCl (for illustration see Fig.3).

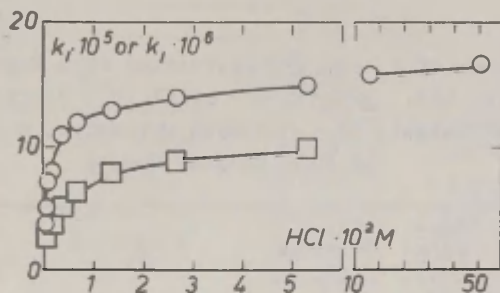


Fig. 3. Dependence of the effective rate constant k for the reaction of HCl with ethanol on the concentration of HCl

○ at 100°C

□ at 75°C

If this phenomenon is interpreted as a sign of proportionality of the observed rate to the concentration of ion pairs ROH_2^+Cl (see Refs. 1-3,6) and it is assumed that the dependence of k on the concentration of HCl is caused by the change in the degree of dissociation, α , of these ion pairs¹⁻³ we can write:

$$k = (1 - \alpha)k_0 \quad \text{and} \quad \alpha = \frac{\lambda}{\lambda + \lambda_0}$$

consequently,

$$k = k_0 - \frac{k_0}{\lambda + \lambda_0} \lambda \quad (1)$$

where k_0 denotes the rate constant for the conversion of ion pairs into the reaction products. If the linearity (1)

between k and λ is held the values of k_0 and k_0/λ_∞ and, consequently, λ_∞ could easily be determined from respective values at the intercept and the slope. From the coefficients of linear regressions in coordinates k, λ and in the range of $[HCl] \leq 0.7$ mol/l the respective k_0 and λ_∞ values were calculated and listed in Table 6. Eq.(1) is held well at these HCl concentrations.

Table 6

Values of k_0 and λ Calculated from Parameters of Eq.(1). $[HCl] \leq 0.7$ mol/l, r - Correlation Coefficient, SD - Standard Deviation, n - Number of Experimental Points

System	Temperature, °C	k_0	λ	r	SD	n
CH ₃ OH+HCl	80	$(2.47 \pm 0.06)10^{-4}$	279.0 ± 3.9	0.994	0.06	12
C ₂ H ₅ OH+HCl	75	$(1.41 \pm 0.02)10^{-5}$	175.2 ± 1.7	0.997	0.03	7
C ₂ H ₅ OH+HCl	100	$(1.87 \pm 0.02)10^{-4}$	234.2 ± 4.1	0.996	0.03	10
C ₃ H ₇ OH+HCl	110	$(4.59 \pm 0.06)10^{-4}$	111.4 ± 5.4	0.992	0.08	6

The λ_∞ value is usually obtained making use of linear extrapolation in coordinates λ, \sqrt{c} or λ, \sqrt{c} . The comparison of the λ_∞ values calculated from parameters of Eq.(1) with those obtained from the extrapolations is represented in Table 7. It is obvious that the values of λ_∞ obtained by these methods are different. This problem has been discussed by several authors (see, e.g., Ref. 17).

Eq.(1) represents a correlation between two independent series of experimental data. Such a correlation indicates that the kinetic and conductometric data are related to one and the same physical object. According to the interpretation given above the observed values of k is proportional

to the fraction of dissociated and the value of λ - to the fraction of undissociated ion pairs.

Table 7

Comparison of the Values of λ_{∞} Calculated Using Eq.(1) with Values Obtained by Linear Extrapolations in Coordinates λ , $\sqrt{\lambda_{\text{HCl}}}$ and λ , $\sqrt{\lambda_{\text{HCl}}}$

Alcohol	Temperature °C	λ_{∞} from		
		Eq.(1)	linearity on $\sqrt{\lambda_{\text{HCl}}}$	linearity on $\sqrt{\lambda_{\text{HCl}}}$
CH ₃ OH	80	279.0 \pm 3.9	307.5 \pm 1.9	332.6 \pm 0.9
C ₂ H ₅ OH	75	175.2 \pm 1.7	154.7 \pm 4.2	173.0 \pm 3.2
C ₂ H ₅ OH	100	234.2 \pm 4.1	206.6 \pm 8.9	234.3 \pm 9.9
C ₃ H ₇ OH	110	111.4 \pm 5.4	77.1 \pm 6.0	95.6 \pm 6.8
CH ₃ OH	25	-	190.9 \pm 2.0	200.5 \pm 3.1
C ₂ H ₅ OH	25	-	78.2 \pm 0.5	84.7 \pm 0.6

But one should keep in mind that the mechanistic scheme represented and Eq.(1) corresponding to this scheme are consistent with experimental data only at relatively low concentrations at HCl. For the best illustration of that are the data for methanol (see Fig. 4).

One can see that the linearity in coordinates k, λ is broken at higher HCl concentrations and the value of k even exceeds the k_0 value obtained by the extrapolation using the data at lower HCl concentrations. Such a trend in the dependence of k on λ cannot be explained proceeding from accepted theory of solutions of strong electrolytes. Therefore an attempt to interpret this inconsistency will be presented in a separate report.

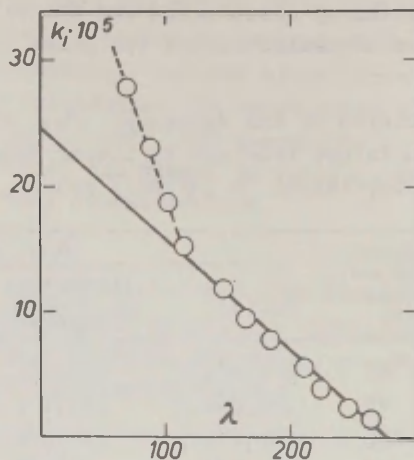


Fig. 4. Plot of k vs. λ for the reaction of HCl with methanol at 80°C.

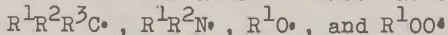
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Application of PPL to Standard Thermodynamic
Properties of Organic Compounds.

14. Heats of Formation of Free Radicals



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The equations for $\Delta H_f^0(298^\circ K, g)$ of free radicals $R^1R^2R^3C\cdot$, $R^1R^2N\cdot$, $R^1O\cdot$ and $R^1OO\cdot$ are derived from PPL and the concept of Ψ -interaction. Standard deviations for the correlations are considerably smaller than errors of experimental ΔH_f^0 values for such compounds. The available experimental data for heats of formation do not confirm the hypothesis of hyperconjugational stabilization of alkyl radicals. The ΔH_f^0 values calculated on the basis of relationships derived are recommended as the "best" estimates for true formation enthalpies of radicals $R^1R^2R^3C\cdot$, $R^1R^2N\cdot$ and $R^1O\cdot$.

The earlier developed concepts¹⁻⁵ are here used for the analysis of the relationships between the chemical structure and heats of formation, $\Delta H_f^0(298^\circ K, g)$, of free radicals $R^1R^2R^3C\cdot$, $R^1R^2N\cdot$, $R^1O\cdot$, and $R^1OO\cdot$; R^1 is any alkyl substituent or H. There are a lot of contradictory data for ΔH_f^0 of such compounds. Therefore it was decided to analyse

all experimental data^{*} which were considered as the independent estimates of true heats of formation with random and/or systematic errors.

The Radicals $R^1R^2R^3C\cdot$.

The ΔH_f^0 values for such radicals, as well as corresponding quantities for alkanes $R^1R^2R^3R^4C$, are assumed to be described by the PPL⁶ using the interaction parameters¹⁻⁵ ψ . In this case the following correlation should exist

$$\Delta \Delta H_f^0(R^1R^2R^3C\cdot) = a_0 + a_1 \sum_i \psi(R^i) + a_2 \sum_{i \neq j} \psi(R^i) \psi(R^j) + a_3 \prod_i \psi(R^i) \quad (1)$$

where $\Delta \Delta H_f^0(R^1R^2R^3C\cdot) = \Delta H_f^0(R^1R^2R^3C) - \sum_i \Delta H_f^0(R^iH)$ and

$a_1 = \psi(\cdot CH_2)$. The coefficients a_0 , a_2 , and a_3 should satisfy the following requirements: $a_0 = \Delta H_f^0(\cdot CH_3)$, and $a_3 = a_2^2$, because of the conditions^{4,6} $a_2 = \alpha_r$ and $a_3 = \alpha_r^2$, where α_r is characteristic of interaction^{4,6} between the substituents.

It was found that the ΔH_f^0 values for 9 of 11 alkyl radicals can adequately be described (See Table 1) with equation (1). Moreover; the limiting condition $a_0 = \Delta H_f^0(\cdot CH_3)$ really fulfils, while $a_2 = a_3 = 0$. Therefore in the limits of accuracy of ΔH_f^0 values the following relationship should exist

$$\Delta \Delta H_f^0(R^1R^2R^3C\cdot) = a_0 + a_1 \sum_i \psi(R^i) \quad (2)$$

As seen from Table 1 and Fig. 1, equation (2) describes ΔH_f^0 values for 9 alkyl radicals with accuracy which exceeds the uncertainties of experimental data. The deviations of points for $(C_2H_5)_2CH\cdot$ and $(CH_3)_3CCH_2\cdot$ perhaps can be explained by systematic errors in the corresponding experimental data.

^{*} The ΔH_f^0 values for these radicals are listed in Table 2. Close values for the same radicals are averaged. The ΔH_f^0 values well described by the derived equations are underlined in Table 2.

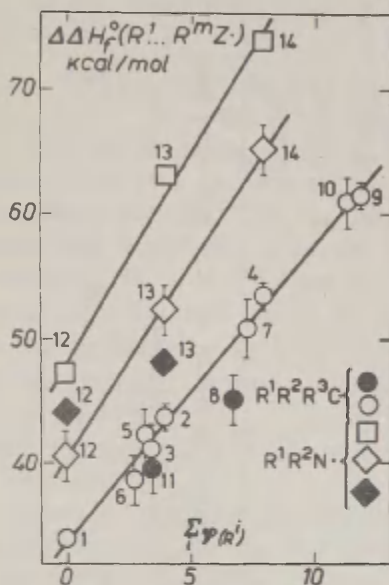


Fig. 1. The relationships between $\Delta\Delta H_f^0(R^1R^2R^3C^\bullet)$ or $\Delta H_f^0(R^1R^2N^\bullet)$ and $\sum_i \psi(R^i)$; \square - the data of Golden D.M. et al.¹⁵;

\diamond - the data of Kerr J.A.¹⁶; \blacklozenge - other data.

1. CH_3^\bullet ; 2. $CH_3CH_2^\bullet$;
3. $C_2H_5CH_2^\bullet$; 4. $(CH_3)_2CH^\bullet$;
5. $n-C_3H_7CH_2^\bullet$;
6. $(CH_3)_2CHCH_2^\bullet$;
7. $C_2H_5(CH_3)CH^\bullet$;
8. $(C_2H_5)_2CH^\bullet$; 9. $(CH_3)_3C^\bullet$;
10. $C_2H_5(CH_3)_2C^\bullet$;
11. $(CH_3)_3CCH_2^\bullet$; 12. NH_2^\bullet ;
13. CH_3NH^\bullet ; 14. $(CH_3)_2N^\bullet$.

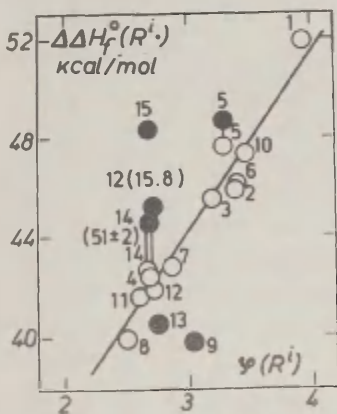


Fig. 2. The correlation between $\Delta\Delta H_f^0(R_i)$ and $\psi(R_i)$ for alkyl radicals: 1. CH_3^\bullet ; 2. $CH_3CH_2^\bullet$; 3. $C_2H_5CH_2^\bullet$; 4. $(CH_3)_2CH^\bullet$; 5. $n-C_3H_7CH_2^\bullet$; 6. $(CH_3)_2CHCH_2^\bullet$; 7. $C_2H_5(CH_3)CH^\bullet$; 8. $(CH_3)_3C^\bullet$; 9. $(C_2H_5)_2CH^\bullet$; 10. $(CH_3)_3CCH_2^\bullet$; 11. $C_2H_5(CH_3)_2C^\bullet$; 12. cyclohexyl; 13. cyclopentyl; 14. cyclobutyl; 15. cyclopropyl

Table 1

The Calculated Parameters of the Correlation Equations (1), (2), (4), (6), (8) and (9) for the $\Delta H_F^0(298^\circ\text{K}, \text{g})$ of Free Radicals^a $\text{R}^1\text{R}^2\text{R}^3\text{C}^\cdot$, $\text{R}^1\text{R}^2\text{N}^\cdot$, R^1O^\cdot , $\text{R}^1\text{OO}^\cdot$.

Compounds	Eqns	a_0	a_1	a_2	a_3	n	r(R)	S_0
$\text{R}^1\text{R}^2\text{R}^3\text{C}^\cdot$	(1)	33.68 \pm 0.98	2.36 \pm 0.33	0.04 \pm 0.13	-0.02 \pm 0.06	9 ^b	0.9999	1.01
	(2)	33.00 \pm 1.01	2.39 \pm 0.15	-	-	11 ^c	0.9821	1.80
		33.65 \pm 0.52	2.39 \pm 0.08	-	-	9 ^b	0.9965	0.88
	(4)	34.29 \pm 0.93	1.18 \pm 0.48	-	-	11 ^c	0.9904	1.40
	(6)	31.56 \pm 1.75	2.39 \pm 0.15	-	-	11 ^c	0.9842	1.79
$\text{R}^1\text{R}^2\text{N}^\cdot$	(8)	48.03 \pm 1.86	3.40 \pm 0.37	-	-	3 ^d	0.9942	2.04
		40.33 \pm 0.37	3.12 \pm 0.07	-	-	3 ^e	0.9997	0.41
R^1O^\cdot	(9)	-11.35 \pm 1.81	7.67 \pm 0.57	-	-	8	0.9836	0.69
$\text{R}^1\text{OO}^\cdot$		-7.37 \pm 4.39	7.95 \pm 1.32	-	-	3	0.9865	1.34

^a For the alkanes the $\Delta H_F^0(298^\circ\text{K}, \text{g})$ values accepted by Stull et al.⁷ are used here.

^b Without of the points for $(\text{CH}_3)_3\text{CCH}_2^\cdot$ and $(\text{C}_2\text{H}_5)_2\text{CH}^\cdot$ radicals.

^c For all the alkyl radicals considered here.

^d The data from the paper¹⁵ of Golden D.M. et al.

^e The data accepted¹⁶ by Kerr J.A.

On the other hand, the following good correlation (see Fig. 2) was found

$$\Delta\Delta H_F^0(R_1) = (22.36 \pm 1.67) + (7.30 \pm 0.54) \psi(R_1) \quad (3)$$

$n = 12; r = 0.9737; s_0 = 0.81 \text{ kcal/mol}$

This correlation considers the unpaired electron of radical center as a certain substituent X (by analogy of monosubstituted alkanes^{2,3} R_1X). The point for $R_1 = (C_2H_5)_2CH\cdot$ deviates from equation (3) in the same direction as that from correlation (2). Such a fact apparently confirms the conclusion of systematic error in the $\Delta\Delta H_F^0$ value for this radical. For cyclohexyl radical, as well as for cyclobutyl radical, one of two (see Table 2) known $\Delta\Delta H_F^0$ values is described by equation (3). In the same time deviations of the points for cyclopropyl and cyclopentyl radicals apparently are random.

The correlation (3) seems to be somewhat formal because of differences⁸ in the geometry of the alkyl radicals R_1 and the corresponding substituents R_1 in alkanes and their monosubstituted derivatives. The parameter a_1 of equation (3) is the measure of ability of the unpaired electron to take part in the ψ -interaction, and parameter a_0 is its additive contribution to the heat of formation.

The Problem of Hyperconjugational Stabilization of Free Radicals

It is assumed⁸ that one of the reasons for the relative stability of $(CH_3)_3C\cdot$ is its stabilization by the hyperconjugational interaction between the H-C-bonds and the unpaired electron. If the hyperconjugational contribution is well described by the α -hydrogen-bonding model⁵⁻¹¹, the equation (4) should exist for the formation enthalpies of alkyl radicals:

$$\Delta\Delta H_F^0(R^1R^2R^3C\cdot) = a_0 + a_1 \sum_i \psi(R^i) + h \sum_i n_H^\alpha(R^i) \quad (4)$$

where $n_H^\alpha(R^i)$ is the number of α -H-atoms in the substituent

R^1 . The condition $h < 0$ is required by virtue of the stabilizing nature of the hyperconjugation (see Ref. 11-14). Equation (4) should take the form (2) in such a case only when its parameters are closely correlated. Indeed, there is a close correlation between these parameters. Moreover, an excellent correlation^{***} (5) is found

$$\sum_i n_H^\alpha(R^i) = (-12.70 \pm 0.98) + (1.84 \pm 0.09) \sum_i \psi(R^i) + \\ + (4.23 \pm 0.35) n_H^\alpha(C^\bullet) \quad (5)$$

$n = 11$; $R = 0.9987$; $s_0 = 0.18$ kcal/mol where $n_H^\alpha(C^\bullet)$ is the number of H-atoms at the radical center.

The following model calculations were then made. On the basis of equation (4) and assumptions: $a_0 = 34.0$ kcal/mol, $a_1 = 3.0$ and $n = -0.5; +0.5; -2.0; +2.0$ kcal/mol, values of $\Delta\Delta H_f^0(R^1R^2R^3C^\bullet)$ were calculated for 11 alkyl radicals.^{***} Then the possibilities to correlate these quantities and the corresponding parameters $\sum_i \psi(R^i)$ only were investigated.

In the case of $h = \mp 0.5$ kcal/mol a good correlation of the type (2) is really observed for all radicals considered. In the case of $h = \mp 2.0$ kcal/mol the relationships between $\Delta\Delta H_f^0(R^1R^2R^3C^\bullet)$ and $\sum_i \psi(R^i)$ split into the sets of the parallel lines (see Figs. 3 and 4). Each of such lines is occupied by the points for the radicals with the same numbers of H-atoms at the radical center. Therefore the correlation (6) should exist because of the relationship (5)

$$\Delta\Delta H_f^0(R^1R^2R^3C^\bullet) = a_0 + a_1 \sum_i \psi(R^i) + a_2 n_H(C^\bullet) \quad (6)$$

As seen from equations (5), (6) and Figs. 3 and 4, the slopes of the parallel lines depend on the sign of the parameter h . It is evident that in the case of $h < 0$ the correlation (2) for all radicals considered here should be worse than in the case of $h > 0$.

^{**} For the radicals which are listed in captions of Figs. . . . 3 and 4.

^{***} For the radicals which are listed in captions of Figs. 3 and 4.

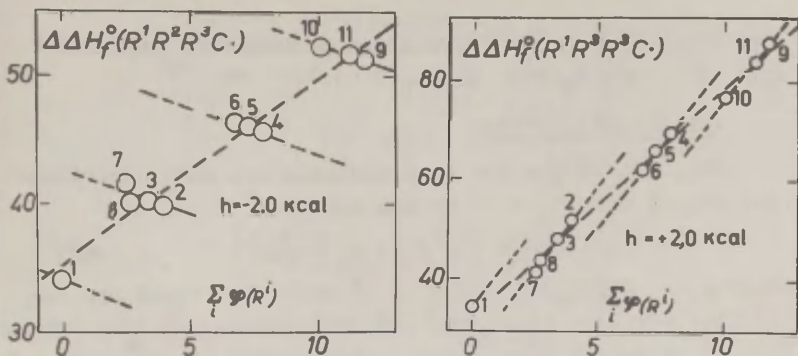


Fig. 3 and 4. The correlations in the cases of the hyperconjugational ($h = -2.0 \text{ kcal/mol}$) and "anti-hyperconjugational" ($h = +2.0 \text{ kcal/mol}$) interactions between radical center of alkyl radical $R^1R^2R^3O\cdot$ and α -H-C-bonds of the substituents R^1 (the results of model calculations). 1. $\text{CH}_3\cdot$; 2. $\text{CH}_3\text{CH}_2\cdot$; 3. $\text{C}_2\text{H}_5\text{CH}_2\cdot$; 4. $(\text{CH}_3)_2\text{CH}\cdot$; 5. $\text{C}_2\text{H}_5(\text{CH}_3)\text{CH}\cdot$; 6. $(\text{C}_2\text{H}_5)_2\text{CH}\cdot$; 7. $(\text{CH}_3)_3\text{CCH}_2\cdot$; 8. $(\text{CH}_3)_2\text{CHCH}_2\cdot$; 9. $(\text{CH}_3)_3\text{C}\cdot$; 10. $(\text{C}_2\text{H}_5)_3\text{C}\cdot$; 11. $\text{C}_2\text{H}_5(\text{CH}_3)_2\text{C}\cdot$.

Now let us assume that the ΔH_F^0 values for $(\text{C}_2\text{H}_5)_2\text{CH}\cdot$ and $(\text{CH}_3)_3\text{CCH}_2\cdot$ contain any considerable errors. In such case there is an analogy between Figs. 1 and 4, but not between Figs. 1 and 3. Indeed, equation (4) with $h = 1.50 \pm 0.58 \text{ kcal/mol}$ holds for all alkyl radicals listed in Table 2. Thus one would have to assume that instead of hyperconjugation there is a destabilizing interaction in the alkyl radicals. The contribution of such an interaction is well described by the model⁹⁻¹¹ of the hyperconjugation. But the point for $(\text{C}_2\text{H}_5)_2\text{CH}\cdot$ deviates from this correlation in the direction of additional stabilization. Experimental data for other alkyl radicals are not available up to date. Therefore the correlation (4) should be considered as rather a formal

one arising from the correlation between the parameters $\sum_i \varphi(R^i)$, $\sum_i n_H(R^i)$, and $n_H(C \cdot)$.

