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C O N T E N T S

COMPLEXING OF SIMPLE POLYETHERS AND POLYACETALS WITH DIETHYLALUMINIUMCHLORIDE

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The donor activity of polymeric ligands different in chemical structure of the class of the simple polyethers and polyacetals in the reaction of the complexing with V-acceptor - diethylaluminiumcloride has been studied by the method of microcalorimetry.

The energy of $p\pi$-conjugation of polyphenyleneoxid has been measured.

In spite of great progress made in quantitative study of the reaction of the complexing of low-molecular donors with V-acceptors, the study of an similar reaction with the polymeric ligands really is only beginning.

Experiment Methods

The methods of the experiment as well as the preparation and the purification of polyethyleneglycol (PEG), diethylaluminiumcloride (DEAC) and of the solvent have been described in detail in an earlier paper.[1]

Polytetrahydrofuran (PTHF), $(-O(CH_2)_4-)_n$, M=7,800 and M=2,160 was synthesized in mass at the temperature of $-30^{\circ}C$, the system tetrahydrofuran - BF_3 - propylene oxide used as a catalyst.

Polydioxolane (PDO), $(-OCH_2-OCH_2-CH_2-)_n$, was obtained in mass by polymerization of dioxolane complex compound of

ether with BF_3 used as a catalyst;

$T = 0^{\circ}C$, M = 34000, M = 17000.

Polytrioxalan (PTO), $(-OCH_2-(OCH_2CH_2)_2-)_n$, was obtained by polymerization in benzene, conc. H_2SO_4 as catalyst; $T = 25^{\circ}C$, M = 5500 and M = 11000.

Polyphenyleneoxide (PPO), $(-O-C_6H_3-)_n$, was obtained from p-bromophenol; M = 1012.

Specimens of polymers were purified by sedimentation. Before the research specimens of polymers were vacuated (10^{-3} - 10^{-5} mm Hg) in the course of several days in a thin layer at $T = 50\text{-}60^{\circ}C$.

The molal concentration of components was changed within a wide range from 10^{-3} to 5.10^{-1} mol/l.

Experimental results

Complex-formation heat of compound 1:1 of polymeric donors with DEAC being under study were taken on Kalvé microcalorimeter.

Table 1 shows thermal effects of the complex formation ($25^{\circ}C$, a solvent - toluene):

$$1/2\ Et_4Al_2Cl_2(solv.) + \left.\begin{matrix} O \\ O \end{matrix}\right\} (solv.) = Et_2AlCl \rightleftarrows \left.\begin{matrix} O \\ O \end{matrix}\right\} (solv.)$$

T a b l e 1

Complex-Formation Heat of Compound 1:1 of Different Donors with DEAC

Donor	α_o	ΔH, kcal/mol
PEG	≥ 1	23.3 ± 0.5
PTHF	~ 1	25.0 ± 0.5
PTO	> 8	23.4 ± 0.5
PDO	> 2.5	23.7 ± 0.5
PPO	≥ 1	17.4 ± 0.5
$(C_2H_5)_2O$		21.7 ± 0.5
$(C_4H_9)_2O$		22.2 ± 0.5

Comment: ΔH is equal to the quantity of heat emitted during the reaction and attributed to monomeric DEAC being in lack (without considering the dissociation heat). $\alpha_o = C_o : C_A$, where C_o and C_A are the molal concentrations of the polymer as calculated on a monomeric link (or an average fragment with an atom of oxygen in the case of PDO or PTO) and monomeric DEAC, respectively.

Discussion

A somewhat larger combination heat of a complex compound (on the average 1.8 kcal/mol) attracts attention in the case of a polymeric donor.

In the literature[2,3] numerous cases of the difference in the activity of the reaction centers, to be found in the macrochain of the low-molecular analog are cited. That is often linked with the electrostatic, spatial and other effects stimulated by neighbouring links ("chain effect") and also with the configuration, conformation and overmolecular organizations of macromolecules.

The difference being observed by us can apparently be explained by "chain effect" since the difference in the heats of the monomeric and polymeric donors was observed for different C_o.

The difference in the donor-activity of the polymeric ligands is insignificant, which is as well observed for low-molecular ethers in the similar reaction with v-acceptors[4].

The value of ΔH for PPO is -17.4 ± 0.5 kcal/mol, while the average value of ΔH for the rest of polymers amounts to -23.8 kcal/mol. The difference is close to 6.4 kcal/mol. Such a great decrease in the heat of complexing is apparently associated with $p\pi$- conjugation.

Comparing the obtained value with the literary data[4] on the energy of $p\pi$-conjugation one can note the proximity of

the Ph-O-R type compounds (where R is the aliphatic radical) to E_c rather than of the Ph-O-Ph compounds.

The proximity of the energy of $p\pi$-conjugation in polymer, which is 6.4 kcal/mol, to the value of E_c for the compounds of Ph-O-R type is apparently associated with the fact that in both cases only one phenylic ring is related to the oxygen atom.

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AN IR-SPECTROSCOPICAL STUDY OF BENZYLIDENEACETONES AND SOME OF THEIR HETEROCYCLIC ANALOGS

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Were measured the IR-spectra of 2-furfurylidene-acetone, substituted benzylidene- and 2-thienylidene-acetones in the solutions of carbon tetrachloride, tetrachlorethylene and in the solid phase. It was found that in solutions these compounds were represented in the form of an equiprobable mixture of s-trans and s-cis conformers. In the crystalline state most of the compounds investigated (with the exception of benzylidene-, p-dimethylaminobenzylidene-, and 5-nitro-2-thienylideneacetones) have the predominant s-trans form. The correlation analysis of carbonyl frequency values (ν_{CO}) was made and higher transmission of electronic effects of substituents was found in benzylideneacetones s-trans-conformers as compared with s-cis ones while for the inverse 2-thienylideneacetone isomers the contrary tendency was observed.

In studying further the conformations and physicochemical properties of α,β-unsaturated ketones according to their constitution /1-3/ we decided to investigate the IR-spectra of substituted benzylideneacetones and some of their analogs (see Table 1). Besides the solution of some problems concerning the conformation of these molecules we have aimed at describing with the help of correlation analysis the influence of heterocyclic radicals and the substituents in benzene and thiophene nuclei on characteristic stretching frequency of the carbonyl group as well as at estimating the transmission of electronic effects in the investigated systems.

Experimental

The carbonyl compounds under investigation were synthesized by the Claisen-Schmidt condensation method of the corresponding aromatic or heterocyclic aldehydes with acetone in alkali medium /4, 5/, with the exception of 5-nitro-2--thienylideneacetone obtained by nitration of 2-thienylideneacetone with nitric acid /6/. All the ketones were ppurified by chromatographying their solutions in the benzene-hexan mixture on aluminium oxide with subsequent fractioning in vacuum or recrystallization from the aqueous methanol.

IR-spectra were measured by the UR-20 spectrophotometer in paraffinum liquidum or KBr tablets and in carbon tetrachloride and tetrachlorethylene solutions with 0.1 M ketone concentration in the 700-1800 cm^{-1} region in cells with the path length of 0.01 cm with windows made of NaCl. The ν_{CO} measurements were repeated 6-8 times and the statistical processing carried out on the confidence level of 0.95 .

Discussion

All the compounds studied here in accordance with the methods of their production are trans-isomers with respect to the arrangement of the substituents at the aliphatic double bonds. This is confirmed by the presence of a characteristic absorption line of extraplane deformation vibrations of trans-ethylene coupling hydrogens at 970-980 cm^{-1} in their spectra.

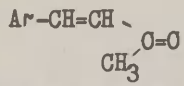
For all the investigated ketones in CCl_4 and C_2Cl_4 solutions at 1600-1700 cm^{-1} three intense absorption bands are observed (for instance see Fig.1). We refer the first band at 1598-1619 cm^{-1} (see Table 1) to double aliphatic bond vibration and two others at 1666-1679 cm^{-1} and 1684-1706 cm^{-1} to stretching vibrations of the carbonyl group of s-trans and s-cis conformers of the compounds studied.

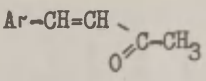
Table 1

Spectral Data for Ketones R-CH=CH-CO-CH_3

No.	R	ν_{CO} cm^{-1} (CCl_4)		$\nu_{C=C}$	ν_{CO} (C_2Cl_4)		$\nu_{C=C}$	ν_{CO} (liq. paraffin		$\nu_{C=C}$
		s-cis	s-trans		s-cis	s-trans		s-cis	s-trans	
I	Phenyl	1697.6*	1674.8*	1614	1697	1679	1614	1695	1681	1612
II	4-Tolyl	-	-	-	1695	1677	1613	1690	1670	1612
III	4-Anisyl	1693.2*	1670.1*	1604	1696	1670	1607**	-	1660	1604
IV	4-Biphenylyl	1696.9*	1674.0*	-	1697	1676	1610**	-	-	-
V	4-Dimethylaminophenyl	1688.9*	1666.0	1603	1690	1666	1603	1679	1657	1590***
VI	4-Chlorophenyl	1699.2*	1677.2*	-	1701	1683	1617	1685	1660	1610
VII	4-Nitrophenyl	1702.0*	1680.8*	-	1706	1684	1614	1691	1668	1597***
VIII	2-Thienyl	1693	1674	1605	1684	1675	1604	1680	1670	1601
IX	5-Methyl-2-thienyl	1692	1672	1602	1693	1673	1599**	1687	1666	1600
X	5-Phenyl-2-thienyl	1695	1676	1601	1693	1674	1598**	-	1662	1605***
XI	5-Chloro-2-thienyl	1695	1677	1604	1696	1677	1601**	-	1665	1615
XII	5-Bromo-2-thienyl	1696	1677	1600	1695	1677	1602**	-	1670	1610
XIII	5-Nitro-2-thienyl	1702	1681	1607	1702	1682	1607	1696	1670	1605***
XIV	2-Furyl	1695	1674	1617	1693	1673	1619	-	1668	1620

* ν_{CO} taken from Ref.4 in which the $\nu_{C=C}$ values are not given ** $\nu_{C=C}$ reported only for s-cis= form; besides the very weak band or bends at 1612-1614 cm^{-1} for VII, IX-XII, and at 1620-1625 cm^{-1} for III and IV ($\nu_{C=C}$ s-trans) are observed. *** Scanned in KBr tablets. tablets.





In a similar way the bands observed in this range for unsaturated ketones are treated elsewhere /4, 7-10/. The low--frequency component of the carbonyl doublet should be attributed to s-trans- and the high-frequency one to s-cis-conformer /7,8/. The reference of the bands of the investigated compounds to ν_{CO} and $\nu_{C=C}$ given here is supported by the fact that for some benzylidene- and 2-thienylideneacetones when passing from solutions in tetrachlorethylene to chloroform solutions two high-frequency bands / ν_{CO} / appreciably shift down to the low-frequency range, while the band at 1598-1619 / $\nu_{C=C}$ / practically does not change its position. It is noteworthy that, as a result of the formation of the hydrogen bond with chloroform, the s-trans-conformer ν_{CO} band undergoes a stronger low-frequency shift (6-13 cm^{-1}) than the ν_{CO} s-cis isomer (3-6 cm^{-1}). The same regularity was noted earlier for chalcones /1/ and regarded /11/ as an indirect proof of the fact that the s-trans-form of α,β-unsaturated ketones possesses larger basicity than s-cis-form. The absorption at 1598-1619 cm^{-1} / $\nu_{C=C}$ / exceeds the carbonyl bands by its intensity for all the ketones. That is why it should be referred to s-cis-form /8/, while the $\nu_{C=C}$ vibrations of s-trans-conformers give in the majority of cases low intensity bands or some bends at 1612-1614 cm^{-1} for heterocyclic ketones and for benzylideneacetones at 1620-1625 cm^{-1} (Fig.1).

The chalkones Ar-CH=CH-CO-C_6H_5 investigated earlier because of the considerable steric hindrance arising between O-hydrogen of an acetophenone fragment and β-hydrogen of the vinylene group, are present in solutions mostly as s-cis-forms /1, 2/. Since in the case of substitution of the benzene nucleus by the methyl group the steric hindrance is being eliminated, for benzylideneacetones the rotation around the single C-C bond situated between the double bonds (O=O and C=C) is being facilitated and benzylideneacetones exist in both conformations simultaneously. The relation between the

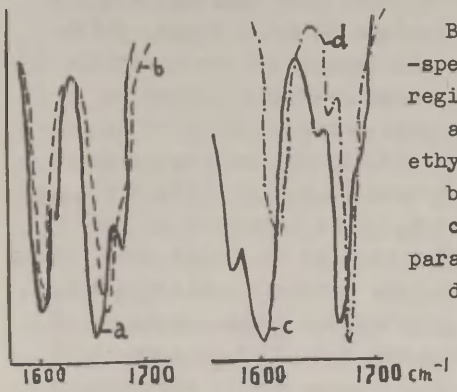


Fig.1

Benzylideneacetone IR-spectrum in the absorption region $\nu_{C=C}$ and $\nu_{C=O}$:

a) solution in tetrachlorethylene;

b) melting;

c) suspension in liquidum paraffinum;

d) crystalline state.

concentrations of the conformers in solutions to a first approximation may be characterized by the ratio of their optical densities in maxima of the corresponding carbonyl bands. The value of the ratio K=Ds-trans/Ds-cis for the ketones studied is on the average I.5. Strictly speaking, this ratio depends not only upon the relative concentrations of two rotation isomers, but also upon the differences in values of molar absorption coefficients of the corresponding ν_{CO} bands. Since it is known that the carbonyl absorption of compounds with the s-trans-configuration is more intensive than that for the s-cis-forms /8/, the value obtained for K differs from unity presumably in the main on account of this factor. Consequently, one can assume as a first approximation that the benzylideneacetones investigated here are present in solutions in the form of an equiprobable mixture of both conformers and this seems to be a consequence of a negligible difference in the energies of the conformers. It confirmes the fact that the ratio of optical densities of ν_{CO} benzylideneacetone bands in the tetrachlorethylene solution does not change with the rise of temperature from 20 to 105° *). It is of interest that for 2-thienylideneacetones and 2-furfurilideneacetone the K ratio is lower and makes 1.2.

*) Only a small decrease of intensity of both bands is observed with the rise of temperature, which is connected with the temperature-dependence of their molar absorption coefficients /13/.

Earlier /1,2/ it was established that chalcone and its analogs exist only in the s-cis-form in solid phase, which seems to correspond better to the demands of dense packing in the crystalline lattice. It was interesting to check up whether this phenomenon would take place in the case of benzylideneacetones and their analogs. In the melt benzylideneacetone measured by us, IR-spectrum (m.p. 33°) (Fig.1,b), as well as for its solutions, the ν_{CO} band intensity of the s-trans-form is much higher than that of the s-cis-form, which is also in good agreement with some recently published data /10/. However in the case of spontaneous crystallization of this ketone melt on NaCl plates the s-trans-form turns to a considerable degree into the s-cis-form, and in the corresponding IR spectrum (Fig.1,d) the ν_{CO} band intensity of the s-cis-isomer considerably exceeds that of the s-trans-conformer. The spectrum of a similar nature is also observed for the benzylideneacetone suspension in liquidum paraffinum (Fig.1,c). Thus,in case of benzylideneacetone the s-cis-from dominates also in the crystalline state over the s-trans-from. It is interesting that on sharp cooling of benzylideneacetone melt to the liquid nitrogen temperature, the metastable crystalline state of this ketone is being presumably obtained, under which the ketone is in the form of a s-trans-conformer /10/. The quantity of the s-trans-form in the crystalline benzylideneacetone also considerably increases while it is pressed into tablets with KBr, the ratio of the bands intensities ν_{CO} s-trans/ν_{CO} s-cis being noticeably dependent on the conditions of the preparation of tablets, i.e. the extent to which the substance is ground with KBr, the time of pressing and the pressure applied. Similar changes of the conformation of organic compounds while they are pressed into tablets of halides of alkali metals was also observed elsewhere /14/.

The possibility of the conformation composition of crystalline benzylideneacetone change in the above example seems to be connected with small energy difference between its s-trans- and s-cis-forms and low melting temperature, the latter facilitates the formation of the so-called "plastic" crystalline state /15/.

In considering the IR-spectra of the substituted benzylideneacetones and their analogs in solid phase it has been found that there is a strong dependence of molecule conformation on the nature of the substituent in heteroaromatic radical or on that of the latter. Quite different is the case with the solutions of these compounds where the conformers ratio changes to a comparatively small degree. Using the comparison ν_{CO} bands intensity of probable conformers as a base*) one may conclude that for 4-dimethylaminobenzylideneacetone (V, Table 1) the s-cis-conformation appreciably prevails, while 4-chlor-(VI), 4-nitrobenzylidene-(VII) and 4--anizalacetones (III) in the solid phase have mainly the s-trans-structure. In the spectra of the lastmentioned compounds the s-trans-form $\nu_{C=C}$ absorption considerably increases (in solutions it is revealed in the form of bends in the high-frequency part of the s-cis-form $\nu_{C=C}$ band only), becoming comparable with or even more intensive than the s-cis-form $\nu_{C=C}$ band, and at the same time the drop of intensity or disappearance of the s-cis-form ν_{CO} bands are observed. For example, it is seen from Figure 2, in anizalacetone spectrum (III) in the solid phase an intensive band at 1634 cm^{-1} (the s-trans-conformer $\nu_{C=C}$) is observed, which in solution is displayed only by a weak bends. At the same time the disappearance of the s-cis-form ν_{CO} absorption is observed. However the presence of some amount of this form can still be

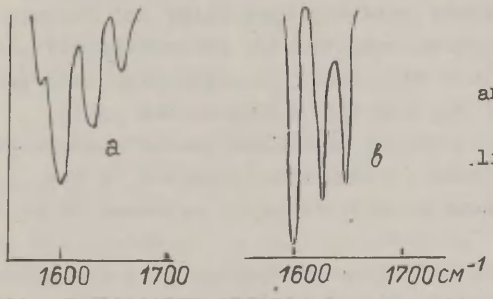


Fig.2

IR-spectrum of anizalacetone.
a) suspension in liquidum paraffinum;
b) KBr-tablete

*) ν_{CO} values in the solid phase are by 6-12 cm^{-1} lower than in solutions.

identified by absorption of $\nu_{C=C}$ at 1601 cm^{-1}, because, as it is known, the s-cis-forms are characterized by a considerably higher intensity of $\nu_{C=C}$ than ν_{CO} /8/. Furfurylideneacetone (XIV), 5-chloro-(XI), 5-bromo-(XII), 5-phenyl-2--thienylideneacetone (X) also have s-trans-conformation in the crystalline state, but crystalline 5-nitro-2-thienylideneacetone (XIII) (KBr tablets) spectrum indicates that the s-cis--form as compared with the s-trans-one prevails substantially. For the lowmelting 4-methylebenzylidene-(II) and 2-thienylidene-(VIII) acetones the nature of the condensed phase (the melt) spectra practically does not differ from those for solutions. All these differences appear to be connected with different crystalline lattice structures of various arylideneacetones.

The investigation if IR benzylideneacetones spectra and of their thiophene and furane analogs in the solid phase makes it possibleto see a number of other peculiarities as well. For example, if for the solutions the $\nu_{C=C}$ absorption intensity of the s-trans-conformers is considerably lower than ν_{CO} (which is in accordance with the data for other α,β-unsaturated ketones /8/),then in the solid phase spectra of furfurylideneacetone (XIV) and some 2-thienylideneacetones (X-XII) the $\nu_{C=C}$ intensity of these forms is at least comparable to the corresponding ν_{CO} absorption. The relative dipole moment changes of these bonds in the process of stretching vibrations, determining their relative intensity, for the molecules in crystalline lattice seem to be considerably different from those of dilute solutions. Consequently, the ratio of intensities of the ν_{CO} and $\nu_{C=C}$ bands in the solid phase spectra, contrary to that of solutions, cannot always serve as a reliable criterion for the determination of the conformation, and ν_{CO} values should primarily be taken into account.

In the spectra of the investigated compounds in the solid phase there appears at 1637-1645 cm^{-1} a distinct absorption band, but of a very low intensity, which is absent in the spectra both of the solutions and of melts. In case of 5--chloro- and 5-bromo-2-thienylideneacetones (XI, XII) and to

a lesser degree for 4-chlorobenzylideneacetone (VI) the intensity of this band rises considerably (see Fig.3). The origin of this band is not connected with the process of pressing as it is also observed in solid phase spectra obtained during the melt crystallization of NaCl plates, and as well in the case of suspension in liquidum paraffinum. It is interesting that some authors /9/ also point out to the appearance in solid phase spectra of some α,β-unsaturated ketones of new bands, although they neither say anything about their position, nor do they interpret their origin. The appearance of the 1637--1645 cm^{-1} band in solid phase spectra of the compounds studied might be connected with the specific interaction in the crystalline lattices.

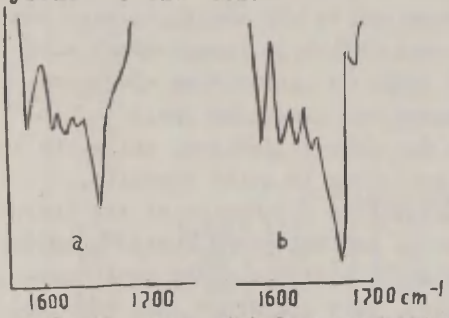


Fig.3

IR-Spectrum of 4-chloro--benzylideneacetone:
a) suspension in liquidum paraffinum;
b) KBr-tablete.

In the case of halogenesubstituted ketones it is not excluded that this intensive absorption will appear in the solid phase at the expense of Fermi resonance of $\nu_{C\text{-}Cl}$ or $\nu_{C\text{-}Br}$ overtone with the adjoining ν_{CO} band, while in solutions the mutual arrangement of these bands for such resonance is not favourable enough.

In the 4-nitrobenzylideneacetone (XII) spectrum in KBr tablets and in suspension in liquidum paraffinum parallel with $\nu_{C=C}$ and ν_{CO} absorption of the s-trans-and some amount of s--cis-conformers a very intensive absorption band at 1712 cm^{-1} and weak bends at $\sim$ 1625 and 1645 cm^{-1} region are observed, which are absent in solution spectra, in this case the peak intensity at 1712 cm^{-1} in the spectrum measured for KBr tablets being considerably higher than in liquidum paraffinum. One can assume that this compound contains the cis-

-isomer (ν_{CO} 1712 cm^{-1} and $\nu_{C=C}$ 1625 cm^{-1}), the amount of which may increase in the process of pressing tablets. This assumption is in accordance with the data /16/ that the presence of a nitrogroup in the benzene nucleus stabilizes the cis-isomers of unsaturated ketones.

Since the relation of the conformers in solutions of different compounds studied here does not substantially change, it was considered both expedient and possible to investigate the dependence of ν_{CO} values of both conformers upon the chemical structure of the ketones. The data given in Table 1 show that the substitution of the benzene nucleus by the thiophene and furan ones in benzylideneacetone is accompanied by a small decrease of ν_{CO} values of both conformers (cf.I with VIII and XIV). This fact point out to the electronodonor character of 2-furyl and 2-thienyl, which is in agreement with the conclusions drawn above /17/. By introducing electronodonor substituents into benzene and thiophene nuclei of unsaturated methylketones the ν_{CO} values decrease, while the influence of the acceptor substituents is quite opposite.

In order to make a quantitative estimation of the influence of substituents in benzene and thiophene nuclei upon the ν_{CO} values, we made a correlation analysis using both monoparameter equations of Hammett, Taft and Brown /18/ and two-parameter equations introduced by Yukava-Tsuno /18/ and Swain-Lupton /19/. The results of the correlation analysis are given in Tables 2 and 3. From the data given in Table 2 it is evident that in the majority of cases the ν_{CO} values correlate rather satisfactorily with different parameters of the substituents (σ, σ°, σ^{+}), and no preference can be given to any of the constants used. In considering the values of reaction constant m obtained both in solutions in CCl_4 and C_2Cl_4, we can clearly observe the tendency of a somewhat higher sensitivity of the s-trans-conformers carbonyl frequency to the influence of the substituents as compared with the s-cis-forms, the ratio of the reaction constants $m_{s\text{-trans}}/m_{s\text{-cis}}$ being 1.11-1.32. A similar regularity was recently observed in studying ν_{CO} values of the s-trans cinnamyl aldehydes and the s-cis-tert.-butylstyrylketones /20/.

Table 2

The Correlation Analysis Data of $\Delta\nu_{CO}$ for *s*-trans (t) and *s*-cis (c) Methyl Ketone Conformers by Hammett, Taft, Brown Equations

	Equations: $y = ax + b$	C	s_a	s_b	s	n
	Benzalacetones					
CCl_4	$\Delta\nu^t_{CO} = 9.3\sigma - 0.04$	0.98	0.7	0.3	0.9	7
	$\Delta\nu^t_{CO} = 10.7\sigma^o - 1.4$	0.93	1.6	0.7	3.3	7
	$\Delta\nu^t_{CO} = 6.0\sigma^+ + 1.2$	0.99	0.4	0.3	0.8	7
	$\Delta\nu^c_{CO} = 8.3\sigma - 1.1$	0.98	0.8	0.4	1.0	7
	$\Delta\nu^c_{CO} = 9.3\sigma^o - 2.0$	0.92	1.6	0.7	3.4	7
	$\Delta\nu^c_{CO} = 5.4\sigma^+ + 0.3$	0.99	0.2	0.2	0.2	7
C_2Cl_4	$\Delta\nu^*_{CO} = 10.8\sigma - 1.3$	0.99	1.9	0.9	5.3	6
	$\Delta\nu^t_{CO} = 10.3\sigma^o - 2.5$	0.99	3.4	1.3	9.2	6
	$\Delta\nu^t_{CO} = 7.1\sigma^+ + 0.4$	0.90	1.0	0.8	3.9	6
	$\Delta\nu^c_{CO} = 8.3\sigma - 0.8$	0.88	0.8	0.4	2.9	6
	$\Delta\nu^c_{CO} = 7.8\sigma^o - 0.3$	0.87	1.1	0.4	2.2	6
	$\Delta\nu^c_{CO} = 5.9\sigma^+ + 1.0$	0.86	3.2	1.4	9.9	6
	2-Thienalacetones					
CCl_4	$\Delta\nu^t_{CO} = 8.8\sigma + 0.6$	0.95	1.4	0.5	1.1	6
	$\Delta\nu^t_{CO} = 7.8\sigma^o + 0.5$	0.94	1.4	0.5	1.3	6
	$\Delta\nu^t_{CO} = 7.3\sigma^+ + 1.5$	0.91	1.6	0.6	1.9	6
	$\Delta\nu^c_{CO} = 10.2\sigma + 0.7$	0.97	1.3	0.4	0.9	6
	$\Delta\nu^c_{CO} = 9.2\sigma^o + 0.5$	0.97	1.1	0.4	0.9	6
	$\Delta\nu^c_{CO} = 8.6\sigma^+ + 1.7$	0.94	1.5	0.6	1.7	6
C_2Cl_4	$\Delta\nu^t_{CO} = 9.6\sigma - 0.4$	0.99	0.5	0.2	0.1	6
	$\Delta\nu^t_{CO} = 8.6\sigma^o - 0.5$	0.99	0.5	0.2	0.2	6
	$\Delta\nu^t_{CO} = 8.3\sigma^+ + 0.6$	0.99	0.5	0.2	0.2	6
	$\Delta\nu^c_{CO} = 9.9\sigma - 0.2$	0.98	1.1	0.4	0.7	6
	$\Delta\nu^c_{CO} = 9.0\ \sigma^o - 0.4$	0.98	0.8	0.3	0.5	6
	$\Delta\nu^c_{CO} = 8.6\sigma^+ + 0.7$	0.98	1.0	0.3	0.7	6

C = the correlation coefficient; s_a, s_b = mean-square errors of parameters a, b; s = standard deviation; n = number of points.

Table 3

The Correlation Analysis Data of $\Delta\nu_{CO}^{t,c}$ for s-trans (t) and s-cis (c) Methyl Ketone Conformers by Yukawa-Tsune, Swain-Lupton Equations

	Equation: $Z = C + ax + by$	C	s_c	s_a	s_b	n
	Benzalacetones					
CCl_4	$\Delta\nu_{CO}^{t} = 0.8 + 6.7\sigma^{o} + 5.1\sigma_R^{+}$	0.97	0.5	0.7	0.9	8
CCl_4	$\Delta\nu_{CO}^{t} = 0.2 + 5.0\mathcal{F} + 10.2\mathcal{R}$	0.95	0.5	0.6	0.4	8
CCl_4	$\Delta\nu_{CO}^{c} = -0.7 + 4.9\sigma^{o} + 5.6\sigma_R^{+}$	0.99	0.3	0.4	0.5	8
CCl_4	$\Delta\nu_{CO}^{c} = 0.4 + 3.4\mathcal{F} + 8.9\mathcal{R}$	0.96	0.5	0.7	0.9	8
C_2Cl_4	$\Delta\nu_{CO}^{t} = 0.9 + 4.8\sigma^{o} + 17.1\sigma_R^{+}$	0.98	0.3	0.7	1.5	6
C_2Cl_4	$\Delta\nu_{CO}^{t} = -1.1 + 5.4\mathcal{F} + 6.7\mathcal{R}$	0.71	3.2	1.4	4.5	6
C_2Cl_4	$\Delta\nu_{CO}^{c} = 0.5 + 9.5\sigma^{o} + 8.5\sigma_R^{+}$	0.80	3.0	1.4	4.6	6
C_2Cl_4	$\Delta\nu_{CO}^{c} = -0.3 + 7.5\mathcal{F} + 7.5\mathcal{R}$	0.88	0.3	1.5	1.4	6
	2-Thienalacetones					
CCl_4	$\Delta\nu_{CO}^{t} = -0.3 + 8.6\sigma^{o} + 5.9\sigma_R^{+}$	0.92	1.1	3.6	1.9	6
CCl_4	$\Delta\nu_{CO}^{t} = -2.1 + 5.4\mathcal{F} + 6.1\mathcal{R}$	0.79	2.1	9.6	4.8	6
CCl_4	$\Delta\nu_{CO}^{c} = 0.1 + 9.6\sigma^{o} + 3.2\sigma_R^{+}$	0.94	0.9	0.9	0.7	6
CCl_4	$\Delta\nu_{CO}^{c} = 0.9 + 5.4\mathcal{F} + 11.9\mathcal{R}$	0.84	1.1	1.6	4.6	6
C_2Cl_4	$\Delta\nu_{CO}^{t} = -0.1 + 8.2\sigma^{o} + 3.4\sigma_R^{+}$	0.99	0.2	0.5	0.3	6
C_2Cl_4	$\Delta\nu_{CO}^{t} = -0.4 + 5.4\mathcal{F} + 9.3\mathcal{R}$	0.87	0.2	1.4	2.0	6
C_2Cl_4	$\Delta\nu_{CO}^{c} = 0.0 + 8.6\sigma^{o} + 3.5\sigma_R^{+}$	0.98	0.2	0.9	0.7	6
C_2Cl_4	$\Delta\nu_{CO}^{c} = 0.2 + 5.0\mathcal{F} + 13.1\mathcal{R}$	0.88	0.2	1.4	5.6	6

C = the correlation coefficient; s_a, s_b, s_c = mean-square errors of parameters a, b, c; n = number of points.