The radicals $R^1R^2N\cdot$

The ΔH_F^0 values for such radicals are well described (see Fig. 1 and Table 1) by the equation

$$\Delta \Delta H_F^0(R^1R^2N\cdot) = a_0 + a_1 \sum_i \varphi(R^i) \quad (7)$$

where $a_0 = \Delta H_F^0(H_2N\cdot)$ and $a_1 = \varphi(HN\cdot)$. But there are two parallel straight lines for the ΔH_F^0 values, one for those found¹⁵ by Golden D.M. et al., and another for those accepted¹⁶ by Kerr J.A. Therefore the data for one set have some systematic error. We assume the data chosen¹⁶ by Kerr J.A. are closer to the true ΔH_F^0 values of the N-radicals. These data fit considerably better equation (17). Moreover, for the radicals $NH_2\cdot$ and $\cdot N(CH_3)_2$ these values coincide well with these accepted¹⁷ on the basis of a wider compilation. As one can see from equations (2) and (7), a linear relationship between the $\Delta \Delta H_F^0$ values for $R^1R^2N\cdot$ and $R^1R^2CH\cdot$ can be formulated. It was done as follows

$$\Delta \Delta H_F^0(R^1R^2N\cdot) = (-2.77 \pm 0.94) + (1.27 \pm 0.02) \times \Delta \Delta H_F^0(R^1R^2CH\cdot) \quad (8)$$

$$s_0 = 0.3 \text{ kcal/mol}$$

The radicals $R^iO\cdot$ and $R^iOO\cdot$

Such compounds can be considered as monosubstituted alkanes R^iX with $X = O\cdot$ and $OO\cdot$. Thus, their ΔH_F^0 values should be well described by the equation^{2,3}

$$\Delta \Delta H_F^0(R^iX) = a_0 + a_1 \varphi(R^i) \quad (9)$$

where $a_0 = \Delta H(X)$ is the additive contribution of X to ΔH_F^0 , and $a_1 = \varphi(X)$ is the measure of the ability of X to take part in the φ -interaction. The correctness of such a hypothesis is evident from Fig. 3 and Table 1. The point for $R^i = H$ considerably deviates from the correlation in the direction of destabilization.

Discussion

The present results demonstrate the applicability to

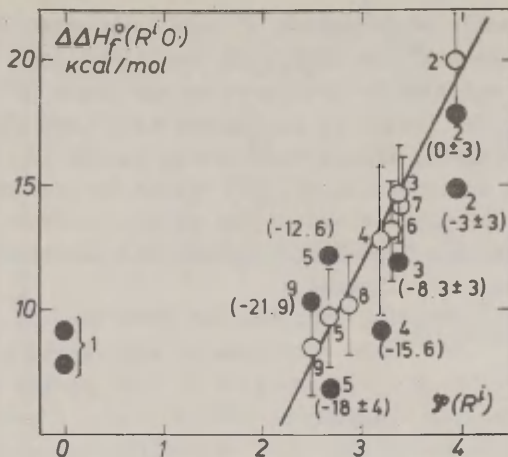


Fig. 5. The relationship between $\Delta\Delta H_f^0(R^iO\cdot)$ and $\psi(R^i)$ (R^i)=; 1. H.; 2. CH₃; 3. C₂H₅; 4. n-C₃H₇; 5. (CH₃)₂CH; 6. n-C₄H₉; 7. i-C₄H₉; 8. s-C₄H₉; 9. t-C₄H₉.

the radicals of the concepts^{1-5, 18} developed earlier for compounds with saturated valence only. The interactions of substituents in the radicals considered here are well described by the ψ -constants although the latter were found from the heats of formation of alkanes. This fact once more proves a wide range of the applicability of the formal interaction type related with ψ -constants for the alkyl substituents. The correlation (3) and its adequacy witness to the proportionality between the energetic characteristics of alkyl substituents and the corresponding radicals. The correlation also shows that the interaction between the unpaired electron and the rest of the alkyl radical R^i can be considered as formally homogeneous with the interaction between corresponding alkyl substituents R^i and the substituent CH₃. The hypothesis⁸ of the hyperconjugational stabilization of the alkyl radicals has no confirmations on the basis of the available experimental data (and their accuracy).

cy) for the heats of formation of such compounds. The deviations of the points³⁸ for $(C_2H_5)_2CH\cdot$ and $(CH_3)_3CCH\cdot$ from correlation (2) can also be discussed on the basis of correlation (6). For the latter it is assumed also that an additional destabilizing interaction occurs in the alkyl radicals, and its contribution to ΔH_f^0 values is proportional to the number of the H-atoms at the radical center. Such an interaction has the formal analogy with interaction observed⁵ for alkenes and alkynes.

The main sources of experimental data for the ΔH_f^0 of radicals are^{16,19,20} mass spectrometry and kinetics of homolytical reactions. For the analysis of the results of such experiments various simplifying assumptions are used. They lead to a vagueness in the ΔH_f^0 values for the radicals (see Table 2). The standard deviations for correlations (2), (8) and (9) are considerably smaller than the uncertainties for the ΔH_f^0 values correlated. Therefore, these correlations can be used as additional criteria for the choice between alternative experimental data. On the basis of these correlations the enthalpies of formation are calculated for the radicals $R^1R^2R^3C\cdot$, $R^1R^2N\cdot$ and $R^iO\cdot$. The calculated values are also listed in Table 2. It can be thought that these quantities are the "best" estimates for the true heats of formation of these radicals. The uncertainties of the values calculated can be regarded as equal to those used for the correlations. On the basis of correlations (2) and (8) the ΔH_c^0 values can be calculated for any radicals $R^1R^2R^3C\cdot$ and $R^1R^2N\cdot$ with branched R^i substituents^{38,39}. Equation (9) can be used for the calculations of thermochemical data for the radicals $R^iO\cdot$ and $R^iOO\cdot$ with any alkyl radical for which the ψ -constant is known or can be calculated (estimated).

³⁸ The absence of large errors in the ΔH_f^0 values for these compounds is assumed.

³⁹ The ΔH_c^0 values for the radicals with strongly branched substituents R^i can deviate from correlation (2) in the stabilizing direction as it takes place⁴ for the alkanes $R^1R^2R^3R^4C$.

Table 2

The Enthalpies of Formation of Free Radicals (298°K, gaseous state, kcal/mol)

Radical	$\Delta H_f^{\circ a}$	n ^b	Ref.	$\Delta H_f^{\circ c}$ calc	Radical	$\Delta H_f^{\circ a}$	n ^b	Ref.	$\Delta H_f^{\circ c}$ calc
1	2	3	4	5	1	2	3	4	5
CH ₃ •	<u>34.0±1</u> 31.5 32.0 30.6±2	2 1 1 1	16,17 21 22 23	33.7	(CH ₂) ₂ CH•	61±3 ^d 51.1±1.0 <u>49±3^d</u>	1 1 1	20,16 29 16	
CH ₃ CH ₂ •	<u>25.7±1</u>	2	16,17	25.2	(CH ₂) ₄ CH•	<u>22±3</u>	1	16	
C ₂ H ₅ CH ₂ •	<u>20.9±2</u> 18.9	2 1	16,23 24	21.5	(CH ₂) ₅ CH•	<u>12±3</u> 15±8	1 1	16 26	
(CH ₃) ₂ CH•	<u>17.6±1</u>	1	16	18.1	H ₂ N•	44±2 47.2 <u>40±2</u>	1 1 1	30 15 16	40.3
n-C ₃ H ₇ CH ₂ •	17.5±2 <u>16.8</u>	1 1	16 25	16.4	CH ₃ HN•	41.6±2 34.3±2 30±2 45.2 48±2	1 1 1 1 1	16 16 17 15 30	34.7
(CH ₃) ₂ CHCH ₂ •	<u>13.8±2</u>	3	16,20,23	13.2	(CH ₃) ₂ N•	<u>29.3±2</u> 28±2	1 1	16 17	29.1
C ₂ H ₅ (CH ₃)CH•	<u>12.6±2.4</u>	4	16,23,26 27	13.0					
(C ₂ H ₅) ₂ CH•	4.7±2	1	23	9.5					
(CH ₃) ₃ C•	<u>7.7±1.3</u>	4	16,20,23, 26,27	8.1					
C ₂ H ₅ (CH ₃) ₂ C•	<u>4.9±2.0</u>	2	23,26	4.5					
(CH ₃) ₃ CCH ₂ •	7.3±2	2	16,23	9.7					

	1	2	3	4	5		1	2	3	4	5
HO•		7.8	1	31		(CH ₃) ₂ CHO•	-18 \pm 4	<u>-15\pm2</u>	1	31, 34	-15.7
		9.3 \pm 1	1	16, 17			-12.6	<u>-17\pm2</u>	1	16	
		8.9	1	32				-18 \pm 2	1	17	
CH ₃ O•		0 \pm 3	4	31(3), 33 ^e	1.4	n-C ₄ H ₉ O•	<u>-20\pm2</u>	-21.9 \pm 0.0	1	16, 34	-16.4
				34		i-C ₄ H ₉ O•	-23.7 \pm 4	5 \pm 2	1	16	-17.7
		<u>2.5\pm2</u>	3	16, 17, 20		s-C ₄ H ₉ O•	6.7	<u>-1.6</u>	1	16	-19.0
		-3 \pm 3	1	33		t-C ₄ H ₉ O•	-19.2	-1.0	1	16	-24.4
C ₂ H ₅ O•		-8.3 \pm 3	4	31(3), 34	-5.7	HOO•			2	17, 31	
		<u>-6.0\pm2</u>	4	16, 17, 31 ^e		CH ₃ OO•			3	31, 34, 16	
		-5.1 \pm 2 ^f	4			C ₂ H ₅ OO•			1	20	
n-C ₃ H ₇ O•		<u>-12.0\pm3</u>	3	16, 31, 34	-11.8	t-C ₄ H ₉ OO•			1	20	
		-15.6	1	31, 34					1	20	

- ^a For the ΔH_F^0 values averaged here the greatest uncertainty interval for the individual ΔH_F^0 values is placed. For the values from literature the corresponding uncertainties are quoted. The ΔH_F^0 values here underlined are used for the calculations of the correlation parameters. These values are considered as the most reliable ones. In Figs. 1, 2, and 5 the light circles correspond to those values. ^b The number of experimental values used to calculate the average in Column 2. The value from quoted reference is brought if $n=1$. ^c The ΔH_F^0 values calculated here from correlations (2), (8), and (9). ^d The ψ -constants for (CH₂)₂CH and (CH₂)₃CH taken do to equal the mean ψ -value for the cyclohexyl and cyclopentyl substituents. ^e "Best" value $\Delta H_F^0(\text{CH}_3\text{O})=0\pm 3$ kcal/mol. ^f The averaged value proceeded from data -4 and -5 \pm 1; -7 \pm 2; -4 \pm 1.0; for which see Refs. 20 and 31.

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VERIFICATION OF EXPERIMENTAL ESTIMATES OF BOND DISSOCIATION ENERGIES

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The simple test (1a) for the verification of the experimental estimates of bond dissociation energies, D_{298}° , is constructed on the basis of the enthalpies of formation for the dissociating compounds. The test is made use of for the analysis of the experimental data for 87 bonds in various compounds. For 58 of the bonds the best estimates for true dissociation energies are selected. The real accuracy for most of such estimates is ± 1 kcal.

For a variety of well-known reasons¹⁻³, the experimental estimates of bond dissociation energies, D_{298}° , have, as a rule, great uncertainties and often contain considerable systematic errors. However, the methods for verification of these estimates are not developed for the moment[■] although the D_{298}° values are the main source for the estimation of ΔH_f° values for free radicals. On the other hand, the great scope of self-consistent experimental information for the heats of formation, $\Delta H_f^{\circ}(298^{\circ}\text{K}, g)$, of organic com-

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[■]One such method, however, exists. It is based on the comparison of different ΔH_f° estimates for the same radical A, when those estimates are derived from different D_{298}° values for various bonds $A-X_1$. The method requires the $\Delta H_f^{\circ}(X)$ values should be well known. That is possible for only a few radicals.

pounds is now accumulated. These data are considerably more accurate than the estimates of D_{298}^0 .

The simple method of verification of experimental estimates for the bond dissociation energies may be constructed bearing in mind the trivial interrelationship between the properties D_{298}^0 and $\Delta H_F^0(298^\circ\text{K}, g)$. Indeed, the dissociation energy, $D_{298}^0(X_1-Y_j)$, for the bond between any X_1 and any Y_j should satisfy the identity

$$\begin{aligned} D^0(X_1-Y_j) - D^0(X_1-H) - D^0(Y_j-H) &= -D_{298}^0(H-H) - \\ &- \Delta H_F^0(X_1Y_j) - \Delta H_F^0(X_1H) - \Delta H_F^0(Y_jH) \end{aligned} \quad (1)$$

In practice it is more convenient to make use of the coordinates of equation (1a) for the analysis of the D_{298}^0 estimates. This is the linear equation with a priori known parameters: $a = -D_{298}^0(H-H)$, and $b = -1.0$.

$$\begin{aligned} \Delta\Delta D^0(X_1-Y_j) &= D^0(X_1-Y_j) - D^0(X_1-H) - D^0(Y_j-H) = \\ &= a + b[\Delta H_F^0(X_1Y_j) - \Delta H^0(X_1H) - \Delta H^0(Y_jH)] \end{aligned} \quad (1a)$$

Let us assume now the $\Delta H_F^0(298^\circ\text{K}, g)$ values for any compounds X_1Y_j , X_1H , and Y_jH are known with high precision, i.e. the condition $s(\Delta H_F^0) \ll s(D_{298}^0)$ fulfils. In this case the deviation of any $\Delta\Delta D^0(X_1-Y_j)$ point from the straight line (1a) will indicate the presence of an error at least in one of the $D^0(X_1-Y_j)$, $D^0(X_1-H)$, and $D^0(Y_j-H)$ estimates. The complete compensation of errors during the calculation of the $\Delta\Delta D_{298}^0(X_1-Y_j)$ values seems to be improbable. Hence the $\Delta\Delta D^0(X_1-Y_j)$ points should be at random distributed around straight line (1a) if the errors in the D^0 estimates are of random nature, too.

In Table 3 the experimental data are presented for dissociation energies of 89[±] single bonds in such compounds only for which the experimental ΔH_F^0 values are known. When several experimental D_{298}^0 values are known for the same

[±]For the $\text{CH}_3\text{CO-H}$ and H-CN bonds the calculated D^0 values are here used (see Ref.³)

bond those are considered to be the independent estimates of the true D_{298}° values. These estimates may contain random and/or systematic errors. The uncertainties for most of experimental data for D_{298}° are assumed³ to be ± 2 kcal. So when the individual estimates for the same bond differ from each other by 4-5 kcal, the averaged one is quoted in Table 3 as the more true estimate of the real D_{298}° value. The experimental D_{298}° estimates for the same bond are often subdivided into some groups. In such cases the averaged value for the every group is quoted in Table 3 despite the fact that the difference between these mean ones may be less than 4-5 kcal. For the D_{298}° values averaged here, the errors of the separate measuring are quoted in Table 3. The thermochemical data of Good⁴ are used for the isomeric pentanes, and the those from a compilation⁵ for the rest of alkanes. For the most of other compounds the $\Delta H_f^{\circ}(298^{\circ}\text{K}, \text{g})$ values earlier selected⁶⁻¹¹ are here used. For the compounds which were not considered by us earlier, the thermochemical data are taken from the original works (see Table 3).

For the $\text{H}-\text{X}_i$ bonds in simple compounds the bond dissociation energies, D_{298}° , used here are quoted in Table 1. These values are calculated from the heats of formation for corresponding atoms, radicals, and compounds. The

$\Delta D_{298}^{\circ}(\text{X}_i-\text{Y}_j)$ values for 69 various bonds X_i-Y_j with $\text{X}_i, \text{Y}_j \neq \text{H}$ were calculated with the help of data from Tables 1 and 3. The relationship between those ones and the corresponding values of $\Delta H_f^{\circ}(\text{X}_i, \text{Y}_j) - \Delta H_f^{\circ}(\text{X}_i, \text{H}) - \Delta H_f^{\circ}(\text{Y}_j, \text{H})$ are shown on Fig. 1^{xxx} where the point for $D^{\circ}(\text{H}-\text{H})$ is also outli-

^{xx}The test (1a) degenerates in trivial identity for $\text{X}_i, \text{Y}_j = \text{H}$.

^{xxx}The corresponding points for the NH_2-NH_2 , $\text{HO}-\text{Cl}$, and $\text{HO}-\text{Br}$ bonds are not shown. The former one lies into the interval of ± 4 kcal, and the others lie into the interval of ± 2 kcal for the straight line (1a).

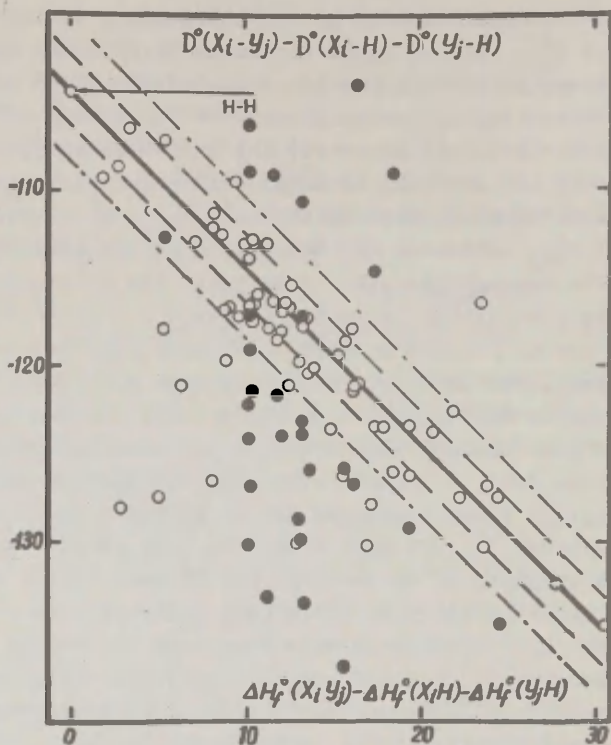


Fig.1. Graphic verification of the experimental estimates for dissociation energies, D_{298}° , of bonds X_1-Y_1 . The full line is the ideal relationship (1a) $y = -104.2 - x$; the dash lines are the uncertainty intervals of ± 2 kcal, and the dot-and-dash lines are the corresponding intervals of ± 4 kcal for theoretical relationship.

● - the duplicated (see Text) $\Delta\Delta D^{\circ}$ values.
(Gaseous state, 298°K,)

ned. The straight line (1a) must pass through this point.

Table 1

Bond Dissociation Energies, $D_{298}^{\circ}(\text{H}-\text{X}_1)$, in Some Simple Compounds HX_1 (kcal, gaseous state)

$\text{H} - \text{X}_1$	D_{298}°	$\Delta H_f^{\circ}(\text{X}_1)$	$\text{H} - \text{X}_1$	D_{298}°	$\Delta H_f^{\circ}(\text{X}_1)$
$\text{H} - \text{H}$	104.2	52.1 ^a	$\text{H} - \text{I}$	71.3	25.5 ^{a,b}
$\text{H} - \text{F}$	135.6	18.1 ^{a,b}	$\text{H} - \text{OH}$	119.2	9.3 ^{b,c}
$\text{H} - \text{Cl}$	103.2	29.1 ^{a,b}	$\text{H} - \text{SH}$	91.7	19.6 ^{b-d}
$\text{H} - \text{Br}$	87.5	26.7 ^{a,b}	$\text{H} - \text{NH}_2$	104.7	40 ^{b,e,f}

^aFrom the compilation¹². ^bThe $\Delta H_f^{\circ}(\text{HX}_1)$ values from Ref.⁶

^cThe $\Delta H_f^{\circ}(\text{X}_1)$ values from Ref.¹³. ^dIt is calculated with the respect to $\text{S}_2(\text{g})$. ^eThe $\Delta H_f^{\circ}(\text{NH}_2)$ value from Ref.³.

^fSee also Ref.¹⁴.

If we assume the uncertainties of $D^{\circ}(\text{X}_1-\text{Y}_j)$, $D^{\circ}(\text{X}_1-\text{H})$, and $D^{\circ}(\text{Y}_j-\text{H})$ estimates are $\approx \pm 2$ kcal (see Ref.³) then the uncertainties of the $\Delta\Delta D_{298}^{\circ}$ values should be¹⁵ within the limits of ± 4 kcal. As seen from Fig.1, the $\Delta\Delta D_{298}^{\circ}$ values for 58 various bonds X_1-Y_j ($\text{X}_1, \text{Y}_j \neq \text{H}$) lie indeed in this interval around the straight line (1a). Moreover, the corresponding values for 43 of those bonds lie within the range of $[-2; +2]$ interval. It corresponds¹⁵ to the uncertainties of ± 1 kcal in the D° estimates used for the calculation of such $\Delta\Delta D_{298}^{\circ}$ values.

Hence, the fitting of the $\Delta\Delta D_{298}^{\circ}$ values within the "error corridor" of ± 2 kcal for the straight line (1a) may be considered as the practical[■] test for the verification of corresponding estimates for dissociation energies of the X_1-Y_j , X_1-H , and Y_j-H bonds. The $D^{\circ}(\text{X}_1-\text{Y}_j)$, $D^{\circ}(\text{X}_1-\text{H})$, and

[■]This test is somewhat weakened because it assumes the relatively small errors in the experimental estimates of bond energies are possible. The rigid test must require the selection of those $\Delta\Delta D^{\circ}$ values only for which the corresponding points will lie on the theoretical straight line $y = -104.2 - x$ (see Eqns.(1) and (1a)).

$D^{\circ}(Y_j-H)$ estimates used here for the calculation of the such $\triangle\triangle D^{\circ}$ values should be considered as the best estimates of the true dissociation energies for the corresponding bonds. The D° values selected in this way are underlined by straight lines in Table 3. The $D^{\circ}(X_1-Y_j)$ values (for $X_1, Y_j \neq H$) underlined in Table 3 by wavy lines correspond to those $\triangle\triangle D^{\circ}$ points which lie within the $[-2;+4]$ and $[-4;-2]$ intervals around the theoretical line (1a). The $\triangle\triangle D^{\circ}$ points blacked on Fig.1 are the alternative ones to those for the same bonds which lie within the $[-2;+2]$ interval. Such points arise when for the same bond several alternative experimental D_{298}° estimates unaveraged by us are considered. Thus, the test (1a) allows the choice of the best estimate to be made between alternative ones for the dissociation energy of the same bond.

The results of the correlation in the coordinates of Eqn.(1a) of the $\triangle\triangle D^{\circ}$ values for the ± 2 and ± 4 kcal intervals are summarized in Table 2.

Table 2

The Coefficients of Eqn.(1a) for the Selected Values of $\triangle\triangle D^{\circ}(X_1-Y_j)$

"error corridor" kcal	a kcal	b	n	r	s_o^a
± 2	-104.59 ± 0.35	-0.99 ± 0.02	43	0.9938	1.28
± 4	-105.28 ± 0.40	-0.97 ± 0.02	54 ^b	0.9877	1.65

^aThe standard error of the regression. ^bWithout the consideration of $\triangle\triangle D^{\circ}(\text{CF}_3-\text{CH}_3)$ and $\triangle\triangle D^{\circ}(\text{CH}_3\text{O}-\text{CH}_3)$. The deviations of these points from the regression derived are greater than those allowed by specified risk level of 5%.

For the $[-2;+2]$ interval, the regression coefficients do not differ significantly from the corresponding theoretical values (see Table 2). Hence, there is the random distribution of $\triangle\triangle D^{\circ}$ points within the interval.

Such distribution arises because the errors of corresponding estimates for the $D^0(X_1-Y_j)$, $D^0(X_1-H)$, and $D^0(Y_j-H)$ are random too. For the $[-4;+4]$ interval, the regression

coefficient a differs significantly from the theoretical one. The distribution of $\Delta\Delta D^0$ points in this interval is asymmetrical one (see Table 2) because the $[-4;-2]$ interval is more crowded (see Fig.1) than that of $[+2;+4]$. From the analysis of the totality of $\Delta\Delta D^0$ points within the $[-2;+2]$ interval it is obvious that the $D^0(X_1-H)$ and $D^0(Y_j-H)$ estimates are more accurate, as a rule, than those for bonds X_1-Y_j with $X_1, Y_j \neq H$. Thus, the preferential deviation of $\Delta\Delta D^0(X_1-Y_j)$ points downwards from the theoretical line $y = -104.2 - x$, but not upwards from it, can arise when the $D^0(X_1-Y_j)$ estimates here used are smaller than the true dissociation energy for the bond X_1-Y_j . The possible reasons for such understated $\Delta\Delta D^0$ values may be the overstated estimates of the activation energies for the reverse reactions in the case of metathetical reactions or the neglect (see, as example, Ref.³) of temperature corrections in the case of activation energies for pyrolytic reactions.

The verificational test here proposed is not the universal one. As example, it is not applicable to the estimates of dissociation energies for the bonds C-N and C-S in nitrocompounds, sulphones, and sulfoxides. However, this test is not also only possible one. A large number of identities which are similar to Eqn.(1) may be constructed for various substituents Z (as example, $Z = CH_3, OH$, etc.)

$$D^0(X_1-Y_j) - D^0(X_1-Z) - D^0(Y_j-Z) \approx - D^0(Z-Z) - \\ - [\Delta H^0(X_1Y_j) - \Delta H^0(X_1Z) - \Delta H^0(Y_jZ)] \quad (3)$$

The applicability of those identities for the verification of various experimental estimates for bond dissociation ener-

³It is obvious that the deviations of most of $\Delta\Delta D^0(X_1-Y_j)$ points (see Table 1, the blacked points) for the alternative $D^0(X_1-Y_j)$ values have the same direction.

Table 3

Experimental Estimates of Dissociation Energies, D_{298}° , for Bonds X_1-Y_j
(gaseous state, kcal)

N ^o	X ₁	Y _j	D ^o (X ₁ -Y _j) ^a	n ^b	Ref.	N ^o	X ₁	Y _j	D ^o (X ₁ -Y _j) ^a	n ^b	Ref.
1	2	3	4	5	6	1	2	3	4	5	6
1	H	H	104.2 ^o	7		13	CN	H	129 ± 3 ^{d,e}		
2	CH ₃	H	103.0 ± 1.0	7	16-23	14	C ₆ H ₅	H	104.5 ± 2.4 ^e	4	48-51
3	C ₂ H ₅	H	97.6 ± 0.8	2	16, 18				110.1 ± 1.3	4	52-55
4	n-C ₃ H ₇	H	98.6 ± 0.6	2	16, 25	15	CNCH ₂	H	86 ± 2 ^e	1	56
5	i-C ₃ H ₇	H	94.5 ± 0.0	2	19, 26				≥ 79	1	57
6	t-C ₄ H ₉	H	90.6 ± 0.9	3	16, 19, 27	16	CH ₃ O	H	100.5 ± 2.1 ⁿ	2	3, 58
7	CH ₂ =CH	H	103.8 ± 1.8 ^e	2	28, 29	17	CHO	H	89 ± 4 ^e	2	59, 60
8	(CH ₃) ₂ CH	H	94.5 ^g						80.2 ± 2.0	3	61-63
	(CH ₃) ₃ CH								74.7	1	64
9	CH ₃ CO	H	88 ± 2 ^{d,e}			18	CCl ₃	H	92.2 ± 3.2 ^f	4	44, 65-67
10	CH ₂ =CHCH ₂	H	86.2 ± 1.8 ^e	2	30, 31	19	O ₆ H ₁₁	H	94.5	2	68, 69
11	C ₆ H ₅ CH ₂	H	84.7 ± 0.6 ^e	3	32-35	20	CH ₂ Cl	H	97 ⁱ	1	66
			77.5	1	36				88 ± 5	1	44
			90.0	1	37	21	CHCl ₂	H	92 ^f	1	66
12	CF ₃	H	106.2 ± 0.3 ^f	5	20, 39-42				75 ± 2	1	44
			103.5 ± 0.4	4	43-46	22	CBr ₃	H	96.0 ± 1.6 ^j	1	70
			109	1	47	23	CH ₃	CH ₃	87.5 ± 2.2	8	72-79

1	2	3	4	5	6	1	2	3	4	5	6
23	CH ₃	CH ₃	80.2 \pm 1.2	2	80, 81	38	I	CH ₃	54.9 \pm 1.5 ¹	5	21, 110-113
			69	1	82	39	Br	CH ₃	67 \pm 0.0 ¹	3	114-116
24	C ₂ H ₅	CH ₃	83.5 \pm 2.1	2	72, 83	40	CH ₃ O	CH ₃	81.0 ^h	1	60
			67.2	1	84	41	OH	CH ₃	90 ¹	1	117
25	n-C ₃ H ₇	CH ₃	86.3	1	85	42	SH	CH ₃	67 \pm 2 ¹	1	118
26	1-C ₃ H ₇	CH ₃	81.6 \pm 1.5	4	86-89	43	NH ₂	CH ₃	91 ¹	1	119
27	t-C ₄ H ₉	CH ₃	80.6 \pm 2.4	3	86, 90, 91	44	C ₆ H ₅ CH ₂	C ₂ H ₅	68.5 \pm 0.5 ^e	1	32
28	(CH ₃) ₂ CH (CH ₃)CH	CH ₃	81.1	1	92				57.5	1	120
29	CH ₂ =CH	CH ₃	85.8 ^e	1	93	45	C ₂ H ₅	C ₂ H ₅	86.3	1	85
			94.0	1	94				78	1	121
30	CH ₃ CO	CH ₃	69.9 \pm 1.6 ^k	5	95-99	46	C ₂ H ₅	I	52.0 \pm 1.4 ¹	6	112, 115, 122- -125
31	CH ₂ =CHCH ₂	CH ₃	60.6 \pm 2.2	2	100, 101				45.0	1	125
			69.5 \pm 2.0 ^e	1	102	47	C ₂ H ₅	Cl	83 \pm 7 ¹	1	126
32	C ₆ H ₅ CH ₂	CH ₃	63.2 ^e	1	103	48	C ₂ H ₅	Br	65 ¹	1	126
			69.9 \pm 0.7	3	32, 104, 105	49	C ₂ H ₅	OH	90	1	117
33	CF ₃	CH ₃	99.7 \pm 2.0 ^f	1	106	50	C ₆ H ₅ CH ₂	n-C ₃ H ₇	66.1 \pm 1.6 ^e	2	32, 127
34	CN	CH ₃	104.6 \pm 0.6 ^e	2	107, 108	51	CH ₃ CO	CH ₃ CO	66.6 \pm 0.8 ¹	2	128, 129
35	C ₆ H ₅	CH ₃	91 ^e	1	72	52	CN	CN	145 \pm 6 ^m	1	131
36	CNCH ₂	CH ₃	72.7 \pm 1.4 ^e	1	56				125 \pm 8	1	132
37	Cl	CH ₃	80 ¹	1	109	53	CHO	CHO	71.5 \pm 0.3 ^m	1	134

1	2	3	4	5	6	1	2	3	4	5	6
54	$i-C_3H_7$	$i-C_3H_7$	<u>76.0</u>	1	92	74	CF_3	Cl	<u>80.3</u> \pm <u>1.0</u>	2	137, 155
55	$t-C_4H_9$	$i-C_3H_7$	<u>73.0</u>	1	86	75	$C_6H_5CH_2$	Cl	<u>70.0</u> ^f	2	156
56	$t-C_4H_9$	$t-C_4H_9$	<u>68.5</u>	1	86	76	$C_6H_5CH_2$	Br	<u>51</u> \pm <u>1</u> ^s		3, 139, 157, 158
57	$CH_2=CHCH_2$	$i-C_3H_7$	<u>~ 54.5</u> ^e	1	135	77	$C_6H_5CH_2$	I	<u>39.5</u> \pm <u>0.7</u> ^f	2	115, 161, 162
58	$i-C_3H_7$	I	<u>46.1</u> ⁱ	1	112				<u>43.7</u>	1	112
59	$CH_2=CHCH_2$	$t-C_4H_9$	<u>65.5</u> ^e	1	136	78	$C_6H_5CH_2$	NH_2	<u>59.4</u> \pm <u>0.6</u> ^t	2	163, 164
60	$t-C_4H_9$	I	<u>45.1</u> ⁱ	1	112	79	$C_6H_5CH_2$	SH	<u>53</u> \pm <u>2</u> ^f	1	118
61	CCl_3	Cl	<u>68</u> \pm <u>3</u> ^f	1	43, 137	80	C_6H_{11}	I	<u>49.2</u> ^u	1	168
62	CCl_3	Br	<u>49.5</u> ⁿ	1	43, 116	81	$n-C_4H_9$	I	<u>49.0</u> ⁱ	1	112
63	$CH_2CH=CH_2$	Br	<u>47.5</u> \pm <u>2.0</u> ^o	1	139	82	$n-C_3H_7$	I	<u>52.0</u> \pm <u>2.8</u> ⁱ	2	112, 169, 170
64	$CH_2=CHCH_2$	I	<u>39.0</u> ^p	1	112	83	CH_3CO	I	<u>50.7</u> ^w	1	171
			<u>35 - 37</u>	1	115	84	CH_2Cl	Br	<u>61.0</u> ^v	1	116
65	$CH_2=CHCH_2$	Cl	<u>59.3</u> ^f	1	140	85	$CHCl_2$	Br	<u>53.5</u> ^v	1	116
66	$CH_2=CHCH_2$	$CH_2=CH$ CH_2	<u>56.0</u> ^q	1	143	86	CBr_3	Br	<u>49.0</u>	1	116
			<u>45.6</u>	1	144				<u>56.2</u> \pm <u>1.8</u> ^x	1	70
67	C_6H_5	Br	<u>70.9</u> ^m	1	146	87	$CHCl_2$	I	<u>42.4</u> ^v	1	168
68	C_6H_5	I	<u>55.5</u> \pm <u>2.1</u> ^m	2	112, 115	88	OH	Cl	<u>60</u> \pm <u>3</u> ^y	1	173
69	C_6H_5	CF_3	<u>103.6</u> \pm <u>2.5</u> ^r	1	147	89	OH	I	<u>56</u> \pm <u>3</u> ^z	1	173
70	C_6H_5	C_6H_5	<u>81</u> \pm <u>8</u> ^m	1	149	90	OH	Br	<u>56</u> \pm <u>3</u> ^z	1	173
71	CF_3	CF_3	<u>94.4</u> \pm <u>4.0</u> ^f	1	150, 151	91	NH_2	NH_2	<u>54.0</u> ^d	1	175
72	CF_3	F	<u>129.3</u> \pm <u>2.0</u> ^f	1	106				<u>60</u> \pm <u>4</u>	1 ⁸	
73	CF_3	Br	<u>70.0</u> \pm <u>0.7</u> ^r	5	152-154						
74	CF_3	Cl	<u>86.1</u> \pm <u>0.8</u> ^r	1	154						

^aFor the D_{298}° values averaged here, the errors of the separate measuring are placed. For the literary values the corresponding uncertainty intervals are quoted. ^bThe number of experimental D° values used here to calculate the average one which is brought in Column 4. The value from quoted reference is brought if $n=1$. ^cSee Table 2. ^dCalculated, see Ref.³. ^eThe $\Delta H_f^{\circ}(298^{\circ}\text{K}, g)$ value from Ref.⁷. ^fThe $\Delta H_f^{\circ}(g)$ value from the compilation in Ref.¹¹. ^gIt is accepted in Ref.³. ^hThe ΔH_f° value from the compilation in Ref.⁸. ⁱThe $\Delta H_f^{\circ}(g)$ value from the compilation in Ref.⁶. ^jFor $\Delta H_f^{\circ}(\text{CHBr}_3)$ two estimates are known: 4 kcal (See Ref.¹³) and 10 kcal (See Ref.⁷¹). The former assumes to be more reliable. ^kThe ΔH_f° value from the compilation in Ref.¹⁰. ^l $\Delta H_f^{\circ}(g) = -78.4 \pm 0.3$ kcal is the mean of the values from Ref. 5, 136. ^mThe ΔH_f° value from our compilation in Ref.¹³³. ⁿ $\Delta H_f^{\circ} = -10.0 \pm 1.5$ kcal is the mean of the values -8.9 (See Ref.⁶⁵) and -11.0 (See Ref.¹³⁸) kcal. ^o $\Delta H_f^{\circ}(g) = 11.8$ kcal from Ref.¹⁴¹. ^p $\Delta H_f^{\circ}(g) = 22.9$ kcal from Ref.¹⁴². ^q $\Delta H_f^{\circ}(g) = 20.0$ kcal from Ref.¹⁴⁵. ^r $\Delta H_f^{\circ}(g) = -167.0$ kcal, the estimate selected¹⁴⁸ by Kolesov. ^s $\Delta H_f^{\circ}(g) = 19.4 \pm 0.8$ kcal is the mean of the values from Ref.^{155, 160}. ^tThe $\Delta H_f^{\circ}(g) = 14$ kcal is the value calculated from $\Delta H_f^{\circ}(l) = 2.0$ (See Ref.¹⁶⁵) and ΔH_v° . The latter is estimated by Klages' method¹⁶⁵; the value of t_b from Ref.¹⁶⁷. ^uThe deviation of experimental estimate of ΔH_f° from the correlation $\Delta \Delta H_f^{\circ}(R_1 I) = f(\varphi_R)$ (See Ref.⁶) is more than the corresponding confidence interval. The $\Delta H_f^{\circ}(\text{C}_6\text{H}_{11}\text{I}, g)$ value here used is calculated on the basis of the former correlation. The constants φ_I and ΔH_I are taken from Ref.⁶. ^v $\Delta H_f^{\circ}(g) = 12$ kcal (See Ref. 71). ^w $\Delta H_f^{\circ}(g) = -31.2$ kcal (See Ref.¹⁷²). ^x $\Delta H_f^{\circ}(g) = 19.5$ is the mean from the values^{71, 138}. ^y $\Delta H_f^{\circ}(g) = -21.2$ kcal is the mean from 3 values (See Ref.¹⁷⁴). ^zThe $\Delta H_f^{\circ}(g)$ values are taken from Ref.¹⁷⁴. ^δ $\Delta H_f^{\circ}(g) = 22.8$ kcal (See Ref.⁹). ^θThe Szwarc's results on pyrolysis (See Ref.¹)

gies will be only limited by the accessibility of the thermochemical data for compounds X_iY_j , X_iZ , and Y_jZ . The practical test based on Eqn.(3) will be applicable to the estimates of $D^0(C-N)$ and $D^0(C-S)$ for nitrocompounds, sulphones, and sulfoxides when $Z = CH_3$, as example.

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THE BASICITY OF SOME PHENOLS AND NAPHTHOLS

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The basicity constants of 8 aromatic hydroxy compounds in aqueous solutions of sulphuric acid have been found by the spectrophotometric method. It has been established that the dependence of the pK_a of polyphenols on the Hammett σ -constants is nonlinear. Depending on the mutual arrangement of hydroxyl groups in the molecule of a base the conjugate acid is in one of the possible forms (oxonium compound, σ - and π -complexes). In the case of asymmetric polyphenols it has the structure of a π -complex.

In studying the azo coupling of 1,2-diazonaphthols with phenols and naphthols in sulphuric acid solutions we supposed that the course of this reaction depends substantially on the behaviour of the azo component. At the same time, no data were available in the literature on the basicity of asymmetric polyphenols and naphthols, except for phenol [1] and phloroglucinol [2].

In this connection, we have studied the basicity of 1,2-, 1,3-, 1,4-, and 1,2,3-polyhydroxybenzene derivatives, 1- and 2-naphthols, and 2,7-dihydroxynaphthalene.

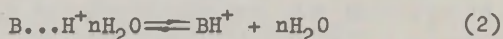
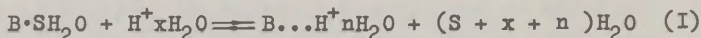
The basicity of compounds (I-VIII) was determined spectrophotometrically [3] in aqueous solutions of sulphuric acid at $25 \pm 0.5^\circ\text{C}$. The values of the acidity function (H_0) for these solutions were determined on the basis of data reported in the literature [4].

As a result of preliminary experiments, it has been established that in sulphuric acid solutions with concentration of up to 80 per cent the spectra of phenols do not

change with time, i.e., no sulphonation or any other processes are observed under the selected conditions.

To check the procedure chosen we measured the basicity of phenol, its pK_a being found to be equal to -6.69; according to literature data [1] the pK_a of phenol is -6.74.

According to investigations reported in the literature [5,6] the protonation of weak bases proceeds by the following scheme:



These authors have found that the spectrophotometric method may be used to determine the constant of the equilibrium corresponding to the Brönsted scheme:



The outcome of this is that the slope of the dependence of $\log \frac{[BH^+]}{[B]}$ on H_0 is equal to 0.79 (Fig.1) and not to unity as it might have been if the objects under study were true Hammett bases.

Table I presents the values of pK_a for the hydroxy compounds studied, which were calculated from the formula:

$$pK_a = H_0 + \log \frac{[BH^+]}{[B]} \quad (4)$$

By analogy with the correlative dependence of the values of pK_a on σ (the Hammett or substituent constants) established earlier for amines [9], we made an attempt to estimate the dependence of pK_a values of polyphenols on σ -values. Fig.2 shows the arrangement of points for polyhydroxybenzene derivatives.

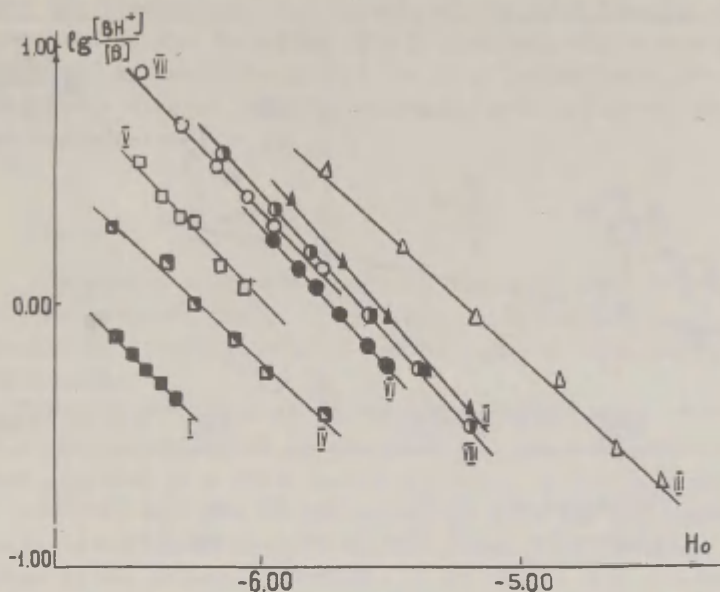


fig 1. The dependence of $\lg \frac{[BH^+]}{[B]}$ on H_0 .