In the case of 2-thienylideneacetones (VIII-XIII) for ν_{CO} values measured in CCl_4 in particular, the corresponding reaction constant m for the s-cis-isomers on the contrary

turned out to be somewhat higher than those for the s-trans--formations (the $m_{s\text{-}cis}$ / $m_{s\text{-}trans}$ ratio being 1.16-1.18). For ν_{CO} VIII-XIII in the tetrachlorethylene solutions m values are practically equal for both conformers, though here too the tendency may be observed to a somewhat higher sensitivity of the s-cis-form carbonyl frequencies to the influence of the substituents in comparison with the s-trans-isomers.

The application of two-parameter equations of the Yukava--Tsuno (1) or Swain-Lupton (2) type

$$\Delta\nu_{CO} = \Delta\nu_{CO}^{H} + m_o\sigma^{o} + m_R\sigma_R^{+} \qquad (1)$$

$$\Delta\nu_{CO} = \Delta\nu_{CO}^{H} + fF + rR \qquad (2)$$

(where σ^{o} are the constants characterizing the inductive influence of the substituted phenyl, σ_R^{+} characterizes the ability of the substituent to direct polar conjugation with the reaction centre, F and R = the constants characterizing the so-called field and resonance effects of the substituents; m_o, m_R, f and r = coefficients of sensitivity to the above-mentioned effects, respectively)

does not essentially improve the correlation coefficients as compared to those for Hammett, Taft, Brown equations (cf. Tables 2 and 3). However, the data given in Table 3 show that of the two types of two-parameter correlation equations for the carbonyl frequencies of benzylidene - and 2-thienylidene-acetones the application of the Yukava-Tsuno type of equation is more preferable. A similar phenomenon is noted for the acetyl derivates of thiophene as well /21/. Comparatively low correlation coefficients in many cases and appreciable errors of the calculated parameters of the correlation equations 1 and 2 (probably due to insufficient number of data and small changes in ν_{CO} values together with a large absolute error in their determination) do not enable one to draw an unambiguous conclusion as to the relative part played by individual components of the electronic effects of the substituents (induction and conjugation effects) in the investigated reaction series. Nevertheless in most cases as in the case of the application of the monoparameter equation one may observe the

tendency to a higher sensitivity of the carbonyl frequency of the s-trans-conformers in the benzylideneacetone series and the s-cis-form in the case of their thiophene analogs - to the influence of the substituents.

To characterize the influence of the vinylene grouping in the studied compounds we compared the carbonyl frequencies of benzylidene- and 2-thienylideneacetones with ν_{CO} of the substituted acetophenones and 2-acetylthiophenes /21/. Such a comparison shows a somewhat different influence of the introduction of the vinylene grouping on ν_{CO} values. E.g., in the case of acetophenones the introduction between the benzene nucleus and acetyl group of a double bond in the s-trans-position to the carbonyl group leads to a considerable decrease of the ν_{CO} values (by 7-12 cm^{-1}), while for the s-cis-conformers the opposite phenomenon is observed (cf., for example, ν_{CO} 1691 cm^{-1} of acetophenone and the same value for I, Table 1). If the first of these facts can be accounted for by the conjugation of the vinylene group with the carbonyl one /22/, the second can be attributed to the direct interaction through the space (the field effect) of the β-hydrogen atom and the carbonyl oxygen present in the s-cis-conformers:

$$\overset{\delta+}{C} \approx C - C \approx O^{\delta-}$$

It is not excluded either that the s-cis- and s-trans-conformer molecules are not equally coplaner.

In the 2-thienylideneacetone series the introduction of the vinylene group leads, as a rule, to the increase of ν_{CO} values of either conformers, as compared to the corresponding substituted 2-acetylthiophenes. The increase is however considerably higher for the s-cis-form, than for the s-trans-form (cf., for example, ν_{CO} values of VIII and of 2-acetylthiophene, 1672 cm^{-1} /21/). This fact is in keeping with the considerations mentioned above.

We have also carried out a comparison of the values of the reaction constants for acetophenones and acetylthiophenes (solutions in CCl_4) /21/ and the corresponding values for both of conformers of their vinylogs (Table 2). Such a compa-

rison makes it possible to determine the vinylene group transmission factor:

$$\pi' = \frac{m_{R-CH=CH-CO-CH_3}}{m_{R-CO-CH_3}}$$

If one takes into account only those reaction series for which the correlation coefficient (in monoparameter equations) is not less than 0.94, the π' value for the s-trans-benzylideneacetones is 0.57-0.58, and for their s-cis-form it is 0.51. In the thienylideneacetone series the π' value for the s-trans-conformers (0.34-0.37) is considerably lower than for benzylideneacetones, while the s-cis-vinylene group transmission factor is 0.40-0.46. These data suggest that the tendency mentioned above of a lower sensitivity to the substituent effects of s-trans-2-thienylideneacetones ν_{CO} values as compared to their s-cis-conformers as distinguished from the opposite tendency in benzylideneacetone series is connected above all with the different transmission of the vinylene grouping electronic effects in both conformers. It may well be that in replacing the benzene nucleus by the thiophene one the steric hindrance should increase (between β-hydrogen atoms of the s-trans-vinylene group and those of the thiophene cycle), which in its turn decreases the coplanarity of these molecules and, consequently, the conjugation degree as well. Such above-mentioned facts as the decrease of K=D ν_{CO} s-trans / /D ν_{CO} s-cis values in passing from benzylidene- to 2-thienylideneacetones, the frequency increase of the carbonyl group valency vibrations of s-trans-2-thienylideneacetones as compared to similar 2-acetylthiophenes are also in agreement with this assumption.

Thus, with the help of the correlation analysis of the ν_{CO} values it was proved possible to reveal some specific differences in the transmission of substituent effects in the molecular systems of benzylidene- and 2-thienylideneacetone s--trans and s-cis-conformers, which are probably connected with some peculiarities of their stereochemistry (the degree of planarity of these systems, the proximity in space of the polar and easily polarized vinylene and carbonyl groups).

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REACTIVITY OP COMPOUNDS WITH DIARYLMETHYLOL GROUP. XXV USE OF CORRELATION EQUATIONS FOR STUDYING I,I-DIARYL-2(N-BENZYLAMINE)ETHANOL IONIZATION IN SULPHURIC ACID

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The ionization of I,I-diaryl-2(N-benzylamine)ethanols has been investigated. The nature of ions formed in concentrated H_2SO_4 is defined making use of the correlation equations. It is shown that the ionization results in forming either doubly charged carbeneammonium ions or singly charged carbenium ions depending on the medium acidity and benzene ring substituents of the diarylmethylol group.

Influenced by H_2SO_4 I,I-diaryI-4-phenylbutanols-I and N-(ω-phenylalkyl)amides of diarylglycolic acids are known to be capable of closing cycles by the intramolecular way.[I] Since in this case the intermediates are carbene ions it is necessary to know the ionization constants of these compounds in concentrated H_2SO_4.

This paper deals with the ionization of I,I-diaryl-2(N-benzylamine)ethanole in the (96% H_2SO_4 + 4% H_2O) - CH_3COOH system.[2]

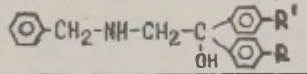
Experimental

The synthesis of 1,1-(N-benzylamine)-ethanols has been described elsewhere.[3] To obtain products with melting points within 1+0.5°C the compounds were purified by recrystallization from suitable solvents. Maximum

equilibrium values of optical density were determined in a way described earlier.[4] Values of λ_{max} associated with measuring optical density and lgε are given in Table I.

Table I

Values of λ_{max} and lg ε for I,I-DiaryI-2(N-benzylamine) ethanols I-X in the (96% H_2SO_4 + 4%H_2O) - CH_3COOH System



N comp.	R	R'	H_2SO_4 concentration %	λ_{max} (nm)	lgε
II	H	CH_3	84-92	430	4.040
III	H	C_2H_5	86-94	475	4.276
IV	H	C_3H_7	86-94	480	4.021
V	H	CH_3O	60-68	455	4.125
VI	H	C_2H_5O	60-68	450	4.090
IX	Br	CH_3	86-94	508	4.236
X	Br	CH_3O	62-70	498	3.955
XIII	CH_3O	CH_3O	50-62	540	4.108

Spectrophotometric measurements have been made with a spectrophotometer, type SF-4, at 20 $\pm$ I°C without using a thermostat.

Results and Discussions

The ionization of I,I-diaryl-2(N-benzylamine)ethanols-I in acidity range within the reach of study (H_R from -5 to -I8) should be determined by two basic factors - the effect of a protonized amine group diminishing strongly the basicity of alcohol hydroxyl, and the nature of substituents in aromatic rings of the diarylmethylol group. This is confirmed by behaviour of solutions of compounds I-XIII in the medium of varying acidity. For example, solutions of Comp. I,VII,VIII,XI and XII do not show the halochromic colour even with the highest concentrations of H_2SO_4 being available. This points to the fact that the ionization does

not take place or is negligible. The other compounds gave coloured solutions during the experiment. Indicator ratios (Q) were measured and the correlation (H_R, lgQ) parameters were estimated for them (Table 2).

Table 2

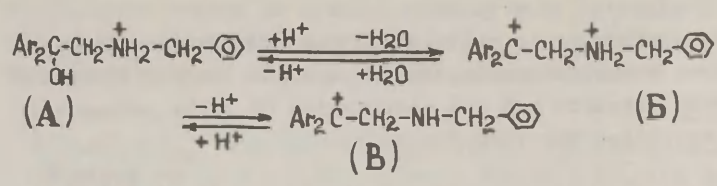
Correlation Parameters of lgQ vs. H_R

Compound	a	b	pK_R^+	r	s	n
II	I6.77	I.020	I6.44	0.998	0.036	5
III	I5.87	0.970	I6.36	0.997	0.050	5
IV	I6.09	0.986	I6.32	0.999	0.030	5
V	II.80	0.967	I2.20	0.994	0.052	5
VI	II.82	0.969	I2.20	0.997	0.037	5
IX	I5.82	0.955	I6.57	0.998	0.04I	5
X	II.42	0.942	I2.I2	0.994	0.056	5
XIII	I0.30	0.906	II.I8	0.999	0.020	5
		0.964				

The table illustrated that these compounds behave in the same manner as carbinol bases do. Thus, the average value of the slope of $lgQ = f(H_R)$ is 0.964.

The pK_R^+ values for compounds II-IV, IX and XIII, estimated from equation $lgQ = a + bH_R$ are in good correlation with σ^+ - constants according to equation $pK_R^+ = -4.02\Sigma\sigma^+ - I7.47$ (I) (r=0.997, s=0.I62). Points for compounds V, VI and X in coordinates σ^+, pK_R^+ of the plot have a deviation of 2-3 pK_R^+ units upwards from this relation. Such pronounced deviations have been reasoned after analyzing the data on ionization of the studied compounds with the help of equations of correlation obtained before.[5]

The ionization equilibrium of compounds I-XIII in H_2SO_4 may be presented by the following scheme:



It is believable a priori that the equilibrium state in this system is apparently dependent on the medium acidity, the nature of Ar and the degree the nitrogen atom is protonated. For example, there would be doubly charged ion Б in the medium of high acidity, no matter what is the nature of Ar determining the value of the positive charge on the carbocation centre. Under these conditions the departure of a proton from ammonium nitrogen is suppressed by the strong protonodonor ability of the medium. However, this ability being reduced, splitting out a proton is possible at a definite positive charge of the carbo-cation centre. In this case ion may arise. The decrease of the positive charge on the carbo-cation centre below a particular value and, as a consequence, the increase of the nitrogen atom basicity may be the cause of forming ion Б even at comparatively low acidity of the medium. The ionization of compounds I - XIII was studied on a basis of these general considerations.

To clear up what ions take part in the equilibrium, the ionization equations of I,I-di(p-anisyl) and I,I-di(p-tolyl) alkanols-I [5] were used. The pK_R^+ value for compound XIII (σ^* for $CH_2-\overset{+}{N}H_2-CH_2C_6H_5$ was taken to be equal to the value for $-CH_2-\overset{+}{N}(CH_3)_3$ viz.- 1.90[6]) estimated by equation $pK_R^+ = -1.76\,\sigma^* - 7.62$ (2) and being equal to -10.96 is in good agreement with the value found by experiment (-11.18).

Since there was no compound with two p-tolyl radicals at carbinol carbon in the investigated series, pK_R^+ value for it was estimated by the correlation equation (I) showing the ionization being influenced by substituents in aromatic rings of the diarylmethylol group (-14.97). At the same time proceeding from the assumption that the amine group is protonized ($\sigma^* = -1.90$[6]) and using Eq.(3), $pK_R^+ = 1.74\sigma^x - 12.04$,

characterizing the inductive effect of substituted alkyl radicals at carbinol carbon[5], we obtain $pK_R^+ = -15.34$ which is comparatively little to differ from the value estimated by Eq.(I).

Having performed similar calculations according to Eqs.(2) and (3) when ions A and B of compound X and I,I-di(p-tolyl)--2(N-benzylamine) ethanol-I are in equilibrium, we obtain pK_R^+ values being equal to -8.37 and -12.78, respectively.* They are significantly different from that found experimentally for compound X and estimated by Eq.(I) for I,I-di(p--tolyl)-2(N-benzylamine) ethanol-I (see above).

The nature of ions taking part in equilibrium during the ionization of compounds V,VI and X becomes clear when analysing experimental and estimated pK_R^+ values. If ions A and Б are in equilibrium, the ionization of compounds V,VI and X should be given by equation (I). However, the pK_R^+ values estimated for these compounds according to equation (I) are greatly different from those found experimentally (-I4.40 and -I2.20; -I4.48 and -I2.20; -I5.00 and -I2.I2 respectively). There is reason to believe that ions of compounds V, VI and X do not have any charge on the nitrogen atom (ions B). This assumption may be verified for compound X and with the help of equation (3) on the ground that the sums of electrophilic constants of substituents in the diarylmethylol groups ($\Sigma\sigma^+$) of this compound and in the reaction series of 1,1-di(p-tolyl)alkanols-I are practically equal ($\Sigma\sigma^+ = -0.6I4$ and -0.602[6] respectively).

What is more, the pK_R^+ values for ionizing compound X according to pattern (A)$\rightleftarrows$(Б) estimated by equations (I) and (3) (-I5.00 and -15.35) and being in admissible agreement also demonstrate that the use of equation (3) for presenting the ionization of compound X in sulphuric acid is quite lawable. Comparison of pK_R^+ values estimated by equation (3) for

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* In view of the fact that we have not found the σ^* value for $CH_2NHCH_2C_6H_5$ in the literature, the latter was equated to σ^* for CH_2NHCH_3(0.427), estimated from σ^* for $NHCH_3$[6] with the use of transmission ratio $\mathcal{Z}^*_{CH_2} = 0.388$.[7]

equilibria (A)⇄(B) and (A)⇄(B) enables one to specify ionization diagram of compound X . The pK_R^+ value for ionizing compound X according to the first pattern is -I2.78 and according to the second one it is - 15.35, whereas the value found experimentally is -I2.I2.

The calculations given above reveal that formation of a single-charge carbenium ion(B)(see the scheme above) is the most probable type of ionizing the compound X.

It is evident that a similar conclusion may be drawn about the nature of ions derived by ionization from compounds V and VI under experimental conditions. True, the equations (3) used for calculation of pK_R^+ values when ionizing nitrogen protonized and non-protonized forms of these compounds, are less proper than for compound X, since differences between $\Sigma\sigma^+$ of substituents in diarylmethylol groups of compounds V and VI, on one hand, and I,I-di(p-tolyl) alkanols-I, on the other hand, are greater than for compound X.

However, the results estimated by equation (I) and presented above in correlation with the experimental data give every reason to believe that during ionization of compounds V and VI ions B are formed as well.

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INTRAMOLECULAR INTERACTIONS IN AMINOAMIDES OF SUBSTITUTED BENZOIC ACIDS

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In the present work it is shown that the nature of substituent in para-position of the aromatic ring of substituted benzoic acids substantially affects diethylamine group basicity of p-$XC_6H_4CON(R)CH_2$-$CH_2N(C_2H_5)_2$ aminoamides. The electronic influence of substituents is transmitted, for monosubstituted amides, via the intramolecular hydrogen bonds of N-H...:$N(C_2H_5)_2$ type and, for disubstituted amides, via the direct dipole-dipole interaction between the carbonyl and amine groups. The pK_a values for both reaction series correlate with the Hammett σ-constants.

It is known that the substitution of hydrogen at the amide nitrogen for the hydrocarbon residue in amide of diaryl glycolic acids substantially affects the spectral characteristics[1], basicity of alcoholic hydroxyl[2] and intramolecular cyclization rate[3].

It might be suggested that such substitution would also influence the amine group basicity in aminoamides. In order to verify the suggestion we studied infrared spectra and basicity of a series of N-diethylaminoethylamides of substituted benzois acid of a common formula p-$XC_6H_4CON(R)CH_2CH_2N(C_2H_5)_2$ (I-XIII) where in the first reaction series R=H; X=H(I), CH_3(II), CH_3O(III), Cl(IV), Br(V), NO_2(VI), NH_2(VII) and in

the second reaction series R=CH_3, X=H(VIII), CH_3(IX), CH_3O(X), Cl(XI), Br(XII), NO_2(XIII).

Experimental

Compounds I-XIII were synthesized by the method of Lüning.[4] Compounds VIII-XIII, not described in the literature, are given in Table I.

Ionization constants were determined by potentiometric titration of compound samples in absolute ethanol with 0.I N $HClO_4$ in the same solvent. The titration was performed with a potentiometer ЛПМ-60М with a standard glass electrode and a silver/silver-chloride electrode filled with saturated solution of KCl in absolute ethanol. The potentiometer was adjusted and the pK_a value and meansquare error were calculated as shown by Albert and Serdgent[5]. The pK_a value for triethylamine, after Exner[6] equal to 8.33, served as a reference point for comparison of ionization constants obtained.

The infrared spectra for 0.01 M solutions of the bases of the synthesized compounds were taken on spectrometer UR-20.

Discussion

The infrared spectra of compounds I-IV indicate the presence of intramolecular hydrogen bonds (IHB) of N-H...: $N(C_2H_5)_2$ type (bands at 3335-3280 cm^{-I}). The compounds VIII-XIII do not adsorb in this range. Substitution of hydrogen at the amide nitrogen for methyl group results in reduction of the valence vibration frequency (νc=o) which is in accordance with the data obtained by other authors[7]. At the same time νc=o in both series as it is seen in Table 2 in which the infrared spectra and ionization constants of the compounds are given, depends on the nature of substituents in the aromatic ring para-position and increases or decreases depending on the electron-donating and electron-withdrawing properties of the substituents.

Table 1

$p\text{-}XC_6H_4CON(CH_3)CH_2CH_2N(C_2H_5)_2$ (VIII - XIII)

Comp.	X	Yield %	b.p. °C/mm	n_D^{20}	Calcd. N,%	Formula	Found N,%
VIII	H	85.2	165/4	1.5162	11.96	$C_{14}H_{22}N_2O$	12.06; 12.20
IX	CH_3	80.7	181-2/6	1.5194	11.28	$C_{15}H_{24}N_2O$	11.13; 11.20
X	CH_3O	83.5	203/6	1.5262	10.60	$C_{15}H_{24}N_2O_2$	10.90; 10.82
XI	Cl	74.6	187/5	1.5348	10.44	$C_{14}H_{21}ClN_2O$	10.60; 10.52
XII	Br	86.3	213/10	1.5420	8.94	$C_{14}H_{21}BrN_2O$	8.97; 8.90
XIII	NO_2	70.0	125-7° (acetone)	---	8.88	$C_{14}H_{22}ClN_3O_3$	8.92; 8.74

Compound XIII is a hydrochloride

Table 2

Infrared Spectra and Ionization Constants of Compounds I-XIII

Comp	$\nu_{cm^{-1}}$	pK_a	Comp.	$\nu_{cm^{-1}}$	pK_a
I	3415.3320.1678	7.18±0.01	VIII	1645	6.76±0.01
II	3415.3330.1678	7.25±0.01	IX	1642	6.84±0.01
III	3415.3330.1675	7.30±0.02	X	1640	6.90±0.02
IV	3415.3335.1682	7.05±0.03	XI	1647	6.63±0.03
V	3415.3335.1684	7.07±0.02	XII	1647	6.68±0.03
VI	3400.3280.1687	6.88±0.01	XIII	1650	6.43±0.01
VII	---	7.42±0.01	-	-	-

The data obtained by infrared spectroscopy do not allow us to regard these variations of $\nu_{C=O}$ as a result of action of any additional mechanisms transmitting the influence of substituents; thus, they may be interpreted in generally accepted terms[8].

It is probable that more reliable information about intramolecular interactions in the compounds of both reaction series may be obtained in studies of basicity of amine groups. It might be expected that owing to the absence of IHB basicity of the aminogroups of the second reaction series compounds would be higher than basicity of the corresponding first reaction series compounds.

But what we actually observed was contrary to expectation (see Table 2) and despite of a considerable distance from the centre the substituent effect in the second reaction series showed itself rather distinctly.

This fact may be explained by admitting existance of direct interaction between the amine group and carbonyl carbon in the second reaction series. The possibility of such intramolecular interaction in open chain compounds has frequently been discussed in the literature [9-14] but the conclusions on the question are contradictory in some cases. Thus, according to Bogatkov et al.[9] in β-aminoketones, $R\text{-}C_6H_4COCH_2\text{-}CH_2N(CH_3)_2$, the methyl group in β-position respective to the amine group leads to an increase of the nitrogen-carbonyl interaction. But Kuznetsov[11] has pointed out that the probability of such interaction in open chain aminoketones is rather small. The results obtained in studies of hydrolysis kinetics and of the carbonyl band properties in infrared spectra of aminoalcohol esters[12] cast doubt on any direct interaction between the amine and carbonyl groups suggested by Kundryutskova et al.[13]. It is obvious that this effect is more distinct in the aminoamide series.[10]

From Table 2 it follows that the pK_a values in both reaction series depend on the nature of substituents in the aromatic ring, the difference in pK_a for most strong electron-donating and electron-withdrawing groups (VII and VI, X and

XIII) reaching as much as 0.5 unit. The distance of substituents from the reaction centre being considerable, the difference cannot be attributed to the induction effect. The probable ways of transmitting the influence of substituents are IHB (1-st reaction series) and direct dipole-dipole interaction between the carbonyl and amine groups (2-nd reaction series). In this case substituent in the benzene ring will influence the positive charge value of the carbonyl group carbon causing increase or decrease in the IHB or dipole-dipole interaction between corresponding groups in the 1-st and 2-nd series. It is probable that this influence is analogous to that observed at ionization of benzoic acids. Indeed, the pK_a values for both reaction series correlate quite satisfactorily with the Hammett σ-constants by equations (I) and (2).

$$pK_a = -0.396\sigma + 7.18 \quad (r=0.980,\ s=0.033) \ldots \quad (I)$$

$$pK_a = -0.446\sigma + 6.76 \quad (r=0.989,\ s=0.023) \ldots \quad (2)$$

This may be regarded as a confirmation of the above suggestions about the mechanism of transmission of the substituent influence on the amine group basicity. It is probable that the possibility of dipole-dipole interaction between the carbonyl and amine groups in the second reaction series compounds results from the amide group relative conformational "toughness" which increases the probability of conformations which are favourable for intramolecular interactions. But in compounds of the first reaction series the dipole-dipole interaction may be hindered by the IHB between the amine group and hydrogen at the amide nitrogen.

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INVESTIGATION OF KINETICS OF ALKALINE HYDROLYSIS OF SUBSTITUTED PHENYL p-TOLUENE SULFONATES

IX Hydrolysis of o-COO^- - Phenyl p-Toluene Sulfonate. Quantitative Interpretation of Salt Effect by Electrostatic Model.

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The rates of the alkaline hydrolysis of o-COO^- - substituted phenyl p-toluene sulfonate in an aqueous solution at various concentrations of electrolyte at 30, 40, 50, 60, 75 and 85°C were measured. In the case of o-COO^- - phenyl p-toluene sulfonate the dependence of logk on the concentration of electrolyte added had two "plateaux" which made a difference comparing with data of all the substrates with charged substituents studied up to date. The values of second-order rate constants extrapolated to pure water, k_0, for the first plateau, $k_{\infty(1)}$, and for the second platean, $k_{\infty(2)}$, as well as corresponding activation parameters E_0, $E_{\infty(1)}$, $E_{\infty(2)}$, log A_0, log $A_{\infty(1)}$ and log $A_{\infty(2)}$ were calculated. An electrostatic model which takes into account the stepwise compensation of the electrostatic interaction present for the reaction between o-COO^- - phenyl p-toluene sulfonate and OH^- ions was suggested. The first plateau corresponded to the reaction between Na^+OH^- ion pairs and substrate RCO_2^-. At higher concentrations of electrolyte the equilibria of formation of both ion pairs, Na^+OH^- and $RCO_2^-.Na^+$ were shifted to the right and in the transition state of two Na^+ ions were present. The reaction between two ion pairs, Na^+OH^- and $RCO_2^-Na^+$,

corresponded to the second plateau. Using most plausible model tested for the transition state the calculated differences of electrostatic contribution of free energy gave the Δ logk values in quantitative accordance with experimental values for the differences $\log k_{\infty}$ (1) - $\log k_o$ and $\log k_{\infty}$(2) - $\log k_o$.

In our preceding papers 1-6 the results of investigation of the kinetics of alkaline hydrolysis of substituted phenyl p-toluene sulfonates and phenyl benzoates with charged substituents depending on the concentration of the neutral electrolyte added have been reported. It was shown that at higher concentration of electrolyte the rate constant reached a limiting value k_{∞}, which did not depend any more on the concentration of ions. It was stated[7] that k_{∞} was to be interpreted as the rate constant for a reaction in which it took part the ion pairs formed from the substrate and/or the reagent. In the same report the value of limiting salt effect, $\Delta \log k_{\infty} = \log k_{\infty} - \log k_o$, was interpreted as a measure of the changes in electrostatic contribution to free energy, $\Delta F^{\neq}_{el}$, due to increasing concentration of electrolyte.

Value of $\Delta F^{\neq}_{el}$ can be evaluated as follows:

$$\Delta F^{\neq}_{el} = q - q_o \qquad (1)$$

where q and q_o denote energies of electrostatic interaction between ionic charges present in the transition and initial state, respectively.

The q-values could be calculated using Eq.(2)

$$q = \frac{Ne^2}{\varepsilon} \sum_{i \neq j} \sum \frac{z_i z_j}{r_{ij}} \qquad (2)$$

where Ne^2=331 kcal/mol, z_i and z_j are ionic charges at atoms with subscripts i and j and r_{ij} is the distance between these charges (A^o). By $\mathcal{E}$ the macroscopic permittivity of solvent is denoted. The sets of ionic charges for substituent as well as for reaction centre include charges introduced by contra-ions present in ion pairs formed from ionic reagents.

The influence of the concentration of electrolyte added on the rate constants of the alkaline hydrolysis of m- and p- COO^- - phenyl p-toluene sulfonates has been reported previously.[6] A good accordance of experimental limiting salt effect, $\Delta \log k_\infty = \log k_\infty - \log k_o$, with the calculated values of electrostatic contribution to the logk value for the reaction between free ions has been observed. This fact can be interpreted as a result of nearly total compensation of electrostatic interaction between charged substituent and reaction centre provided the ion pairs of type $RCO_2^-.Na^+$ are the reactive species.

In the present work the influence of the neutral electrolyte added on the rates of the alkaline hydrolysis of o-COO^- - phenyl p-toluene sulfonate at different temperatures was investigated. An attempt to interpret quantitatively the peculiar result obtained (two plateaux observed in the plots of logk vs. electrolyte concentration) has been made making use of Eq. 11).

EXPERIMENTAL

o-COOH-phenyl p-toluene sulfonate was prepared from p-toluene sulfonyl chloride and salicylic acid in an alkaline aqueous solution similary with the preparation of m- and p-COOH-phenyl p-toluene sulfonates described previously.[6] M.p 154-157°C (154-156°C handbook[8]). Found %: C 57.86, 58.04; H 4.03, 4.16. Calculated %: C 57.52; H 4.12.