TABLE I The Basicity Constants of Some Aromatic Hydroxy Derivatives

Phenol		pK_a	Amine		pK_a
I	Phenol	-6.69 ± 0.05	Aniline		4.58 [7]
II	Pyrocatechol	-5.73 ± 0.02	o-Aminophenol		4.73 [8]
III	Resorcinol	-5.19 ± 0.04	m-Aminophenol		4.30 [8]
IV	Hydroquinone	-6.21 ± 0.05	p-Aminophenol		5.65 [8]
V	Pyrogallol	-5.93 ± 0.03			
VI	1-Naphthol	-5.72 ± 0.02			
VII	2-Naphthol	-5.60 ± 0.03			
VIII	2,7-Dihydroxynaphthalene	-5.59 ± 0.03			
IX	Phloroglucinol	-3.86 [8]			

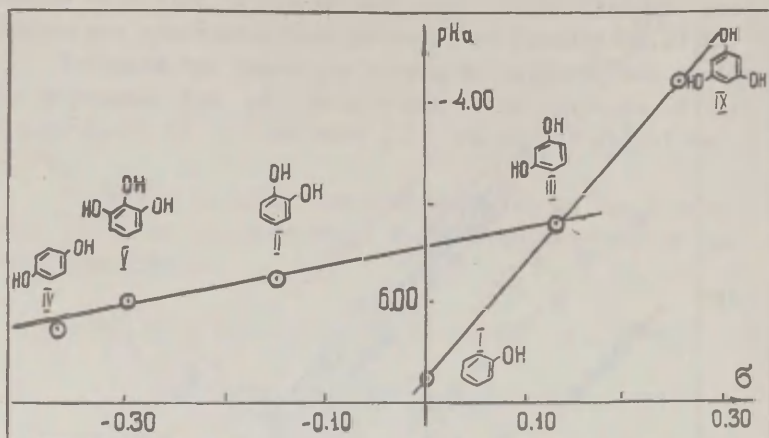


Fig.2 The dependence of the values of pK_a of some polyphenols on σ (the Hammett or substituent constant)

It turned out that if the protonation of asymmetric polyhydroxyphenols proceeded with the formation of an oxonium compound, as has been found for phenol [I], then the point corresponding to the parameters of the latter would have been on a single straight line with those of (II)-(V). Besides, the changes in the basicity of phenol caused by the introduction of hydroxyl groups into it would probably correspond to the changes that occur in aniline when hydroxyl groups are incorporated into it (see Table I).

On the other hand, it has been established earlier that the protonation of phloroglucinol and its ethers involves the formation of a σ -complex, which accounts for such a sharp increase of the basicity upon introduction of two hydroxyl groups into the phenol molecule at the meta-position [2,10]. The deviation of the point of phloroglucinol from the straight line (II-V) is a proof that this mechanism of protonation is also inapplicable to asymmetric polyphenols. On the strength of this, we think

that the protonation of compounds of the II-V type is accompanied by the formation of a π -complex, which is also supported by small changes in the band intensity of the electronic spectra taken in sulphuric acid solutions in the region close to pK_a .

Experimental

Sulphuric acid solutions were prepared from chemically-pure grade sulphuric acid; their concentration was checked by potentiometric titration using a JNM-60M potentiometer.

A weighed sample of the substance under study (1-2 mg) was dissolved in the corresponding sulphuric acid solution in a 25-ml measuring flask. After an hour a cell (1 cm) was filled with this solution and thermostated for 30 minutes at $25 \pm 0.5^\circ$. Then a spectrum was taken on the interval between 230 and 280 nm with a spectrophotometer (C Φ -4a), and after an hour the measurement was repeated.

The values of pK_a were calculated after Haldna [3] .

The values of Hammett σ -constants were taken from the literature [11] .

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REACTIVITY OF COMPOUNDS WITH DIARYLMETHYLOL GROUP

XV. IONIZATION CONSTANTS FOR N-(β -OXYETHYL)- AND
N-(β -ARYLOXYETHYL) AMIDES OF DIARYL GLYCOLIC ACIDS

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Ionization of N-(β -oxyethyl)- and N-(β -aryloxyethyl) amides of diaryl glycolic acids has been studied by spectrophotometrical method. It was shown that in the range of 60 to 70% of the H_2SO_4 concentration stabilization of the carbonium carbon atom by unshared electron-pair of the oxygen atom in the ether group exerts influence on the ionization of the N-(β -phenoxyethyl) amides. In case of weakening nucleophilicity of the latter the stabilizing effect vanishes.

It is known that in some reactions substituents may influence the stabilization of transition state or intermediates by means of full or partial of reaction centre. Numerous examples of such a influence are described in the works of Winstein et alia [1] and other authors [2].

In the process of studying of acid-base interaction

In the process of studying the acid-base interactions of compounds containing diarylmethylol groups [3,4] we made an attempt to find out how these interactions are influenced by an oxygen-containing group introduced in β -position of the nitrogen-containing radical in N-alkylamide of diaryl glycolic acid.

For this purpose three series of compounds of a common formula $(R' - \text{C}_6\text{H}_4)_2 - \underset{\text{OH}}{\text{C}} - \text{CONH}(\text{CH}_2)_2\text{OR}$ were studied.

These series differ from each other by substituents at the oxygen atom[§]:

$R=H$; $R^1=H$ (I), $p-CH_3$ (II), $m-CH_3$ (III), $p-CH(CH_3)_2$ (IV), $p-CH_3O$ (V), $p-C_2H_5O$ (VI), $p-F$ (VII), $p-Cl$ (VIII), $p-Br$ (IX) (the first reaction series).

$R=C_6H_5$; $R^1=H$ (X), $p-CH_3$ (XI), $p-CH_3O$ (XII), $p-C_2H_5O$ (XIII), $p-F$ (XIV), $p-Cl$ (XV), $p-Br$ (XVI) (the second reaction series).

$R=p-ClC_6H_4$; $R^1=H$ (XVII), $p-CH_3$ (XVIII), $m-CH_3$ (XIX), $p-CH(CH_3)_2$ (XX), $p-CH_3O$ (XXI), $p-C_2H_5O$ (XXII), $p-F$ (XXIII), $p-Cl$ (XXIV), $p-Br$ (XXV) (the third reaction series).

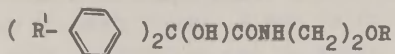
Halochromy is characteristic of compounds with diaryl-methylol group [5]. Halochromy of compounds of the second reaction series (X-XVI) has the particular character. Thus at high concentration of H_2SO_4 halochromic colour appears immediately after mixing the solutions X-XVI with H_2SO_4 . Being not stable the colour of solutions of compounds X, XI, XIV-XVI disappears very soon.

If we dissolve these compounds in 60-70% H_2SO_4 the colourless solution gradually acquires a steady colour and its intensity reaches its maximum in two or three days. Spectral characteristics of solutions of compounds X-XVI in H_2SO_4 of different concentrations are listed in Table 1. It is noteworthy that λ_{max} of compounds X, XI, XIV-XVI, depending on the H_2SO_4 concentration, are either close to each other (60-70% H_2SO_4) or distinguish essentially by their value and approach to the λ_{max} value for corresponding compounds I, II, VII-IX, XVII, XVIII, XXIII-XXV. It may be connected with different character of stabilization of carbonium ions in solutions of H_2SO_4 of different concentrations.

By spectrophotometrical method in systems H_2SO_4 +4% of H_2O (A) and (96% H_2SO_4 +4% H_2O) - CH_3COOH (B) for compounds

[§]Syntheses and constants of these compounds are to be found in the journal "Chemistry and Chemical Technology (in print).

T a b l e I
Electronic spectra of N-(β -oxyethyl)- and
N-(β -aryloxyethyl) amides of diaryl glycolic acids



N comp.	R	R'	System (B)		System (A) 60-70% H ₂ SO ₄	
			λ_{max}	$\lg \epsilon$	λ_{max}	$\lg \epsilon$
II	H	p-CH ₃	520	4.53		
IV	H	p-CH(CH ₃) ₂	520	4.54		
V	H	p-CH ₃ O	544	4.72		
VI	H	p-C ₂ H ₅ O	550	4.81		
VII	H	p-F	498	4.40		
VIII	H	p-Cl	540	4.60		
IX	H	p-Br	580	4.40		
X	C ₆ H ₅	H	514	4.00	490	3.54
XI	C ₆ H ₅	p-CH ₃	514	4.22	490	3.88
XII	C ₆ H ₅	p-CH ₃ O	540	4.41	540	4.65
XIII	C ₆ H ₅	p-C ₂ H ₅ O	540	4.46	540	4.80
XIV	C ₆ H ₅	p-F	496	4.26	490	4.03
XV	C ₆ H ₅	p-Cl	550	5.18	490	4.40
XVI	C ₆ H ₅	p-Br	580	4.98	490	4.32
XVIII	p-ClC ₆ H ₄	p-CH ₃	506	4.58		
XX	p-ClC ₆ H ₄	p-CH(CH ₃) ₂	516	4.46		
XXI	p-ClC ₆ H ₄	p-CH ₃ O	540	4.83		
XXII	p-ClC ₆ H ₄	p-C ₂ H ₅ O	540	4.92		
XXIII	p-ClC ₆ H ₄	p-F	488	4.56		
XXIV	p-ClC ₆ H ₄	p-Cl	556	4.67		
XXV	p-ClC ₆ H ₄	p-Br	580	4.81		

X-XVI indicator relations (Q) are determined and dependence of $\lg Q$ from the acidity function H_R for the medium [6] has been studied. The parameters of correlation $\lg Q$ a- bH_R are calculated by means of the least-squares method (Table 2).

In the system (A) at the H_R range from -9 up to -11.26 the average of the slope of the regression line, the parameter " \bar{g} " for compounds X, XI, XIV is close to unit (1.030). All these compounds have equal λ_{\max} value (490 nm) and they remain stable over the whole range of H_R . For compounds X and XVI in 70-75% of H_2SO_4 (H_R from -11.52 up to -12.82) λ_{\max} are not constant and change from 496 to 506 nm and that is why the determination of the above-mentioned dependence loses its meaning. However, in 84-92% of H_2SO_4 λ_{\max} become constant and parameter " \bar{g} " is close to unit (1.049).

In the system (B) at concentrations of H_2SO_4 from 42 to 70% the quantity " \bar{g} " for the compounds X, XI, XIV, XVI is considerably different from unity (0.443), though for XII and XIII, which have strong electrodonor substituents ($p-CH_3O-$ and $p-C_2H_5O$), " \bar{g} " equal 0.997 and 1.025, respectively. The behavior of XV and XVI at high concentrations of H_2SO_4 is analogous to that described for system (A).

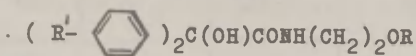
Such behavior of compounds X, XI, XIV-XVI in solutions of H_2SO_4 indicates that under the certain acidity of environment for some compounds the acid-base equilibrium is complicated by some additional effect. The same phenomenon was observed earlier in studying the ionization of di-(p -anisyl)- and di-(p -tolyl)alkyl carbinols [7].

As in compounds X-XVI there are some groups unequal by their basicity, it may be suggested that, depending on the acidity of the environment different protonated forms take part in equilibria.

The most important of them are listed in Table.

For example if the acidity is rather low (up to 50% H_2SO_4) compounds XII and XIII form an equilibrium system consisting of forms "a" and "b" which is characterized by the constant K [4].

T a b l e 2
Parameters of correlation $\lg Q = a - \ell H_R$
for N-(β -oxyethyl)- and N-(β -aryloxyethyl) amides
of diaryl glycolic acids ($t=20\pm 1^\circ\text{C}$)



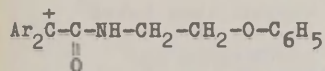
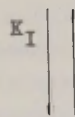
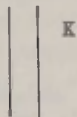
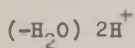
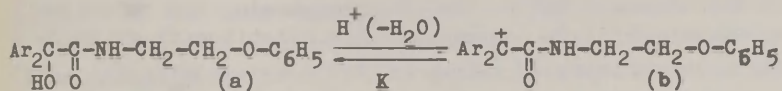
N comp.	R	R'	The interval of acidity	Sys-tem	-a
I	2	3	4	5	6
II	H	p-CH ₃	-10.75-12.81	B	12.239
IV	H	p-CH(CH ₃) ₂	-10.75-12.81	B	11.785
V	H	p-CH ₃ O	-5.10-6.54	B	6.037
VI	H	p-C ₂ H ₅ O	-5.10-6.54	B	5.811
VII	H	p-F	-12.81-14.52	B	12.299
VIII	H	p-Cl	-15.43-17.24	B	16.945
IX	H	p-Br	-15.15-17.24	B	15.632
X	C ₆ H ₅	H	-9.70-11.26	A	10.396
XI	C ₆ H ₅	p-CH ₃	-9.18-11.26	A	9.873
XII	C ₆ H ₅	p-CH ₃ O	-5.87-7.06	B	6.190
XIII	C ₆ H ₅	p-C ₂ H ₅ O	-5.59-6.70	B	6.673
XIV	C ₆ H ₅	p-F	-9.70-11.26	A	10.829
XV	C ₆ H ₅	p-Cl	-15.71-17.24	B	17.396
XVI	C ₆ H ₅	p-Br	-15.71-17.24	B	17.323
XVIII	p-ClC ₆ H ₄	p-CH ₃	-11.40-13.23	B	10.270
XX	p-ClC ₆ H ₄	p-CH(CH ₃) ₂	-10.75-12.81	B	11.957
XXI	p-ClC ₆ H ₄	p-CH ₃ O	-5.87-6.70	B	6.120
XXII	p-ClC ₆ H ₄	p-C ₂ H ₅ O	-5.59-6.54	B	5.373
XXIII	p-ClC ₆ H ₄	p-F	-11.73-13.64	B	13.576
XXIV	p-ClC ₆ H ₄	p-Cl	-15.15-16.20	B	14.050
XXV	p-ClC ₆ H ₄	p-Br	-15.15-16.20	B	18.244

T a b l e 2 (continuation)

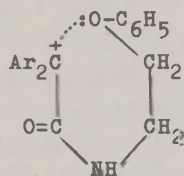
N comp.	$-\beta$	$-pK_R^0$	χ	α	n
	7	8	9	10	11
II	1.022	11.985	0.999	0.030	7
IV	0.989	11.916	0.998	0.043	7
V	1.025	5.890	0.988	0.078	6
VI	1.040	5.587	0.999	0.022	6
VII	0.872	14.120	0.997	0.038	6
VIII	1.038	16.326	0.988	0.100	6
IX	0.961	16.266	0.993	0.078	7
X	1.021	10.182	0.997	0.065	5
XI	0.987	10.003	0.991	0.098	5
XII	0.995	6.220	0.997	0.083	7
XIII	1.025	6.510	0.986	0.066	6
XIV	1.083	10.330	0.998	0.040	5
XV	1.028	16.922	0.993	0.069	5
XVI	1.069	16.204	0.999	0.027	5
XVIII	0.847	12.130	0.994	0.058	6
XX	0.984	12.151	0.998	0.042	6
XXI	1.017	6.020	0.986	0.050	5
XXII	0.972	5.530	0.992	0.042	5
XXIII	1.098	12.360	0.997	0.057	6
XXIV	0.904	15.520	0.997	0.026	5
XXV	1.133	16.100	0.995	0.042	5

Scheme

Acid-base equilibria for N-(β -phenoxyethyl)
amides of diaryl glycolic acids



(d)



(c)

Under such conditions other forms must practically be absent because the acidity of the medium [8] is too small for the formation of form "d" and the formation of form "c" is impossible due to insufficient electrophilicity of carbonium ions. All this is confirmed by the fact that λ_{\max} of solutions of these compounds in H_2SO_4 have the same value as the basic amides of diaryl glycolic acids [4]. Besides the point for compound XII on the diagram showing the relationship between the Taft σ -constants for substituents at amide nitrogen in substituted amides of di-(p-anisyl)glycolic acid and pK_{R^+} [9], lies near the regression line which means that the oxygen atom of ether is not protonized.

When the acidity is higher (up to 70% H_2SO_4) in water solution the equilibrium is established slowly - during two or three days and probably includes the forms "a", "b", and "c". Due to low concentration of ions "b" in the medium of such acidity the accumulation of ions "c", which can be followed spectrophotometrically, requires much time. Ion "c" is more stable in comparison with ion "b" because the specially favourable electron pair of oxygen atom takes part in this stabilization.

The evaluation of the concentration of ions "d" based on Arnett data on simple ether 8 allows to draw a conclusion that in 70% H_2SO_4 the share of ions "d" is not more than 0.01 M and so their influence on equilibrium is very little. However, in the medium of 75% H_2SO_4 and somewhat higher, the concentration of ions "d" is more considerable and its presence in the system influences the equilibrium of compounds XV and XVI.

All this explains the shift of λ_{\max} .

When the acidity is high (84-92% H_2SO_4) the protonization of the ether oxygen is so full that the formation of ions "b" and consequently ions "c" becomes impossible (compounds XV and XVI). Obviously, in the system the equilibrium $\text{"a"}\text{H}^+ + \text{H}^+ \rightleftharpoons \text{"d"} + \text{H}_2\text{O}$ is established which can be quantitatively characterized also by the constant K.

It may be suggested that the ions of compounds X, XI, XIV-XVI in 60-70% H_2SO_4 have both electrophilic and nucleo-

philic centres active enough, and that is why the latters can interact with each other through space. All this decreases the substituents contribution to the stabilization of ion charge as it is confirmed by the data of UV-spectra (Table I) and by increasing ionization constants by some powers of ten in comparison with corresponding compounds of the first and the third reaction series.

In the first and the third reaction series ionization in H_2SO_4 goes without any peculiarities observed at the compounds I, XI, XIV-XVI (see Table 2). Here the average slopes ($\bar{\rho}$) are close to unit (0.992 and 0.995 respectively). The pK_R values correlate well with the electrophilic Brown-Okamoto constants (Table 3).

T a b l e 3
The parameters of correlation pK_a vs. σ^+

Reaction series	ρ	ρ^+	pK_R^0	s	n
I.	0.996	-5.96	-14.96	0.441	6
2. XII, XIII, XV, XVI	0.997	-5.71	-15.03	0.395	4
3.	0.981	-5.45	-14.39	0.750	7

The parameters of correlation between pK_R^+ and σ^+ , determined in system (B) for the compounds XII, XIII, XV, and XVI of the second reaction series and also for the first and the third series show that under the reversible acid-base interactions the main part in stabilization of carbonium ion is played by the substituents in diarylmethylol group,

In the case of compounds of the first reaction series the basicity of the primary alcohol is such that under conditions of the experiment it must be practically fully protonated [10] and as a result of that, the oxygen atom has no nucleophilic properties. In the third reaction series the nucleophilicity of this atom lowers the I-effect of the chlorine atom in the para-position.

E x p e r i m e n t a l

For spectrophotometrical measurements the compounds by means of the repeated crystallization were brought to purity corresponding to the interval on the melting temperature

less than 1°, and were kept in exicator under pressure of 20 mm Hg. The UV spectrophotometer SF-4 has been used at 20-1°. Determinations of maximum and equilbrial values of optical densities for the solutions with unstable halochromic colour were carried out as reported earlier [4].

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INTERRELATION OF STRUCTURAL EFFECTS IN THE REACTIONS
OF ARYLSULPHONIC ACID ANHYDRIDES WITH ARYL AMINES

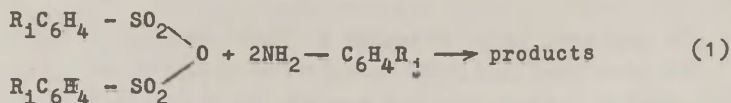
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The kinetics of the interaction of various substituted arylsulphonic acid anhydrides with aromatic amines in nitrobenzene at 25° was studied. The data obtained on the dependence of the transition state structure upon substituents in the reagent molecules were discussed from the point of view of the "reacting bonds" rules in terms of a simple single-stage substitution mechanism. The change in the position of the transition state at the reaction coordinate has been shown to be mainly due to the interrelation structures of nucleophile and the acyl portion of the substrate.

With a view to obtain information about the change in the nature of the transition state depending on the structure of reagents in the reaction of nucleophilic substitution at tetracoordinate sulphur the kinetics of reactions of various substituted arylsulphonic acid anhydrides with aromatic amines in nitrobenzene at 25° was studied.



The feature of the reaction series in question consists in a simultaneous change in three structure fragments usually varied in the nucleophilic substitution reactions; nucleophile structure, that of leaving group and that of the acyl portion of the substrate. The reaction rate under consideration was found to obey a second-order kinetics ¹. The rate constants (subscript in k_{ij} refers to the series of reactions with varying substituent in both the anhydride and aryl amine) are summarized in Table 1.

The correlation of the rate constants with the parameters, characterizing the substituents in reagents was carried out in accordance with the equations

$$\lg k_{ij} = \lg k_{cj} + \rho_j^\circ \sigma_1^\circ, \quad (2)$$

$$\lg k_{ij} = \lg k_{ie} + \rho_1^\circ \sigma_j^\circ, \quad (3)$$

where ρ_j° and ρ_1° are sensitivity constants of the individual reaction series to the substituents R_i and R_j characterized by inductive constants σ_1° and σ_j° in the case of j -th arylamine and i -th anhydride, respectively.

The correlation parameters of the data in Table I according to the equations (2) and (3) are listed in Table 2. It follows from these data that the sensitivity of reaction (1) to the structure effects of the attacking nucleophile (ρ_1°) increases when the electron-withdrawing substituents are introduced in the molecule of arylsulphoacid anhydride, i.e. as its reactivity increases. On the other hand, the sensitivity of reaction (1) to the variation of the arylsulphoacid anhydride structure ρ_j° (simul-

Table 1

Values of $k_{1j} \cdot 10^3$ (l/mol·sec)*) for the Reaction of Substituted Arylsulphonic Acid Anhydrides with Aromatic Amines in Nitrobenzene at 25°

$R_1 \backslash R_j$	H	N	3-Cl	N	3,5- (COOCH ₃) ₂	N	3-NO ₂	N	3-NO ₂ - 5-COOCH ₃	N
4-CH ₃	91.6 \pm 2.3	6	12.3 \pm 0.3	6	4.77 \pm 0.16	6	1.62 \pm 0.05	7	0.36 \pm 0.05	6
H	311 \pm 5	7	25.6 \pm 0.8	5	10.2 \pm 0.9	6	3.69 \pm 0.10	8	0.68 \pm 0.05	5
4-Cl	1360 \pm 10	7	140 \pm 4	6	44.1 \pm 0.5	5	12.7 \pm 0.6	5	2.90 \pm 0.10	6
3-NO ₂	-		-		796 \pm 12	4	185 \pm 2	5	33.4 \pm 2.3	5

*) Values of k_{1j} are listed with standard deviations. N is the number of points.

Table 2.

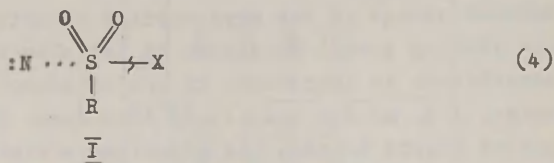
Correlation Parameters of the Rates of the Arylamine Acylation by the Arylsulphonic Acid Anhydrides with the Substituent Constants (σ_1^o , σ_j^o)
According to Eqns. (2) and (3); r - Correlation Coefficient

Parameters of Eq. (2)				Parameters of Eq. (3)			
R_j	$\lg k_{cj}$	ρ_j^o	r	R_1	$\lg k_{10}$	ρ_1^o	r
H	-0.53 ± 0.004	2.74 ± 0.05	0.994	4-CH ₃	-1.034 ± 0.004	-2.45 ± 0.05	0.9995
3-Cl	-1.59 ± 0.03	2.54 ± 0.03	0.998	H	-0.530 ± 0.004	-2.75 ± 0.04	0.9998
3,5-(COOCH ₃) ₂	-1.97 ± 0.02	2.60 ± 0.13	0.997	4-Cl	0.135 ± 0.050	-2.83 ± 0.05	0.999
3-NO ₂	-2.43 ± 0.01	2.40 ± 0.04	0.998	3-NO ₂	1.49 ± 0.04	-3.11 ± 0.18	0.998
3-NO ₂ -5-COOCH ₃	-3.10 ± 0.02	2.27 ± 0.13	0.997				

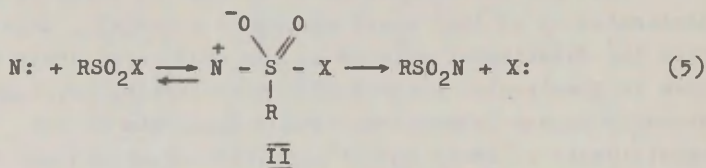
taneous change in the acyl portion structure and that in the leaving group) decreases as the electron withdrawing substituent is introduced in the molecule of the acylated amine, i.e. as its reactivity decreases. Hence, some interaction occurs between the structure effects of the substituents, respectively in acyl portion and those of the leaving group of the arylsulphoacid anhydride R_1 , on the one hand, and the substituent effects R_j in arylamine, on the other hand.

Let us consider the data obtained in terms of the applicability of the "reacting bonds" rules [2,3], which predict the substituent effects on the transition state structure in bimolecular nucleophilic substitution reactions. Recently in our laboratory, the interaction of the substituents in reactions of acylation of arylamines by acyl halides of substituted benzoic acid derivatives has been studied [4, 5]. This is an illustration of applicability of the above-mentioned rules to nucleophilic substitution at the unsaturated (carbonyl) carbon. The works of Rogne [6, 7] on the influence of the reagent structure on the nucleophilic substitution reactions at the unsaturated sulphonyl sulphur (interaction of substituted in ring derivatives of benzenesulphonyl chloride with arylamines [6] and pyridines [7] of various structure) were published almost at the same time. In the foregoing works [5, 6] the influence of substituents in nucleophile and substrate molecules on the transition state structure is discussed.

A priori two kinetically hardly distinguishable mechanisms are possible for the bimolecular nucleophilic substitution reactions at sulphonyl sulphur. One of them consists in direct single-step displacement of the leaving group of the substrate by the nucleophile ($:N$) through the transition state of the type I^- [8].



The second possible mechanism includes the formation of the pentacoordinate intermediate II [9] at the first stage followed by breakdown of II to products



The presence of the intermediates of type II is not detected by any physico-chemical methods. Nevertheless the possibility of its existence, in principle, is assumed in the studies of many workers [9] including the investigations of our laboratory [10]. For the reaction type in question such a situation is also possible when the free energy of the intermediate II is close to that of the transition state I.

In such a case significant differences in the structure of the transition state and that of the intermediate are not bound to occur [11]. Taking into account this and the difficulties of the interpretation of the obtained results within the framework of Scheme (5) we shall consider the behaviour of the correlation parameters ρ_i° and ρ_j° in terms of simple single-stage substitution mechanism involving the transition state I; though, in principle, the obtained results of the multiple correlation may be accounted for in terms of the step-wise mechanism.

First, let us decide upon the change in the ρ_i° -val-

ues under the influence of the substituents R_1 . In accordance with the foregoing rules [3] the introduction of an electron-withdrawing substituent into the leaving group of arylsulphonic anhydride ($X = SO_2C_6H_4R_1$) should facilitate the decrease in the $N \cdots S$ -bond order in the transition state \bar{I} . As a result of this the sensibility of the reaction to the nucleophile structure should decrease. The observed change in ρ_1° (see Table 2) reflects the overall effect. Inasmuch as the absolute value of ρ_1° increases as the electron-withdrawing properties of the substituents R_1 in anhydride molecule grow, one may conclude that the extent of $N \cdots S$ -bond making in the transition state \bar{I} is changed to a greater extent when effected by a substituent in acyl portion than in the leaving group.

Now let us consider the behaviour of the ρ_j° -values. The parameter ρ_j° is complex and reflects the overall sensibility of the reaction rate to the simultaneous variation of the leaving group structure $(\rho_j^\circ)_X$ and that of the acyl portion $(\rho_j^\circ)_R$, i.e.

$$\rho_j^\circ = (\rho_j^\circ)_X + (\rho_j^\circ)_R^{**}) \quad (6)$$

^{**}) An additional term, $\propto (\rho_j^\circ)_X (\rho_j^\circ)_R$, which reflects the change in reaction sensitivity caused by the interaction of R and X, should be added to Eq.(6). However in the been shown [12] that the sensitivity of the reaction between p-anisidine and arylsulphonic acid chlorides ($\rho_{X=Cl}=0.74$) coincides with that of the reaction of p-anisidine with arylsulphonic acid bromides ($\rho_{X=Br}=0.76$). Hence, the interaction of R and X appears to be negligible and, consequently, the term $\propto (\rho_j^\circ)_X (\rho_j^\circ)_R$ in Eq.(6) is close to zero.

As it is seen from Table 2, ρ_j° decreases with the growing electron-withdrawing properties of the substituent R in the attacking arylamine.

After Harris and Kurz [3] the introduction of an electron-withdrawing substituent into the attacking nucleophile decreases the bond order with the leaving group. Hence, the value of $(\rho_j^\circ)_X$ must increase.

The change of the term $(\rho_j^\circ)_R$ depending on the substituent in the nucleophile will be determined by in what extent the $N \cdots S$ bond making competes with the breaking of the $S \rightarrow X$ bond. If the bond making prevails over the bond breaking the value of $(\rho_j^\circ)_R$ should decrease as the reactivity of arylamine decreases (Cf. [4,6]). This experimentally observed decrease in the ρ_j° value with introducing an electron-withdrawing substituent in the arylamine molecule indicates that this change is mainly due to (ρ_j°) . Hence, the change in the amine structure effects to a larger extent on the reaction rate sensitivity to the variation of substituents in acyl portion than in the leaving group, with the tendency of increasing the $S \rightarrow X$ bond breaking in comparison with the $N \cdots S$ bond making occurring as the arylamine reactivity reduces.

Thus, it follows from all these considerations that the change in the transition state structure (the shift along the reaction coordinate) is determined mainly by the interrelation between the nucleophile structure and that of the acyl portion of the substrate.

EXPERIMENTAL

All the arylsulphonic acid anhydrides under study were prepared and purified for kinetic investigations as described previously [1].

Aniline [13], nitrobenzene [1], 3-chloraniline [14],

3-nitro-aniline [14], 3,5-dicarbomethoxy-aniline [15], and 3-nitro-5-carbomethoxy-aniline [15] were purified according to the known procedures.

The rate of the reaction under investigation was determined by potentiometric titration of the unreacted arylamine by the sodium nitrite in the medium of hydrochloric acid[4]

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ON THE MECHANISM OF THE PROCESS OF SULPHAMIDE FORMATION.
THE KINETIC ISOTOPE EFFECT.

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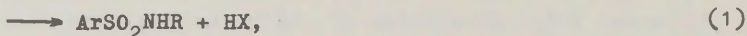
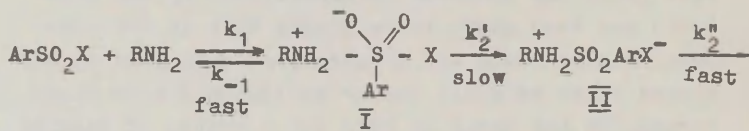
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The kinetics of the interaction between p-toluenesulphobromide and p-anisidine and its N,N-di-deuteroanalog in benzene, nitrobenzene and their 50 per cent mixture (by volume) at 25°C has been investigated. The primary kinetic isotope hydrogen effect (when the N-H-bond is substituted by the N-D-bond) has been shown to be absent both in the non-catalytic reaction and in reaction, catalysed by the second amine molecule and by arylsulphanilide being formed. On the basis of this and a number of results previously obtained on the influence of structural effects and polar properties of medium on the rate of sulphamide formation, the general base catalysis mechanism without proton transfer in the rate limiting stage is discussed.

In a series of our previous papers [1-11] we have already discussed the mechanism of both the bimolecular non-catalytic reaction and the accompanying trimolecular (catalysed by the second molecule of the nucleophile) reaction of arylsulphoacid derivatives with aliphatic [1-4] and aromatic [5-11] amines. The question of the role of proton transfer from the N-H-bond of the amine being acylated in

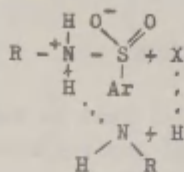
the mechanism under discussion is, in particular, of importance. On the ground of the lack of the primary kinetic isotope hydrogen effect (on substituting the N-H-bond by the N-D-bond [10]), a conclusion was drawn, that the hydrogen departure from the N-H-bond in the bimolecular interaction process takes place in the rapid non-rate-limiting stage. Hence, the N-H-bond is not a "reacting bond" *) and its breaking does not influence significantly the structure of the transition state. This fact together with a number of other previously discussed data [1-11] suggested as the most likely mechanism one involving the formation of pentacoordinate intermediate (I) from the reagents in the first rapid equilibrium stage followed by the removal of the leaving group which limitates the overall rate which results in forming of protonated sulphamide (II), that quickly loses a proton in the fast completing stage:



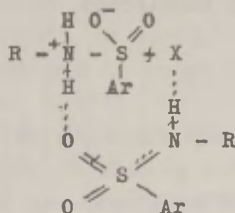
where X = Cl, Br, OSO₂Ar; R = Ar, Alk.

The catalysis by the second amine molecule was considered [3, 4, 8, 11] as a result of a bifunctional assistance in the breakdown of the intermediate I through the cyclic transition state of type III

*) Reacting bond is a bond that is either broken or is formed immediately at the reaction centre [12].



III



IV

The latter mechanism is consistent with the following findings: low sensitivity of catalytic reaction rate to the electronic structure of R in the catalysing amine molecule [5] and to the influence of the polar properties of medium [11]; high sensitivity to the steric environment at the N-atom in the catalysing amine molecule (in reaction with secondary amines, unlike primary ones, the catalysis by the second amine molecule does not occur) [3, 6]; decelerating the catalytic reaction rate with temperature increase [1, 3, 4]. An analogous cyclic mechanism (see IV) was also suggested for the arylsulphanilide-catalysed process [8].

For a further check of the catalysis scheme in question it seems interesting to study the kinetic isotope effect of hydrogen in reactions catalysed by the second amine molecule and by arylsulphamide. With this end in view, we have studied the kinetics of the interaction between p-toluene sulphobromide and p-anisidine and its N,N-dideutero-derivative in solvents that appreciably differ one from another in polarity: in benzene, nitrobenzene, and their 50 per cent mixture (by volume) at 25°C. The acylation rate of undeuterated amine in the given solvents has already been studied earlier [6, 7, 14]. However, to compare with reactivity of the undeuterated and deuterated derivatives more correctly the experiments were repeated under strictly

identical conditions.

RESULTS AND DISCUSSION

It was shown earlier [5-7, 10, 14] that in the general case the overall interaction rate of arylsulphobromides with aromatic amines can be represented as

$$w = (k_2 + k_3 [\text{Ar}'\text{NH}_2] + k_a [\text{ArNHSO}_2\text{Ar}']) [\text{ArSO}_2\text{Br}] [\text{Ar}'\text{NH}_2], \quad (2)$$

where k_2 (1/mol.sec) is the bimolecular non-catalytic reaction rate constant, k_3 and k_a (l²/mol².sec) are the rate constants of trimolecular processes catalysed by the second amine molecule and arylsulphanilide respectively. The relationship between the two pathways varies greatly with the polarity of solvent so that in benzene [6] the dominant role is played only by trimolecular processes (k_3 and k_a), in 50 per cent mixture of benzene and nitrobenzene [5, 7] - by processes characterised by k_2 and k_3 , and in nitrobenzene - only by the bimolecular reaction (k_2). The corresponding rate constants calculated as described elsewhere [5-7, 14] are listed in Table 1. The values of isotope effects characterised by the k_H/k_D ratio are also given there.

With allowance for the confidence intervals it can be said that all three reaction pathways are characterised by approximately equal values of the isotope hydrogen effects which are less than unity in all the cases. This is suggestive of the fact that the numerical value of the k_H/k_D -ratio is associated either solely with the exhibition of the secondary isotope hydrogen effect (cf. [10]) or with the exhibition of primary effect in conjunction with the secondary one, the contribution of the former being very

Table I

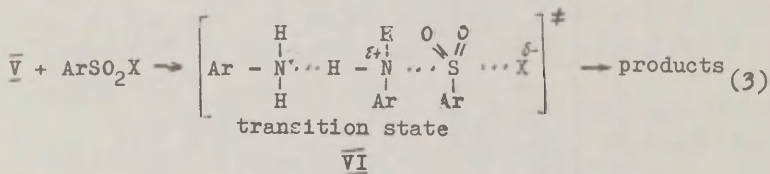
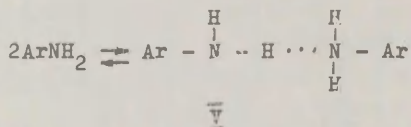
Rate constants^{*} of non-catalytic (k_2 , l/mol.sec), amine-catalysed (k_3 , l²/mol².sec) and arylsulphanilide-catalysed (k_a , l²/mol².sec) reaction of p-toluene sulphobromide with p-anisidine in various solvents at 25°C

Media	Amine	p-Anisidine		N,N-Dideutero-p-anisidine		k_H/k_D
	Constants	$k \cdot 10^3$	N	$k \cdot 10^3$	N	
Benzene	k_3	1.93 ± 0.33	8	3.34 ± 1.08	8	0.55 ± 0.28
	k_a	22.1 ± 0.90	8	37.6 ± 4.1	8	0.60 ± 0.09
50 per cent mixture of benzene-nitrobenzene	k_2	7.2 ± 0.2	7	8.4 ± 0.1	7	0.86 ± 0.03
	k_3	53.6 ± 4.6	7	58.3 ± 2.9	7	0.92 ± 0.12
Nitrobenzene	k_2	54.2 ± 0.4	17	65.0 ± 0.4	19	0.83 ± 0.01

* Rate constants values are listed with the standard deviations;

N - number of points.

small. It follows from the statement above that the N-H-bond in arylamine is not affected much in the rate-limiting stage both under non-catalytic (of. [10]) and catalytic conditions. From the point of view of the "solvation rules" [12, 13] (according to which the primary isotope effect does not occur if a) hydrogen is transferred between atoms of the same nature b) hydrogen does not form "reacting bonds" in the transition state) the latter statement does not agree with the previously discussed bifunctional mechanism of the action of the catalysts in question (see III and IV). In our opinion, the absence of the primary catalytic isotope hydrogen effect in the reaction catalysed by the second amine molecule may agree with such a scheme of general base catalysis which does not involve the proton transfer in the rate-limiting stage. This can be made more illustrative if the scheme for the concerted (3) rather than step-wise (1) mechanism of substitution at sulfonyl sulphur is resorted to



The catalysing amine molecule which forms the H-bond with the amine molecule serving as a reagent (complex V) increases the nucleophilicity of the attacking nitrogen atom. This leads to the fact that the N-S-bond is formed at a

longer distance, than in the non-catalytic reaction. The transition state becomes reagent-like to a greater extent and hence, to reach it a lower activation energy is necessary as compared to the non-catalytic reaction. In such a situation the difference in the zero-point vibrational energy of the N-H-bond varies very little in changing over from the initial state (V) to the activated state VI. Furthermore, since the hydrogen taking part in the formation of the N-H-bond is located between the atoms of equal electronegativity (N-atoms) then according to the "solution rules" [12] the primary kinetic isotope hydrogen effect must be absent here. In the case of the amine catalysed reactions the fact that the transition state is reagent-like to a considerable extent may also explain those effects (e.g. low sensitivity to the catalyst structure [5] and to polar properties of medium [11], etc.), which were interpreted earlier [3, 4, 8, 11] as conforming the bifunctional mechanism of catalysis [3, 4, 8, 11]. The bifunctional mechanism of catalysis by the second amine molecule also seems to be doubtful because of the geometry of the intermediate X (or the transition state similar to it in the case of a concerted substitution mechanism). Recently, a trigonal-bipyramidal structure of the transition state in the nucleophilic substitution at the sulphonyl sulphur [15] with the attacking (in our case RNH_2) and leaving (X) groups in axial positions has been preferred in literature. The distance between two axially located ligands (an angle of 180°) is appreciably longer than that between two equatorially (an angle of 90°) located ligands (see, for example, Ref. 16). Because of this, the N-H-bond length in the catalyst (amine) is hardly long enough to ensure formation of H-bonds with the entering and leaving groups which results in acyclic structure of type III.

of arylsulphanilide may be higher than that of arylamine.

It is difficult to explain why the general base contribution in accordance with VI and VII alters the structure of the transition state so much (as far as reagent-like) comparing with the catalytic reaction for which the transition state seems to be highly reagent-like on the basis of high sensibility of the latter reaction to the influence of the nucleophile structure [5], that of the leaving group [20, 21], and polar properties of medium [9].

It is natural that a question arises whether one can interpret the absence of the primary isotope hydrogen effect in the reaction in question reasoning from the step-wise mechanism of substitution at sulphonyl sulphur rather than the concerted one. It seems possible if one assumes that the rate determining stage is altered under the influence of the general base catalysis, and the breakdown of the intermediate I (stage, characterized by the rate constant k_2 in Scheme (1)) in the non-catalytic reaction and the formation of intermediate (stage, characterized by the rate constant k_1 in Scheme (1)) in the reaction catalysed by the second amine molecule serve as the rate-determining stage. In such a situation along the reaction coordinate we shall actually deal with the single transition state that is more or less reagent-like rather than product-like.

Thus, the available data do not make it possible to conclude convincingly whether process catalysed by the second amine molecule and arylsulphanilide involve a pentacoordinate intermediate of type I on the reaction path or they proceed by the mechanism of concerted substitution (as, for example, the transition state of VI reflects it).

EXPERIMENTAL

The reagents [6, 10] and the solvent [10] were prepared for kinetic investigations as described earlier. Analysis for deuterium in the N-D₂-group of N,N-dideutero-p-anilidine was performed from IR spectra (see Ref.22). a rule, deuterium amounted to no less than 96-97 per cent. The precautions which were taken when working with deuterated derivatives are described in detail elsewhere [10]. The procedure of kinetic measurements consisted in the potentiometric titration of the bromide ion formed after the reaction had been inhibited by diluted nitric acid [6].

(Translated from Russian by V. T. Kolyadny)

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CATALYSIS BY TERTIARY AMINES IN REACTION
OF SULPHAMIDE FORMATION.
KINETIC ISOTOPE EFFECT.

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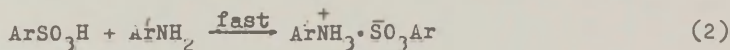
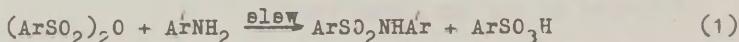
A high catalytic activity of pyridine and N,N-dimethyl-p-toluidine in the reaction of p-chlorobenzenesulphonic acid anhydride with m-nitroaniline in nitrobenzene at 25°C has been found. The intensity of catalytic action in reactions with anhydrides, bromides, and chlorides of arylsulphonic acids has been compared. The catalytic properties of tertiary and primary amines are correlated with the nature of the leaving group and the substrate. The kinetic hydrogen isotope effect has been shown to be absent on substituting the N-D-bond for the N-H-bond in the arylamine being acylated. From the experimental results the nucleophilic mechanism of catalysis has been assumed.

In order to continue investigations 1,2 of catalytic reactions of nucleophilic substitution at the tetracoordinate atom of sulphur, the kinetics of reactions of anhydride of p-chlorobenzenesulphonic acid with m-nitroaniline and N,N-dideutero-m-nitroaniline in the presence of various admixtures of pyridine and N,N-dimethyl-p-to-

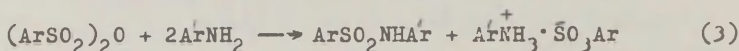
luidine in solution of nitrobenzene at 25°C has been studied.

RESULTS AND DISCUSSION

The interaction of anhydrides of arylsulphonic acids with aromatic amines in nitrobenzene under non-catalytic conditions [3, 4] is in compliance with the scheme:



Or totally



Here the reaction rate is not complicated by a catalytic action of the initial reagents or the acylation products, as in another case [1, 2], and is described by a simple equation of the second order [3, 4]. If a tertiary amine is added to the medium the stoichiometry of the process can satisfy equations (1) or (2) which depends on the relationship of the concentrations and basicities of the amine being acylated and the catalyst being added, and on the solubility of their salts as well (cf. [1]).

Catalysis by pyridine. The catalytic action of this tertiary amine was investigated in rather great detail earlier in reactions of amide formation with chlorides and bromides of arylsulphonic acids [1, 2] on the one hand and with acyl halides [5] and anhydrides [6] of carboxylic acids on the other hand. It is interesting to note that in the case of carbonyl compounds, an appreciable difference was observed in the behaviour of pyridine as a catalyst depending on whether the chloride

and bromide of carboxylic acid or the anhydride of this acid were used as an acylating reagent. The acylation of amine was often not only accelerated by the anhydrides as in the case of reactions of acyl halides [5] but it was even decelerated under the influence of the tertiary amine added [6]. It was especially interesting in this connection to compare the catalytic behaviour of pyridine in the reaction of sulphamide formation with acyl halides and anhydrides of arylsulpho-acids, respectively.