The method used for kinetic measurements has been previously described[2,9]. The alkaline hydrolysis of o-COO^- - phenyl p-toluene sulfonate in an aqueous solution was investigated. Various NaOH and neutral electrolyte concentrations at different temperatures were applied under pseudouni-molecular conditions. The range of NaOH concentrations and the conditions used for the spectrophotometric rate measurements are listed in table 1. NaCl was used most as neutral electrolyte added. At 75°C some experiments were carried out using $NaClO_4$, too.

The second-order rate constants k, were calculated from pseudo-first-order rate constants[1], k_I, $k=k_{I/C_{NaOH}}$.

The dependence of logk on the concentration of electrolyte (expressed conventionally in form of $\sqrt{\mu}$, where μ is the ionic strength) at 40, 50, 60, 75 and 85°C are shown in Fig. 1.

T a b l e 1

Conditions for Kinetic Measurements. The initial value of the extinction coefficient for o-COO^- - phenyl p-toluene sulfonate (25°C) $\varepsilon_0 = 0$; change of the extinction coefficient during the reaction $\Delta\varepsilon = 4500$; wave-lengthe 294 nm.

Temperature °C	Limits of NaOH concentration range, M
30.0	1.08 - 2.2
40,0	0.83 - 2.2
50.0	0.014- 1.65
60.0	0.016- 1.08
75.0	0.022- 0.46
85.0	0.016- 1.08

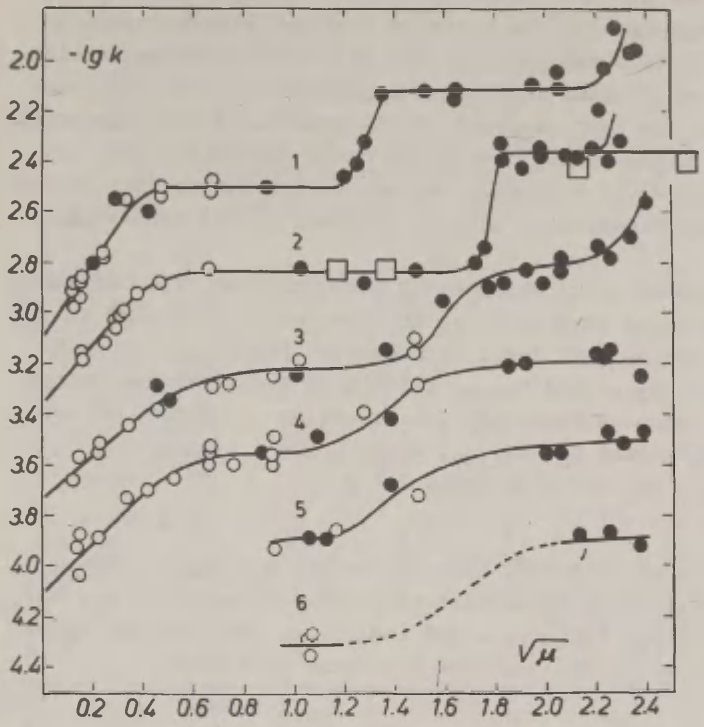


Fig. 1. Dependence of logk on $\sqrt{\mu}$ for the alkaline hydrolysis of o-COO^--phenyl p-toluene sulfonate 1:85°C; 2:75°C; 3:60°C; 4:50°C, 5. 40°C, 6. 30°C

○ = without NaCl

● = NaCl added

□ = $NaClO_4$ added

As we can see the curves for o-COO^-- phenyl toluene sulfonate representing the plots of logk vs. electrolyte concentration form two plateaux. For all other substrates with charged substituent investigated previously only one such a plateau has been observed. It is remarkable that the points obtained using $NaClO_4$ lie in the curve determined by the points for NaCl. Therefore one can be quite sure that anions of neutral electrolyte are not involved in the transition state.

The values of k_o obtained by ectrapolation of second-order rate constants to pure water from dependences of logk vs. $\sqrt{\mu}$, initial slope, φ, of these dependences; the values of rate constants $k_{\infty(1)}$ and $k_{\infty(2)}$ related to the first and second plateau, respectively; and corresponding parameters of Arrhenius equations E_o, $E_{\infty(1)}$, $E_{\infty(2)}$, $logA_o$, $logA_{\infty(1)}$, $logA_{\infty(2)}$, are given in Table 2.

T a b l e 2

Values of Slopes φ. Rate Constants, k_o, $k_{\infty(1)}$, $k_{\infty(2)}$ and corresponding Parameters of Arrhenius Equation, E_o, $E_{\infty(1)}$, $E_{\infty(2)}$, $logA_o$, $logA_{\infty(1)}$, and $logA_{\infty(2)}$, for Alkaline Hydrolysis of o-COO^- - Phenyl p-Toluene Sulfonate

Temperature °C	φ*	$k_o \cdot 10^4$ $M^{-1} \cdot sec^{-1}$	$k_{\infty(1)} \cdot 10^4$ $M^{-1} \cdot sec^{-1}$	$k_{\infty(2)} \cdot 10^4$ $M^{-1} \cdot sec^{-1}$
30.0			0.51±0.04	1.32±0.06
40.0			1.29±0.05	3.32±0.17
50.0	1.22±0.46	0.76±0.09	2.84±0.09	6.81±0.90
60.0	0.80±0.47	1.80±0.90	6.07±0.34	15.0 ±0.7
75.0	0.93±0.16	4.80±0.42	14.4 ±0.4	43.5 ±1.4
85.0	1.37±0.16	8.50±0.51	32.2 ±0.9	77.8 ±2.4

E_o=15.527 ± 569 $logA_o$ = 6.42 ± 0.37
$E_{\infty(1)}$=15.711 ± 343 $logA_{\infty(1)}$= 7.07 ± 0.23
$E_{\infty(2)}$=15.819 ± 200 $logA_{\infty(2)}$= 7.55 ± 0.13

*Experimental initial slope of the dependences of logk on $\sqrt{\mu}$

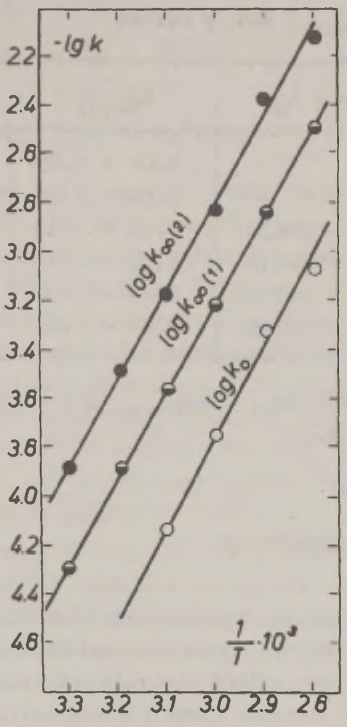


Fig. 2. Dependence logk on 1/T for the alkaline hydrolysis of o-COO^--phenyl p-toluene sulfonate

Limits of the $\sqrt{\mu}$ change used for calculation of values k_o, $k_{\infty(1)}$, $k_{\infty(2)}$ and φ are given in Table 3.

T a b l e 3

Range of Variable $\sqrt{\mu}$ Used in Calculating the k_o, $k_{\infty(1)}$, $k_{\infty(2)}$, and φ Values

Temperature °C	φ and k_o	$k_{\infty(1)}$	$k_{\infty(2)}$
30.0		1.04 - 1.05	2.10 - 2.20
40.0		0.90 - 1.20	1.80 - 2.50
50.0	0 - 0.330	0.60 - 1.10	1.70 - 2.60
60.0	0 - 0.240	0.70 - 1.40	1.80 - 2.20
75.0	0 - 0.330	0.65 - 1.50	1.80 - 2.30
85.0	0 - 0.235	0.60 - 1.20	1.40 - 2.20

The dependences of $\log k_o$, $\log k_{\infty(1)}$ and $\log k_{\infty(2)}$ on 1/T are represented in Fig. 2.

DISCUSSION

In the case of alkaline hydrolysis of m- and p-COO^- - phenyl p-toluene sulfonates the experimental difference $\Delta \log k_\infty = \log k_\infty - \log k_o$ and electrostatic contribution to the logk for the reaction between ions calculated from Eq.(1) were found to be very close to each other. This fact shows that the formation of ion pairs at higher concentration of electrolyte leads to $\Delta F^{\neq}_{el}=0$. This simple approach applied to o-COO^--phenyl p-toluene sulfonate enables us to estimate the limiting value of salt effect only. The presence of two plateaux can be considered as a result of the partial and stepwise compensation of the electrostatic interaction between charged substituent and reaction centre. Proceeding from this assumption corresponding calculation were carried

out for different plausible models of the transition state in reactions between free ions, the OH^- ion and ion pair RCO_2^-. Na^+, ion pair Na^+OH^- and substrate RCO_2^-, and ion pairs RCO_2^-. Na^+, and Na^+OH^-. The total reaction scheme was assumed as follows:

$$RCO_2^- + OH^- \xrightarrow{k_0} \quad (3)$$

$$RCO_2^- \cdot Na^+ + OH^- \xrightarrow{k_1} \quad (4)$$

$$RCO_2^- + Na^+OH^- \xrightarrow{k_2} \quad (5)$$

$$RCO_2^- \cdot Na^+ + Na^+OH^- \xrightarrow{k_3} \quad (6)$$

The values of q_0 and q were calculated using the computer "Nairi-2". The special programme has been prepared to calculate Cartesian coordinates of atoms in the molecule, the distances between those atoms and the sum of all coulombic interactions between ionic charges, localized on atoms. These calculations were performed using following sets of interatomic distances.[10] $C_{Ar}-C_{Ar}=1.40A^o$; $C_{Ar}-CO_2^-=1.48A^o$ (benzoic acid); $C_{sp^3}-O=1.23A^o$ (in the CO_2^- group); $S-O=1.70A^o$; $S=O(S^{2+}-O^-)=1.43$ (See Ref. 11,12); $C_{Ar}-O=1.47A^o$ (amino phenol) and of valency angles[10]: $\angle SOC_{Ar} = \angle C_{Ar}C_{Ar}O = \angle O_{Ar}O_{Ar}(CO_2^-) = \angle(OCO)^- = 120^o$.

In the model of the initial state a tetrahedric configuration for sulfur atom was accepted. In the model of the transition state the oxygen atoms of the $^{2+}S(O^-)_2OH$ group were symmertrically localized around the sulfur atom all in one and the same plane perpendicular to the plane defined with the help of atoms in the fragment, $S-O-C_{Ar}$, and to the phenylic cycle bonded to the sulfur atom (Table 5).

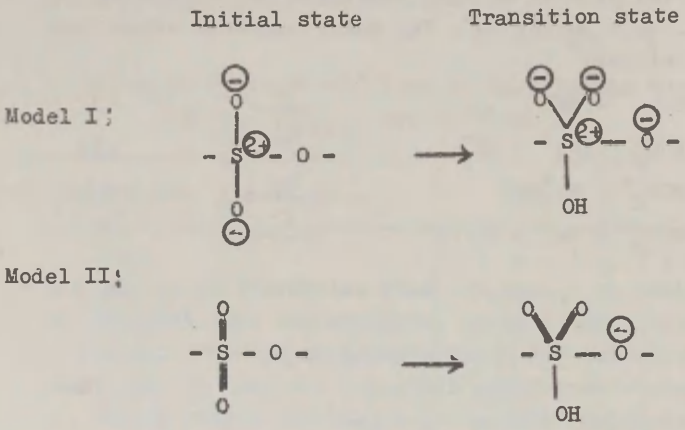
In the transition state the distance between the sulfur and the phenoxy oxygen atoms was assumed to be equal the arithmetical mean value calculated as follows:

$$r^{\neq}_{S-O^-} = \frac{r^k_S + r^k_O}{2} + \frac{r^v_S + r^v_O}{2} = 2.46A^o$$

By r^k_S and r^k_O the covalency radii of the sulfur and oxygen atoms use denoted respectively; r^v_S and r^v_O are the corresponding Van-der-Waals radii.

7

Two different models for the charge distribution of the reaction centre were tested:

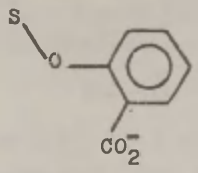


For reaction (5) the Na^+ ion present in the transition state at the reaction centre was considered to be located at equal distances from both the negatively charged oxygen atoms of the $^{2+}S(O^-)_2OH$ group.

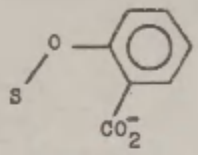
In the case of the model I (initial state) the oxygen atoms of the $^{2+}S(O^-)_2OH$ group were regarded as situated at the maximum distance from the CO_2^- substituent. In the model of ion pairs of type RCO_2^-. Na^+ the Na^+ ion was considered to be located in the same plane with the CO_2^- group at equal distances from both the oxygen atoms. For the Na^+ ion the cristallographic radius r_{Na^+} =0.98 A^o (see Ref. 10) and for oxygen atom the Van-der-Waals radius $r_{O^-}=r_O$=1,38A^o (see Ref. 13) were used. The distance between the centres of charges of opposite sign present in ion pairs Na^+OH^- was set equal to the sum of the values of r_{Na^+} and r_{O^-} (2,36)A^o).

For the initial and the transition state cis- and trans-conformations, caused by the rotation around the C_{Ar}-O bond

were considered:



trans



cis

Conformations with sulfur atoms shifted out of the plane of the o-C_6H_5 group were not considered.

For the reaction between ion pairs RCO_2^- . Na^+ and Na^+. OH^- different positions for the Na^+ ion in transition state were tested:

1. In one and the same plane with the phenylic cycle, the phenoxy oxygen atom and the CO_2^- group between negatively charged phenoxy and carboxy oxygen atoms (A).
2. In that plane at the negatively charged oxygen atom at the greatest possible distance from the CO_2^- group (B).
3. Between negatively charged oxygen atoms of phenoxy, CO_2^-, and $^{2+}S(O^-)_2OH$ groups in the plane perpendicular to the plane for phenylic cycle and the phenoxy oxygen atom (C).
4. Between negatively charged oxygen atoms of the $^{2+}S(O^-)_2OH$ group in the same plane with those and sulfur atom (D).

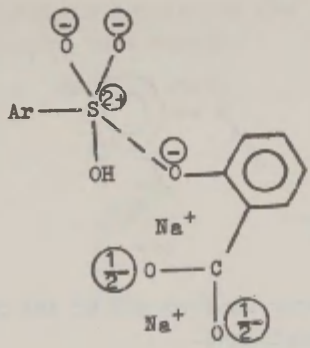
For models A, B C and D the trans-conformation was considered, only.

For model II different localizations for the second Na^+ ion in the transition state were tested as shown in schemes A, B and C.

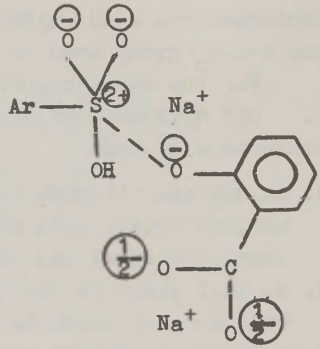
The q and q_0 values were calculated according to Eq(1) taking into account the temperature dependence of the macroscopic value of permittivity[14].

The values of $\Delta F^{\neq}_{el}$ (defined by Eq.(1)) for reactions (3)-(6) and different models and conformations were calculated. In the case of reactions (5) and (6) the electrostatic interaction in the ion pair Na^+OH^- initial state was taken

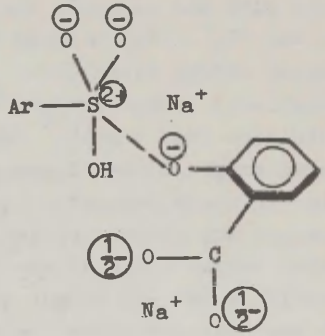
(A)



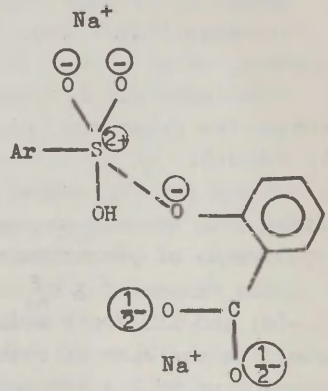
(B)



(C)



(D)



into account. The change in the electrostatic energy, $\Delta\Delta F^{\neq}_{el}$, due to the substituent effect, was calculated from the difference:

$$\Delta\Delta F^{\neq}_{el} = \Delta F^{\neq}_{el} - \Delta F^{\neq\,o}_{el}$$

where $\Delta F^{\neq\,o}_{el}$ is the change in the electrostatic energy for the unsubstituted compound (for model II $\Delta F^{\neq\,o}_{el}=0$)

From the $\Delta\Delta F^{\neq}_{el}$ values obtained the corresponding values of Δ logk or Δ logk(cis) and Δ logk(trans) were calculated:

$$\Delta \log k = -\frac{\Delta\Delta F^{\neq}_{el} - \Delta\Delta F^{o\neq}}{2.3\ RT}$$

$$\log k(cis) = -\frac{\Delta\Delta F^{\neq}_{el} - \Delta\Delta F^{o\neq}_{el}(cis)}{2.3\ RT}$$

$$\log k(trans) = -\frac{\Delta\Delta F^{\neq}_{el} - \Delta\Delta F^{o\neq}_{el}(trans)}{2.3\ RT}$$

in which $\Delta\Delta F^{\neq}_{el}$ is the change in the electrostatic energy for any reaction of the set (4)-(6), $\Delta\Delta F_{el}{}^{o\neq}$ or $\Delta\Delta F^{o\neq}_{el}$(cis) and $\Delta\Delta F^{o}_{el}$(trans) correspond to the reactions between two ions (reaction 3) in accordance with model II and with cis- and trans-conformations of model I, respectively. These calculated Δ logk values can be compared with the differences $\Delta \log k_{\infty(1)} = \log k_{\infty(1)} - \log k_{o}$ and $\Delta \log k_{\infty(2)} = \log k_{\infty(2)} - \log k_{o}$, calculated from the experimental data.

The total electrostatic contribution to the free energy of activation expressed in logk scale was calculated as follows:

$$\Delta \log k_{c}(calc) = -\frac{\Delta\Delta F^{o\neq}}{2.3RT}$$

The results of the calculations are listed in Table 4.

For the sake of well-defined localization of ionic charges for models A,B,C and for D of the transition state the Cartesian coordinates of the corresponding atoms are given in Table 5. The origin of coordinates was fixed at the carbon atom in o-position of the phenylic cycle (with index 1), the

Table 4

Experimental $\Delta \log k_{\infty\,(1)}$ and $\Delta \log k_{\infty\,(2)}$ Values and Calculated $\Delta \log k_o$, $\Delta \log k$, $\Delta \log k(cis)$ $\Delta \log k(trans)$ Values for Different Models of the Transition State. Numbers (1) and (2) in the first column correspond to the number of Na^+ ions in the transition state (for reactions involving ion pairs). For reaction (6) the first Na^+ ion is always localized at CO_2^- group, for the localization of second Na^+ ion different positions are considered (see Text).

Model	Quantity	Reaction	Temperature °C		
			30.0	50.0	85.0
Experiment [e]	$\Delta \log k_{\infty\,(1)}$ [f]		0.49[a]	0.57	0.59
	$\Delta \log k_{\infty\,(2)}$		0.89[a]	0.95	0.98
I, cis, (0)	$\Delta \log k_o$	3	-0.90	-0.93	-0.97
trans, (0)	$\Delta \log k_o$	3	-1,15	-1,18	-1.23
II	$\Delta \log k_o$	3	-1.02	-1.05	-1.10
I, cis, (1)	$\Delta \log k$ (cis)	4	0.30	0.32	0.33
	$\Delta \log k$ (trans)	4	0.55	0.57	0.59
trans, (1)	$\Delta \log k$ (cis)	4	0.50	0.52	0.53
	$\Delta \log k$ (trans)	4	0.75	0.76	0.79
II, (1)	$\Delta \log k$	4	0.66	0.68	0.71

I, trans, (1)	Δ logk (cis)	5	0.24	0.25	0.26
	Δ logk (trans)	5	0.49	0.50	0.52
I, trans, (2), A	Δ logk (cis)	6	0.70	0.73	0.75
	Δ logk (trans)	6	0.95	0.98	1.01
I, trans, (2), B	Δ logk (cis)	6	0.25	0.25	0.27
	Δ logk (trans)	6	0.50	0.50	0.53
I, trans, (2), C[b]	Δ logk (cis)	6	1.01	1.05	1.09
	Δ logk (trans)	6	1.26	1.28	1.35
I, trans, (2), C[c]	Δ logk (cis)	6	0.81	0.84	0.88
	Δ logk (trans)	6	1.06	1.09	1.14
I, trans, (2), C[d]	Δ logk (cis)	6	0.88	0.91	0.95
	Δ logk (trans)	6	1.13	1.16	1.21
I, trans, (2) D	Δ logk (cis)	6	0.59	0.61	0.64
	Δ logk (trans)	6	0.84	0.86	0.89
II, trans, (2), A	Δ logk	6	0.44	0.45	0.47
II, trans, (2), B	Δ logk	6	0.19	0.20	0.21
II, trans, (2) C[b]	Δ logk	6	0.34	0.36	0.38

[a]Calculated from data at higher temperature using Arrhenius equation
[b]Distance $Na^+(10) - \bar{O}(3) = 2.36A^\circ$; $\angle Na^+(10)\bar{O}(3)\ C(2) = 140^\circ$
[c]Distance $Na^+(10) - \bar{O}(3) = 2.36A^\circ$; $\angle Na^+(10)\bar{O}(3)\ C(2) = 90^\circ$
[d]Distance $Na^+(10) - \bar{O}(3) = 1.85A^\circ$; $\angle Na^+(10)\bar{O}(3)\ C(2) = 150^\circ$
[e]Configuration (cis, trans) for the reactive compound is shown
[f]Configuration (cis, trans) for the reaction (3) is shown

Table 5

Cartesian Coordinates of Charged Atoms for Transition State in Accordance with Models A,B,C, and D

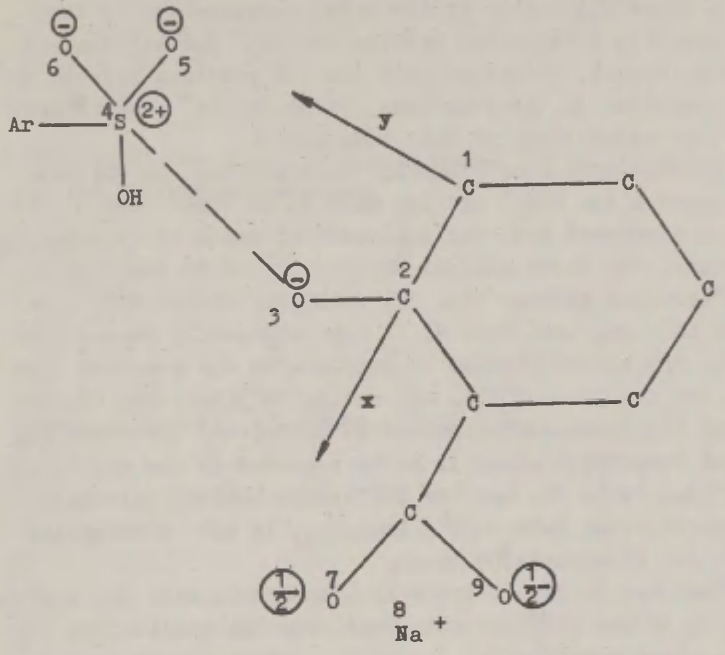
Indexes of atoms and models	X	Y	Z
O^- (3)	2.135	1.273	0
S^{2+} (4)	0.905	3.404	0
O^- (5)	-0.167	2.784	-0.715
O^- (6)	1.978	4.023	-0.715
$O^{1/2-}$ (7)	4.175	-0.147	0
Na^+ (8)	6.240	-1.212	0
$O^{1/2-}$ (9)	4.175	-2.278	0
Na^+ (10), A	4.371	2.087	0
Na^+ (10), B	-2.049	0.907	0
Na^+ (10), C^a	3.047	2.852	-1.530
Na^+ (10), C^b	2.135	1.273	-2,380
Na^+ (10), C^c	3.315	3.334	-1.552
Na^+ (10), D	0.863	3.380	-2.776

[a] Distance $Na^+(10)$-O(3)=2.36A°; $\angle Na^+(10)\bar{O}(3)C(2)=140°$

[b] Distance $Na^+(10)$-$\bar{O}$(3)=2.36A°; $\angle Na^+(10)\bar{O}(3)C(2)= 90°$

[c] Distance $Na^+(10)$-$\bar{O}$(3)=2.85A°; $\angle Na^+(10)\bar{O}(3)C(2)=150°$

X-axis proceeds along the bond between carbon atoms with indexes 1 and 2, the x,y plane was determined by atoms with indexes 1,2 and 3. The Z-axis was directed perpenticularly down from this plane.



Examination of the data from Table 4 enables us to draw following conclusion.

1. Using model II for the reaction centre it is impossible to explain the presence of two plateaux characteristic for the experimental dependence of logk on $\sqrt{\mu}$.

2. Calculated value of $\Delta \log k_o$ for cis-conformation is in good agrement with the experimental value of $\Delta \log k_\infty$ (2)

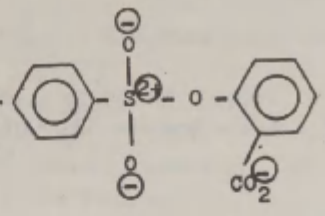
Nevertheless, the absolute F values calculated show that the trans- conformation is more stable. Consequently, the latter is to be considered more plausible. The calculated value of $\Delta \log k_o$ for trans-conformation exceeds the $\Delta \log k_{\infty\,(2)}$ value. Therefore one can say the presence of two Na^+ ions in the transition state for the reaction between ion pairs (reaction 6) does not result in the total compensation of the electrostatic interaction between the CO_2^- substituent and reaction centre, characteristic for the reaction between two ions (reaction 3). Nevertheless, these two Na^+ ions compensates the major part of this interaction.

3. The calculated value of $\Delta \log k$(trans) of the reaction between ion RCO_2^- and ion pair Na^+OH^- (reaction 5) is in good agreement with the experimental value of $\Delta \log k_{\infty\,(1)}$. Evidently, the first plateau may correspond to reaction 5. But a parallel pathway viz. the reaction between RCO_2^-. Na^+ on the OH^- ions (reaction 4) is not necesserily impossible.

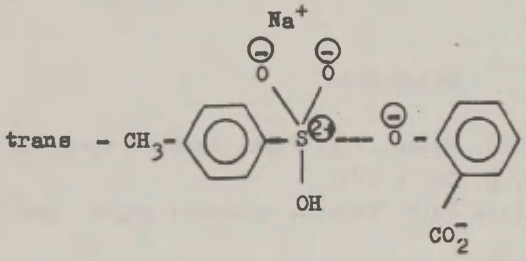
4. The second plateau corresponds to the reaction between two ion pairs RCO_2^-. Na^+ and Na^+OH^- (reaction 6). As much as the trans-conformations is considered structure (A) for the transition state is to be regarded as the most plausible (see Table 4). But the difference between calculated and experimental values of $\Delta \log k_{\infty\,(2)}$ is not substantial either for structures (C) and (D).

The results of our investigation demonstrate the applicability of the electrostatic model for the qualitative (two plateaux) and quantitative (heights of these plateaux) interpretation of the dependence of the rate constants of the alkaline hydrolysis of o-COO^--substituted phenyl p-toluene sulfonate upon the concentration of neutral electrolyte. It is also possible to draw some conclusions on the detailed structure of the initial and transition states. The most probable scheme for processes determining the peculiarity and the parameters of total reaction can be represented by the sum of reactions (3), (5) and (6) with following specifications:

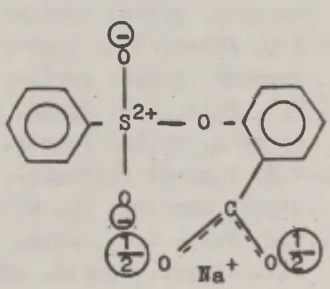
a) RCO_2^- = trans - CH_3 -



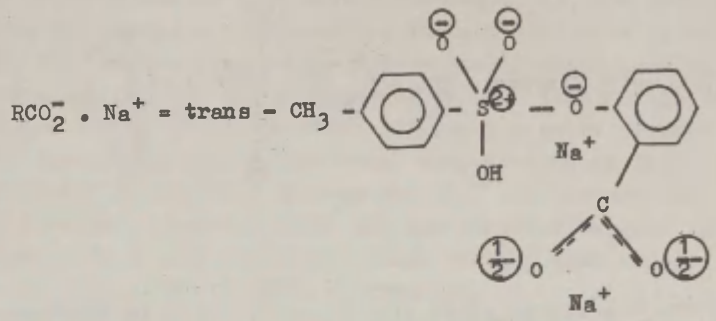
b) The transition state of the reaction (5) is expressed by the following structure:



c) $RCO_2^- \cdot Na^+$ = trans - CH_3-



d) The transition state of reaction (6) is expressed by the structure:



It is not superfluous to mention that the primary salt effect as additionaly shown in the present work cannot be described even qualitatively in terms of Debye-Hückel--Brönsted

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INVESTIGATION OF KINETICS OF ALKALINE HYDROLYSIS OF SUBSTITUTED PHENYL p-TOLUENE SULFONATES

X Hydrolysis of o- and p-SO_3^--Phenyl p-Toluene Sulfonates at Various Temperatures in Water

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The rates of the alkaline hydrolysis of o- and p-SO_3^- -substituted phenyl p-toluene sulfonates at 40, 50, 60, 75 and 85°C were measured. The influence of the electrolyte added was studied at 60 and 85°C. No considerable dependence of the values of the second-order rate constants on the added electrolyte concentration in the range of 0.004 to 4.5 M was dedected.