It follows from Fig. 1 (here and hereafter a , b and m are the initial concentrations of anhydride, arylamine and catalyst in mol/l) that the introduction of pyridine into the reaction mixture results in a very sharp increase in the rate of sulphamide formation. Attention should be paid to the fact that in the beginning the pyridine-catalyzed reaction proceeds extremely rapidly. For instance, on adding 0.005 mol/l of the catalyst the quantitative yield of amide was detected after a minute. Notice that the $m = a$ concentration relation takes place in the experiment given above. Under the conditions when $m < a$ (see curves 2, 3 and 4 in Fig. 1) some extent of transformation of the reagents is also achieved very quickly, and that extent is slightly larger than m in number but still it is not in line with the quantitative yield of sulphamide. Hereafter, the process of acylation proceeds at a measurable rate which is appreciably higher (curves 2, 3, and 4 in Fig. 1) than the non-catalytic reaction rate (curve 1 in Fig. 1). Thus, there can be no doubt about the significant catalysis by pyridine in the reactions in question. But it is necessary to find out by what such an unusual character of the kinetic curves in Fig. 1 can be explained. Taking into account the fact that the basicity of pyridine ($pK_a = 5.2$, water, 25° [7]) is considerably greater than that of *m*-nitroaniline ($pK_a = 2.5$, water, 25° [7]) the assumption is forced upon one that as arylsulphonic acid is formed it quantitatively binds the catalyst converting it

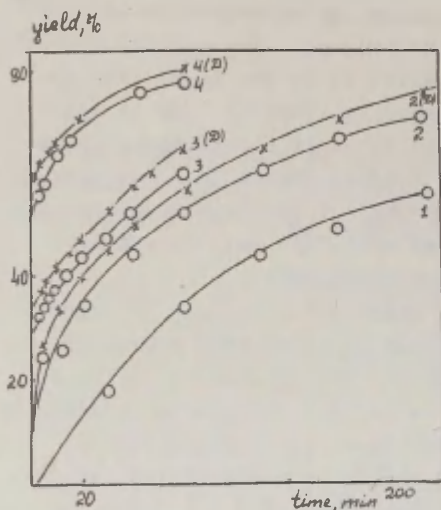


Fig. 1. Kinetics of the interaction of anhydride of p-chlorobenzenesulpho-acid with m-nitroaniline and its N,N-deutero derivative (symbol D) in the presence of pyridine in nitrobenzene at 25° (2a = b = 0.01)
1. m = 0; 2. m = 0.001;
3. m = 0.0015; 4. m = 0.003.

into the non-active state which results in a decrease in the reaction rate. At this the stoichiometry of acylation must satisfy equation (1). Then the expression for the over-all acylation rate should be written in the form:

$$\frac{dx}{dt} = [k_0 + k_N(m - x)](a - x)(b - x), \quad (4)$$

where k_0 (1/mol.sec) and k_N (l²/mol².sec) are the rate constants of the non-catalytic^{*} and tert. amine-catalyzed reactions, respectively; x (mol/l) is the concentration of the acid formed. It follows from (4) that the effective second order constant, $k_{eff.}$ (1/mol.sec) equals

$$k_{eff.} = k_0 + k_N(m - x). \quad (5)$$

^{*}) For the reaction of p-chlorobenzenesulphoacid anhydride with m-nitroaniline in nitrobenzene $k_0 = (1.27 \pm 0.06) \cdot 10^{-2}$ (1/mol.sec) and with its N,N-dideuteroanalogue $(1.48 \pm 0.08) \cdot 10^{-2}$ 1/mol.sec [3].

In accordance with Eq.(5) the k_{eff} -value calculated from the second-order equation (considering the stoichiometry of Eq.(1) should be linearly dependent on x as long as x becomes equal to m (the whole of the catalyst will be bound). From this moment on k_{eff} should approximate to k_0 (5).

However, as it was mentioned above, in every kinetic experiment even the first experimentally recorded point corresponds with the yield of the reaction product which is larger than m , and the constant k_{eff} corresponding to this value of x exceeds the value of k_0 appreciably. Later on in the course of time k_{eff} falls less markedly with x (Fig. 2) without reaching the value of k_0 even at high degrees of conversion of the reagents. Such a character of the change in k_{eff} appears to be associated with the fact that the expected stoichiometry of reaction (1) does not remain unchanged throughout the development of the catalytic process. Indeed, since in such experiments there was shortage of pyridine as compared to the amount of nucleophile ($m < b$) the effective bonding of the catalyst in the initial period must be accompanied by a sharp change in the relationship of the concentrations which as reaction proceeds creates a situation when $m \ll b$. Under such conditions bonding of the acid formed may take place partially at the expense of *m*-nitroaniline which supplies the solution with a quantity of catalyst. The latter seems to be the reason for the greater rate of acylation in comparison with the non-catalytic reaction even when $x > m$. It is not excluded that the complex character of the change in k_{eff} with time is also partially due to the inhibiting action of the *p*-chlorobenzenesulpho-acid anion accumulated in the reaction if the mechanism of catalysis has nucleophilic nature (cf. [2, 8]).

Since k_{eff} falls very sharply with changing in x (see Fig. 2), extrapolation of it to the zero time ($x \rightarrow 0$ when $t \rightarrow 0$) results in a great uncertainty of the inter-

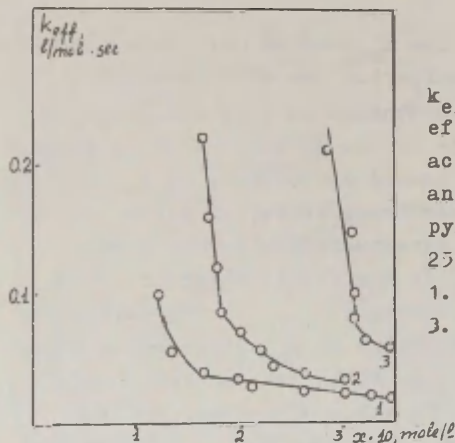


Fig. 2. Dependence of k_{eff} on x for the reaction of *p*-chlorobenzenesulohonic acid anhydride with *m*-nitroaniline in the presence of pyridine in nitrobenzene at 25° ($2a = b = 0.01$).
 1. $m = 0.001$; 2. $m = 0.0015$; 3. $m = 0.003$.

cept and, hence, in a very low accuracy of k_N calculated from k_{eff} . Therefore the catalytic activity of pyridine in the reaction under discussion is evaluated only very approximately. If the rectilinear nature of the initial portions of the curves in Fig. 2 also remains in the range of small x -values (not recorded in the experiment), the k_N -value can be evaluated graphically from the equation

$$\frac{k_{\text{eff}}(m_1) - k_{\text{eff}}(m_2)}{m_1 - m_2} = k_N \quad (6)$$

where $k_{\text{eff}}(m_1)$ and $k_{\text{eff}}(m_2)$ are the values of the observed rate constants in the experiments with pyridine concentrations m_1 and m_2 at concentrations of x equal for both the experiments, respectively. The quantity k_N can be presented as a numerical value of the slope of the initial portion of a straight line in coordinates k_{eff}, x . The two ways lead to a tentative value of k_N which is not less than $1 \cdot 10^3 \text{ l}^2/\text{mol}^2 \cdot \text{sec}$. It would seem that the difficulties mentioned can be avoided if one employs a catalyst at a higher concentration than that of the acylating agent ($m > a$). However, under such conditions the rate turned

Table I

Kinetics of the interaction of m-nitroaniline and N,N-di-deutero-m-nitroaniline with p-chlorobenzenesulphonic acid anhydride in the presence of N,N-dimethyl-p-toluidine in nitrobenzene at 25° ($2a = b = 0.01$; $k_{\text{eff.}}$ - in l/mol.sec).

Time in minutes	m = 0.0010		m = 0.0015		m = 0.0025		m = 0.0035	
	$x \cdot 10^4$	$k \cdot 10^2$	$x \cdot 10^4$	$k \cdot 10^2$	$x \cdot 10^4$	$k \cdot 10^2$	$x \cdot 10^4$	$k \cdot 10^2$
m-Nitroaniline								
1	-	-	-	-	7	26.90	-	-
2	6	10.95	-	-	10	23.90	16	35.20
3	7	8.70	10	13.10	14	19.7	20	31.9
4	8	7.60	11	10.99	-	-	-	-
5	9	6.96	12	9.80	17	15.3	25	23.7
10	11	4.40	15	6.50	21	10.3	30	18.6
15	12	3.2	-	-	-	-	34	16.1
20	-	-	18	4.10	24	6.3	-	-
30	-	-	-	-	26	4.9	-	-
		$k' = 0.18 \pm 0.02$	$k' = 0.23 \pm 0.02$		$k' = 0.35 \pm 0.05$		$k' = 0.52 \pm 0.09$	

$$k_N^H = (156 \pm 10) \text{ l/mol}^2 \cdot \text{sec}^2$$

N,N-Dideutero-m-nitroaniline								
1	-	-	-	-	-	-	14	41.7
2	-	-	-	-	-	-	17	38.2
3	9	11.6	11	14.6	-	-	20	31.9
4	10	9.8	13	13.5	-	-	-	-
5	11	8.8	14	11.8	20	19.2	24	25.3
10	13	5.4	17	7.6	24	12.7	30	18.7
15	15	4.3	-	-	-	-	33	15.1
20	26	3.5	20	4.8	27	7.7	-	-
30	-	-	-	-	29	5.8	36	9.2
		k'=0.21±0.01		k'=0.28±0.02		k'=0.49±0.02		k'=0.62±0.05

$$k_N^D = (178 \pm 3) \text{ l/mol}^2 \cdot \text{sec}^2$$

out to be so high that it could not be measured using the procedure employed.

Catalysis by N,N-dimethyl-p-toluidine. Owing to an appreciably smaller catalytic activity of this amine as compared to pyridine we have managed to investigate the kinetics of catalytic reaction of sulphamide formation in the initial period too (Table 1). That permitted the data to be analyzed in accordance with kinetic equation (5). Figure 3 shows that

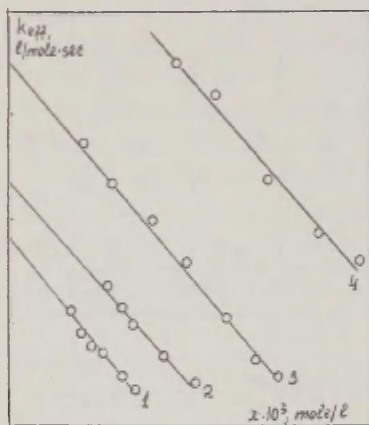


Fig. 3. Dependence of k_{eff} upon x for the reaction of anhydride of p-chlorobenzenesulphonic acid with m-nitroaniline in the presence of N,N-dimethyl-p-toluidine in nitrobenzene at 25° ($2a = b = 0.01$).

1. $m = 0.001$; 2. $m = 0.0015$;
3. $m = 0.0025$; 4. $m = 0.0035$.

there is a linear relation between k_{eff} and x . This is in accordance with the fact that in the initial parts of the kinetic curves which (these parts), in reality, were treated the stoichiometry of the reaction is close to that reflected by equation (1). The slopes in Fig. 3, according to equation (5), give numerical values of k_N , and the intercepts correspond to the complex constants (collected in Table 1).

$$k' = k_0 + k_N m \quad (7)$$

The values of k_N for the non-catalytic reactions of anhydride of p-chlorobenzenesulphonic acid with m-nitroaniline and its deuterio analogue were calculated from equation (7) whose validity is illustrated by Fig. 4. The

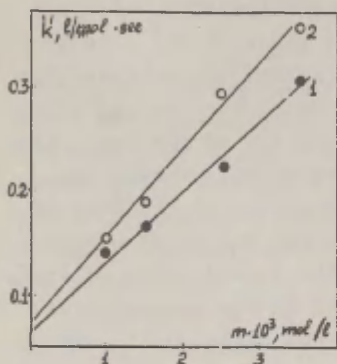
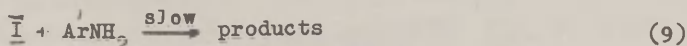
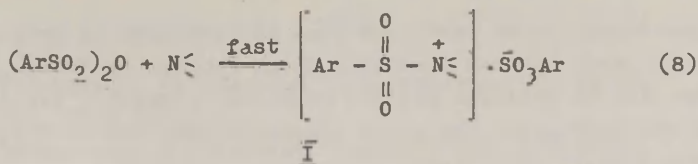


Fig. 4. Dependence of k' on m for the reaction of p-chlorobenzenesulpho-acid anhydride with m-nitroaniline (1) and its deuterioanalogue (2) catalyzed by N,N-dimethyl-p-toluidine in nitrobenzene at 25°.

values of k_N calculated from the slopes in the coordinates k_{eff}, X from equation (5) coincide with the values of k_N calculated from Eq.(7) which testifies to the validity of the kinetic expression for the rate of (4) in this particular case. Earlier, reasoning from investigation of the medium effects [1, 2] and changes in the structure of pyridine bases [9] on the rate of the acylation reaction of aryl amines by halides of arylsulphonic acids, the reaction being catalyzed by these pyridine bases, considerations were voiced in favour of the nucleophilic mechanism of catalysis. In studying the tertiary amine-catalyzed reactions of formation of amides of carboxylic acids the probability of exhibiting the nucleophilic mechanism of catalysis was found [6, 10, 11] to increase with the improving ability to loose the leaving group in the substrate. Since the arylsulphonate anion in anhydrides of arylsulpho-

acids is a far more easily separated group than the halide ion in acyl halides [3, 4], there is a reason to believe that nucleophilic mechanism of catalysis is especially probable. Indeed, the intensity of the catalytic action of pyridine ($k_N/k_O \approx 10^5$) and even N,N-dimethyl-p-toluidine ($k_N/k_O = 1.2 \cdot 10^4$) is considerably higher in the reaction discussed here than in the case of the pyridine catalysis in reactions with arylsulphobromide ($k_N/k_O \approx 10^2 \div 10^3$) [2]. At the same time, an opposite situation is characteristic of general-base mechanism of catalysis (see, for example, Refs. 12-14) i. e. the probability of catalysis increases here in reactions of substrates with hardly departed leaving groups. Thus, for example, in the case of reaction of sulphamide formation in the non-polar medium (benzene) the catalytic action of the second amine molecule which can be explained only in terms of the general base mechanism of catalysis rather than the nucleophilic one (see the previous report [15]) occurs only in acylation by chlorides [16] and bromides [17] of arylsulpho-acids and is absent in acylation by anhydrides [4] of these acids. It is also significant that catalytic action by the second amine molecule does not occur at all, when the range of the variation of the basicity of the amine [3, 4, 18, 19] acylated is wide enough, for the process of sulphamide formation in a polar solvent (nitrobenzene) in which a high catalytic effect of tertiary amines is revealed both in employing anhydrides of arylsulphonic acid (present studies) and in using halides of arylsulpho-acids [2, 8]. All the above considerations permit nucleophilic mechanism of catalysis by tertiary amines to be postulated in the aminolysis of anhydrides of arylsulphonic acids. The following scheme reflects its gist:



According to this scheme the addition product of the catalyst and the acylating agent I is further attacked by the nucleophile ArNH_2 . In this case the catalyst regeneration at the expense of the substitution by the entering nucleophil can take place either simultaneously or by the addition - elimination mechanism through the pentacoordinate intermediate (see [15, 20]).

The data on the isotope effect registered in substituting deuterium for hydrogen in the nucleophilic reagent [14] are often used in literature to identify the nucleophilic and general base mechanisms of catalysis in reactions of nucleophilic substitution. It has been shown [14], among other things that the isotope effect with substituting D_2O for H_2O in hydrolysis of dialkyl phenyl phosphate is close to unity for nucleophilic catalysis by tertiary amines and it is about 2 and greater for general base catalysis. The primary kinetic isotope effect is absent in the N,N-dimethyl-p-toluidine ($k_{\text{N}}^{\text{H}}/k_{\text{N}}^{\text{D}} = 0.87 \pm 0.07$ from the data of Table I) and also pyridine-catalyzed reaction of sulphamide formation which we have studied (cf. the kinetic curves for the reaction with m-nitroaniline and its N,N-dideutero analogue in Fig. 1). This, hence, is not inconsistent with assuming nucleophilic mechanism of catalysis. True, the absence of the primary kinetic isotope effect, in terms of the considerations given by Swain [21] can be consistent with an alternative scheme of general

base catalysis on condition that the transfer of hydrogen takes place between identical atoms (which, in principle, may also be realized for the reaction in point). But still, in the aggregate, the above arguments lead one to prefer nucleophilic catalysis.

EXPERIMENTAL

m-Nitroaniline, N,N-dideutero-m-nitroaniline [3], anhydride of p-chlorobenzenesulphonic acid [4], pyridine [22], and nitrobenzene [3] were prepared for the kinetic investigations by previously described procedures.

N,N-Dimethyl-p-toluidine as a sulphate was crystallised from 10 per cent sulphuric acid and decomposed by alkali. The product was distilled, the medium fraction being collected; b. p. 210-211° ([7], volume II, p. 990). The analytical control of the prepared solutions of the reaction components, rate measurements [3], and isolation of reaction products [17] were carried out as described earlier.

It was established by check experiments (cf. [1, 22]) involving the determination of the amount of unreacted arylamine in the process of catalytic acylation providing the reaction is practically completed that there were possible side reaction of hydrolytic decomposition of anhydride of arylsulphonic acid in the presence of the catalyst within the time necessary for completing reaction of sulphamide formation.

Translated from Russian by V.T. Kolyadnyi.

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IONIZATION MECHANISM OF STRONG ACIDS. TRICHLORO-
ACETIC, 2,4,6-TRINITROBENZOIC, AND PICRIC ACIDS
IN AQUEOUS SULPHURIC ACIDM. M. Karelson, V. A. Palm, R. Hjob,
and Ü. L. Haldna

Received

Ionization of trichloroacetic, picric and 2,4,6-trinitrobenzoic acids was investigated differential-conductometrically and spectrophotometrically in aqueous solutions of sulfuric acid. In the case of first of them both anionic and acidic forms of acid have the equilibria of complexing with hydrated proton in the solution. The simultaneous treating of the conductometric and the spectrophotometric data of trichloroacetic acid gives the value $pK_a = -0.56 \pm 0.03$ for the dissociation constant (by the H^+ acidity scale).

The dissociation of picric and 2,4,6-trinitrobenzoic acids proceeds by Brönsted scheme of acid-base equilibrium. Nevertheless, we should take into account the ability of the nonionized form of the acid to form the complexes by hydrated proton (as in the case of 1,3,5-trinitrobenzene). The following values of the dissociation constant were calculated: $pK_a = -0.10 \pm 0.02$ for picric acid and $pK_a = -0.17 \pm 0.03$ for 2,4,6-trinitrobenzoic acid (by the H^+ acidity scale).

The reaction series of dissociation of carboxylic acid is an important source for obtaining new values of inductive σ^{se} -constants. In determining the parameters of the linearity between pK_{a} and σ^{se} values the essential point is that for trichloroacetic acid.¹ Many various values of its dissociation constant can be found in the literature, e.g. -0.76 and 0.89 (see Refs. 2 and 3, respectively). It was taken note of a pronounced nonadditivity of the inductive effect of the halogen atoms at the α -halogen-substituted carboxylic acids, if to use the most spread values.¹

Consequently, it is important to obtain more reliable data about the dissociation of trichloroacetic and other strong acids. From this point of view this work is a supplement and logical continuation of the previous communication².

In particular we were interested in picric and 2,4,6-trinitrobenzoic acids. Various pK_{a} values available are also characteristic of the first of them.⁴

Two experimental methods were used in this work:

a) Differential conductometry, which is based on the determination of the influence of little additions of the substance investigated on the electrical conductivity of the strong mineral acid (H_2SO_4) aqueous solutions.

b) Spectrophotometrical measurement of the molar extinction coefficient of the substance in aqueous H_2SO_4 .

Experimental

Trichloroacetic acids was synthesized at the Laboratory of the Kinetics and Catalysis, Tartu State University.

The melting point of the purified product was 57.5°C.

Picric acid was recrystallized three times from the water-ethanol (1:1) up to the melting point of 121.5°C.

2,4,6-Trinitrobenzoic acid was recrystallized several times from the cold acetone-water up to the melting point of 220.0°C.

Bromoacetic and pivalic acids were used as models for the conductometric investigation of the complexing of

carboxylic group with hydrated proton.

Bromoacetic acid of the chemically pure grade was purified by recrystallization from cold ethanol up to the melting point of 50.2°C.

Purified product of the pivalic acid had a melting point 163.5°C.

UV absorbances were taken with a spectrophotometer (Hitachi Model EPS-3T) at 25°±0.2°C. The cell length was 0.1 or 1 cm.

The aqueous solutions of sulphuric acid were prepared from concentrated H₂SO₄ of the special pure grade and redistilled water by weighing.

Figs. 1, 2, and 3 show the typical absorption curves for three investigated acids (trichloroacetic, picric, and 2,4,6-trinitrobenzoic acids). Indicator ratios were calculated by the formula

$$I_{Sp} = \frac{\epsilon_{AH} - \epsilon}{\epsilon - \epsilon_{A^-}} \quad (1)$$

where ϵ_{AH} and ϵ_{A^-} denote the extinction coefficients of nonionized and anionic forms of the acid, respectively, ϵ is the extinction coefficient of the investigated solution of the acid.

The ϵ values at λ_{max} of substance investigated were used. The I_{Sp} values are given in Table 1.