From the second-order constants the values of activation parameters E and logA, as well as the σ^o constants for o- and p-SO_3^- - phenyls were calculated.

In our preceding papers [1-7] the investigation of the dependences of the alkaline hydrolysis rates of o-, m-, p-$N(CH_3)_3^+$-, o-, m-, p-O^- -, o-, m- and p-CO_2^- - phenyl p-toluene sulfonates, m-, p-$N(CH_3)_3^+$ -; m- and p-O^- - phenyl benzoates, and $N(CH_3)_3^+$ - substituted alkyl benzoates on the concentration of neutral electrolyte added, have been reported. In most cases at the higher electrolyte concentration the rate constant reached a limiting value, k_∞, which did not depend any more on the concentration of ions. However, no considerable dependence of the alkaline hydrolysis rates of o- and p-O^- - phenyl p-toluene sulfonates on the added neutral

electrolyte concentration was observed.[2]

It was stated[8] that the value of the limiting salt effect, $\Delta\log k_{\infty} = \log k_{\infty} - \log k_{o}$, was to be interpreted as the difference between the reactivity of free ions and ion pairs or other interionic associates. The limiting change in logk, $\Delta\log k_{\infty}$, should be calculated, as an electrostatic contribution to the free energy of activation expressed in the logk scale.

This study was undertaken in order to get information on the influence of the neutral electrolyte added upon the alkaline hydrolysis rate constants of o- and p-SO_3^- -substituted phenyl p-toluene sulfonates.

p-SO_3Na - phenyl p-toluene sulfonate was prepared from p-toluene sulfonyl chloride and Mg-salt of phenol-p- sulfonic acid.[9] Found %: C 43.62; 43.36; H 3.21; 3.15. Calculated %: C 44.57; H 3.17.

o-SO_3K-phenyl p-toluene sulfonate was prepared by an analogous way from K-salt of phenol-o-sulfonic acid. Found %: C 42.22; 41.97; O 28.18; H 3.27; 3.26. Calculated %: C 42.74; O 26.30; H 3.01.

The method used for kinetic measurements has been previously described.[10] The alkaline hydrolysis rates of o- and p-SO_3^-- phenyl p-toluene sulfonates in an aqueous solution at various NaOH concentrations was investigated under pseudo-unimolecular conditions at 40, 50, 60, 75 and 85°C. The dependence of the rate constant on the electrolyte concentration was examined at 60 and 85°C. NaCl was used as neutral electrolyte added. The range of NaOH concentrations and the conditions used for the spectrophotometric rate measurements are given in Table 1.

In the case when NaCl was not added the values of the second-order rate constants were obtained as slopes of the straight lines in coordinates k_I and C_{NaOH} (see Fig.1). When NaCl was added the second-order rate constants k were calculated from the pseudo first-order rate constants k_I: $k = k_I / C_{NaOH}$. For comparision the arithmetical mean values

Table 1

Conditions for Kinetic Measurements. Limits of NaOH concentration range, used wave-length, λ ; the initial value of the extinction coefficient (25°C), ε_o; change of the extinction coefficient during the reaction $\Delta\varepsilon$

	p-SO_3^- - phenyl p-toluene sulfonate	o-SO_3^- - phenyl p-toluene sulfonate
Temperature °C	NaOH concentration range, M	
40.0	0.23 - 1.10	0.06 - 0.23
50.0	0.08 - 0.23	0.06 - 0.23
60.0	0.016 - 0.11	0.023 - 0.12
75.0	0.016 - 0.058	0.012 - 0.060
85.0	0.004 - 0.16	0.0058- 0.04
λ(nm)	255	255
ε_o	1800	3300
$\Delta\varepsilon$	25200	9800

from all the second-order constants including constants measured in the presence of NaCl were found at 60 and 85°C.

The values of the second-order rate constants of the alkaline hydrolysis of o- and p-SO_3^- - phenyl p-toluene sulfonates and corresponding parameters of the Arrhenius equation, E and logA, are given in Table 2.

Fig. 2 and 3 illustrate the dependences of logk on $\sqrt{\mu}$ (μ =ionic strength) for p- and o- SO_3^- - phenyl p-toluene sulfonates at 60 and 80°C. The plots of logk vs. 1/T for p- and o-SO_3^- - phenyl - p-toluene sulfonates are given in Figure 4.

As shown in Figs. 2 and 3 no significant dependence of the bimolecular alkaline hydrolysis rate upon concentration of electrolyte added in the range from 0,002 to 4,5 M for p- and - o-SO_3^- - phenyl p-toluene sulfonates was observed. The data in Table 2 allow us to draw the same conclusion.

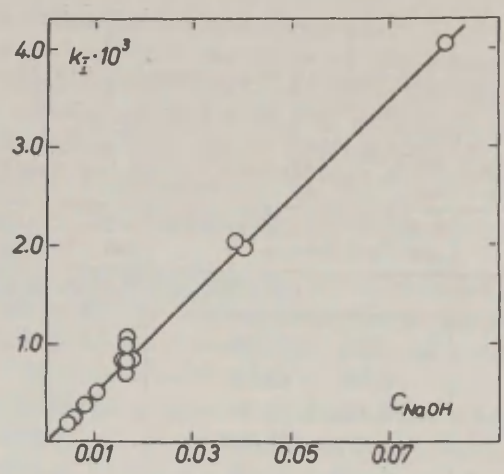

Fig. 1. The dependence of the pseudo-first-order rate constant k_1 for the alkaline hydrolysis of p-SO_3^--phenyl p-toluene sulfonate upon NaOH concentration at 85°C

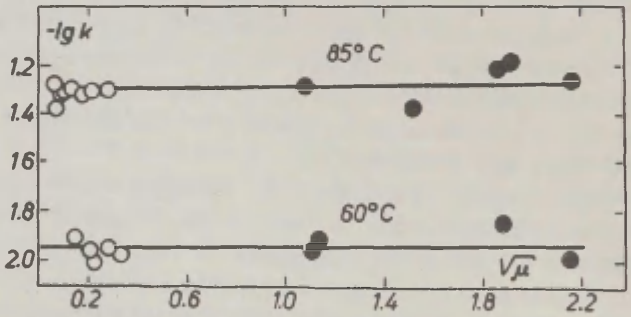

Fig. 2. The dependence of logk on $\sqrt{\mu}$ for the alkaline hydrolysis of p-SO_3-phenyl p-toluene sulfonates

○ = without NaCl

● = NaCl added

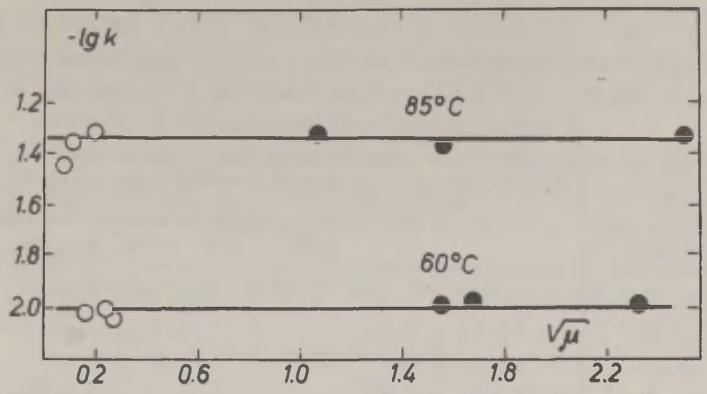

Fig. 3. The dependence of logk on $\sqrt{\mu}$ for the alkaline hydrolysis of o-SO_3^--phenyl p-toluene sulfonates

○ = without NaCl

● = NaCl added

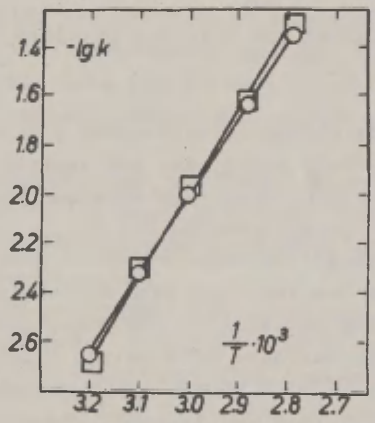

Fig. 4. The dependence of logk on 1/T for the alkaline hydrolysis of p- and o-SO_3^--phenyl p-toluene sulfonates

□ = point for p-SO_3^--phenyl p-toluene sulfonate

○ = point for o-SO_3^--phenyl p-toluene sulfonate

Table 2

Values of the Second-Order Rate Constants and Parameters of Activation for Alkaline Hydrolysis of p- and o-SO_3^- - Phenyl p-Toluene Sulfonates

	p-SO_3^--phenyl p-toluene sulfonate	o-SO_3^--phenyl p-toluene sulfonate
Temperature °C	$k.10^3$ ($M^{-1}.sec^{-1}$)	
40.0	2.11 ± 0.23	2.19 ± 0.07
50.0	5.14 ± 0.06	4.40 ± 0.10
60.0	10.8 ± 0.6	10.0 ± 0.04
	11.4 ± 0.5*	9.90 ± 0.30*
75.0	24.0 ± 0.9	22.0 ± 0.3
80.0	50.3 ± 0.9	44.0 ± 0.5
	50.6 ± 0.2*	43.6 ± 0.4*
E	15 135 ± 490	14 520 ± 400
logA	7.92 ± 0.32	7.49 ± 0.26

* Calculated including the k values obtained in the presence of NaCl

The values of rate constants calculated including rate constants in case of NaCl added, are not essentially different from the values of rate constants obtained as slopes of the straight lines in coordinates k_I and C_{NaOH}.

In preceding papers[6,7] the electrostatic model has been used for calculation of the limiting salt effect including the case distinguished by two plateaux in the relationship between the logk and $\sqrt{\mu}$ values. In the case of alkaline hydrolysis of p-and o-SO_3^- - p-toluene sulfonates the positive salt effect was assumed. However, it was not dedected. Considering the electrostatic model the independence of the interionic reaction rate constants can be observed in two cases: either there is no ion pair formation from both ionic reagents or the formation of ion pairs from both reagents is almost completely

shifted to the right. The former or the latter condition must be satisfied in the whole electrolyte concentration range. So far no other facts were available to prove any of the conditions mentioned above.

The results of our preliminary work demonstrate that the equilibrium $Na^+ + OH^- \rightleftharpoons Na^+OH^-$ was shifted to the left at the lowest electrolyte concentrations and to the right at the highest.

Therefore it is apparent that in the present case the equilibrium

$$RSO_2O^- + Na^+ \rightleftharpoons RSO_2O^-Na^+$$

must be shifted to right in the range of the whole electrolyte concentration of 0.004 to 4.5 M. Such a kind of condition seems to be quite improbable. So far no respective conductometric measurements have been made.

Consequently, including the previously dedected absence of the salt effect in the case of the alkaline hydrolysis of o- and p-O^- - phenyl p-toluene sulfonates, four cases are known so far in which the addition of a neutral electrolyte over a wide range of concentration does not influence the rate constants of the interionic reactions at all. Therefore the feature of so called primary salt effect requirs further investigations.

As to the Brönsted - Debye - Hückel theory it is evident that its applicability to quantitative or even qualitative interpretation of facts observed previously and in the present work, is out of the question.

From the second-order rate constants the values of σ^o constants for p- and o-SO_3^- - phenyls were calculated (Table 3). The values of $\log k_o$ (for unsubstituted compound) and ρ, reported previously[6,10,11] were used. The calculated values of σ^o for p- and o-SO_3^- - phenyls are given in Table 3.

Table 3

Values of σ^{o} Constants for p- and o-SO_3^- - Phenyls

Temperature °C	Substituted phenyl	
	p-SO_3^-	o-SO_3^-
40.0	0.335	0.359
50.0	0.379	0.339
60.0	0.386	0.367
75.0	0.307	0.281
85.0	0.358	0.294
	av.=0.351	av.=0.328

For p-SO_3^--phenyl the following σ^{o} values have been reported[12]:
0.37(μ=0.1)*
0.19(μ=0.01)*
0.09(μ=0.0001)*

* Values of σ^{o} constants calculated from the values of pKa for p-SO_3^--sulfobenzoic acid.

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INVESTIGATION OF KINETICS OF HYDROLYSIS OF BENZOATES

V Alkaline Hydrolysis of p- and m-COO^--Phenyl Benzoates

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The rates of the alkaline hydrolysis of p- and m-COO^---substituted phenyl benzoates in an aqueous solution at various concentrations of electrolyte at 15, 25, 40, and 50°C were measured. The influence of added electrolyte upon the hydrolysis rates in detail was studied at 25 and 50°C. No significant dependence of the values of the second-order rate constants on the concentration of electrolyte added in the range of 0.002 to 4.5 M was dedected. From the second-order rate constants obtained the values of the activation parameters E and logA as well as the values of σ^o constants for p- and m-COO^- - substituted phenyls were calculated.

This study is a continuation of the systematic examination of salt effects in reactions between substrates with charged substituents and ionic reagents.[1-9] In most cases studied up to now higher electrolyte concentration the rate constant reached a limiting value, k_∞, which did not depend any more on the concentration of ions. At the same time, no considerable dependence of the rates of alkaline hydrolysis of p-O^--, o-O^--, p-SO_3^-- and o-SO_3^--substituted phenyl p-toluene sulfonates on the concentration of the neutral electrolyte added was observed.[2,8] Therefore it seemed desirable to examine the influence of the concentration of neutral electrolyte on the rates of the alkaline hydrolysis of p- and

m-COO^--phenyl benzoates. Benzoates were prepared from benzoyl chloride and corresponding oxybenzoic acids in pyridine solution.

p-COO^--phenyl benzoate, m.p. 227°C.
Found %: C 68.11; O 26.84; H 4.19. Calculated %: C 69.42; O 26.42; H 4.16.

m-COO^-- phenyl benzoate, m.p 132°C. Found %: C 67.14; O 26.43; H 3.93. Calculated %: C 69.42; O 26.42; H 4.16.

The spectrophotometric rate measurements were carried out using spectrophotometer CΦ - 4A equipped with a photoelectric multiplier and a recorder of type LP as earlier described. An aqueous solution under pseudounimolecular conditions at 15, 25, 40 and 50°C was investigated, various NaOH and neutral electrolyte (NaCl) concentrations applied. The dependence of the rate constant on the electrolyte concentration was examined at every temperatures, in detail at 25 and 50°C. The range of NaOH concentrations and the conditions for the spectrophotomectric rate measurements are given in Table 1.

T a b l e 1

Conditions for Kinetic Measurements. Limits of NaOH concentration range, used wave-length, λ; the initial value of the extinction coefficient (25°C), ε_o ; change in the extinction coefficient during the reaction, $\Delta\varepsilon$.

Temperature °C	p-COO^--phenyl benzoate	m-COO^--phenyl benzoate
	NaOH concentration range, $M.10^3$	
15.0	2.47 - 19.6	2.47 - 18.5
25.0	2.47 - 24.7	2.47 - 18.5
40.0	2.47 - 19.6	2.45 - 12.3
50.0	1.2 - 9.82	2.45 - 12.3
λ (nm)	275	310
ε_o	3 990	720
$\Delta\varepsilon$	7 280	2 800

In case without NaCl the values of the second-order rate constants were obtained as slopes of the straight lines in coordinates k_I and C_{NaOH} (see Fig. 1). In cases with NaCl

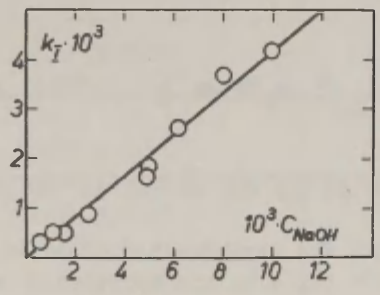

Fig. 1 The dependence of the pseudo-first-order rate constant k_I of the alkaline hydrolysis of p-COO^-- phenyl benzoate on NaOH concentration at 25°C

the values of second-order rate constants k were calculated from the pseudo-first-order rate constants k_I; $k=k_I/C_{NaOH}$. From these calculated values the arithmetic means were found.

The values of ordinary second-order rate constants and the activation parameters E and logA are given in Table 2. For comparision the values of the second-order rate constants measured in the presence of NaCl are presented in Table 2.

Figs. 2 and 3 illustrate the lack of dependence of logk on $\sqrt{\mu}$ (μ-ionic strength) for p- and m-COO^- - phenyl benzoates.

The plots of logk vs. 1/T for p- and m-COO^- - phenyl benzoates are given in Fig. 4.

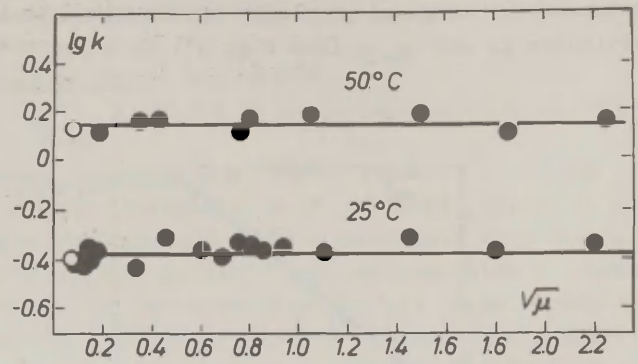

Fig. 2. The dependence of logk on $\sqrt{\mu}$ for the alkaline hydrolysis of p-COO^--phenyl benzoate

○ = without NaCl ($\sqrt{\mu} < 0.10$)

● = NaCl added

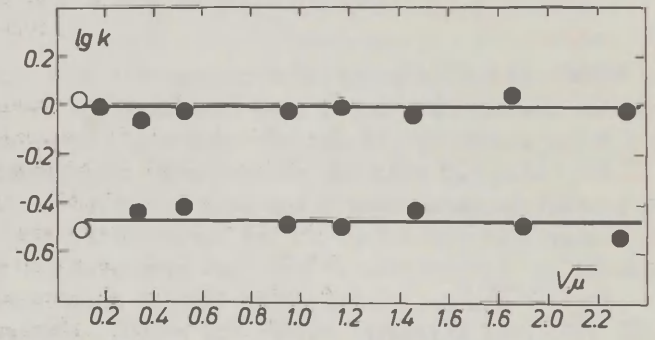

Fig. 3. The dependence of logk on $\sqrt{\mu}$ for the alkaline hydrolysis of m-COO^--phenyl benzoate

○ = without NaCl ($\sqrt{\mu} < 0.15$)

● = NaCl added

Table 2

Values of Rate Constants and Activation Parameters

Temperature °C	p-COO^--phenyl benzoate	m-COO^--phenyl benzoate
	k.10 ($M^{-1}.sec^{-1}$)	
15.0	2.20 ± 0.04	1.69 ± 0.19
	3.40 ± 0.08*	2.55 ± 0.10*
25.0		3.09 ± 0.41
	4.00 ± 0.09*	3.47 ± 0.11*
40.0	8.74 ± 0.28	6.38 ± 0.60
	10.2 ± 0.4*	6.35 ± 0.22*
50.0	13.4 ± 0.2	10.8 ± 0.9
	14.7 ± 0.4*	10.0 ± 0.3*
E	9 576 ± 190	9 670 ± 240
logA	6.61 ± 0.14	6.57 ± 0.17

* Values of k for reaction NaCl added

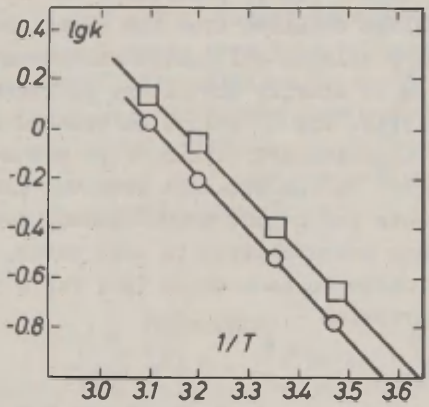

Fig. 4. The dependence of logk on 1/T for the alkaline hydrolysis of p- and m-COO^---phenyl benzoates

□ = point for p-COO^--phenyl benzoate

○ = point for m-COO^--phenyl benzoate

As one can see in Figs. 2 and 3 no significant dependence of the values of rate constants on concentration of electrolyte added in the range of 0.002 to 4.5 M for p- and m-COO^--phenyl benzoates was dedected. The data in Table 2 allow us to draw the same conclusion. The values of rate constants in case of NaCl added are not essentially different from the rate constants obtained as slopes of the straight lines in coordinates k_I and C_{NaOH} (not more than 0.07 logarithmic units).

Earlier[6] the dependence of the rate constants of the alkaline hydrolysis of p- and m-COO^--phenyl p-toluene sulfonates upon the concentration of electrolyte added has been investigated. For both p- and m-COO^--phenyl p-toluene sulfonates a plateau has been appeared in the dependence of logk on $\sqrt{\mu}$. From the rate constants extrapolated to pure water, k_0, and from those for plateau, k_∞, the corresponding values of σ^o and σ_∞^o have been calculated.

For comparision the σ^o values for p- and m-COO^--phenyls were calculated from the rate constants of the alkaline hydrolysis of substituted phenyl benzoates. The comparing of two sets of σ^o values obtained from the alkaline hydrolysis cate constants of p-toluene sulfonates and bezoates, respectively, enables us to clarify the nature of reacting species in studied hydrolysis. The σ^o values calculated from the rate constants of the alkaline hydrolysis of p- and m-COO^--phenyl benzoates and the σ^o values obtained from the alkaline hydrolysis rate constants for p- and m-COO^--phenal p-toluene sulfonates after their extrapolation to pure water, k_0, were found to be very close to each other (see Table 3).
The following expression

$$(\sigma^o)^S_{CO_2^-} = (\sigma^o)^B_{CO_2^-} \neq (\sigma_\infty^o)^S_{CO_2^-}$$

is valid for both, p- and m-COO^--phenyls. Symbols B and S denote the alkaline hydrolysis of benzoates and p-toluene sulfonates respectively used for calculating the σ^o values.

Table 3

Values of σ^o Constants for p- and m-COO-Phenyls

Temperature °C	The σ^o values calculated from the alkaline hydrolysis rate constants, k, for			
	phenylbenzoates		phenyl p-toluene sulfonate	
	p-COO^-	m-COO^-	p-COO^-	m-COO^-
15.0	-0.051	-0.172	av. σ^o=-0.122	av. σ^o=-0.195
25.0	-0.043	-0.164	av. σ^o_∞ =0.207*	av. σ^o_∞ =0.122*
40.0	-0.090	-0.203		
50.0	-0.129	-0.237	For the calculation of σ^o see Ref. 6.	
	av.= =-0.078	av.= =-0.194		

* Calculated from the k_∞ values

It is assumed that the rate constants of interionic reaction, extrapolated to pure water belong to the reaction between free ions. Consequently, the reaction of alkaline hydrolysis of p- and m-COO^--phenyl benzoates can be considered as a reaction between free ions - reagent OH^- and substrate of type RCO_2^-. Nevertheless it is not superfluous to note that for the proof of such a conclusion conductometric measurements are needed. Hitherto it is impossible to understand why an interionic reaction can be insensible to the concentration of neutral electrolyte.

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SOME FORMAL RELATIONSHIPS BETWEEN SALT EFFECTS OF SUBSTRATES WITH CHARGED SUBSTITUENT

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The influence of the added electrolyte concentration on the alkaline hydrolysis rates of substituted phenyl tosylates (p-toluene sulfonates) and that of benzoates with a charged substituent in the phenylic group, were compared. Linear relationships were found between following quantities: lgk ($CH_3C_6H_4SO_2OC_6H_4X^{\pm}$) and lgk ($C_6H_5CO_2C_6H_4X^{\pm}$); lgk_∞ and lgk_o; $\triangle lgk_\infty$ and lgk_o; $\triangle lgk_\infty$ ($CH_3C_6H_4SO_2OC_6H_4X^{\pm}$) and $\triangle lgk_\infty$ ($C_6H_5CO_2C_6H_4X^{\pm}$); $\triangle lgk_\infty$ and $\sigma_X^{o\pm}$, where $X^{\pm}$ denotes the ionic substituent. In all the cases the substrate with positively or negatively charged substituent obeys one and the same relationship.

In our preceding papers[1-9] the data of the systematic investigations of the influence of the neutral electrolyte concentration on the alkaline hydrolysis rates of o-, m- and p-substituted phenyl tosylates and phenyl benzoates with a charged substituent ($N(CH_3)_3^+$, SO_3^-, CO_2^-, O^-) have been reported. In most cases at higher electrolyte concentrations the rate constant reached a limiting value, k_∞, which did not depend any more on the concentration of ions. At the same time no considerable dependence of the alkaline hydrolysis rates of o-O^--, p-O^--, o-SO_3^-- and p-SO_3^--phenyl tosylates and m-CO_2^-- and p-CO_2^-- phenyl benzoates upon the added neutral electrolyte concentration was observed. It is necessary to emphasize that the existence or the lack of salt effect of a charged substituent depends on the studied reaction. At the alkaline hydrolysis of p- and m-CO_2^-- phenyl tosylates

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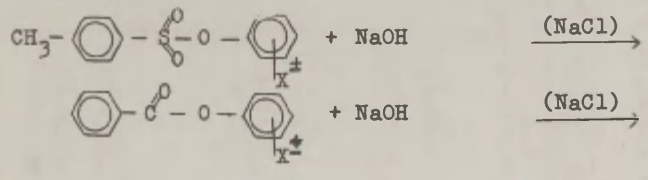
a considerable salt effect was observed. At the same time, for the alkaline hydrolysis of p- and m-CO_2^- - phenyl benzoates no significant dependence of the values of rate constants on the added electrolyte concentration was dedected. On the other hand, in the case of p-O^- - phenyl tosylate the salt effect was not observed. However, for the alkaline hydrolysis of p-O^- - phenyl benzoate quite a "normal" salt effect appeared. Similar situation was reported by Eaborn and coworkers[11,12] for the reaction between benzyltrimethylsilanes ($Me_3SiCH_2C_6H_4X^{\pm}$) and sodium hydroxide. The study of m-PMe_3^+ - compound[12] showed that there was in fact a small decrease of rate constant with increasing alkali concentration ($\Delta \lg k_\infty \approx 0.1$). A considerably larger salt effect ($\Delta \lg k_\infty > 0.6$), in the opposite direction with increasing NaOH concentration was noted for the reaction involving the negatively-charged $Me_3SiCH_2C_6H_4CO_2^-$ ions.[11]

From these facts is apparent, like we have mentioned already on several occasions, the theory of Debye-Hückel-Brönsted, even as a qualitative interpretation, cannot be applied to the influence of the added neutral electrolyte (or the lack of it) on the interionic reaction rates of substrates with a charged substituent.

It has been stated[10] that the value of limiting salt effect, $\Delta \lg k_\infty = \lg k_\infty - \lg k_o$, should be interpreted as the difference between the reactivity of free ions and ion pairs (or other interionic associates) and calculated as an electrostatic contribution to the free energy of activation expressed in lgk scale. On certain occasions the electrostatic model enables us to interpret quantitatively the observed salt effects,[5-7,10] even those including two plateaux in plots of lgk vs. electrolyte concentration.[7] However, so far the electrostatic model based on the electrostatic interaction between charged substituent and reaction centre, has not been applied successfully to all the salt effects observed at alkaline hydrolysis of substituted phenyl tosylates and benzoates.

In the present work the influence of the charged substituent as well as the influence of the neutral electrolyte concentration on the alkaline hydrolysis rates of substituted phenyl tosylates and on those of phenyl benzoates:



were compared with each other.

The lgk_o, lgk_∞ and Δlgk_∞ values for the alkaline hydrolysis of phenyl tosylates and phenyl benzoates in on aqueous solution at 50°C are given in Table 1. By k_o the rate constant obtained by extrapolation of second-order rate constants to pure water is denoted; k_∞ is the limiting rate constant at higher electrolyte concentrations (for plateau); $\Delta \log k_\infty = lgk_\infty - lgk_o$. All the rate constants represented in Table 1 were obtained for the alkaline hydrolysis of tosylates and benzoates, NaOH acting as a reagent and NaCl as a neutral electrolyte.

The $\sigma^o_{X^\pm}$ and $(\sigma^o_\infty)_{X^\pm}$ values, calculated from lgk_o and lgk_∞ for the alkaline hydrolysis of phenyl tosylates and phenyl benzoates are recorded in Table 2.

The comparision of the lgk_o, lgk_∞ and Δlgk_∞ values resulted in linear relationships between following quantities:

1. $lgk_{OH}(CH_3C_6H_4SO_2OC_6H_4X^\pm)$ and $lgk_{OH}(C_6H_5CO_2C_6H_4X^\pm)$
2. lgk_∞ and lgk_o
3. Δlgk_∞ and lgk_o
4. $\Delta lgk_\infty (CH_3C_6H_4SO_2OC_6H_4X^\pm)$ and $\Delta lgk_\infty(C_6H_5CO_2C_6H_4X^\pm)$

The parameters of linear relationships (1)-(4) are given in Table 3.