Conductometric method and equipment has been described previously⁵. The quantity

$$y = \frac{k \cdot 10^3}{[AH]} \left(\frac{1}{R_0 + \Delta R} - \frac{1}{R_x} \right) \quad (2)$$

is calculated, where

k - cell constant (cm⁻¹),

R_0 - resistance of the solution before the addition of investigated substance AH,

R_x - resistance of the solution after the addition of substance AH,

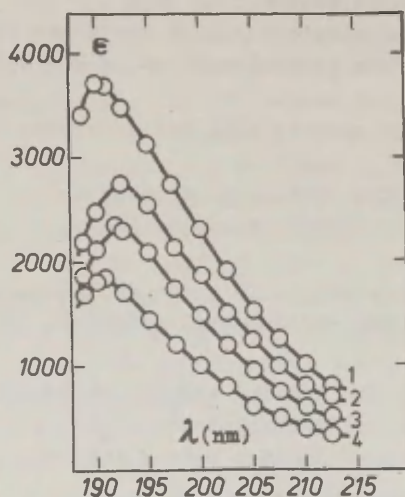


Fig. 1.

UV spectral absorption
curves of trichloroacetic
acid in

- 1 - water
- 2 - 8.87% H_2SO_4
- 3 - 20.0% H_2SO_4
- 4 - 35.8% H_2SO_4

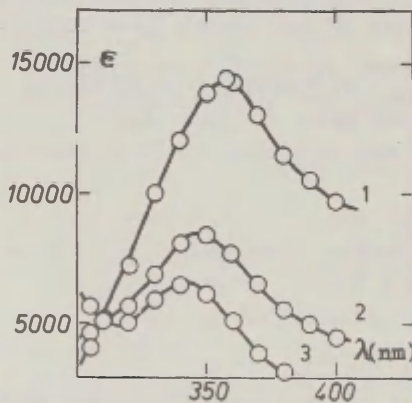


Fig. 2.

UV spectral absorption
curves of picric acid in

- 1 - water
- 2 - 9.84% H_2SO_4
- 3 - 23.09% H_2SO_4

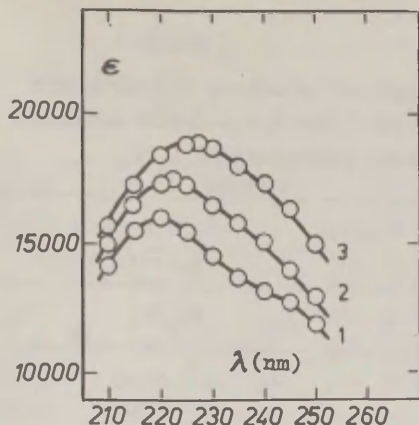


Fig. 3

UV spectral absorption curves of 2,4,6-trinitrobenzoic acid in

- 1 - water
- 2 - 9.18% H_2SO_4
- 3 - 37.9% H_2SO_4

ΔR - change in the solution resistance, due to the dilution of the solution, after the addition of substance AH,

$[\text{AH}]_0$ - stoichiometric concentration of added substance.

One can show that the addition of an organic acid that can form complexes $\text{A}^-(\text{H}_3\text{O}^+)_2$ and $\text{AH}\cdot\text{H}_3\text{O}^+$, and whose dissociation may result in the ions H_3O^+ and A^- , to the aqueous H_2SO_4 determines the following structure of the quantity y^* .

$$y = (\lambda_{\text{H}_3\text{O}^+} + \lambda_{\text{A}^-}) \frac{[\text{A}^-]}{[\text{AH}]_0} + (\lambda_{\text{AH}\cdot\text{H}_3\text{O}^+} - \lambda_{\text{H}_3\text{O}^+}) \frac{[\text{AH}\cdot\text{H}_3\text{O}^+]}{[\text{AH}]_0} \quad (3),$$

where $\lambda_{\text{H}_3\text{O}^+}$, λ_{A^-} , $\lambda_{\text{AH}\cdot\text{H}_3\text{O}^+}$ denote mobilities of the proton, the anion, and the complex between hydrated proton and acid molecule, respectively; $[\text{A}^-]$ and $[\text{AH}\cdot\text{H}_3\text{O}^+]$ are molar concentrations of the respective particles.

The conductometric measurements were carried out at

* H_3O^+ denotes hydrated proton.

Table 1

Spectrophotometric indicator ratio, I_{sp} , (1) for trichloroacetic, picric, and 2,4,6-trinitrobenzoic acids in aqueous solutions of H_2SO_4

Trichloroacetic acid		Picric acid		2,4,6-Trinitrobenzoic acid	
$\%H_2SO_4$	I_{sp}	$\%H_2SO_4$	I_{sp}	$\%H_2SO_4$	I_{sp}
2.10	13.7	2.43	2.43	1.22	7.28
4.50	6.49	3.02	3.05	2.43	4.27
5.89	6.06	4.20	2.12	3.42	2.87
7.06	4.78	4.78	1.89	5.93	1.52
7.80	3.89	5.93	1.31	6.62	1.42
8.87	3.25	6.50	1.20	7.65	0.93
11.10	1.85	7.63	0.951	9.82	0.81
12.00	1.84	8.75	0.800	10.75	0.87
13.00	1.32	9.84	0.688	11.50	0.53
14.47	1.22	10.90	0.558	13.10	0.45
15.90	1.08	11.45	0.528	16.25	0.35
17.00	0.970	11.96	0.500	19.02	0.234
20.00	0.661	13.02	0.385	20.14	0.184
21.30	0.605	14.05	0.328	22.23	0.208
		15.07	0.237	24.42	0.165
		17.14	0.141	27.21	0.137
		19.02	0.102		

Table 2

Differential conductivities, γ , for trichloroacetic, picric, and 2, 4, 6-trinitrobenzoic acids[‡]

Acid $\%H_2SO_4$	Trichloroacetic acid	Picric acid	2,4,6-Trinitro- benzoic acid
0	362.7 \pm 3.1	384.0 \pm 1.9	388.8 \pm 4.2
1.19	-	330.8 \pm 3.7	256.9 \pm 5.1
2.08	295.2 \pm 0.9	275.2 \pm 3.2	229.7 \pm 6.3
2.44	290.5 \pm 2.7	262.5 \pm 2.1	212.6 \pm 4.3
3.02	265.4 \pm 1.4	-	-
4.45	239.3 \pm 4.1	224.1 \pm 1.2	190.5 \pm 6.1
4.81	-	202.0 \pm 2.2	128.9 \pm 14.9
5.57	227.1 \pm 4.7	-	-
6.61	196.8 \pm 3.2	121.5 \pm 4.9	93.2 \pm 2.7
6.76	-	107.1 \pm 4.4	79.9 \pm 11.1
7.76	150.4 \pm 2.8	105.5 \pm 6.2	57.8 \pm 4.7
8.66	-	68.6 \pm 2.7	10.2 \pm 4.2
10.35	106.2 \pm 0.4	-	-
14.72	-	-92.5 \pm 3.9	-94.0 \pm 3.7
15.56	18.4 \pm 2.9	-	-
21.73	-75.5 \pm 0.9	-	-
22.80	-	-272.5 \pm 5.4	-249.2 \pm 6.8
26.99	-162.3 \pm 1.7	-349.4 \pm 2.9	-341.6 \pm 5.2
31.90	-205.6 \pm 2.9	-415.0 \pm 10.2	-395.8 \pm 7.3
38.61	-249.2 \pm 1.3	-	-
40.35	-	-505.2 \pm 4.7	-593.0 \pm 6.1
47.11	-250.6 \pm 2.7	-547.7 \pm 1.6	-702.5 \pm 4.5
54.02	-247.9 \pm 3.1	-598.2 \pm 4.4	-782.6 \pm 3.9
64.60	-198.5 \pm 4.2	-638.6 \pm 3.7	-
66.03	-	-685.7 \pm 7.1	-872.1 \pm 2.9

[‡] Mean square root deviations from arithmetic means at degree of freedom $f = 2$.

Table 3

Differential conductivities, γ , for pivalic and bromoacetic acids in aqueous solutions of H_2SO_4 [‡]

Acid $\% \text{H}_2\text{SO}_4$	Pivalic acid	Bromoacetic acid
1.19	-26.5 [±] 3.7	-23.7 [±] 2.9
2.08	-40.2 [±] 7.0	-33.9 [±] 4.5
4.45	-64.5 [±] 1.9	-55.1 [±] 3.2
6.76	-92.5 [±] 6.0	-76.2 [±] 1.7
8.66	-115.4 [±] 2.9	-93.2 [±] 4.4
10.35	-131.6 [±] 2.2	-102.2 [±] 3.5
14.72	-169.9 [±] 3.1	-135.5 [±] 5.7
17.02	-185.1 [±] 5.9	-150.3 [±] 3.2
21.70	-211.6 [±] 3.2	-168.8 [±] 7.0
26.99	-232.5 [±] 1.7	-185.5 [±] 0.6
31.90	-245.2 [±] 4.0	-196.2 [±] 4.1
38.61	-	-199.7 [±] 3.1
40.35	- 249.7 [±] 3.5	-
47.11	-247.5 [±] 5.1	-201.6 [±] 4.2
54.02	-250.9 [±] 4.2	-195.4 [±] 3.2
66.03	-219.6 [±] 7.2	-153.6 [±] 4.9

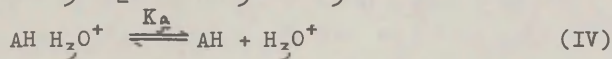
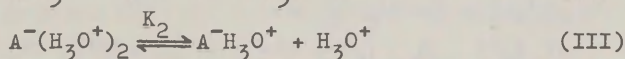
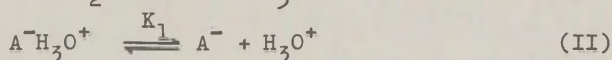
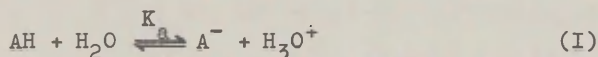
[‡] Mean square root deviations from arithmetic means at degree of freedom $f = 2$.

25±0.2°C, held with the precision of ±0.001°C. The following values of the cell constant were used: 20cm⁻¹; 213 cm⁻¹, 3008 cm⁻¹. The values of γ are given in Tables 2 and 3.

Results and Discussion

A. Trichloroacetic acid

It was observed² that trichloroacetic acid in aqueous solutions of the sulfuric acid had different spectrophotometric (I_{Sp}) and conductometric (defined as $I_c = \frac{\gamma_{AH}}{\kappa_{\infty(AH)}}$) indicator ratio values. Specially was noted that the quantity I_c changes from positive to negative (the γ values changes the sign) in the more concentrated solutions of H₂SO₄. This phenomenon was interpreted² as a result of simultaneous dissociation and complexing with the H₃O⁺ of the trichloroacetic acid molecule. Then there must be following equilibria in the solution:



with the equilibrium constants:

$$K_a = \frac{[A^-] \cdot a_{H_3O^+}}{[AH] \cdot a_{H_2O}} \quad (4)$$

$$K_1 = \frac{[A^-] \cdot a_{H_3O^+}}{[A^- \cdot H_3O^+]} \quad (5)$$

$$K_2 = \frac{[A^- \cdot H_3O^+] \cdot a_{H_3O^+}}{[A^- \cdot (H_3O^+)_2]} \quad (6)$$

$$K_p = \frac{[AH] a_{H_3O^+}}{[AH \cdot H_3O^+]} \quad (7)$$

where $[A^-]$, $[AH]$, $[A^- \cdot H_3O^+]$, $[A^- \cdot (H_3O^+)_2]$ and $[AH \cdot H_3O^+]$ are the molar concentrations of respective forms, $a_{H_3O^+}$ is activity of the hydronium ion, a_{H_2O} is activity of water.

Assuming that the complexing with hydrated proton does not affect the molar extinction coefficients of the anionic and acidic form of the acid AH, we can show that the spectrophotometric indicator ratio (1) has the following content:

$$I_{Sp} = \frac{[A^-] + [A^- \cdot H_3O^+] + [A^- \cdot (H_3O^+)_2]}{[AH] + [AH \cdot H_3O^+]} \quad (8)$$

If to take into consideration the mass balance of the acid AH, quantity y can be written as

$$\begin{aligned} y([A^-] + [A^- \cdot H_3O^+] + [A^- \cdot (H_3O^+)_2]) + \\ + y([AH] + [AH \cdot H_3O^+]) = \\ = \lambda_1 [A^-] - \lambda_2 ([A^- \cdot (H_3O^+)_2] + [AH \cdot H_3O^+]) \end{aligned} \quad (9)$$

where $\lambda_1 = \lambda_{H_3O^+} + \lambda_{A^-}$ and $\lambda_2 = \lambda_{H_3O^+} - \lambda_{A^- \cdot (H_3O^+)_2} = \lambda_{H_3O^+} - \lambda_{AH \cdot H_3O^+}$. By combining the equations (8) and (9), we get $(yI_{Sp} + y)([AH] + [AH \cdot H_3O^+]) = \lambda_1 [A^-] - \lambda_2 ([A^- \cdot (H_3O^+)_2] + [AH \cdot H_3O^+])$

Then, by using definitions of equilibrium constants (4-7), after simple transformations of the latter equations, we get:

$$\frac{y(I_{Sp} + 1) a_{H_3O^+}}{a_{H_2O}} = K \lambda_1 - \frac{K_a}{K_1 K_2} \lambda_2 a_{H_3O^+}^2 -$$

$$- \frac{1}{K_{\beta}} [y(I_{Sp} + 1) + \lambda_2] \frac{a_{H_3O^+}^2}{a_{H_2O}} \quad (10)$$

From this equation one can find the numerical values of the constants K_a , K_1K_2 and K_{β} , but only if the quantities $a_{H_3O^+}$ are known for the aqueous sulfuric acid solutions. In our last work⁷ we noticed that the complexing equilibria between nitro-group and hydrated proton could be described by the acidity function $H_{\beta} = -\lg a_{H_3O^+}(\beta) = \frac{[H_2O^+]}{a_{H_2O}^2}$. Now, by using the differential conductometric data for bromoacetic and pivalic acids we can show that the function H_{β} is useful also for describing of complexing equilibria between hydrated proton and carboxyl group.

The quantity I_c

$$I_c = \frac{[AH]}{[AH \cdot H_3O]} = \frac{y_{\max} - y}{y} \quad (11)$$

(concentration of the anion for these acids in merely acidic media is practically zero), must result in validity of the following equation for these acids:

$$\lg I_c = H_{\beta} - pK_{\beta} \quad (12)$$

Least-squares treatment of data leads to the following results:

$$pK_{\beta} = -0,12 \pm 0,02; \quad \operatorname{tg} \alpha = \frac{d \lg I_c}{d H_{\beta}} = 1,09 \pm 0,06;$$

$$r = 0,993; \quad s\% = 3,1 \quad \text{for the pivalic acid and}$$

$$pK_{\beta} = -0,14 \pm 0,02; \quad \operatorname{tg} \alpha = 1,02 \pm 0,05; \quad r = 0,991; \quad s\% = 3,7$$

for the bromoacetic acid.

The difference of quantities $\operatorname{tg} \alpha = d \lg I_c / d H_{\beta}$ from unity is experimentally undetectable. Therefore, the function H_{β} can be used for describing the complexing equilibria between proton and carboxyl group. If to extend this propitious circumstance to the carboxylate group, one can pro-

cess the data for trichloroacetic acid by Eq.(10), considering ${}^a\text{H}_3\text{O}^+ = \text{h}_\beta$. Least-square treatment of the data up to concentration of 25% (wt.) H_2SO_4 , gives:

$$K_a = 3,63 \pm 0,22, \quad K_1 K_2 = 26,7 \pm 7,3, \quad K_\beta = 1,6 \pm 0,3, \\ r = 0,991, \quad s\% = 4,3.$$

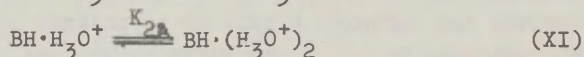
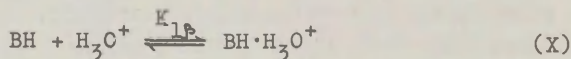
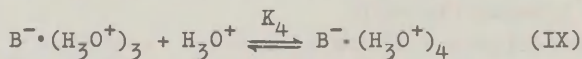
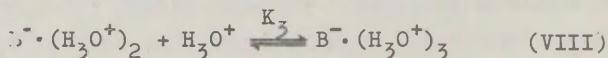
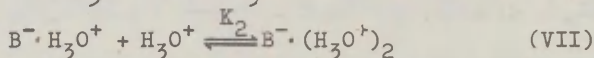
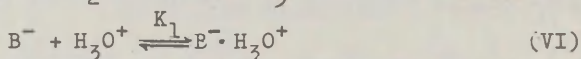
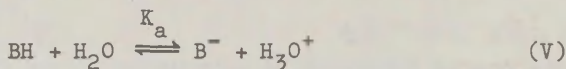
The value of K_a is in a good agreement with the value, which was obtained by using the Raman spectroscopy in concentrated solutions of the trichloroacetic acid: $K_a^{\text{Sp}} = 3,2 \pm 0,1$ (see Ref. 8).

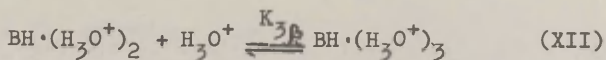
Corresponding value of $\text{p}K_a = -0,56 \pm 0,03$ is a little, but experimentally detectable different from the additive value ($\text{p}K_a^{\text{add.}} = -0,92$).

B. Picric and 2,4,6-trinitrobenzoic acids.

As it has been established the nitro group also is able to form complex with the hydrated proton.⁷ This fact must be taken into consideration when one wants to compare the differential-conductometric and spectrophotometric data.

Let the molecule of the picric or 2,4,6-trinitrobenzoic acid which contains three nitro-groups and one dissociable acidic group, be denoted as BH. Then the following equilibria should occur in the solution of the strong acid:





The corresponding equilibrium constants are:

$$K_a = \frac{[\text{B}^-] a_{\text{H}_3\text{O}^+}}{[\text{BH}] a_{\text{H}_2\text{O}}} \quad (12)$$

$$K_1 = \frac{[\text{B}^-] a_{\text{H}_3\text{O}^+}}{[\text{B}^- \cdot \text{H}_3\text{O}^+]} \quad (13)$$

$$K_2 = \frac{[\text{B}^- \cdot \text{H}_3\text{O}^+] a_{\text{H}_3\text{O}^+}}{[\text{B}^- \cdot (\text{H}_3\text{O}^+)_2]} \quad (14)$$

$$K_3 = \frac{[\text{B} \cdot (\text{H}_3\text{O}^+)_2] a_{\text{H}_3\text{O}^+}}{[\text{B}^- \cdot (\text{H}_3\text{O}^+)_3]} \quad (15)$$

$$K_4 = \frac{[\text{B}^- \cdot (\text{H}_3\text{O}^+)_3] a_{\text{H}_3\text{O}^+}}{[\text{B}^- \cdot (\text{H}_3\text{O}^+)_4]} \quad (16)$$

$$K_{1p} = \frac{[\text{BH}] a_{\text{H}_2\text{O}}}{[\text{BH} \cdot \text{H}_3\text{O}^+]} \quad (17)$$

$$K_{2p} = \frac{[\text{BH} \cdot \text{H}_3\text{O}^+] a_{\text{H}_3\text{O}^+}}{[\text{BH} \cdot (\text{H}_3\text{O}^+)_2]} \quad (18)$$

$$K_{3p} = \frac{[\text{BH} \cdot (\text{H}_3\text{O}^+)_2] a_{\text{H}_3\text{O}^+}}{[\text{BH} \cdot (\text{H}_3\text{O}^+)_3]} \quad (19)$$

If to assume that the complex-formation with the proton brings about no changes in the extinction coefficients of the anionic and undissociated forms of the acid, the spectrophotometrical indicator ratio may be written as

$$I_{Sp} = \frac{[B^-] + [B^{\cdot-}H_3O^+] + [B^{\cdot-}(H_3O^+)_2] + [B^{\cdot-}(H_3O^+)_3] + [B^{\cdot-}(H_3O^+)_4]}{[BH] + [BH \cdot H_3O^+] + [BH \cdot (H_3O^+)_2] + [BH \cdot (H_3O^+)_3]} \quad (20)$$

The conductometric quantity y has following form:

$$y = (\lambda_{H_3O^+} + \lambda_{A^-}) [B^-] + (\lambda_{B(H_3O^+)_2} - \lambda_{H_3O^+}) [B^{\cdot-}(H_3O^+)_2] + \\ + [BH \cdot H_3O^+] + (\lambda_{B \cdot (H_3O^+)_3} - 2\lambda_{H_3O^+}) ([B^{\cdot-}(H_3O^+)_3] + \\ + [BH \cdot (H_3O^+)_2]) + (\lambda_{B \cdot (H_3O^+)_4} - 3\lambda_{H_3O^+}) ([B^{\cdot-}(H_3O^+)_4] + \\ + [BH \cdot (H_3O^+)_3]) \quad (20a)$$

It is accepted (see Ref. 9), that $\lambda_{B^{\cdot-}(H_3O^+)} = \lambda_{BH \cdot H_3O^+}$, and so on (because the dimensions of corresponding particles are approximately equal).