Table 1

The lgk_o, lgk_∞ and Δlgk_∞ Values for Alkaline Hydrolysis of Substituted Phenyl Tosylates and Phenyl Benzoates. Aqueous Solution at 50°C, NaOH Acting as a Reagent and NaCl as a Neutral Electrolyte

Substituent $X^{\pm}$	$CH_3C_6H_4SO_2OC_6H_4-X^{\pm}$ *			$C_6H_5CO_2C_6H_4-X^{\pm}$ *		
	lgk_o	lgk_∞	Δlgk_∞	lgk_o	lgk_∞	Δlgk_∞
2-$N(CH_3)_3^+$	0.518 (1)	0.079 (1)	-0.60	-	-	-
3-$N(CH_3)_3^+$	-1.198 (1)	-1.542 (1)	-0.34	1.116 (3)	0.48 (3)	-0.64
4-$N(CH_3)_3^+$	-1.420 (1)	-1.816 (1)	-0.40	1.085 (3)	0.55 (3)	-0.54
2-SO_3^-	-2.357 (8)		0			
4-SO_3^-	-2.290 (8)		0			
2-CO_2^-	-4.119 (7)	-3.547 (7)	0.57	-0.95 ***	-0.55 ***	0.40
		-3.168 (7)	0.95			
3-CO_2^-	-3.229 (6)	-2.671 (6)	0.56	0.034 (9)		0
4-CO_2^-	-3,086 (6)	-2.594 (6)	0.50	0.124 (9)		0
3-O^-	-4.440 **	-3.778 (2)	0.76	-0.508 (3)	-0.24 (3)	0.27
4-O^-	-4.310 (2)		0	-0.537 (3)	-0.26 (3)	0.27

* References in brackets

** Calculated by Arrhenius equation

*** More detailed data of the alkaline hydrolysis of 2-CO_2^--phenyl benzoate will be published elsewhere

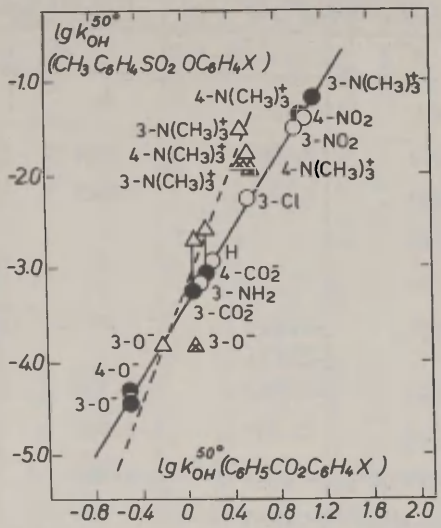


Fig. 1. Dependence of lgk for the alkaline hydrolysis of tosylates on lgk for the alkaline hydrolysis of phenyl benzoates. H_2O at 50°C.

O, uncharged substituents
●, charged substituents, k_o used
△, charged substituents, k_∞ used
◬, charged substituents, k_o corrected by intramolecular electrostatic interaction

The Fig. 1 illustrates the relation between lgk for the alkaline hydrolysis of substituted phenyl tosylates and corresponding values for substituted phenyl benzoates at 50°C. Using the k_o values for substrates with a charged substituent the points for all the m- and p-substituted substrates with

Table 2

Calculated $\sigma^{o}_{X^{\pm}}$ and $(\sigma^{o}_{\infty})_{X^{\pm}}$ Values for Alkaline Hydrolysis of Phenyl Tosylates and Phenyl Benzoates. Aqueous Solutions.

Substituent $X^{\pm}$	$CH_3C_6H_4SO_2OC_6H_4-X^{\pm}$ *		$C_6H_5CO_2C_6H_4-X^{\pm}$ *	
	$\sigma^{o}_{X^{\pm}}$	$(\sigma^{o}_{\infty})_{X^{\pm}}$	$\sigma^{o}_{X^{\pm}}$	$(\sigma^{o}_{\infty})_{X^{\pm}}$
2-$N(CH_3)_3^+$	1.946	1.683		
3-$N(CH_3)_3^+$	1.042	0.798	1.094	0.304(50°C)
4-$N(CH_3)_3^+$	0.880	0.655	1.025	0.386(50°C)
2-SO_3^-	0.328			
4-SO_3^-	0.351			
2-CO_2^-	-0.687	-0.354 -0.133	-1.361(50°C)	-0.77(50°C)
3-CO_2^-	-0.195	0.122	-0.194	
4-CO_2^-	-0.122	0.207	-0.078	
3-O^-	-0.874(50°C) -1.263(85°C)	-0.488(50°C) -0.591(50°C)	-0.886	-0.57
4-O^-	-0.815		-0.833	-0.58

* The $\sigma^{o}_{X^{\pm}}$ values were calculated as arithmetic means from the $\sigma^{o}_{X^{\pm}}$ values found from the kinetic data for different temperatures, otherwise the corresponding temperature is given in brackets.

a charged substituent (3-$N(CH_3)^+$, 4-$N(CH_3)^+$, 3-CO_2^-, 4-CO_2^-, 3-O^-) fell on the same straight line established for substrates with uncharged m- and p- substituents (r=0,998, see Table 3). The correlation does not become worse if to include substrates with charged substituent (see Table 3).

It was mentioned above that for the alkaline hydrolysis of 4-O^-- phenyl tosylate the salt effect had not been dedected. Since the point for 4-substituent falls on the

Table 3

Parameters of Linear Relationship of Type $y=a+bx$ (H_2O, 50°C)

y/x	Position and nature of substituents	a	b	r	s
lgk_{Tos}/lgk_{Benz}	uncharged meta-, para-	-3.415 ± 0.041	1.998 ± 0.061	0.997	0.048
lgk_{Tos}/lgk_{Benz}	uncharged meta-, para- and charged meta-, para-	-3.363 ± 0.028	1.904 ± 0.040	0.998	0.077
lgk_{∞}/lgk_{o} Tosylates	charged meta-, para-	-0.798 ± 0.164	0.632 ± 0.058	0.984	0.157
$\Delta lgk_{\infty}/lgk_{o}$ Tosylates	charged meta-, para-	-0.826 ± 0.165	-0.390 ± 0.056	0.970	0.152
lgk_{∞}/lgk_{o} Benzoates	charged meta-, para-	0.012 ± 0.019	0.467 ± 0.026	0.994	0.043
$\Delta lgk_{\infty}/lgk_{o}$ Benzoates	charged meta-, para-	-0.003 ± 0.022	-0.533 ± 0.026	0.995	0.041
$\Delta lgk_{\infty}^{Tos}/\Delta lgk_{\infty}^{Benz}$	charged meta-, para-	0.399 ± 0.097	1.295 ± 0.190	0.989	0.135
	charged meta-, para- ortho-	0.410 ± 0.050	1.315 ± 0.103	0.994	0.096
$\Delta lgk_{\infty}^{Tos}/\sigma_{X}^{o}{}^{\pm}$	charged meta-, para-	0.314 ± 0.060	-0.673 ± 0.088	0.968	0.142
$\Delta lgk_{\infty}^{Benz}/\sigma_{X}^{o}{}^{\pm}$	charged meta-, para-	-0.095 ± 0.018	-0.455 ± 0.023	0.995	0.044

straight line obtained for other charged and uncharged m- and p-substituents using the k_o value for the alkaline hydrolysis of 4-O^- - phenyl benzoate, a conclusion can be drawn that the rate constant in the case of 4-O^-- phenyl tosylate characterizes the reaction between ions.

Using the k_∞ values in the same coordinates the points for substrates with a positively charged substituent (3-$N(CH_3)_3^+$, 4-$N(CH_3)_3^+$), except that for 3-O^-- substituent, deviate from the common straight line defined by the uncharged m- and p- substituents.

The points for lgk_∞ probably define an other line which across the common straight line at the point corresponding to 3-O^- - substituent. The points for charged substituents also deviate from the common plot for uncharged and charged substituents after correcting the lgk_o values in view of electrostatic interaction between charged substituent and reaction centre in activated state equal for tosylates and benzoates.

Recently it has been stated[13] that in the case of different aliphatic organic acids the introduction of electrostatic correction into the pK_a values for acids with charged substituent results in an inductive attenuation factor of carbon atom, $Z^*_{CH_2}$, common for acids with uncharged and charged substituents, but different for every reaction series. Such a result is, in principle, different from conclusion drawn from the present data on the alkaline hydrolysis of substituted phenyl tosylates and phenyl benzoates. In the case of ionic reagent the reactivity of substrates with charged m- and p-substituent depends on the substituent quite "normally", and, maybe mere formally, does not differ from that of substrates with uncharged m- and p- substituent. At the same time, in the case of reaction in which the ion pairs take part the reactivity of substrates with charged substituent cannot be described by the dependence for substrates with uncharged m- and p- substituents.

In Figs. 2 and 3 the dependence of lgk_∞ on lgk_o for the alkaline hydrolysis of substituted phenyl tosylates and that for substituted phenyl benzoates at 50°C are shown. In both the cases tosylates and benzoates the points for substrates with positively and negatively charged substituent lie on a common straight line (see Table 3). In the case of alkaline hydrolysis of tosylates points for substrates with $2\text{-}N(CH_3)_3^+$- and $2\text{-}CO_2^-$- substituent fall off the linear relationship determined by substrates with m- and p-substituents. Using in the case of $2\text{-}CO_2^-$- phenyl tosylate the values of lgk_o and lgk_∞ for two plateau separately and puting $lgk_o = lgk_{\infty(1)}$ for $2\text{-}CO_2^-(2)$ point, the corresponding points, denoted by $2\text{-}CO_2^-(1)$ and $2\text{-}CO_2^-(2)$ lie on the plot for m- and p-substituents (see Fig. 2). For $2\text{-}CO_2^-$- phenyl benzoate the falloff is negligible.

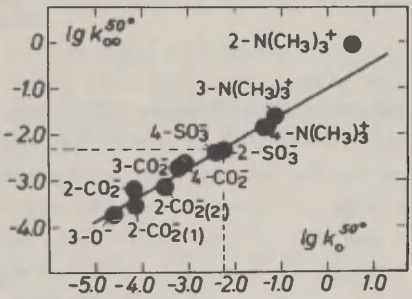


Fig. 2. Dependence of lgk_∞ on lgk_o for the alkaline hydrolysis of phenyl tosylates. H_2O at 50°C. For $2\text{-}CO_2^-$- phenyl tosylate the following lgk_o and lgk_∞ values were used.
Point $2\text{-}CO_2^-$: lgk_o and $lgk_{\infty(2)}$ (on the second plateau)
Point $2\text{-}CO_2^-(1)$: lgk_o and $lgk_{\infty(1)}$ (on the first plateau)
Point $2\text{-}CO_2^-(2)$: $lgk_{\infty(1)} = lgk_o$ and $lgk_{\infty(2)}$

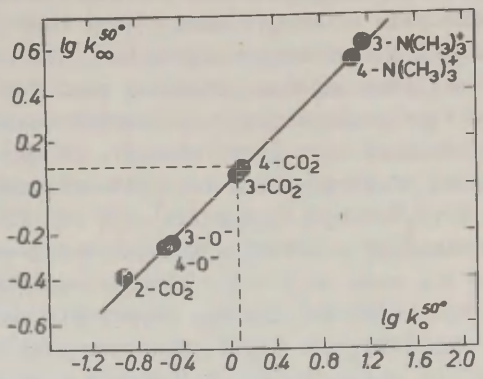


Fig. 3. Dependence of lgk_∞ on lgk_o for the alkaline hydrolysis of phenyl benzoates H_2O at 50°C.

The linear relationship between lgk_∞ and lgk_o has an isoparametric point determined by condition $lgk_\infty = lgk_o$. On one side of it remain the substrates having a positive salt effect and on the other - substrates with negative salt effect (see Figs. 4 and 5). At the point $lgk_\infty = lgk_o$ the rate constant of the interionic reaction does not differ from the rate constant of the reaction in which it took part ion pairs (or ion pair). This is exactly the point in which it fall the rate constant values for 4-SO_3^-- and 2-SO_3^-- substituted compounds in the case of alkaline hydrolysis of phenyl tosylates

$$lgk(SO_3^-) = lgk_o(SO_3^-) = lgk_\infty(SO_3^-)$$

and 3-CO_2^- - and 4-CO_2^- - substituted compounds in the case of alkaline hydrolysis of phenyl benzoates

$$lgk(CO_2^-) = lgk_o(CO_2^-) = lgk_\infty(CO_2^-)$$

for which the salt effects were not observed.

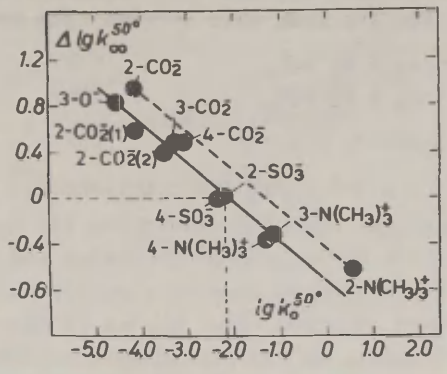


Fig. 4. Dependence of Δlgk_∞ on lgk_o for the alkaline hydrolysis of phenyl tosylates. H_2O at 50°C. For 2-CO_2^--phenyl tosylate the following lgk_o and Δlgk_∞ values were used.
Point 2-CO_2^-: lgk_o and $\Delta lgk_\infty = lgk_{\infty(2)} - lgk_o$
Point 2-CO_2^-(1): lgk_o and $\Delta lgk_\infty = lgk_{\infty(1)} - lgk_o$
Point 2-CO_2^-(2): $lgk_o = lgk_{\infty(1)}$ and $\Delta lgk_\infty = lgk_{\infty(2)} - lgk_{\infty(1)}$

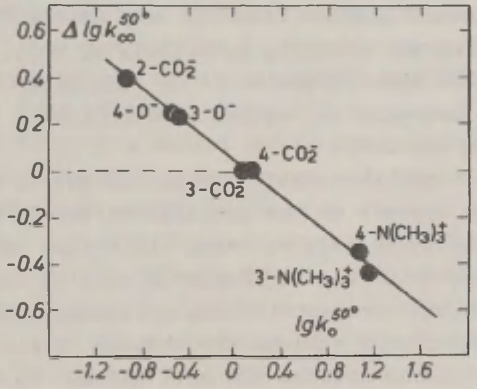


Fig. 5. Dependence of Δlgk_∞ on lgk_o for the alkaline hydrolysis of phenyl benzoates. H_2O at 50°C.

Linear relationship between the Δlgk_∞ and lgk_o values (Figs. 4 and 5) follows from that between lgk_∞ and lgk_o. If

$$lgk_\infty = a_1 + b_1\, lgk_o \qquad (1)$$

$$\Delta lgk_\infty = a_2 + b_2\, lgk_o \qquad (2)$$

$$\text{then } a_1 = a_2 \text{ and } b_2 = b_1 - 1 \qquad (3)$$

The values of a and b for the relationships (1) and (2) in Table 3 demonstrate that the conditions (3) are accomplished for alkaline hydrolysis of tosylates and benzoates. In the case of o-substituted compounds deviation from the dependence (2) were observed (Fig. 4), as it was the case at dependence (1) (Fig.2). In the linear relationship between Δlgk_∞ and lgk_o the values of the alkaline hydrolysis rate constants for 4-SO_3^- - and 2-SO_3^-- phenyl tosylates (Fig.4) and for 4-CO_2^-- and 3-CO_2^--phenyl benzoates (Fig.5) correspond to the point at $\Delta lgk_\infty = 0$ as it could be expected. It is noteworthy that for the tosylates and benzoates the conditions $lgk_\infty = lgk_o$ and $\Delta lgk_\infty = 0$ are met in the case of the charged substituent similar to the reaction centre in the activated state.

A linear relationship

$$\Delta lgk_\infty(CH_3C_6H_4SO_2OC_6H_4X^{\pm}) = a + b\,\Delta lgk_\infty(C_6H_5CO_2C_6H_4X^{\pm}) \qquad (4)$$

was found (Fig.6). The dependence (4) can be regarded as a linear free energy relationship, resulted from salt effects. The Δlgk_∞ values for the alkaline hydrolysis of tosylates and those of benzoates are different. It is remarkable that dependence (4) does not pass the origin of coordinates (a=0,399 and b=1.30, see Table 3).

So far it is not understandable why the extent of a salt effect or lack of it depends on the specific nature of a studied reaction. However it is apparent that the values of salt effects for one reaction series regularly depends on the same quantities for the other reaction series, including positive and negative salt effects as well as the absence of it. Due to the linear relationship between the salt effect values

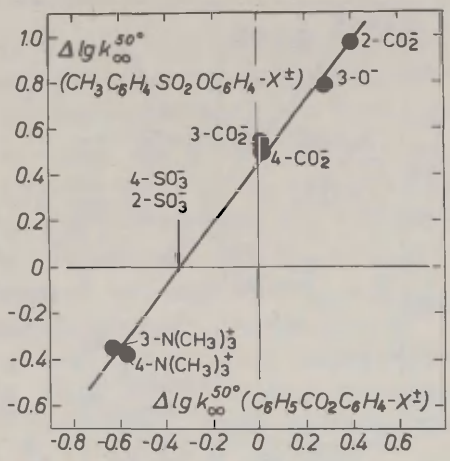


Fig. 6. Dependence between $\Delta \lg k_{\infty}$ for the alkaline hydrolysis of phenyl tosylates and $\Delta \lg k_{\infty}$ for the alkaline hydrolysis of phenyl benzoates. H_2O at 50°C.

for two different reaction series it is possible to predict the values of salt effect for a substrate with a charged substituent in one of these series, for which no experimental data are available. For instance, from the dependence (4) follows that a substrate with SO_3^- substitutent in the case of the alkaline hydrolysis of substituted phenyl benzoates should have a negative salt effect(-0.31), usually characteristic for the substrates with positively charged substituent.

The relation between $\Delta \lg k_{\infty}$ and $\sigma^{o}_{X^{\pm}}$ (Fig. 7) calculated from the corresponding k_o values enables us to construct a common scale of $\Delta \lg k_{\infty}$ for the alkaline hydrolysis of both tosylates and benzoates. The respective equations can be written as follows:

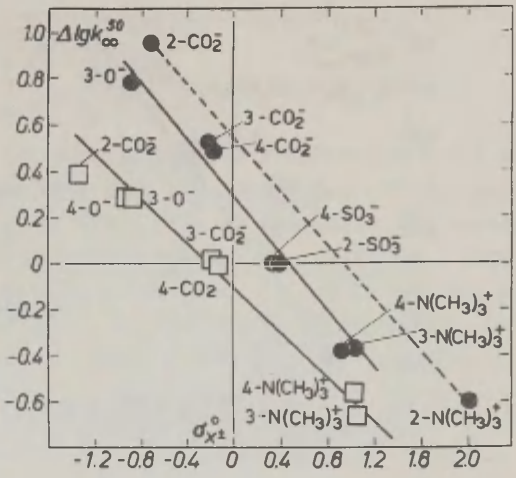


Fig. 7. Dependence of $\Delta \lg k_{\infty}$ on $\sigma^{\circ}_{X\pm}$ for the alkaline hydrolysis of phenyl tosylates and that for phenyl benzoates. H_2O at 50°0.

0, phenyl tosylates
□, phenyl benzoates

$$\Delta \lg k_{\infty} = a + b\sigma^{\circ}_{X\pm} \qquad (5)$$

or $$\Delta \lg k_{\infty} = \Delta \lg k^{\circ}_{\infty} - \rho_{\infty} \sigma^{\circ}_{X\pm} \qquad (6)$$

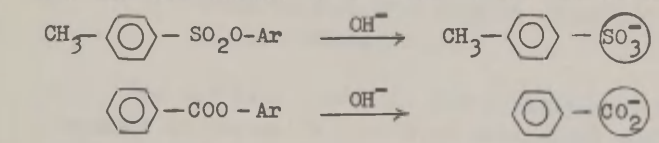
$$\Delta \lg k_{\infty} = \rho_{\infty} (\sigma^{\circ}_{cr} - \sigma^{\circ}_{X\pm}) \qquad (7)$$

The values of $a = \Delta \lg k^{\circ}_{\infty}$ and $b = -\rho_{\infty}$ for the alkaline hydrolysis of tosylates and benzoates are given in Table 3. In the case of tosylates and benzoates on condition that $\sigma^{\circ}_{X\pm} = 0$, the value of $\Delta \lg k_{\infty}$ is different from zero, $\Delta \lg k_{\infty} \neq 0$. For

$\sigma^{o}_{X^{\pm}} = 0$ the equation $\Delta \lg k_{\infty} = \Delta \lg k^{o}_{\infty}$ can be rewritten:

$$\Delta \lg k^{o}_{\infty} = \rho_{\infty} \sigma^{o}_{cr}$$

From the $\Delta \lg k^{o}_{\infty}$ and ρ_{∞} values the σ^{o}_{cr} values for both the reaction series can be calculated. For tosylates $\sigma^{o}_{cr} = 0.46$ and for benzoates $\sigma^{o}_{cr} = -0.21$. Considering the deviations of $\Delta \lg k^{o}_{\infty}$ and ρ_{∞} (see Table 3) one can draw a conclusion that the value of $\sigma^{o}_{cr} = 0.46$ corresponds nearly to the $4\text{-}SO_3^-$ - substituent and $\sigma^{o}_{cr} = -0.21$ to the $3\text{-}CO_2^-$ - or the $4\text{-}CO_2^-$ - substituent. So, $\sigma^{o}_{cr} = \sigma^{o}_{4\text{-}SO_3^-}$ for the alkaline hydrolysis of tosylates and $\sigma^{o}_{cr} = \sigma^{o}_{4(3)\text{-}CO_2^-}$ for that of benzoates. Consequently, in the case of alkaline hydrolysis of both tosylates and benzoates critical substituent having $\Delta \lg k_{\infty} = 0$ corresponds to a group formed from the reaction centre as a result of one of the reactions:



It is necessary to emphasize that the considered groups, $-SO_3^-$ and $-CO_2^-$, are not in the same benzene cycle with charged substituent.

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THE APPLICATION OF THE INDICATOR OVERLAP METHOD TO WEAK BASES PROTONATED ACCORDING TO THE DEHYDRATION SCHEME

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It has been demonstrated that approximate pK_a values of thermodynamic significance may be obtained using indicator overlap method for weak bases whose protonation occures according to the dehydration scheme.

The basicity constants for a variety of weak bases in aqueous strong acids are often determined making use of Hammelt acidity function H_c.[1] But the values of this function obtained with weakly basic indicators ($pK_a < -3$) do not reflect the activity of protons in acid-water mixtures because for these solutions the H_o function is determined by the dehydration equilibria

$$B...H^+.nH_2O \rightleftharpoons BH^+.mH_2O+(n-m)H_2O \qquad (1)$$

and it describes the changes in water activity in these solutions.[4-6] From this point of view some doubts may arise about the nature of the basicity constants, obtained using the acidity function H_o. First of all that can be said about the pK_a values of weakly basic Hammett's indicators (with $pK_a < -3$). However, these pK_a values seem to be rather close to the respective thermodynamic ones. Evidence for that comes from different sources. So the pK_a values for polysub-

stituted anilines, calculated using additivity of the substituent effects, have shown to be rather close to the pK_a values obtained by the overlap method.[7] The consistency of the indicator overlap method with linear free energy - enthalpy correlations represents another kind of evidence for the thermodynamic significance of pK_a values determined by the overlap method.[8,9] It is the purpose of the present paper to discuss the nature of pK_a values obtained by indicator overlap method for weak bases, protonated in aqueous strong acids according to Eq.(1). It is well known that in the series of weak bases B_1, ... B_{N-1}, B_N, ... B_i used for the acidity function determination the basicity constants of two adjacent indicators B_{n-1} and B_N are related to each other by the following equation.[1]

$$pK_{a,B_N} = pK_{a,B_{N-1}} + \log I_{N-1} - \log I_N + \Delta \qquad (2)$$

where I_{N-1} and I_N are the indicator ratios for B_{N-1} and B_N, respectively. The last term on the right of Eq.(1) is a function of activity coefficients

$$\Delta = \log \frac{f_{B_{N-1}} \cdot f_{HB_N^+}}{f_{B_N} \cdot f_{HB_{N-1}^+}} \qquad (3)$$

Assuming that the molar extinction coefficients for $B.bH_2O$ and $B...H^+.nH_2O$ have the same value, the spectrophotometrically determined indicator ratio would be given by

$$I = \frac{[B.bH_2O] + [B...H^+.nH_2O]}{[BH^+.mH_2O]} \qquad (4)$$

At low acid concentrations $[B.bH_2O] \gg [B...H^+.nH_2O]$ and so for this case Eq.(2) enables us to calculate the thermodynamically significant pK_{a,B_N} values because it is not unreasonable to assume that in the series of chemically similar bases $\Delta = 0$.

In solutions containing more than 30% (w/w) H_2SO_4 or $HClO_4$ $[B.bH_2O] \ll [B...H^+.nH_2O]$.[5]

For this range of acid concentrations Eq.(4) reduces to

$$I = \frac{[B...H^+.nH_2O]}{[BH^+.mH_2O]} \qquad (5)$$

The concentration $[B...H^+.nH_2O]$ is proportional[6] to the $[B.bH_2O]$

$$[B...H^+.nH_2O] = [B.bH_2O] \cdot \frac{h}{K_{\beta,B}} \qquad (6)$$

where h is the acidity scale for the equilibrium between $B.bH_2O$ and $B...H^+.nH_2O$; $K_{\beta,B}$ is the constant for this equilibrium.

Using Eqs.(5) and (6) we can write for indicators N and N-1

$$I_N = \frac{[B_N.bH_2O]}{[HB_N^+.mH_2O]} \cdot \frac{h_N}{K_{\beta,B_N}} \qquad (7)$$

$$I_{N-1} = \frac{[B_{N-1}.bH_2O]}{[HB_{N-1}^+.mH_2O]} \cdot \frac{h_{N-1}}{K_{\beta,B_{N-1}}} \qquad (8)$$

It follows from Eqs.(7),(8) and (2) that for acid solutions considered

$$pK_{a,B_N} = pK_{a,B_{N-1}} + \log \frac{[B_N.bH_2O]}{[HB_N^+.mH_2O]} - \log \frac{[B_{N-1}.bH_2O]}{[HB_{N-1}^+.mH_2O]} +$$

$$+ \log h_N - \log h_{N-1} + pK_{\beta,B_{N-1}} - pK_{\beta,B_N} + \Delta \qquad (9)$$

In the series of chemically similar indicators it is reasonable to assume that $\log h_N - \log h_{N-1} = 0$ and $\Delta = 0$. Consequently, the deviation of the pK_{a,B_N} (Eq.(9)) from the

respective thermodynamic value is in first approximation given by the difference $pK_{\beta,B_N} - pK_{\beta,B_{N-1}}$.

The stability constants for H-bonded complexes (K_β) are rather insensitive to the basicity of the electrondonors.[10,11] In accord with this the experiment has shown that for any pair of weak bases (B_N and B_{N-1})[5]

$$\left| pK_{\beta,B_N} - pK_{\beta,B_{N-1}} \right| < 1 \qquad (10)$$

Now it is evident that for a series of chemically similar indicators the deviations of pK_{a,B_N} (Eq.(9)) from the respective thermodynamic values do not exceed $\pm$ 1 pK_a unit (if Δ=0). That is just the range of deviations between the pK_a-s for polysubstituted anilines calculated using the principle of additivity of substituent effects and those obtained by the indicator overlap method.[7]

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INFLUENCE OF REAGENT STRUCTURE ON ACYLATION RATE OF ALCOHOLS IN PRESENCE OF TERTIARY AMINES*

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By potentiometric and spectrophotometric methods the kinetics of reaction of benzoyl chloride with some alcohols in presence of different tertiary amines was investigated. The reaction rate depended on both inductive and steric effects of substituents in alcohols and in amine-catalyst molecules. These facts as well as positive ρ^* values confirmed the hypothesis surmised previously about a nucleophilic mechanism of catalysis. The influence of the alcohol and amine structure was completely additive. Some possible explanations of it were proposed.

Effect of tertiary amines on the reaction of acyl chlorides with alcohols is shown in some papers.[2] However, no quantitative description of dependence between the catalytic activity of aliphatic amines and their structure is available either the data about the interrelation between the reagent structure and the reaction rate. Hence, continuing our preceding investigations[1], we studied the kinetics of reaction of benzoyl chloride with alcohols (I-VII) in presence of

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*Part IV from the series "Influence of structure of aliphatic alcohols on their reactivity". For the preceding paper see Ref. 1.

different tertiary amines. As objects the substances were selected which had the well-known inductive and steric characteristics varying rather widely.

Experimental

The alcohols investigated (I-VII), benzoyl chloride and the solvents (tetrachloroethylene, toluene, acetone, acetonitrile) were purified as described by us before[1]. 1-Phenyl--3-dialkylaminopropins (VIII, X) were prepared by Mannich reaction from phenylacetylene, paraforme and appropriate secondary amines[3]. ω-Phenylalkyl-dimethylamines (XII,XIV) were prepared from appropriate bromides and dimethylamine[4]. N-Methylpiperidine was prepared as described by Unkovsky et al[5]. The constants of all substances prepared were in accordance with those available in literature. The purity of alcohols and amines was controlled by GLC (ChL-69 with catharometer, the 1mx4mm column with 10% Carbowax-6000/Celite, gas-carrier is He.

The method of kinetic measurements was described in a preceding paper[1]. The pH-stat and spectrophotometric methods were used. The rate constants determined by both methods coincided well with each other to verify the results obtained. The accuracy of these constants was characterized by the confidence interval which was calculated by methods described in Refs. 6 and 7. The coefficients of polylinear equations were calculated by least-squares method.

Since the hydrochlorides of tertiary amines formed in course of reaction were low dissoluble in tetrachloroethylene the reaction mixture was heterogeneous. To examine the independence of the reaction kinetics of this heterogeneity we performed the comparative experiments both with an intensive mixing and without one. The coincidence of the rate constants obtained (see Table 1) was an evidence that no diffusion limitations were in our experiments.

Table 1

Influence of Mixing on the Acylation Rate

($C_o^{RCOCl} = C_o^{alc} = 0.05-0.1$ mol/l, $C_o^{am} = 0.1-0.25$ mol/l)

ROH	Amine	$K \cdot 10^2$ $M^{-2}sec^{-1}$	
		With mixing	Without mixing
CH_3OH	$(C_2H_5)_3N$	5.6±0.5	5.7±0.4
$CH{\equiv}CCH_2OH$	$(C_4H_9)_3N$	3.0±0.2	3.1±0.2
$CH{=}CCH_2OH$	$C_5H_{10}NCH_3$	19±2	20±3

Discussion

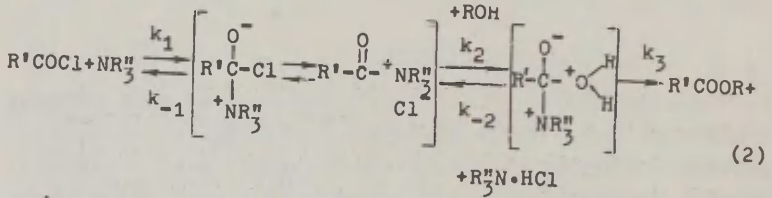
The results of kinetic measurements presented in Table 2 allow to characterize the system investigated rather completely. It may be seen that the reaction rate is depended on both inductive and steric effects of substituents in the molecules of alcohols and amines-catalysts. The calculation of two-parameter Taft equation (1) by means of least-squares method for alcohols (I-III, V-VII) lead to good correlations (see Table 3).

$$\lg K = \lg K_{10} + \rho_1^* \sigma_{(R)}^* + \delta_1 E_{s(RCH_2)} \qquad (1)$$

The positive ρ^* and the large sensibility of reaction to steric effects confirm the hypothesis surmised previously[1] about a nucleophilic mechanism of the tertiary amines catalysis (2)

Alcohols Acylation in Presence of Tertiary Amines in

Alcohols ROH					
NN	R	σ^*	$-E_s$ for RCH_2	VIII $C_6H_5C{\equiv}CCH_2NEt_2$	IX Bu_3N
				$\Sigma\sigma^*$ 0.46	-0.39
				$-E_N$ 3.4	4.5
I	$C_6H_5CH_2CH_2$	0.080	0.45	0.065±0.005	0.45±0.02
II	$CH_3OCH_2CH_2$	0.190	0.42	0.065±0.005	-
III	$C_6H_5CH_2$	0.215	0.38	0.13±0.01	1.5±0.2
IV	Cl_3CCH_2	0.960	?	0.22±0.03	-
V	$ClCH_2CH_2$	0.385	0.48	0.22±0.03	-
VI	CH_3	0.205	0.07	0.33±0.05	2.6±0.2
VII	$CH{\equiv}CCH_2$	0.600	0.64	0.39±0.02	3.0±0.2



(2)

As an argument in behalf of nucleophilic catalysis may be considered the data received about the influence of tertiary amines structure on the rate reaction. The calculations of this data were performed by means of modifyed Taft equation (3) in which the E_N constants equal to E_s values for isosteric groups $R_1R_2R_3C$ were used as measure of steric accessibility of amines $R_1R_2R_3N$.[8]

$$\lg K = \lg K_{2,0} + \rho_2^*\Sigma\sigma^* + \delta_2 E_N \qquad (3)$$

Table 2

Tetrachloroethylene at 25° ($K \cdot 10^2$, $l^2 mol^{-2} \cdot sec^{-1}$)

Amines				
X $C_6H_5C{\equiv}CCH_2NMe_2$	XI Et_3N	XII $C_6H_5CH_2NMe_2$	XIII $C_5H_{10}NMe$	XIV $C_6H_5CH_2CH_2NMe_2$
0.66	-0.3	0.215	-0.14	0.08
1.8	3.8	2.23	3.0	2.3
1.4±0.2	1.2±0.1	2.6±0.2	3.7±0.2	4.0±0.3
-	1.3±0.1	-	-	4.4±0.2
2.3±0.2	2.4±0.2	5.0±0.3	6.6±0.3	8.1±0.3
-	4.2±0.6	-	-	14±1
-	4.2±0.5	-	-	14±1
5.8±0.5	5.9±0.3	13.6±0.5	19±1	22±2
5.5±0.6	7.1±0.2	12±2	20±2	22±1

This equation was recently proved to hold for the reaction of benzoyl chloride hydrolysis in presence of tertiary amines.[9] The present results listed in Table 4 show that the steric structure of amines has great importance in their reactivity. This is considered as an evidence in behalf of nucleophilic mechanism of catalysis.

It claims attention the fact that φ_1^* and δ_1 values which characterize the influence of alcohol* structure on the reaction rate do not depend on the amine used as well

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* As before[1] the steric effect of alcohols ROH is characterized by the E_s values for RCH_2 groups which are roughly isosteric to RO groups. The data for trichloroethanol (IV) was not included because of absence of E_s value for $Cl_3C\,CH_2$ group.

Table 3

Influence of Amine Structure on Correlation Parameters by Eq.(1)

Amine	lgK_o	ρ^*	δ	r	S
$C_6H_5C{\equiv}CCH_2NEt_2$	-2.85±0.13	2.17±0.35	1.37±0.34	0.962	0.12
Et_3N	-1.59±0.12	2.12±0.32	1.30±0.32	0.966	0.11
$C_6H_5CH_2CH_2NMe_2$	-1.01±0.11	2.09±0.30	1.41±0.30	0.971	0.10

Table 4

Influence of Alcohol Structure on Correlation Parameters by Eq.(3)

Alcohol	lgK_o	ρ^*	δ	r	S
$C_6H_5CH_2CH_2OH$	1.04±0.24	-2.04±0.18	0.94±0.07	0.989	0.12
$C_6H_5CH_2OH$	1.13±0.28	-2.07±0.21	0.87±0.09	0.983	0.14
CH_3OH	1.70±0.19	-2.09±0.15	0.92±0.06	0.992	0.09
$CH{\equiv}CCH_2OH$	1.55±0.18	-2.06±0.44	0.87±0.06	0.992	0.09

as ρ_2^* and δ_2 values which characterize the influence of amine structure on the reaction rate do not depend on the alcohol acylated (Table 4). That proves the influence of structure of both reaction components-alcohol and amine-upon their rate to be additive. In other words, that signifies that the combined influence of alcohol and amine structure is described by the correlation equation (4) of no cross-terms.

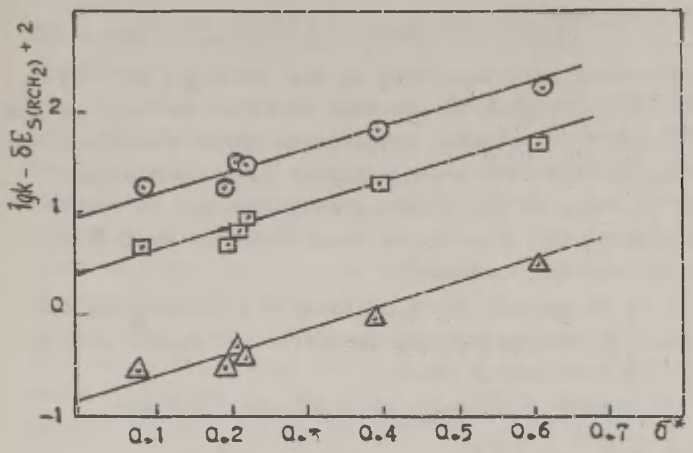

Figure 1.Plot of the rate for catalytic esterification of alcohols vs. their atructure.△-$C_6H_5C{\equiv}CCH_2NEt_2$,□-$Et_3N$, ○-$C_6H_5CH_2CH_2NMe_2$

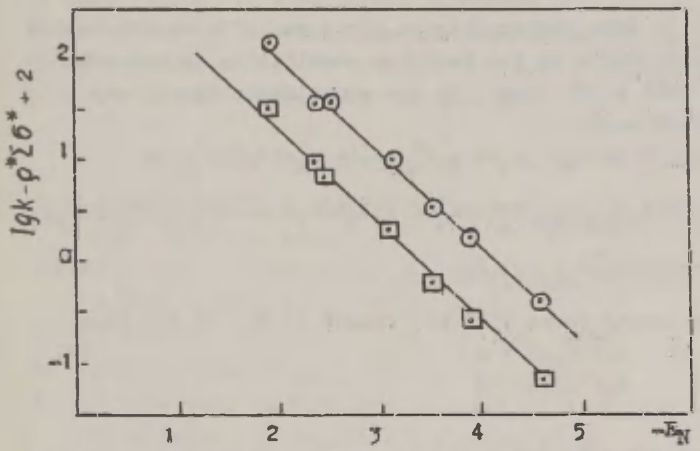

Figure 2.Plot of the rate for catalytic esterification of alcohols vs. amine structure. ,□-$C_6H_5CH_2CH_2OH$,○-CH_3OH

$$\lg k = 1.22+2.13\sigma^{*}_{(R)}+1.36E_{S(RCH_2)}-2.07\Sigma\sigma^{*}_{(R'')}+0.91E_N \qquad (4)$$

On the other hand according to the principle of polylinearity (PPL)(see Ref.10),in this equation it must be expected the presence of some cross-terms which described the interaction of different acting factors with each other. Formally, in terms of PPL this contradiction may be resolved if we assume the existing at least one more acting factor, the solvent for instance*.

Then if we neglect for simplicity the cross-terms described the interaction between inductive and steric effects the Eq.(5) will be taking place,

$$\lg k = \lg k_o + \rho'_1\sigma^{*}_{(R)} + \delta'_1E_{S(RCH_2)} + \rho'_2\Sigma\sigma^{*}_{(R'')} + \delta'_2E_N + sS +$$
$$+ a'_1\rho'_1\rho'_2\sigma^{*}_{(R)}\Sigma\sigma^{*}_{(R'')} + a'_2\delta'_1\delta'_2E_{S(RCH_2)}E_N + a'_3s\rho'_1\sigma^{*}_{(R)}S +$$
$$+ a'_4s\rho'_2\Sigma\sigma^{*}_{(R'')}S + a'_5s\delta'_1E_{S(RCH_2)}S + a'_6s\delta'_2E_NS + a'_7s\rho'_1\rho'_2\sigma^{*}_{(R)}\Sigma\sigma^{*}_{(R'')}S +$$
$$+ a'_8s\delta'_1\delta'_2E_{S(RCH_2)}E_NS \qquad (5)$$

where S is some characteristic (or a sum of characteristics) of solvent and s ie the reaction sensibility to variation of it. Just as S= const. in our experiments Eq.(5) may be written as Eq.(6).

$$\lg k = (\lg k_o + sS) + (1 + a'_3sS)\rho'_1\sigma^{*}_{(R)} + (1 + a'_4sS)\rho'_2\Sigma\sigma^{*}_{(R'')} +$$
$$+ (1 + a'_5sS)\delta'_1E_{S(RCH_2)} + (1 + a'_6sS)\delta'_2E_N + (a'_1 + a'_7sS)\rho'_1\rho'_2\sigma^{*}_{(R)}\Sigma\sigma^{*}_{(R'')} +$$
$$+ (a'_2 + a'_8sS)\delta'_1\delta'_2E_{S(RCH_2)}E_N \qquad (6)$$

Then the cross-terms will be absent if Eq.(7) are real,

$$a'_1 = a'_7sS = 0 \qquad (7)$$
$$a'_2 + a'_8sS = 0$$

or

$$S = -\frac{a'_1}{a'_7s} = -\frac{a'_2}{a'_8s} \qquad (8)$$

---

*Mathematically, the same results are received if an acting factor is temperature, acyl chloride structure etc.

This condition may casually have maintained just for the acylation of benzoyl chloride in tetrachloroethylene at 25° and therefore Eq.(4) takes place.

In respect of the physical meaning of these facts they seemingly indicate in terms of the alsolute rate reaction theory the constant polarity and steric characteristic of transition state. It may be more or less speculatively explained if the participation of solvent in the transition state to take into account also. So in accordance with an Hammond postulate increasing reactivity of initial compounds must lead to more reagent-like and consequently to less polar transition state. However that may diminish their solvation and the grade of cnarge delocalization in solvate sphere. Consequently the relative polarity of transition state will be increased. If the both effects compensate each for other more or less completely no dependence of the polarity of transition state and the ς^* and $\delta^*_{\neq}$ values consequently upon the reactivity of substrates will be observing as it takes place. Analogously increasing steric exactions of reagents may be represented to compensate for decreasing solvation grade. Then steric characteristic of the transition state will be constant.

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EFFECT OF SOLVENTS ON GRIGNARD REACTION
XIV. The Schlenk Equilibrium

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It was shown that the position of the Schlenk equilibrium was determined by solvation of the particles involved in the equilibrium. A principale way to calculate the Schlenk equilibrium constants was indicated.

At present there is no more doubt that all the particles which take part in the Schlenk equilibrium.

$$2\ RMgX \rightleftharpoons R_2Mg + MgX_2\ ,$$

are involved in the interactions between Grignard reagent and various substrates, e.g. ketones and nitriles.[1-3]

Since the particles R_2Mg and RMgX are of different reactivity, the total reactivity of the system is susceptible to and determined by the position of the Schlenk equilibrium.

Evidently, the influence of the halogen atom on the reactivity of Grignard reagent is mainly realized through its influence on the position of the Schlenk equilibrium.

A comparision of the data for the reactivity of alkylmagnesium halides with those for the position of the Schlenk equilibrium in diethyl ether and tetrahydrofurane corroborates the statement above. The comparative reactivity data are comprised in Holm's work[4]. The constant of Schlenk equilibrium in diethyl ether strongly depends on the halogen,[5] similarily to the reactivity of Grignard reagent. As to the tetrahydrofurane solutions, in known cases[6-8] the ratio of the concentration of the particle RMgX to that of R_2Mg varies from 1 to 3 and is little dependent on the halogen. Accord-

ingly, in reactions of n-butylmagnesium halides with acetone, methylacetate, or azobenzene in tetrahydrofurane[4] the rate of the chloride exceeds that of the bromide only by 5–40%.

The Schlenk equilibrium constant,

$$K_S = \frac{[RMgX]^2}{[R_2Mg][MgX_2]} ,$$

depends on the solvent noticeably as it can be seen from Table 1. Smith and Becker[6] suggest that the position of the Schlenk equilibrium in different solvents is determined by the differences in the solvation of particles involved in the equilibrium. If it is so, the Schlenk equilibrium constant will be determined by the basicity of the solvent and acidity of the particles.

T a b l e 1

The Constants of the Schlenk Equilibrium in Solutions of RMgBr

Solvent	R=C_2H_5- t=25°C	R=C_6H_5- t=25°C	R=2-$CF_3C_6H_4$- t=-50°C
Tetrahydrofurane	5.1[a]	3.8[a]	10.5[b]
2-Methyltetrahydrofurane	...	2.3[b]	31[b]
Dimethoxyethane	...	6.1[c]	...
Diethyl ether	484[a]	62[a]	324[b]
Diethyleneglycole diethyle ether	...	>1500[b]	...

[a] data of Smith and Becker[5,6]
[b] data of Evans and Fazakerley[8]
[c] data of Psarras and Dessy[9]

In a previous paper[10] we proposed a formulation of the effective basicity as follows

$$B^{*} = \varphi_0 + \varphi_1 B + \varphi_2 B\, E_S^o , \qquad (1)$$

where B is a measure of electron-donating properties of the base and $E_S^{o'}$ is its isosteric constant. The ratio

$$\varphi_1 / \varphi_2 = \varphi^*$$

is characteristic of the substrate and determines the scale of effective basicity of the solvents in respect of the substrate. The constant φ^* is called[10] index of effective acidity.

Symmetrically to the formula for effective basicity (1) we may express the effective acidity as follows

$$A^* = \beta_0 + \beta_1 A + \beta_2 A\, E_S^{o'} ,$$

where A is a measure of electron-accepting properties of the acid and constants β are characteristic of the reference base. Construction of the scale of constants A is connected with a number of difficulties, the most noteworthy of them is caused by the polyvalency of many Lewis acids including magnesium compounds.

In the case of the latters a comparision of acidity of particles involved in the Schlenk equilibrium is of practical interest. Since the steric requirements of the acids of any Schlenk system do not differ considerably, one can assume that

$$A \sim \varphi^*$$

and, as far the index of effective acidity includes also the steric effects[10], that

$$A^* = \beta_0 + \beta_1 \varphi^* \qquad (2)$$

The relationship (2) is probably valied in the case of the solvents with moderate steric effects.

If the position of the Schlenk equilibrium is mainly determined by solvation of the particles involved in the equilibrium, the problem will be restrected to the differences in effective acidity of the particles.

Expressing the Schlenk equilibrium constant through the constants of the solvation equilibria of the particles

we obtain

$$\lg K_S = 2 \lg K_{RMgX} - \lg K_{R_2Mg} - \lg K_{MgX_2} \qquad (3)$$

It was found earlier[10] that the constants of the solvent replacement equilibria correlated well according following equation

$$\lg K = A_o + b B^* .$$

Analogously we may put

$$\lg K = C_o + c A^* . \qquad (4)$$

Then it follows from Eqs. (2) - (4) that

$$\lg K_S = \gamma (2\varphi^*_{RMgX} - \varphi^*_{R_2Mg} - \varphi^*_{MgX_2}), \qquad (5)$$

where γ is a characteristic constant of the solvent.

Unfortunately, there is no bulk of data to check the validity of Eq.(5). Recently[10] we calculated from experimental data some values of the indeces of effective acidity, φ^* (Table 2). In the same work the correlation (6) was found

$$\varphi^* = 10.1 + 2.4\, E_S^{o\prime} + 0.6 \sum \sigma^*, \qquad (6)$$

where $E_S^{o\prime}$ is the isosteric constant of organomagnesium compound and $\sum\sigma^*$ is the sum of inductive constants of the substituents linked with the magnesium atom. By means of Eq. (6) one can try to estimate the indeces of effective acidity for magnesium bromide and phenylmagnesium bromide. Assuming magnesium bromide to be isosteric to the group $-CHBr_2$ we used for it the value[11] $E_S^{o\prime} = -2.5$. Analogously we estimated for phenylmagnesium bromide $E_S^{o\prime} = -2.2$ and so obtained for magnesium bromide $\varphi^* = 7.4 \pm 0.6$ and for phenylmagnesium bromide $\varphi^* = 6.9$. The latter value agrees well with $\varphi^* \leq 7$ based on the experimental data[10].

Making use of the values of φ^* from Table 2, the corresponding values of Schlenk equilibrium constants from Table 1, and Eq.(5) we obtained the following values of γ for diethyl ether: from the data for ethylmagnesium bromide $\gamma = 3.0$ and from the data for phenylmagnesium bromide $\gamma = 3.6$.

In the same way we obtained the corresponding γ values equal to 0.8 and 1.2 for tetrahydrofurane.

Table 2

Indeces of Effective Acidity for Some Magnesium Compounds

Compound	φ^*
$MgBr_2$	7.4
PhMgBr	6.9
EtMgBr	6.4
Ph_2Mg	5.9
Et_2Mg	4.5

Taking into consideration the assumptions made in deduction of Eq.(5) and the inaccuracy of estimating the φ^* values, one should admit that the γ values obtained from different systems coincide quite satisfactorily. Consequently, the Schlenk equilibrium constant is actually determined by solvation of the particles involved in the equilibrium. It also follows that the values of the Schlenk equilibrium constant can be calculated from the indeces of effective acidity and an empiric constant for the solvent.

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THE IHDOLYL-3-PHENYLMETHYLCATIOHS

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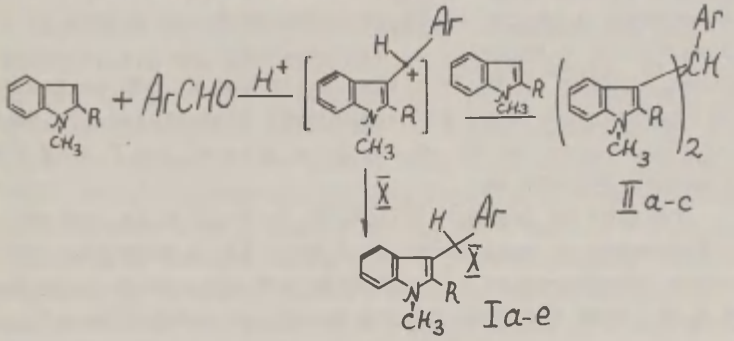
By methods of UV- and visible spetroscopy and cryoscopy it was established that 1-methyl-2-carboxy-3-(α-X-benzyl) indoles and di(1-methyl-2-carboxyindolyl-3)-phenylmethanes convert into (1-methyl-2-carboxyindolyl-3)-phenylmethylcations in concentrated sulfuric acid. The values of pK_{R^+} from indolyl-3-phenylmethylcations were calculated by employing of acidity function (C_0), which has been evaluated for the equilibria: diphenylmethanol + $H^+ \rightleftharpoons$ diphenylcation + H_2O.

With the help of the acidity function for diphenylcarbinols the pK_{R^+} values were calculated for the studied indolyl-3-phenylmethyl cations.

It is known that the reactions of indoles with aromatic aldehydes are catalyzed by acids and lead to diindolylphenylmethanes (II) [1]. Recently, we proved that the derivates of indolyl-3-phenylcarbinoles (I) can be obtained at under certain conditions in acid medium in a high yield [2].



The behaviour of substances I and II (where X = OH, OCH_3, Cl; R = COOH) in solutions of H_2SO_4 was investigated in order to prove the formation of indolyl-3-phenylmethylcations as intermediates in this reaction. When substances I and II were dissolved in sufficiently concentrated H_2SO_4, a new spectroscopic species appeared which strongly absorbed in the visible region of the spectrum. An increase of optical density of the solution took place as far as all the initial substance converts into carbonium ion (Fig.1).

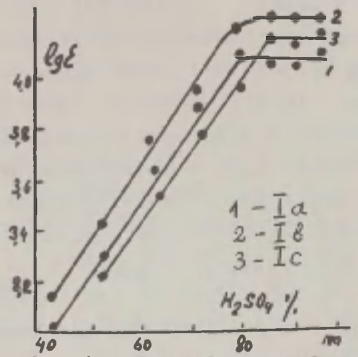


Fig. 1. Plot of the molar extinction coefficient I a,b,c against % H_2SO_4 at λ_{max}.

The absorption of a free initial substance was negligible at λ_{max} of carbonium ion. It was found that a solutions of substances I and II at concentrations 1.10^{-4} – 1.10^{-3} obey Beer's law. It proves the independence of ratio Q=concentration of carbonium ion)/(concentration of non-ion species) on concentration of initial substance.

We and Deno with his coworkers [3] did not discover any difference in behaviour of carbinoles (X = OH) and chlorides (X = Cl), hence in the experimental work mainly chlorides were used as more stable for keeping. A change of UV-spectrum with the growth of concentration of H_2SO_4 (Fig. 2) was expressed by the increase of optical density in the visible region and at 300 nm. However, when initial substance was completely dissociated (70,5% H_2SO_4) the curve did not change in a plot of log ε vs % H_2SO_4 for region 440-460 nm.

The plot of log Q = f(% H_2SO_4) (Fig. 3) is typical for behaviour of weak bases in H_2SO_4 [4]. A practical measurable concentration of carbonium ion appears in more than 52% H_2SO_4 even for more strong bases. An estimation of the

pK_{R^+} value may be carried out by employing overlapping indicators i.e. substances of the same structure but dissociating in a diluted solution of H_2SO_4. Such a complete number of indolyl-3-phenylmethylcarbinoles was not obtained therefore the pK_{R^+} value was evaluated from relation

$$pK_{R^+} = C_0 + \lg Q \quad (1),$$

where C_0 = acidity function of H_2SO_4 solution, obtained for equilibrium: diphenylcarbinol (diphenylmethylchloride) + $H^+ \rightleftharpoons$ diphenylmethylcation + H_2O (HCl), for diphenylmethylchlorides are more similar with indolylphenylmethylchlorides I a-e. A correlation of pK_{R^+} and σ-constant of substituents in the phenyl ring expressed by equation:

$$pK_{R^+} = -5.18 - 10.5$$

($r = 0.95$), which negligibly differs from the equation for diphenylmethylcarbinols [5]: $pK_{R^+} = -5.636 - 13.2$. Therefore,

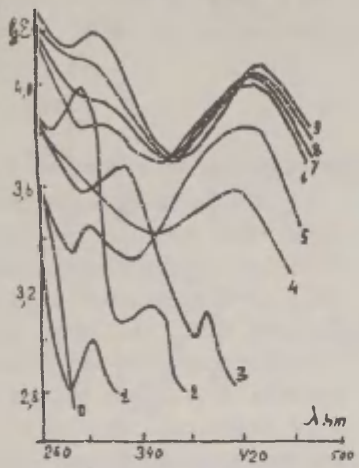
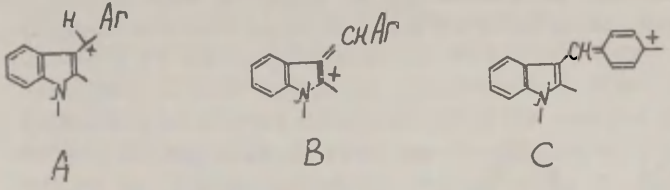


Fig. 2. UV-spectrum of sibstance Ia in H_2SO_4 of the following concentrations (%): 0 - 0; 1 - 18; 2 - 30; 3 - 42; 4 - 55; 5 - 62; 6 - 70; 7 - 78; 8 - 84; 9 - 90; 10 - 96.

1 -methyl-2-carboxyindolyl-3-group increases the stability of carbonium ion as compared to a phenyl-group, by 2.7 units of pK. Using of σ^+-constants improved the correlation($r=0.97$), thus indicating the existence of resonance structure with a positive charge in the phenyl ring (C). However, the exchange reaction of X-group yielded products, according to structures of carbonium ions A and B, except structure C. For example, chlorine in 1-methyl-2-carboxy-3-(α-chlorbenzyl) indole was replaced by hydroxy, alkoxy, acetoxy, thioalkyl groups, while the action of KCN caused a decarboxylation and then formation

of 1-methyl-2-cyano-3-benzylindole.



A B C

That proves the existence of a carbonium ion in structure B.

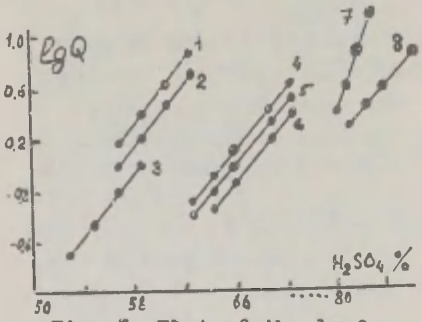
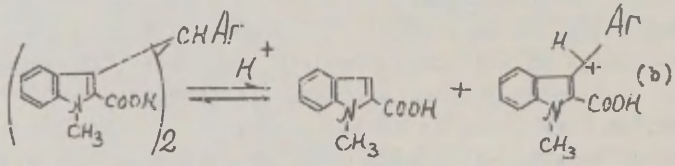


Fig. 3. Plot of the lg Q against % H_2SO_4 for
1 - IIb; 2 - Ia;
3 - IIc; 4 - Ie;
5 - IIa; 6 - Ib;
7 - Ic; 8 - Id.

It is interesting to note the ability of di-(indolyl-3)-phenylmethanes (II) to make colour solutions of H_2SO_4 similarly tc to substance (I). Their UV-spectra in visible region were identical. The only coloured specie which could be common for these two structure is indolyl-3--phenylmethylcation, formed by reaction (b).

1-methyl-2-carboxyindole under experimental conditions cannot be protonated and its solutions in H_2SO_4 are colourless. We obtained the following Vant-Hoff's coefficients in case of conc.H_2SO_4: 1-methyl-2-carboxyindole i = 1.0; di(1-methyl-2-carboxyindolyl-3)phenylmethane i = 2.8 ($i_{theoretical}$ = 3,0).



An additional evidence of existence of equilibrium (b) resulted from experiments in which to solution of diindolylphenylmethane (II) in H_2SO_4 KCl and 1-methyl-2-carboxyindole were added (Fig. 4). A reduction of optical density at 458 nm occurred both for KCl and for 1-methyl-2-carboxyindole, the efficiency of 1-methy-2--carboxyindole was 10^3 times more as compared to KCl. In the plot of lg ε vs % 1-methyl-2-carboxyindole for 62%, 64%, 66% H_2SO_4 the curve was a straight line, as indolylphenylmethylcation and 1-methyl-2-carboxyindole took part in equilibrium (b).

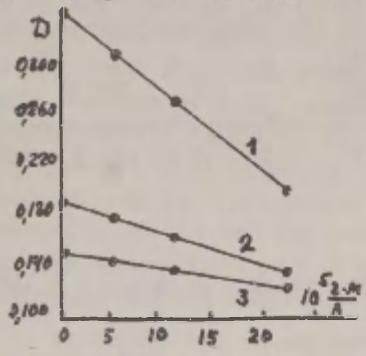


Fig. 4

The optical density of substance IIa in the presence of 1-methylindole-2-carbonic acid 1 - 66%, 2 - 64%, 3 - 62% H_2SO_4.