By using the definitions (12-19), we can rewrite Eq. (20) as

$$I_{Sp} = \frac{[B^-] (1 + \frac{a_{H_3O^+}}{K_1} + \frac{a_{H_3O^+}^2}{K_1 K_2} + \frac{a_{H_3O^+}^3}{K_1 K_2 K_3} + \frac{a_{H_3O^+}^4}{K_1 K_2 K_3 K_4})}{[BH] (1 + \frac{a_{H_3O^+}}{K_{1\beta}} + \frac{a_{H_3O^+}^2}{K_{1\beta} K_{2\beta}} + \frac{a_{H_3O^+}^3}{K_{1\beta} K_{2\beta} K_{3\beta}})} \quad (21)$$

or

$$\frac{I_{Sp} a_{H_3O^+}}{K_a a_{H_2O}} = \frac{1 + \frac{a_{H_3O^+}}{K_1} + \frac{a_{H_3O^+}^2}{K_1 K_2} + \frac{a_{H_3O^+}^3}{K_1 K_2 K_3} + \frac{a_{H_3O^+}^4}{K_1 K_2 K_3 K_4}}{1 + \frac{a_{H_3O^+}}{K_{1\beta}} + \frac{a_{H_3O^+}^2}{K_{1\beta} K_{2\beta}} + \frac{a_{H_3O^+}^3}{K_{1\beta} K_{2\beta} K_{3\beta}}} \quad (22)$$

It is very difficult to obtain individual constants, K , from the last equation (8-parameter treatment). Therefore some restricting assumptions should be used. At first, we utilize the data for the merely concentrated (up to

20 w.%) H_2SO_4 solutions, in spite of this restriction the interval of the I_{sp} changes is too large (see Table 1). We can exclude equilibria (IX) and (XII), because the corresponding equilibrium constant for the model substance and that for 1,3,5-trinitrobenzene should be comparable to each other and large enough to allow us to neglect the $\text{TNB} \cdot 3\text{H}_3\text{O}^+$ formation ($\text{pK}_{\text{TNB}}^{\text{TNB}} = -2.93$, as shown earlier⁷).

Consequently, the spectrophotometric data for picric and 2,4,6-trinitrobenzoic acids can be treated by the following equation:

$$\begin{aligned} \frac{I_{\text{sp}}}{a_{\text{H}_2\text{O}}} (a_{\text{H}_3\text{O}^+} + \frac{a_{\text{H}_3\text{O}^+}^2}{K_{1\text{p}}} + \frac{a_{\text{H}_3\text{O}^+}^3}{K_{1\text{p}}K_{2\text{p}}}) = \\ = K_a + \frac{K_a}{K_1} (a_{\text{H}_3\text{O}^+} + \frac{a_{\text{H}_3\text{O}^+}^2}{K_2} + \frac{a_{\text{H}_3\text{O}^+}^3}{K_2K_3}) \end{aligned} \quad (23)$$

Since the reaction series in question is little sensitive to the substituent effects we take $K_{1\text{p}}$ and $K_{2\text{p}}$ as equal to the respective dissociation constants for the first and the second steps of dissociation for 1,3,5-trinitrobenzene: $K_{1\text{p}} = 3.32$; $K_{2\text{p}} = 31.5$ (see Ref. 7).

If to assume that $K_2 = K_{1\text{p}}$ and $K_3 = K_{2\text{p}}$ we can calculate numerical values of quantities in brackets on the left and right sides of Eq. (23). As is seen in Table 4, quantity $(I_{\text{sp}}/a_{\text{H}_2\text{O}}) (a_{\text{H}_3\text{O}^+} + a_{\text{H}_3\text{O}^+}^2/K_{1\text{p}} + a_{\text{H}_3\text{O}^+}^3/K_{1\text{p}}K_{2\text{p}})$ is constant for picric and 2,4,6-trinitrobenzoic acids on the investigated interval (H_2SO_4 from 0 up to 20 % by weight) and numerically equal to the corresponding value of the dissociation constant K_a (see Eq. (24)).

We can observe that this result is independent of the assumption $K_2 = K_{1\text{p}}$ and $K_3 = K_{2\text{p}}$, as the right side of Eq. (24) is constant independently of the changes in the argument value.

The pK_a values for picric ($\text{pK}_a = -0.10 \pm 0.02$) and 2,4,6-trinitrobenzoic acids ($\text{pK}_a = -0.17 \pm 0.03$) are a little more negative than the earlier values (see Refs. 4, 10).

Quotient $\frac{K_a}{K_1} \approx 0$, i.e. $K_1 \gg K_a$ (since $K_a \neq 0$). This fact indicates that equilibrium (VI) (and, consequently, equilibria (VII - IX) also) can be neglected in this interval of the H_2SO_4 concentration. If the restrictions made in our treatment are true, it means that dissociation of these acids occurs by Brönsted scheme and only nonionized forms of acid take part in equilibria of complex-formation with proton.

Table 4

Calculation of the K_a values for picric and 2,4,6-trinitrobenzoic acids on condition the left side of

Eq.(23) is constant

$$X = (I_{Sp}/a_{H_2O})(h_3 + h_3^2/3.32 + h_3^3/104.5); h_3 = [H_3O^+]/a_{H_2O}^2$$

Picric acid		2,4,6-Trinitrobenzoic acid	
% H_2SO_4	X	% H_2SO_4	X
2.43	1.19	2.43	1.45
4.20	1.36	3.42	1.45
5.93	1.23	5.93	1.43
6.50	1.24	6.62	1.49
7.63	1.22	7.65	1.30
8.75	1.26	9.82	1.53
9.84	1.29	11.50	1.29
11.96	1.31	13.10	1.40
14.05	1.17	16.25	1.61
17.14	1.05	19.02	1.41
$K_a = 1.25 \pm 0.06$		$K_a = 1.47 \pm 0.09$	

One can show that the processing of conductometric data gives analogous results.

If to take into account equilibria (V, X - XII) with the dissociation constants (12, 17-19), Eq.(20a) can take another shape:

$$K_a = \frac{y^2 a_{H_3O^+} + \frac{(\lambda_2 + y) a_{H_3C^+}^2}{K_{1e}} + \frac{(\lambda_3 + y) a_{H_3O^+}^2}{K_{1e} K_{2e}}}{(\lambda_1 - y) a_{H_2O}} \quad (24)$$

where $\lambda_1 = \lambda_{B^-} + \lambda_{H_3O^+}$, $\lambda_2 = \lambda_{H_3O^+} - \lambda_{BH \cdot H_3O^+}$, $\lambda_3 =$
 $= 2\lambda_{H_3O^+} - \lambda_{BH \cdot (H_3O^+)_2}$,

Using the differential-conductometric data at concentrations of H_2SO_4 up to 20% (by weight), quotient K_a remains practically constant. For picric acid ($\lambda_1 = 334$; $\lambda_2 = 270$; $\lambda_3 = 575$ are estimated on the bases of an earlier work⁹):

$$K_a = 1.21 \pm 0.12.$$

For 2,4,6-trinitrobenzoic acid ($\lambda_1 = 368$; $\lambda_2 = 275$; $\lambda_3 = 580$, see Ref. 9.):

$$K_a = 1.37 \pm 0.13.$$

These values practically coincide with respective spectrophotometrical values. Such an accordance between the results of two independent experimental methods indicates, in our opinion, that the pK_a values obtained are reliable and the assumptions made properly.

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ON THE RATIO BETWEEN ISOMERIC ALDEHYDES IN OLEFIN HYDROFORMYLATION PRODUCTS

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Kinetics of isobutene hydroformylation reaction has been investigated. 3-Methylbutanal, 2,2-dimethylpropanal and isobutane activation parameters have been determined. On the basis of experimental and literature data analysis antibatity of the change in selectivity and reactivity of the system in olefin hydroformylation processes has been revealed.

Homogeneous olefin hydroformylation at elevated temperatures (100–200°) and CO and H₂ pressures of 100–300 atm in the presence of cobalt carbonyls is known to be the most common method for olefin-based production of aldehydes. The first investigations on isobutene hydroformylation reaction were carried out in order to determine the principal possibility to obtain products of neopentyl structure. Later on several reports were published (1–3) on the ratio between the obtained isomeric aldehydes and the factors that influence the pivalic aldehyde yield. The mechanism of olefin hydroformylation reactions has been investigated well enough. The reaction rate is of first order for the olefin and the catalyst (2,4). However, the problem of isomer ratio in hydroformylation reaction is still open for discussion. Therefore, it seemed interesting to carry out quantitative investigation of the temperature dependence of parallel reactions for aldehyde formation of different structure and to examine the ratio between these isomers.

Experimental

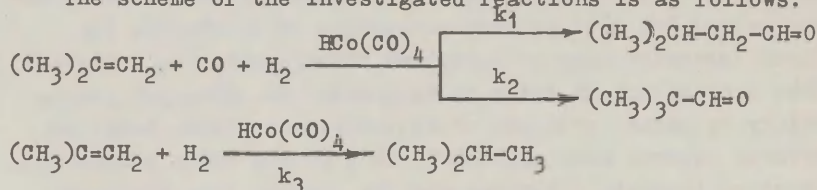
The experiments were carried out in a perfect mixing reactor under synthesis-gas pressure of 300 atm (CO:H₂=1:1);

samples were taken from gaseous and liquid phases. The catalyst $\text{Co}_2(\text{CO})_8$ was prepared beforehand in toluene solution. The reaction was initiated by injection of an olefin dose into the reactor. The analysis of the liquid phase was done by gas-liquid chromatography on Chromatograph LHM-7A with a thermal conductivity detector and temperature programming; the column length was 4 m. Styrene and divinyl benzene (DVB) copolymer (DVB content of 40 per cent and specific area of $200 \text{ m}^2/\text{g}$) was used as a sorbent. Gas analysis was carried out by selective absorption of individual mixture components: CO_2 , O_2 , CO , C_4H_8 . Isobutane was detected with GLC instrument HL-4.

Results and Discussion

Time-dependent concentrations of isobutene, isovaleric and trimethyl acetic aldehydes, and isobutane were obtained with the help of the above given technique. (Figure 1).

The scheme of the investigated reactions is as follows:



At constant synthesis-gas and catalyst concentration a system of first-order reaction equations corresponds to this scheme. Kinetic constants of the reaction rates were evaluated by means of differential methods of experimental data analysis. The least-squares method applied to the temperature dependence of rate constants of the above-mentioned reactions made it possible to determine the values of Arrhenius equation parameters:

$$\ln k_1 = (21.0 \pm 1.8) - (20000 \pm 2000)/RT;$$

$$\ln k_2 = (22.2 \pm 2.0) - (24000 \pm 2000)/RT;$$

$$\ln k_3 = (30.0 \pm 3.0) - (30000 \pm 2000)/RT;$$

where k_1 , k_2 , k_3 are rate constants of the corresponding reactions in min^{-1} .

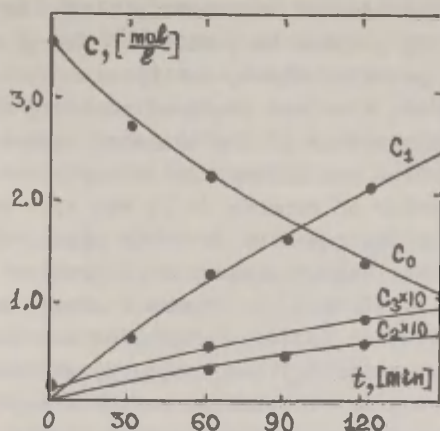


Figure 1. Comparison of experimental (dots) and calculated results for isobutene conversion (C_0) into 3-methylbutanal (C_1), 2,2-dimethylpropanal (C_2) and isobutane (C_3). Conditions: $T = 388^\circ\text{K}$, $C_0 = 0.1$ weight per cent, synthesis-gas ($\text{CO}:\text{H}_2=1:1$) pressure - 300 atm.

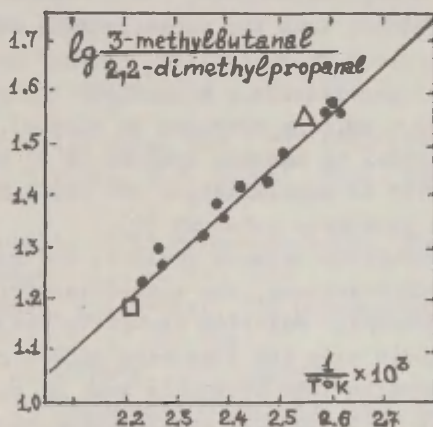


Figure 2. Relationship between the $\log(3\text{-methylbutanal}/2,2\text{-dimethylpropanal})$ and reciprocal temperature.

● - experimental data; Δ - Wender data (1);
 \square - Knapp data (2).

In investigation of unsymmetric olefin hydrogenation a very interesting problem is a ratio of the produced isomeric aldehydes. As practice shows, mainly straight chain aldehydes are obtained, that are produced contrary Markovnikov rule. However, the amount of the branched isomer ranges depending upon reaction conditions. As it has already been mentioned in a number of reports (2,5) the most important factor influencing the ratio of isomeric products is the reaction temperature. Higher temperatures promote the formation of more branched structures. Figure 2 shows the relationship between the obtained isomeric aldehydes and temperature. Data obtained by Wender (1) and Knapp (2) are also given. Thus, with the decrease in temperature and, correspondingly, the decrease in the activity of the system its selectivity as related to less branched aldehydes increases. Activation energy relationship also evidences in favour of this fact.

Now we refer to the literary data on the influence of the catalytic complex structure on the process selectivity. If we compare selectivity on cobalt carbonyl to that on cobalt carbonyl phosphine complex, i.e., when a strong δ -donor ligand is introduced into the corresponding coordination sphere one can see that $\text{HCo(CO)}_3\text{PR}_3$ "works" more selectively, giving, almost quantitatively a straight chain isomer contrary to Markovnikov rule as compared to HCo(CO)_4 , which gives the branched isomer in amounts from 20 to 40 per cent. HCo(CO)_4 activity is approximately 200 times higher than that of cobalt phosphine catalyst (6).

Such a comparison between activity and selectivity in hydroformylation reactions, the rate-determining stage of which is electrophilic addition (substitution) of the catalyst to the olefin with the formation of π -complex followed by its isomerisation into δ -complex make it possible to draw an analogy with electrophilic substitution reactions in an aromatic nucleus which also proceed through π -complex formation and its conversion into a true intermediate δ -complex. An empirical Brown rule (7) for electrophilic substitution is well known; this rule determines the ratio between activity

of a system and its selectivity:" the higher the reagent activity the lower is its selectivity". On the basis of modern ideas one can consider selectivity in electrophilic aromatic substitution reactions to be so much higher as more transitive is the state, determining the reaction rate, like δ -complex, in which the degree of a new bond formation is the greatest.

Thus, in olefin hydroformylation reactions on cobalt hydrocarbonyls $\text{HCo}(\text{CO})_4$ forms, apparently, an "early" transition state, which is more like η^5 -complex and in which a degree of a bond formation is not high, therefore it quickly and unselectively converts into δ -complex, while a cobalt phosphinio complex forms a more "late" transition state (nearer to δ -complex), in which a degree of a bond formation is high and therefore it makes greater demands to electron distribution in reagents. When taking into account that a less active (more selective) hydrocarbonyl gives almost completely the addition product contrary to Markovnikov rule one can conclude that in the transition state hydrocarbonyls are polarized predominantly by the type $\text{H}^{\delta-}(\text{Co}(\text{CO})_3\text{X})^{\delta+}$, where $\text{X} = \text{OO}, \text{PR}_3$.

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A NEW MODEL FOR SOLUTIONS OF ELECTROLYTES
(Preliminary Communication)

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A new model is proposed which permits to describe quantitatively the equivalent conductivities of aqueous solutions of electrolytes of various valence type over the whole concentration range.

Many problems on organic reactivity and mechanisms cannot be solved without the help of fundamental concepts of the theory of strong electrolyte solutions. It has been pointed out that insisting necessity to take into account ionic association has arisen for many cases¹⁻³. Classical approach based on Milner-Debye-Hückel ionic atmosphere model, is often unsuitable for this purpose. Moreover, there are many difficulties in interpretation of various properties (activity coefficients, electric conductivity etc.) of the electrolyte solutions even of moderate concentrations with the help of them⁴⁻⁹.

Čeleda¹⁰ had demonstrated that a universal empirical relationship is hold for the equivalent electric conductivities of relatively concentrated aqueous electrolyte solutions :

$$\lambda = \lambda_0 e^{-2,3Vc} \quad (1)$$

or

$$\lg \lambda = \lg \lambda_0 - Vc \quad (1a)$$

where λ denotes equivalent conductivity of the solution, c is the concentration of electrolyte in this solution (in g-equiv/l), λ_0 and V' are constants characteristic for given

electrolyte at given temperature.

One can prove that Eq(1) has a simple physical meaning. Let us postulate that for any pair of opposite charged ions there exists constant, independent of the concentration of electrolyte, probability P to be in electric-conductive state. Mobilities (λ_0) of ions in such a state are also assumed to be concentration-independent. Proceeding from these postulates following equation can be derived for the equivalent conductivity:

$$\lambda = \lambda_0 \cdot P N_A \cdot c \quad (2)$$

where N_A is Avogadro's number and c is concentration of electrolyte (in g-equiv/l). Eqs (2) and (1) are mathematically identic ($e^{-2,3V} = P N_A$). Statistical treatment of experimental data for 50 aqueous electrolyte solutions (of various valence types at various temperatures) confirms high reliability of the Čeleda relationship (1). Correlation coefficients are higher than 0.99, standart deviations vary in range of 1 to 4 per cents of maximal change of the processed quantity (λ). Treatment was carried out for the concentration range, where systematical deviations from the regression line for the points of more concentrated solutions were undetectable. Such deviations with the positive sign were observed for diluted solutions (see Fig.1).

In terms of above-mentioned interpretations, one can state that under these conditions either the ratio of conducting particles to non-conducting ones is not determined by probability law (Čeleda relationship) or ion mobilities do change (increase). It is important to point out that in the region of concentrations, where deviations from Čeleda relationship are quantitatively detectable, the fraction of pairs of ions in conducting state (estimated by extrapolation from Eq (1)) is close to unity (> 0.99).

One can prove that experimental deviations of λ -values from the straight line, defined by Eq(1a), can quantitatively be interpreted assuming that in the region the Čeleda relationship is hold practically all ions are associated

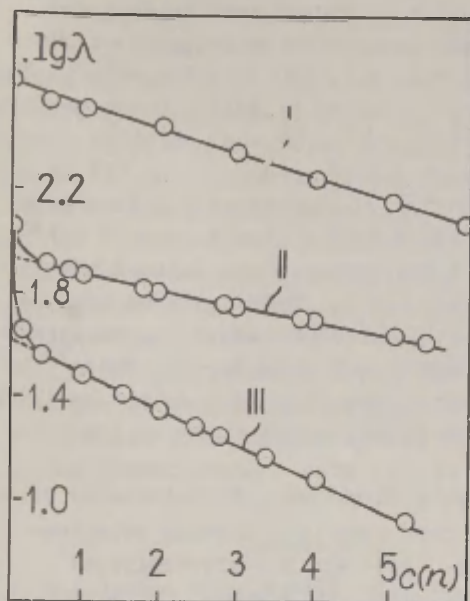


Fig.1. Equivalent electrical conductivities on the coordinates of the Čeleda relationship.

I - HClO_4 , 25°C
 II - NaCl , 18°C
 III - MgSO_4 , 18°C

and in the region of diluted solutions, where the deviations from this relationship are detectable ion associates could be identified with ion pairs. The deviations from Čeleda law can be interpreted as a result of dissociation of such ion pairs: mobility of free ions is larger as that for the ion pairs in conducting state. Dissociation ratio of ion pairs can be expressed:

$$\alpha = \frac{\Delta\lambda}{\Delta\lambda_\infty} \quad (3)$$

where

$$\Delta\lambda = \lambda - \lambda_\chi,$$

$$\Delta\lambda_\infty = \lambda_\infty - \lambda_\chi,$$

λ is observed equivalent conductivity of the solution, λ_χ is equivalent conductivity of the solution calculated (extrapolated) from the Eq(1).

λ_∞ is limiting conductivity for electrolyte at infinite dilution.

If this model is true, i.e. activity coefficients and mobilities of free ions are concentration-independent, we must conclude that the Ostwald dilution law, $K = \alpha^2 c / (1 - \alpha)$, is valid if α is expressed as given by Eq(3). Consequently, the linearity in coordinates $\Delta \lambda^2 c, \Delta \lambda$ shall exist:

$$\Delta \lambda^2 c = K \Delta \lambda^2 - K \Delta \lambda_{\infty} \Delta \lambda \quad (4)$$

Our statistical examination of experimental data showed that such a linearity is valid with a high degree of reliability ($r > 0.99$, $s = 1$ to 5 per cents of the maximal change of the correlated parameter $\Delta \lambda^2 c$) in the case of aqueous electrolyte solutions. Values of dissociation constants of ion pairs (K) found are rather different for the Fuoss¹¹ or Shedlovsky¹² values. Nevertheless, this fact is not striking because the different definitions of associates - ion pairs had been accepted.

Free energies of ion pair formation ΔF calculated from K -values obtained can be described by following relationship common for 1:1-, 1:2-, 2:1- and 2:2-electrolytes:

$$\Delta F = -2,3RT \lg K = (1.60 \pm 0.05) + \frac{331 z_a z_k}{\epsilon (r_a + r_k)} - (4.75 \pm 0.11) \Delta H_s^0 \quad (5)$$

where z_a and z_k denote charges of anion and cation, respectively, r_a and r_k are their crystallographic radii^{13, 14}, ϵ is a macroscopic dielectric constant of medium (water) at given temperature¹⁵, ΔH_s^0 is the sum of the hydration enthalpies of ions forming ion pair. Consequently, in order to describe quantitatively obtained pK -values, one should introduce only two additional empirical parameters, if to take into account electrostatic interaction in ion pair (the second term in the right side of Eq(5)). The last term in Eq(5) might be interpreted as the free energy of partial desolvation of ions forming the ion pair. As is seen from Eq(5), this free energy is proportional to the quantity ΔH_s^0 and consists of $0,47 \pm 0,01$ per cents of the latter.

The adequacy of the model proposed for the description of the electric conductivity of aqueous electrolyte solutions allows us to draw following conclusions:

(1) Aqueous electrolyte solution contains equilibrium mixture of free ions and ion aggregates. The latter formations are practically identical with ion pairs in the concentration range where free ions are detectable conductometrically. Starting from relatively moderate concentrations of electrolyte it is present practically only in the state of ion associates (pairs).

(2) Two states for ionic associates are possible, one of which is able to conduct electricity. Ratio of the ion associations in these two states is given by a simple probability law.

(3) Mobilities and activity coefficients of the free ions are concentration-independent.

Detailed presentation of the results of the treatment of the conductometric data will be published elsewhere.

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