Experimental

1. An estimation of pK_R+ for (1-methyl-2-carboxyindolyl-3-)-phenylmethyl cations

An aliquot of 0.10 g (3.10^{-5} moles) carbinole Ib in 10ml ethanol was dissolved, a sample of 0.1 ml of the obtained solution was taken and added to test-tubes, containing 18+-+96% conc.H_2SO_4. The reference cell contained all the components except substance Ib. The cells were brought to $20\pm0.2^{\circ}C$, and the resdings of optical density in UV and visible region were taken on CF-16 spectrophotometer. The obtained results are shown in Fig.1. For calculation of the pK_R+ values the spectrum of the solution was taken in the range of H_2SO_4 concentration 62.3+70% at 1.5 per cent intervas. In each case the concentration was chosen in such a way that the ionized form

Table

The Basicity of 1-CH_3-2-COOH-3-(α-X-benzyl)-indoles (Ia-e) and Di(1-CH_3-2-COOH-indolyl-3)-phenylmethanes (IIa-c)

№	Compound	pK_{R^+}	$\frac{d \lg Q}{d H_2SO_4}$	r	S	λ nm	ε
Ia	1-CH_3-2-COOH-3-(α-hydroxy-o-chlorbenzyl)-indole	-8.1±0.4	1.2	0.99	0.09	460	$1.0 \cdot 10^4$
Ib	1-CH_3-2-COOH-3-(α-hydroxybenzyl)-indole	-10.7±0.4	1.2	0.98	0.09	460	$1.8 \cdot 10^4$
Ic	1-CH_3-2-COOH-3-(α-chlor-p-NO_2-benzyl)-indole	-13.0±0.8	2.4	0.95	0.10	440	$1.14 \cdot 10^4$
Id	1-CH_3-2-COOH-3-(α-chlor-m-NO_2-benzyl)-indole	-13.9 ±0.4	1.6	0.96	0.11	425	$11.4 \cdot 10^4$
Ie	1-CH_3-2-COOH-3-(α-chlor-p-chlorbenzyl)-indole	-10.6±0.4	1.2	0.98	0.09	460	$3.5 \cdot 10^4$
IIa	Di(1-CH_3-2-COOH-indolyl-3)-phenylmethane	-10.5±0.5	1.2	0.96	0.09	458	$2.0 \cdot 10^4$
IIb	Di(1-CH_3-2-COOH-indolyl-3)-o-chlorphenylmethane	-8.1±0.5	1.2	0.96	0.08	460	$1.06 \cdot 10^4$
IIc	Di(1-CH_3-2-COOH-indolyl-3)-p-methoxyphenylmethane	-6.2±0.3	1.2	0.97	0.10	535	$3.1 \cdot 10^4$

content should change from 25% to 75%. The pK_R+ value was calculated from Equation (1), where C_0 is acidity function [3], $\lg Q = Di/(D_{max} - Di)$, where Di is optical density for the measuring concentration of H_2SO_4 at λ_{max} = 458 nm; D_{max} is optical density for 90-96 % H_2SO_4, when all the carbinol is in a from of carbonium ion. Average relative error is 5% or 0.5 units pK_R+ (see Table). The slope of indicator ratio as a function of H_2SO_4 concentration ($d \lg Q/d H_2SO_4$) is satisfactorily constant, except the substance containing NO_2- group. A good linearity of the function $\lg Q = f(H_2SO_4)$ follows from the correlation coefficient (r) and the standard deviation (S). In the two last columns of the Table one can see the wave-lenght (λ) at which the measurings were carried out, and the molar extinction coefficient (ε).

2. Cryoscopic measurments

An ordinary technique was used [6]. The highest temperature, which the mixture reached at the moment of crystallization was used as the freezing point. It was difficult to determine the freezing point by melting the mixture, since the solution was strongly coloured.

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HYDROGEN BOND ENERGY IN ICE I CALCULATED BY THE METHOD OF THE ELECTROSTATIC INTERACTIONS BETWEEN THE PARTIAL CHARGES

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The importance of the hydrogen bond in the case of many chemical processes is well known.[1] Need for a well working model of the hydrogen bond arises in various areas of chemical investigation (from the examination of the properties of the molecular crystals[2] up to exploring of the influence of the hydroxyl-containing solvents on the rate of chemical reactions [3]).

Considerable progress in describing of the properties of the hydrogen bond by use of the quantum-mechanical CNDO and ab initio methods has been made during last years.[4] Unfortunately, because of the insufficient precision and excessive complication, these methods are still unsuitable in solving many interesting problems. For that reason, various empirical functions of the hydrogen bond potential energy are widely used.[5,6]

In previous works[7,8] one of us has proposed a model of the electrostatic interaction between atomic partial charges in molecule. It was established that by this model enthalpies of formation (at $0^{\circ}K$) of alkanes and fluoromethanes (i.e.for the compounds containing covalent chemical bonds) could be calculated within the limits of experimental error. In view of this it is of interest to prove this model for describing the other types of chemical bonds, e.g. the hydrogen and donor-acceptor bonds. In the present work we make an attempt

to use the method of electrostatic interactions between partial charges for calculating the potential energy of the hydrogen bond between the water molecules in ice I. It should be noted that a strong argument against the full - electrostatic description of the hydrogen bond (formerly proposed by L. Pauling[9]), has been presented. Namely the lenght of the hydrogen bond is notably shorter than the sum of the van der Waals radii of the atoms forming this bond.[10,11] As it has been pointed out, the repulsion energy between the atoms at the distance of hydrogen bond is far greater than the calculated energy of electrostatic stabilization.[10] This fact must be taken into account in constructing simple models of the hydrogen bond.

Let us assume that the total hydrogen bond energy, E_H, consists of two parts:

a) energy of electrostatic interaction, E_{el},

b) covalent bonding energy, E_{cov}.

Thus, $E_H = E_{el} + E_{cov}$. (1)

Consequently, if the experimental value of E_H is known, and if one can calculate the quantity E_{el}, contribution of the covalent part to total energy of the structure formed by hydrogen bonds could be evaluated according to Eq.(1).

The must exact experimental value of the energy of the structure with hydrogen bonds is the one of ice. Numerically it is equal to the sublimation enthalpy of the ice:

at 298 K $\Delta H^{\circ}_{subl} = 12.232$ kcal/mol[12]

at 0 K $\Delta H^{\circ}_{0\,subl} = 11.300$ kcal/mol[13]

If to take into consideration the difference between the zero - point energies of the ice and the water vapor

$\Delta H^{\circ}_{0\,subl} = 13.412$ kcal/mol[6]

Unfortunately, exact calculation of the lattice energy of ice I cannot be realized in practice because there are great mathematical difficulties in computing the Madelung

constant for its structure, based on the internal distribution of the charges in the water molecules. Therefore we had investigated the convergence of the electrostatic interaction energy between of the fixed water molecule in the structure of ice I and the water molecules on the consecutive layers around its.

Thus, the first layer contains 4 water molecules bonded directly with the fixed molecule, the second layer contains 12 molecules bonded over the one with the fixed molecule and so on (see Table).

The electrostatic interaction energy between the two water molecules was calculated according to the following formula:

$$E_{el} = \frac{Ne^2}{\varepsilon} \sum_{i \neq j} \sum \frac{q_i q_j}{r_{ij}} \qquad (2)$$

in which q_i and q_j are the values of the partial charges in interacting molecules, r_{ij} is the distance between these charges, N is Avogadro's number, e is the electronic charge, and ε is the dielectric constant of the medium, taken equal to unity.

It is clear that information on the distribution of the charges in the water molecule is needed for the practical calculations. This distribution can be calculated provided(similar to that in case of alkanes and fluoromethanes, as it was pointed out above) that the total heat of formation of water, $\Delta H^{o}_{o(H_2O)}$, is equal to the intermolecular electrostatic interaction energy between the partial charges on its molecule. Then we can write:

$$\Delta H^{o}_{o(H_2O)} = Ne^2 q_H^2 \left(-\frac{4}{r_{OH}} + \frac{1}{r_{HH}}\right) + \frac{4 q_H \mu_e \cos\varphi}{4.8\, r^2_{OH}} \qquad (3)$$

In Eq.(3) μ_e denotes dipole moment caused by one unshared electron pair of the oxygen atom, q_H is the partial charge localized on the hydrogen atom, r_{HH} and r_{OH} are distances between the corresponding atoms, φ is the angle formed by the OH-bond and the dipole μ_e.

Another equation we can obtain from the expression for the total dipole moment of water molecule μ_{H_2O} is as follows.

$$\mu_{H_2O} = -4.8 \cdot 2 \cdot r_{OH} \cdot q_H \cdot \cos(\gamma/2) + 2\mu_: \cos(\Theta/2) \quad (4)$$

Here γ denotes the angle between the two OH-bonds, and Θ is the angle between two dipoles $\mu_:$. Following numerical values of the constants were used in calculation:

$$\Delta H^\circ_{c(H_2O)} = -57.1 \text{ kcal/mol}^{16}, \quad r_{OH} = 0.9584 \text{ Å}^{17}$$

$$\gamma = 104^\circ 27'^{17} \quad \mu_{H_2O} = 1.846 \text{ D}.^{18} \quad \Theta \text{ and } \varphi$$

were regarded as the tetrahedrical angles.

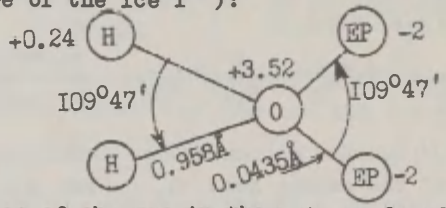
The solution of the system of Eqs.(3) and (4) gives the following values for the quantities to be determined*:

$$q_H = +0.241 \text{ (units of elementary charge)}$$

$$\mu_: = 0.427 \text{ D}$$

In fact, the dipole $\mu_:$ was assumed to be a point dipole. But, since the program used by the computation of electrostatic energies was accomodated to calculation of the sum of electrostatic interaction energies between point charges, we have to assume that the charge at the negative tip of dipole is equal to - 2 (charge of the unshared electron pair). This value results in the dipole lenght of 0.0435 A°.

Finally, for the immediate calculations the following electrostatic model of the water molecule was used (it was taken into account that tetrahedric angles are realized in the structure of the ice I[19]):



* Distribution of charges in the water molecule, obtained here, can be found by the use of independent methods as described elsewhere.[23,24]

In calculation of the distances between partial charges of different water molecules the structure of ice I was adopted (by J.D. Bernal and R.H. Fowler[19] with the distance $r_{O\cdots H-O} = 2.76$ Å [19,20]).

In this work we calculate the electrostatic interaction energy between fixed molecule and 5 closest layers of water molecules around it. These layers contain a total of 158 water molecules (see Table). In calculations by the formula (2) we use the standart program elaborated by us for the computer "Nairi-2".

In finding the interaction energy between molecules, it was taken into account that every molecule in the structure of ice I can have different configurations with respect to others. With the help of the calculations of the residual entropy of the ice, L. Pauling had shown that all the configurations of water molecules in the ice I structure are equivalent to each other.[21] For that reason, in calculations of the interaction energy of every two water molecules, all these configurations had been taken into account with the equal statistical weights. The results of calculations are presented in Table.

T a b l e

Electrostatic Interaction Energy Between the Fixed Water Molecule and the Molecules in the n-th Layer Around it in the Structure of Ice I, Calculated According to Formula (2) (in kcal/mol)

Layer (n)	Number of the water molecules in the layer	$E_{el}(n)$	$\sum_n E_{el}$
1	4	-13,356	-13,356
2	12	- 4,946	-18,302
3	25	- 2,978	-21,280
4	44	- 0,806	-22,086
5	73	- 0,428	-22,514

It can be seen from the obtained data that the interaction energy declines sharply at distant layers (despite of the increased number of water molecules in the layer). Moreover, in all probability, it must be asserted that the given series of the electrostatic interaction energies at infinity ($n \longrightarrow \infty$) approaches the doubled value of the ice sublimation energy. Electrostatic energy for the one molecule of water is equal to a half of the magnitude, calculated by us, because every pair interaction energy is shared between the two water molecules. Consequently, the total lattice energy of the ice is equal to its electrostatic part, and the covalent energy should be taken equal to zero.

On the other hand, as it was pointed out above, contribution of the covalent part of energy to the formation of hydrogen bond must be highly considerable if to evaluate the energy not from the energy level of the isolated atoms, but from the level of the repulsion energy at distance between atoms in lattice. Therefore, we make an attempt to find out the contribution of the covalent energy to the total potential energy of the hydrogen bond.

Let us assume that the dependence of the covalent potential energy value on the bond lenght can be presented by the well-known Morse function:

$$E_{cov} = D\left\{1 - \exp\left[-\beta(r - r_o)\right]\right\}^2 - D \qquad (5)$$

where D denotes the depth of the covalent potential cavity, β is a characteristic constant, r and r_o are the given distance between atoms and the distance at the minimum of the covalent energy respectively.

Denoting the distance between the oxygen and hydrogen atoms at minimum of total energy in ice by r^*, we have (see Table and Fig. 1):

$$D\left\{1 - \exp\left[-\beta(r^* - r_o)\right]\right\}^2 - D = 0 \qquad (6)$$

From this equation we get the following requirement for quantity β :

$$\beta = -\frac{\ln 2}{r^* - r_o} \qquad (7)$$

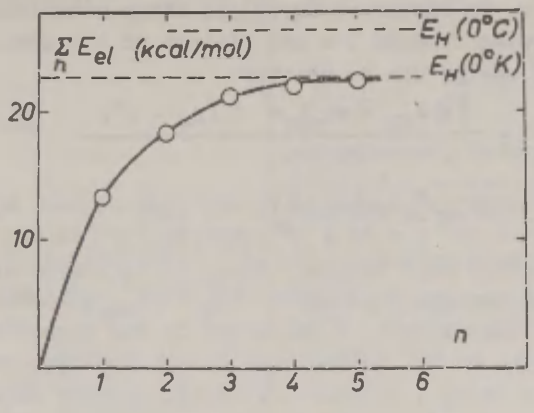


Fig. 1
Relationship of the electrostatic interaction energy between the fixed molecule and the molecules in the n-th layer around it in the structure of ice I.

On the other hand, principle of the total energy minimum must be written in form:

$$\left(\frac{\partial E_H}{\partial r}\right)_{r = r^*} = 0 \qquad (8)$$

If to take into account Eq.(1), and imply, that E_{cov} and E_{el} are independent functions from the distance parameter r, we can get following requirements:

$$\left(\frac{\partial E_H}{\partial r}\right)_{r = r^*} = \left(\frac{\partial E_{el}}{\partial r}\right)_{r = r^*} + \left(\frac{\partial E_{cov}}{\partial r}\right)_{r = r^*} = 0 \qquad (9)$$

Changing E_{cov} for that in Eq.(5) we get:

$$\left(\frac{\partial E_{el}}{\partial r}\right)_{r = r^*} + 2\,D\beta e^{-\beta(r^* - r_o)}\left[1 - e^{-\beta(r^* - r_o)}\right] = 0, \qquad (10)$$

from which we obtain

$$D = -\frac{\left(\partial E_{el}/\partial r\right)_{r=r^*}}{2\beta e^{-\beta(r^* - r_o)}\left[1 - e^{-\beta(r^* - r_o)}\right]} \qquad (11)$$

Finally, in virtue of Eq.(7)and after numerical operations following formula for the minimum of the covalent part of the bond energy can be written:

$$D = \frac{(\partial E_{el}/\partial r)_{r=r^{*}} \cdot (r_0 - r^{*})}{2.7728} \qquad (12)$$

The quantity r^{*} is known in the case of the hydrogen bond in ice I ($r^{*} = 1.80$ Å).[20] From Eq.(12) it can be seen that information only on quantity r_0 is wanted to calculate the D value. Partial derivative $(\partial E_{el}/\partial r)_{r=r^{*}}$ can be obtained by the graphical method as the slope of the dependence of E_{el} from r in site of r^{*}. In the case of the hydrogen bond in ice, calculations of E_{el}, proceeded by us by varying of r, gave:

$$\left(\frac{\partial E_{el}}{\partial r}\right)_{r = r^{*}} = 6.65 \frac{\text{kcal}}{\text{mol Å}}$$

Doing reasonable assumptions on the values of quantity r_0, one can evaluate the maximal value of D.

Evidently

$$r^{*} < r < r_v,$$

where r_v denotes the sum of the van der Waals radii of the atoms forming hydrogen bond. From the definition of r_v we get another condition:

$$E_{cov}(r_v) \approx 0$$

Consequently, if to take into account the form of the Morse function (See Fig. 2), the maximal estimate of r_0 is as follows.

$$r_0 = \frac{r^{*} + r_v}{2} \qquad (13)$$

Putting numerical values into Eq (13), ($r^{*} = 1.80$ Å[20] and $r_v = 2.60$ Å[1]), we get $r_0 = 2.20$ Å. Then quantity D = 0.931 kcal/mol (See Eq. (12)) and $\beta = 1.730$ (from Eq.(7)).

Therefore the Morse function for the covalent contribution to the hydrogen bond energy can be written as follows:

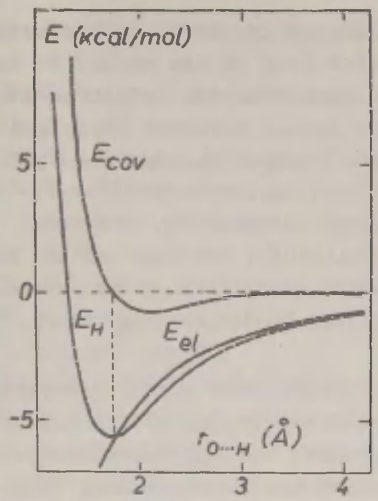


Fig. 2

Relationship between the potential energy E_H in ice I and the distance $r_{O\ldots H}$.

E_{el}=calculated by Eq.(2)

E_{cov}=calculated by Eq.(14)

$$E_{cov(ice)} = 0.931\left\{1 - \exp\left[-1.730(r-2.20)\right]\right\}^2 - 0.931 \qquad (14)$$

From Fig. 2 it can be seen that in the case of $r > r^{\equiv}$ the contribution of the covalent part to total energy is surprisingly little and the main part of the bond energy results from electrostatic stabilization.

However, it should be noted that from the latter result one must not conclude that covalent forces are of little importance in forming of hydrogen bond. On the contrary, due to the compensation of the repulsive forces by covalent forces the donor and acceptor molecules approach the more nearer distance to each other whereas the electrostatic stabilization forces markedly increase.

It can be shown (see Fig. 2) that at the distance $r^{\equiv}$ corresponding to the total energy minimum, covalent part of energy has zero value, which corresponds to that of isolated atoms. In other words, electrostatic energy "pushes" the system through the cavity of the covalent part of potential

energy on the other brink of this cavity. Further shortening of the distance r evokes a greater loss of the energy on account of the repulsion as the gain from the electrostatic energy part. If this, by oneself little covalent hydrogen bond be lacking, then equilibrium between the van der Waals repulsion and electrostatic attraction forces will be established at the markedly greater distances, r, and total gain of the energy should be negligible. For that reason the appearing of the covalent hydrogen bond leads to an essential energetic effect, although the latter has secondary, electrostatic nature.

Now, knowing the shape of the covalent energy potential function and proceeding from the distribution of the partial charges in the interacting molecules, one can calculate both the lenght of the hydrogen bond and the corresponding energetic effect. A check on the validity of the model described above for constructing the quantitative theory of the hydrogen bond and specific solvation conditioned by the latter will be described elsewhere.

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DESCRIPTION OF THE IONIC HYDRATION WITH HELP OF THE MODEL OF THE INTERACTING PARTIAL CHARGES IN MOLECULES

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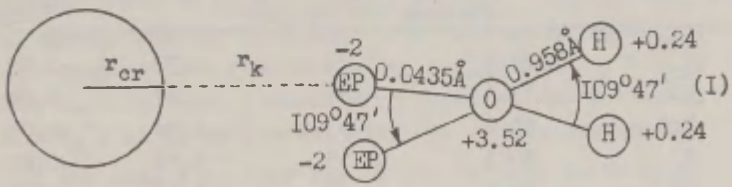
In the previous work[1] we had presented an electrostatic model of the water molecule and theory of hydrogen bonding, based on the calculation of the electrostatic interaction energy between the partial charges in interacting water molecules.[2,3] In this work we propose a check-up of the water molecule model and the before-used theory for fully different type of chemical interaction, viz. the hydration of ions.

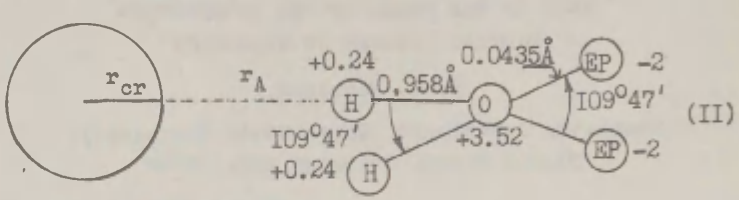
The quantities $\Delta H_{0,1}$ as the interaction energy of an ion and the water molecule in gaseous phase for some univalent anions and cations have been measured of high accuracy with the help of mass-spectrometry by P.Kebarle and coworkers.[4] Without doubt, these quantities have a clearer physical interpretation than quantities ΔH_h^o, which describe energetical effect of transport of an ion from the gaseous phase to the liquid water.

We had used following models for the charge distribution and structure of complexes formed by an ion and the water molecule.

In the case of cations:



In the case of anions:



(II)

Quantity r_{cr} denotes cristallographic radius of ions in these scheme.[6]

Consequently, we had used the distribution of the partial charges of the water molecule in unperturbed state, i.e. as described in the previous work[1]. The charge of the ion was localized on its centre. It should be noted that experimental information about the distances r_A and r_k be lacking actually.

T a b l e

Comparison of the Quantities $r_{k(A)} + r_{cr}$ (I,II) with the Crystallographic Radii r_{or} for some Univalent Ions

Ion	$\Delta H^4_{O,1}$ (kcal/mol)	$r_{K(A)} + r_{cr}$ (Å)	r_{cr} (Å)	$r_{K(A)}$ (Å)
Li^+	34	1.48	0.78	0.70
Na^+	24	1.71	0.98	0.73
K^+	17.9	2.03	1.33	0.70
Rb^+	15,9	2.16	1.49	0.67
Cs^+	13,7	2.31	1.65	0.66
	Average for cations			0.68±0.02
F^-	23,3	1,31	1.33	-0.02
Cl^-	13,1	1,85	1.81	0,04
Br^-	12,3	1,93	1.96	-0,03
J^-	10.2	2.15	2,16	-0,01
OH^-	22.5	1.33	1.40[7]	-0.07
	Average for anions			-0.02±0.03

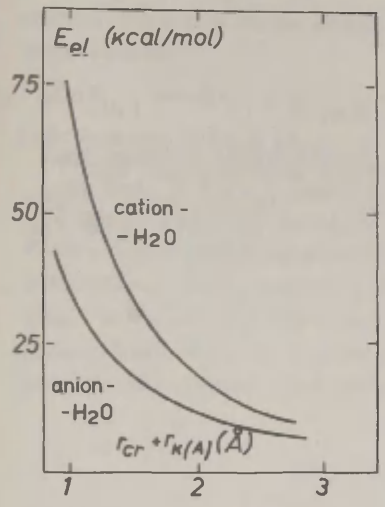


Fig. 1

Relationship between the electrostatic interaction energy (1) and the distance $r_{K(A)^+} r_{cr}$

For that reason we had chosen the following way in which to test the models described above. Proceeding from the structures (I) and (II), we had calculated electrostatic interaction energies according to the formula:

$$E_{el} = 331\ q_i \sum_j \frac{q_j}{r_{ij}}, \text{(kcal/mol)} \qquad (1)$$

where q_i denotes the ion charge, q_j are partial charges in the water molecule, r_{ij} is distance between charges i and j at various values of $r_k + r_{cr}$ and $r_A + r_{cr}$. Corresponding potential energy curves, obtained by us, are given in Fig.1.

Let compare then quantities $(r_k + r_{cr})$ and $(r_A + r_{cr})$ for some different ions, which correspond to the values of E_{el} at $\Delta H_{0,1}$ in these curves, with the crystallographic radii of the same ions (see Fig. 2 and Table). In view of experimental uncertainity ($\pm$ 1 kcal/mol), we can assert that $r_k = 0.68$ Å and $r_A = 0$.

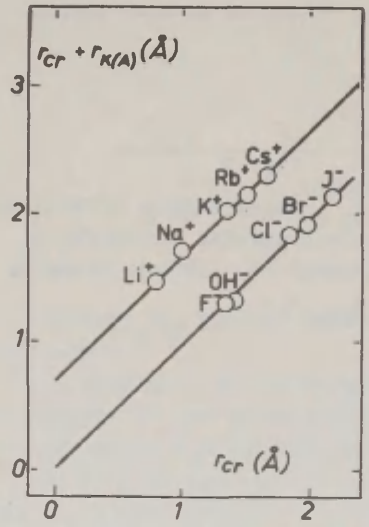


Fig. 2.

Relationship between the values $r_{A(K)} + r_{cr}$ and the crystallographic radii r_{cr} for some ions.

Consequently, in the framework of the model described above the hydrogen atom which forms a bond with the anion must be found at the distance of the crystallocraphic radius from the centre of the latter. Likewise it is very interesting that the size of the distance r_k=0.68 Å is practically that of the covalent radius of the oxygen (0.66 Å[8]).

Therefore, making some physically realistic assumptions, one can calculate the energy of bond between an ion and the water molecule according to the electrostatic model described already[1-3].

In connection with the use of quantities $\Delta H_{0,1}$ one should pay attention to quite an interesting relationship. P.Kebarle et al.[9] have observed certain closeness in change of quantities ΔH_h^o and $\Delta H_{0,1}$. However, if to use quantities $\sum \Delta H_{0,1}$ and $\sum \Delta H_h^o$ for neutral electrolytes instead of individual ion values (such a comparison is more correct, because for getting ΔH_h^o from $\sum \Delta H_h^o$ various unexperimental

assumptions are to be made) we can establish following linear correlation:

$$\Sigma\Delta H_{0,1} = (-20.7 \pm 2.1) + (0.355 \pm 0.012)\Sigma\Delta H_h^\circ \qquad (2)$$

for various alkali halides.

The intercept of this linearity is equal to $2\,\Delta H^\circ_{vap}(H_2O) = -20.791$ [10] within the limits of experimental error. Consequently, for the comparison of $\Sigma\Delta H_{0,1}$ with the quantities $\Sigma\Delta H_h^\circ$ (corresponding to a liquid phase) one must take into account the heat of vaporization of two water molecules which will be bonded with ions of the 1:1 electrolyte, because the former quantities are referred to gaseous phase.

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EFFECT OF THE NATURE OF NUCLEOPHILIC AGENT ON THE SUBSTITUTION RATE OF CHLORINE ATOM IN sym-TRIAZINE CHLORO-DERIVATIVES

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There was studied the rate of interaction of sym-triazine chloro derivatives with seven nucleophilic groups, viz. OH^-, CH_3O^-, $C_6H_5S^-$, $C_6H_5O^-$, $p\text{-}CH_3C_6H_4O^-$, $m\text{-}CH_3C_6H_4O^-$, $p\text{-}ClC_6H_4O^-$. Nucleophilic reactivity was demonstrated to be determined not only by basicity but also by polarizability of compounds. In the chlorotriazine series the relative reactivity of nuoleophilic agents is slightly dependent on the substrate; however, it differs considerably from the relative nucleophilie reactivity of the same reagents in the series of nitrochlorobenzenes. This phenomenon is accounted for by the smaller contribution of polarizability in the case of nitrogen-containing heterocycles.

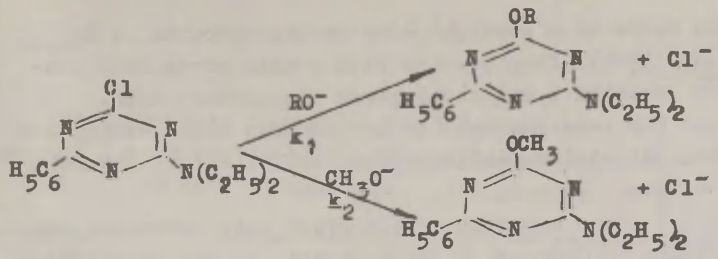
Continuing the studies of nuoleophilic substitution reactions in the series of sym-triazine chloro derivatives [1,2], we investigated the influence of various nuoleophilic agents upon substitution rate. The following nuoleophilic agents were studied in methanol solution: methoxy ion, phenoxy ion, p-chlorophenoxy ion, and m- and p-cresol anions. 2-Chloro-4-phenyl-6-diethylamino-sym-triazine (Compound I) served

as substrate in these experiments. In order to find out the degree to which the regularities discovered retain after the change of substrate, another set of experiments was conducted utilizing two nucleophilic agents (methoxy and phenoxy ions) and five compounds belonging to the series of substituted chloro derivatives of sym-triazine (Compound I and Compounds II-V in Table 2).

Since it does not seem possible to study interaction of sym-triazine chloro derivatives with hydroxyl in methanol solution, we used a mixed solvent, dimethylsulphoxide/water, for the experiments with this nucleophilic agent. We investigated thiophenoxy ion in the same medium. This ion, according to the available data [3] is remarkable due to its unusually high nucleophilic ability in the series of nitrochlorobenzenes. To compare the results obtained in different media, we also did measurements with phenoxy ion in the same solvent. From the practical considerations, we chose 2-chloro--4-ethylamino-6-diethylamino-sym-triazine (Compound VI) as a substrate for the experiments in the mixed solvent. When studying substitution reaction in methanol we had to take into account a number of factors. After the introduction of a nucleophilic reagent to methanol, equilibrium between methoxy ion and nucleophilic anion arises:

$$RO^- + CH_3OH \overset{K}{\rightleftharpoons} ROH + CH_3O^- \qquad (1)$$

Therefore, two parallel reactions occur, with RO^- and CH_3O^- anions (2,3). The ratio of products of these reactions is determined not only by k_1 and k_2, but also by K.



(2)

(3)

It was shown [4] that the rate of substrate transformation for this kind of reactions is described by the following expression:

$$W = [A] \cdot [R] \; \frac{k_1 + k_2 K \dfrac{[CH_3OH]}{[ROH]}}{1 + K \dfrac{[CH_3OH]}{[ROH]}} \qquad (4)$$

[R] is the concentration of base, equal to the sum of concentrations of both anions, [A] is the concentration of chlorotriazine, $[CH_3OH]$ and [ROH] are the equilibrium concentrations of methanol and nuoleophilic compound.

Therefore the apparent second-order rate constant is:

$$k_{exper} = \frac{k_1 + k_2 K \dfrac{[CH_3OH]}{[ROH]}}{1 + K \cdot \dfrac{[CH_3OH]}{[ROH]}} \qquad (5)$$

In the case when $K \cdot \dfrac{[CH_3OH]}{[ROH]}$ is small compared to unity, Equation 5 transforms into Equation 6:

$$k_{exper} = k_1 + k_2 K \frac{[CH_3OH]}{[ROH]} \qquad (6)$$

This leads to a straight line in the coordinates k_{exper} vs. $[CH_3OH]/[ROH]$. Intersection with y-axis gives rate constant for reaction 2 and slope gives the product $k_2.K$.

Since the rate constant of interaction with methoxy ion can be determined independently, one can calculate the equilibrium constant from Eq.(1).

Table 1 gives apparent second-order rate constants for the reactions of Compound I with phenol, p- and m-cresols, and p-chlorophenol. As an example, Fig. 1 shows the dependence of apparent rate constant for the reaction of Compound I with m-cresoxy ion on the ratio $[CH_3OH]/[ROH]$. In all other cases rate constants also obey linear relationship. This indicates that in the studied range of concentrations the expression $K.\frac{[CH_3OH]}{[ROH]}$ is small in comparison with unity.

Table 2 presents apparent second-order rate constants for interaction of chlorotriazines with phenoxy ions at various concentrations of phenol. Table 3 compares true rate constants of interaction with phenoxy ion calculated from Eq. (6) with constants of interaction with methoxy ion. As follows from Table 3, the relative reactivity of methoxy and phenoxy ions slightly depends on substrate in the series of sym-triazines, Compound V, however, deviates to a certain degree from the general relationship.

In the mixed solvent dimethylsulphoxide/water, which was used for comparing nucleophilic reactivities of three anions, viz. hydroxyl, phenoxy ion, and thiophenoxy ion, an equilibrium between two ions establishes as well:

$$RO^- + H_2O \rightleftharpoons ROH + OH^- \qquad (7)$$

Therefore, two parallel reactions occur, with RO^- and CH_3O^- anions (2,3). The ratio of products of these reactions is determined not only by k_1 and k_2, but also by K.

Table 1

Apparent Rate Constants for Interaction Compound I with Nucleophilic Agents in Methanol at 56°C (l/mol·sec)

Phenol		m-Cresol		p-Cresol		p-Chlorophenol	
ROH	$k \cdot 10^3 \pm 5\%$	HOH	$k \cdot 10^3 \pm 5\%$	ROH	$k \cdot 10^3 \pm 5\%$	ROH	$k \cdot 10^3 \pm 5\%$
0.00995	4.45	0.01452	5.19	0.00865	7.46	0.01033	1.90
0.01120	4.11	0.01645	5.03	0.01063	6.61	0.01256	1.41
0.01597	3.47	0.02040	4.27	0.01256	5.95	0.01548	1.36
0.01668	3.07	0.02346	4.16	0.01847	5.06	0.02095	1.07
0.01946	2.71	0.02831	3.57	0.02255	5.22	0.02096	0.89
0.02607	2.58	0.03296	3.55	0.03383	4.27	0.02774	0.94
0.02638	3.11	0.03972	3.20	0.03935	4.39	0.04162	0.77
0.03894	2.57	0.04760	2.87	0.04616	3.96		
0.04721	2.33	0.06063	2.36	0.05903	3.34		
0.04822	1.62			0.06355	2.86		
0.06973	1.90			0.06762	2.39		

Since in the case of thiophenol the equilibrium of Reaction 7 shifts completely towards the formation of thiophenoxy ion [5] one may rule out interaction of Compound VI with hydroxyl and assume that the experimentally determined second order rate con-

stant equals k_2. Rate constant for phenoxy ion was calculated from Eq(6). Relationship between rate constant of the reaction and phenol concentration is given in Table 4. Rate constants of interaction of Compounds I and VI with all studied nucleophilic agents in corresponding solvents are presented in Table 5.

Table 2

Apparent Rate Constants for Interaction of 2-Chloro-R-6-diethylamino-sym-triazines with Phenol at 56°C (l/mol·sec)

No.	II		III		IV		V	
R	C_2H_5		C_3H_5NH		C_2H_5ONH		CH_3ONH	
ROH	$k \cdot 10^3 \pm 5\%$	ROH	$k \cdot 10^3 \pm 5\%$	ROH	$k \cdot 10^3 \pm 5\%$	ROH	$k \cdot 10^3 \pm 5\%$
0.01539	4.40	0.00980	1.71	0.01585	5.52	0.01901	5.73
0.02039	3.73	0.01395	1.26	0.01857	4.43	0.02042	6.05
0.02346	3.50	0.01907	1.02	0.01887	6.84	0.02474	4.96
0.03058	2.89	0.02083	1.04	0.01931	5.89	0.02965	5.51
0.05320	2.75	0.02225	1.37	0.02377	4.43	0.03605	4.85
0.06430	1.69	0.03285	0.66	0.02921	4.29	0.03711	3.95
0.06560	1.91			0.03537	3.46	0.05303	3.78
0.02061	3.67			0.04824	2.83	0.08741	2.73
0.10003	1.26					0.13342	2.07
0.16460	1.00						

Table 3

Methanolysis and Phenolysis Rate Constants
for Various Substituents
in the Series of Chlorotriazines

No.	$k_{meth} \cdot 10^3 \pm 5\%$, l/mol·sec	$k_{phen} \cdot 10^4 \pm 5\%$, l/mol·sec	k_{meth}/k_{phen}
I	25.72	16.06	16.1
II	22.71	10.18	22.3
III	0.635	0.317	20.1
IV	2.62	1.53	17.1
V	2.04	1.98	10.3

Table 4

Apparent Rate Constants of Compound VI
Phenolysis in DMSO/water Solution at 94°C
(l/mol·sec)

ROH	0.01394	0.01606	0.02481	0.04613	0.07556	0.09734	0.14890
$k \cdot 10^4$	9.30	9.64	9.75	9.18	8.23	8.84	7.52

We made an attempt to compare reactivities of all nucleophilic agents studied in the present work. We have already found that relative reactivity in the series of sym-triazines is slightly dependent on solvent.[5] Therefore, knowing the reactivity ratios for phenoxy ion towards other nucleophilic

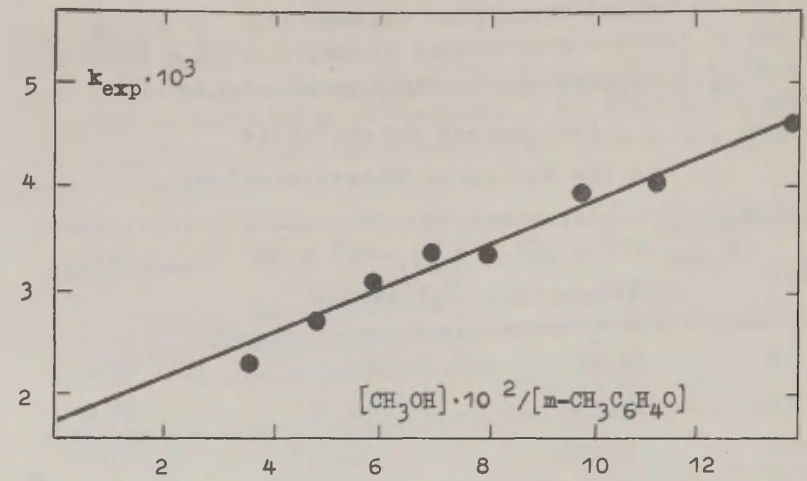


Fig.1. Apparent phenolysis constant of compound 1 vs. m-cresoxy ion concentration

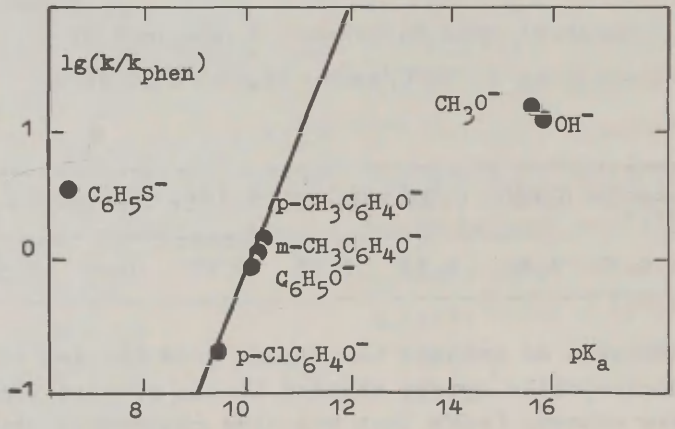


Fig.2. Brönsted relationship in the series of chlorotriazines.

Table 5

Reactivity of Some Nucleophilic Agents in Interaction with Chloro Derivatives of sym-Triazine

Nuoleophilic agent	Compound I in methanol at 56°		Compound VI in DMSO/water at 94°		Relative reactivity	pK_a *
	$k \cdot 10^3$ l/mol·sec	$K \cdot 10^4$	$k \cdot 10^3$ l/mol·sec	$K \cdot 10^5$		
CH_3O^-	25.70±0.42				16.06	15.5
$p\text{-}ClC_6H_4O^-$	0.33±0.14	2.43±0.34			0.21	9.38
$m\text{-}CH_3C_6H_4O^-$	1.7 ±0.12	8.84±0.39			1.07	10.08
$p\text{-}CH_3C_6H_4O^-$	2.40±0.27	7.39±0.85			1.50	10.14
$C_6H_5O^-$	1.61±0.15	4.52±0.47	0.82±0.04	1.86±0.80	1.00	9.98
$C_6H_5S^-$			2.97±0.21		3.63	6.50
OH^-			10.69±0.91		13.07	15.75

* Literature data [12]

agents in varicue solvents, we may arrange all nuo-leophilic agents in a single row. Calculation results ars given in Table 5, interaction rate constant for phenoxy ion being taken as unity. The Bröneted equation wae used in order to compare the data obtained (see Fig.2). The Bröneted relation holds only in the series of phenol derivatives (r = 0.995). The equation can be expressed in the following way:

$$\log k = -13.84 + 1.10\ pK_a$$

Nucleophilic agents OH^-, CH_3O^-, $C_6H_5S^-$ deviate from this relationship. The lack of linear correlation for nucleophilic agents of other types indicates that the Hammett equation is in essence satisfied. Therefore, polarizability of compounds exerts strong influence on nucleophilic reactivity. Unfortunately, the Edwards equation [6] cannot be used for calculations because of the lack of data on oxidation potentials and molecular refractions of these nucleophilic agents. One may say, however, that polarizability plays a less important role than in reactions of nitrochlorobenzenes. The most easily polarizable ion $C_6H_5S^-$ is a more reactive nucleophilic agent than CH_3O^- or OH^- (see Ref.7). However, in our case it reacts 4 times slower than hydroxyl. Therefore, any equation taking polarizability into account (of the Sven-Scott type [8]) should not correlate nitrogen--containing heterocyclic compounds by means of parameters found for aromatic systems [9]. A similar phenomenon was noticed by Illuminati [10] in the case of nucleophilic substitution in the series of chloroquinolines. The smaller contribution of polarizability into nucleophilic reactivity of these anions is evidently accounted for by greater positive charge

of carbon atom in nitrogen-containing heterocyclic compounds compared to nitrochlorobenzenes.

EXPERIMENTAL

Solvents

Dimethylsulphoxide was distilled in vacuum. Methanol was absolutised by heating over calcined CaO and subsequent distillation. Absolute alcohol was dryed over magnesium and distilled.

Reagents

All reagents were purified by vacuum distillation. Sodium methylate solutions were prepared by solving a weighed amount of freshly cut metallic sodium in methanol in dry nitrogen atmosphere. Sodium methylate solutions were prepared before each experiment.

Kinetic experiments were conducted by mixing 25 ml of a solution of reagents with 25 ml of 0.01 N chlorotriazine solution. The solution of reagents was prepared in the following manner. A weighed amount of phenol, taken in excess with respect to the base, was added to a solvent containing sodium methylate (for the experiments in methanol solution) or sodium hydroxyde (for the experiments in a mixed solvent DMSO/ /water); the solution was diluted to the 50 ml mark and equilibrated for 30 minutes in thermostat at the temperature of the experiment.

The moment of joining these two solutions was taken as the onset of experiment. During the course of the reaction 8-9 samples were taken. The reaction medium in the samples was neutralised with 0.1 N HNO_3

and cooled. The reaction was followed by the accumulation of chlorine ions in the solution. Chlorine was titrated by a potentiometric method utilizing LPM-60M meter. When studying the reactivity of thiophenoxy ion the analysis procedure was somewhat more complex. Since thiophenol hindered potentiometric determination of chlorine ions, it was withdrawn according to a previously described technique [11]. The sample was neutralized with 0.1 N HNO_3, and carbon tetrachloride was added (20 ml). The water layer was separated and extracted with ether (25 ml). The organic layer was washed with water, and the water extracts were mixed. Ten drops of concentrated nitric acid and 1 ml of concentrated hydrogen peroxide were added after that. Next day the samples were titrated with silver nitrate.

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KINETICS AND MECHANISM OF THE REACTION OF HCl WITH ABSOLUTE ALIPHATIC ALCOHOLS

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For 2-methyl-1-propanol a linear correlation between kinetic and conductometric data was observed. The concentration of ion pairs was calculated from kinetic data and the dependence of the rate constant upon the concentration was obtained.

In the case of methanol, ethanol and 1-propanol the dependence was similar to those obtained previously from comparison of kinetic and conductometric data.

It was shown that for 1-propanol and 2-methyl-1-propanol the ratio of the rate constant k_{nc}, related to the ion pairs in nonconductive state, to k_c, related to ion pairs in conductive state, either is equal to or less than unity.

The dependence of lgk upon σ^* and E_s constants for six alcohols, ROH, at 120°C was investigated.

In our recent report[1] it has been shown that the effective rate constant for the reaction of an aliphatic alcohol with HCl is determined by two parallel reactions one in participation of ion pairs in the conductive and the other in nonconductive state.

For the reaction of HCl with methanol or ethanol the respective constants were calculated. A sharp decrease was observed in the rate constant k_{nc}, related to ion pairs in nonconductive state when passing from methanol to ethanol.

Table 1

Effective Rate Constants, $k(sec^{-1})$, and Equivalent Conductivites, Λ, for the Solutions of HCl in Absolute 2-Methyl-1-propanol. The rate constants are determined by conductometric method

N№	$[HCl]\ M \times 10^3$	$\Lambda^{25°}$	$\Lambda^{85°}$	$k^{85°} \times 10^6$
1	1,353	-	-	5.9*
2	1,012	-	-	5.5*
3	679	-	-	5.5*
4	445	-	-	5.5*
5	128	5.0	4.9	6.0*
6	87	-	-	5.4*
7	62.7	4.9	5.5	5.6
8	31.3	5.7	5.9	5.2
9	28.3	-	-	4.5*,a
10	15.6	6.1	6.4	4.8
11	7.8	8.4	8.6	4.5
12	3.9	9.7	9.6	4.3
13	1.9	10.3	11.2	3.8

*Calculated from data reported by Tsvetkova.[4]

[a] Not taken into account as obviously low value.

This work was aimed to study more closely the kinetics of the reaction between HCl and 1-propanol or 2-methyl-1-propanol and to make an attempt to give a more general scheme of this reaction.

Experimental

The methods of experiment and of the purification of alcohols hawe been described earlier.[2,3]

The experimental data for 2-methyl-1-propanol are represented in Table 1. For the data on 1-propanol see preceding paper.[2]

Discussion

In our preceding work[2] on dilute solutions of HCl in methanol, ethanol or 1-propanol linear dependences of the first-order rate constants, k (sec^{-1}), upon equivalent conductivities, Λ, of respective solutions were observed. As it proceeds from the data presented in Table 1 a similar linearity can be seen for the solution of HCl in 2-methyl-1-propanol in the concentration range of 1.9×10^{-3}–0.128M at 85°C ($k_o^{85°}=(7.39\pm0.30)\times10^{-6}$; r=0.968; SD=0.21).

In the case of 1-propanol and 2-methyl-1-propanol the data processing according to the new model of strong electrolyte[5], as it had been made for methanol and ethanol[1], so far was not possible, although the Čeleda's relationship was valid in this case too. By the data available it was possible to estimate the Λ_o values as given in Table 2.

T a b l e 2

The Values of Λ_o Estimated by Extrapolation from Čeleda's Relationship (see Ref.1) for the Solutions of HCl in 1-Propanol and 2-Methyl-1-propanol. For comparison the Λ_o Values for Methanol and Ethanol are Represented, too

Alcohol	[HCl] M	Λ_o^{25}	Λ_o
$(CH_3)_2CHCH_2OH$	0.03–0.13	6.2±0.1	6.3±0.1 (85°)
C_3H_7OH*	0.04–0.18	≈17.8	≈12.5 (110°)
C_2H_5OH	0.2 –1.5	24.0± 0.8	36.9±1.5 (100°)
CH_3OH	0.5–2.0	97.0±3.9	134.0±3.9 (80°)

* For 1-propanol at 25°C Λ_o is estimated by the Goldschmidt's work.[7] For 110°C the Λ_o value, since sufficient number of experimental data lack, turns out to be rather rough.

As we can see from Table 2 the absolute values of λ_o decrease when passing from methanol to 2-methyl-1-propanol and the linearity between $\lg\lambda$ and HCl concentration is held already when $[HCl] \leq 0.2$ M.

At the same time a very slight dependence of k on the concentration of HCl is observed (e.g. for 1-propanol at [HCl] = 1.40 M $k^{110^o} = 4.4 \times 10^{-4}\ sec^{-1}$, at [HCl] = 0.09 M $k^{110^o} = 4.1 \times 10^{-4}\ sec^{-1}$).

The above-mentioned facts, on the one hand, result in an increase in relative experimental errors, and, on the other hand, may indicate that the dissociation of ion pairs is shifted towards lower concentration of HCl.

In view of data on methanol and ethanol we can expect that the ratios of k_{nc}/k_c (k_{nc} and k_c are rate constants in case of ion pairs being in nonconductive and conductive states, respectively) remain, with slight decreases, close to unity when passing from ethanol to higher alcohols.

If $k_{nc}/k_c = 1$ the effective k value obtained from data at high concentration of HCl should be fit both the states of ion pairs, i.e. $k = k_{nc} = k_c$. If $k_{nc}/k_c < 1$, then $k = k_c$.

In addition to the comparison of conductometric and kinetic data one can try to formulate the relationship between observed K values and the concentration of ion pairs calculated from the kinetic data.

The equilibrium of the dissociation of ion pairs is as follows

$$ROH_2^+Cl^- \overset{K}{\rightleftharpoons} ROH_2^+ + Cl^- \qquad (1)$$

The dissociation constant for ion pairs takes shape:

$$K = \frac{[ROH_2^+][Cl^-]}{[ROH_2^+\ Cl^-]} \qquad (2)$$

The dependence of the k value upon the degree of ion pair dissociation can be written as follows.

$$k = k_o\ (1 - \alpha), \qquad (3)$$

in which k_o = the rate constant for the ion pair decomposition.

Regarding the water concentration as extremely small, we may write:

$$[ROH_2^+] = [Cl^-] = \alpha[HCl] \qquad (4)$$

Denoting the analytic concentration of HCl by $[HCl]_o$, the fractions of free ions, (α), and ion pairs ($1-\alpha$) turn out to be as follows:

$$\alpha = \frac{[ROH_2^+]}{[HCl]_o} \qquad (5) \quad \text{and} \quad 1-\alpha = \frac{[ROH_2^+Cl^-]}{[HCl]_o} \qquad (6)$$

Stoichiometrical equation for HCl has the shape:

$$[HCl]_o = [Cl^-] + [ROH_2^+Cl^-] \qquad (7)$$

After changing for the respective quantities and simple transformations in Eq.(2) we obtain Eq.(8), which represents straight line in coordinates $k, \sqrt{k}/[HCl]_o$.

$$k = k_o - (\sqrt{K}k_o)\sqrt{k}/[HCl]_o, \qquad (8)$$

Data processing in terms of Eq.(8) over the concentration range of HCl for methanol ($[HCl]=0.9\times10^{-3}$–3.6 M), ethanol ($[HCl]=0.2\times10^{-3}$–2.3 M), 1-propanol ($[HCl]=0.14\times10^{-2}$–1.4M) and for 2-methyl-1-propanol ($[HCl]=1.9\times10^{-3}$–1.35 M) resulted in relationships illustrated by Figs. 1 and 2.

Initial data for methanol, ethanol and 1-propanol have been reported ealier,[1,2] those for 2-methyl-1-propanol are taken from Table 1.

As we can see from Figs., Eq.(8) is followed for 1-propanol at 110°C and for 2-methyl-1-propanol at 85°C. For methanol at 80°C (above $[HCl]\approx 0.4$ M) and for ethanol at 100°C (above $[HCl]\approx 0.5$ M) the linearity was broken as a result of a change in the ratio of k_{nc} to k_c.[1] As we could expect the greatest deviation was observed for methanol.

Comparision of this values with those calculated earlier[2] is given in Table 3.

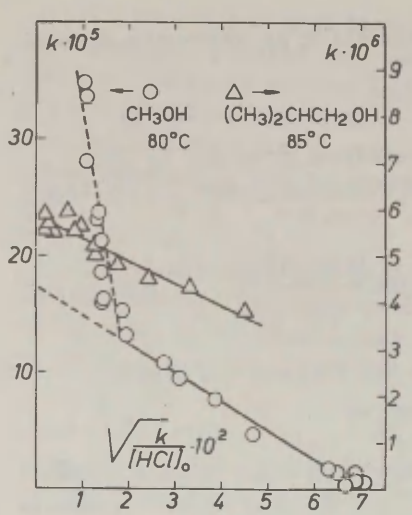


Fig. 1. Relationship in the coordinates of eq.(8) for the solutions of HCl in methanol and 2-methyl-1-propanol.

T a b l e 3

Results of Data Processing for Eq.(8). r=Correlation Coefficient, SD=Standard Deviation

ROH	k_o	r	SD	k_o *
CH_3OH 80°C	$(1.71\pm0.05)\times10^{-4}$	0.993	0.60	$(2.47\pm0.06)\times10^{-4}$
C_2H_5OH 100°C	$(1.67\pm0.00)\times10^{-4}$	0.989	0.07	$(1.87\pm0.02)\times10^{-4}$
C_3H_7OH 110°C	$(4.43\pm0.00)\times10^{-4}$	0.996	0.06	$(4.59\pm0.06)\times10^{-4}$
$(CH_3)_2CHCH_2OH$ 85°C	$(5.82\pm0.09)\times10^{-6}$	0.947	0.22	$(7.39\pm0.30)\times10^{-6}$

* Calculated from the relationship between k and λ (see Ref.2)

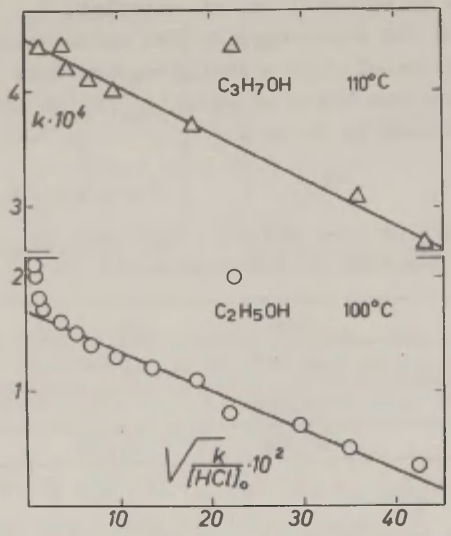


Fig. 2. Relationship in the coordinates of Eq.(8) for the solutions of HCl in ethanol and 1-propanol

The obtained results once more support the assumption that the rates of studied reaction of aliphatic alcohols with HCl are, in fact, limited by dehydration of ion pairs, in other words, the structure of activated complex must be close to that of ion pairs. There is no doubt any more that the reaction involves ion pairs of two states.[1]

Consequently, the effective k values, except reactions with methanol or ethanol, estimated at high HCl concentration ($[HCl] \approx 1{,}5M$), may be accepted as characteristics of ion pairs in conductive state. They can be put to use in consideration of reactivity of alcohols.

In the case of methanol we can calculate k_o from the value of k. Since the dependence of ion pairs dissociation constant k for methanol only slightly varied with temperature,[2] calculation was based on ratio k_{nc}/k_c at 80°C. The results are presented in Table 4.

Table 4

The Values of lgk (see Ref. 3), lgk_c and lgk_{nc} for the Reaction of HCl with Methanol

Temp. °C	lgk	lgk_c	lgk_{nc}
110	-2.50	-2.80	-2.20
120	-2.20	-2.55	-1.89
130	-1.88	-2.18	-1.58

For ethanol K value sharply decreases with increasing temperature.[2]

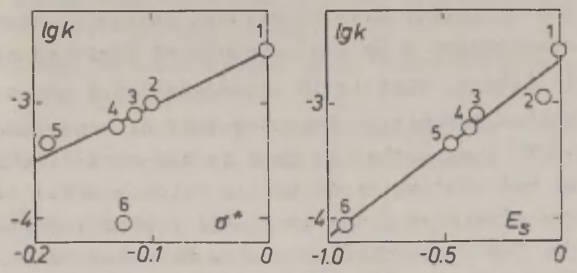
Calculating $k_o^{120°}$ from the kinetic data in the concentration range of HCl of 0.03-2.3 M at that temperature the linearity in coordinates $k, \sqrt{k}/[HCl_o]$ was held over the whole concentration range. The calculated value $lgk_o^{120°} = -2.97$ is close to the effective value $lgk^{120°} = -2.95$. That is in accordance with the assumption made.

Fig. 3 presents the dependence of lgk upon σ^* for six alcohols, ROH (CH_3OH, C_2H_5OH, C_3H_7OH, C_4H_9OH, $(CH_3)_2CHOH$ and $(CH_3)_2CHCH_2OH$) at 120°C. As we can see there is no general linearity for all the substituents R dealt with.

On the other hand, a satisfactory linearity between lgk and E_s for substituents R could be observed according to Eq.(9).

$$lgk = lgk^o + \sigma E_s \qquad (9)$$

The results of data processing by regression analysis in terms of Eq.(9) are presented in Table 5 and illustrated by Fig. 4.



Figs. 3 and 4. The lgk-dependences for reaction of HCl with alcohol at 120°C upon the inductive Taft constant σ^{*} (Fig.3) and upon the steric constant E_s (Fig. 4).

1, CH_3OH; 2, C_2H_5OH; 3, C_3H_7OH; 4, C_4H_9OH; 5, $(CH_3)_2CHOH$; 6, $(CH_3)_2CHCH_2OH$

Table 5

The Results of Data Processing According to Eq.(9)

Temp. °C	lgk^{o}	ρ^{*}	r	SD
110	-2.97±0.11	1.41±0.22	0.952	0.17
120	-2.66±0.77	1.45±0.16	0.977	0.12
130	-2.32±0.07	1.60±0.15	0.983	0.11

*For the values of inductive and steric constants see Ref.8. Values of lgk_c for methanol are taken from Table 4, for the other alcohols from an ealier work [3].

Using the steric constant E_s^{o} instead of E_s the correlation becomes worse (at 120°C r = 0.964; SD = 0.17, as shown earlier[9]). It is caused mainly because of the deviation of the point for R = $CH(CH_3)_2$.

Validity of Eq.(9) made it rather probable that the effect of substituent R in the molecule of reacting alcohol had a steric nature. That is in accordance with the conception that the nucleophilic attack of the chlorine ion, which belongs to ROH_2^+, upon the ion pair is the rate-limiting step. In this case the studied reaction can be classified as $A_{Alk}2$.

From the linearity given by Eq.(9) probably deviates the lgk value for 2-methyl-2-propanol. Expected value of lgk for the linear relationship (9) must be close to -5. In view of data on lgk calculated from the activation parameters reported by Tsvetkova[4] (lgk^{120°=-2.4) and by Savolainen[10] (Igk^{120°=-1.6) the above-mentioned alcohol reacts faster than we can see from Eq.(9).

In point of fact the lgk values reported by these two authors are rather different.

However, Bennett and Reynolds[11] noted that the reaction of HBr with 2-methyl-2-propanol proceeded a hundred time faster than with methanol.

Evidently, in that case a change in reaction mechanism occured.

After all, it should be emphasized that in our case the effect of substituent R in ROH_2^+. Cl^- cannot be distinguished from that of R as constitute of the solvent molecule.

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KINETICS OF THE GRIGNARD REAGENT FORMATION. 1. SUPPLEMENTARY KINETIC PARAMETERS AND MECHANISM OF THE REACTION

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The more precise and complete experimental data on reaction rates of magnesiumorganic compound formation are reported. It was once more confirmed that after an induction period the reaction rate in etheral solutions is proportional to the concentration of halide, ethyl ether and the effective surface of the metal, and the reaction being of the third order. The reaction mechanism of magnesiumorganic compound formation was specified. The reaction scheme of radical nature involving two parallel chains seems to be the most acceptable one to interpret our kinetic data.

In our preceding papers[1] the data of preliminary kinetics measurements have been reported and the problems of the Grignard reagent formation mechanism discussed. In this study the above-mentioned problems are discussed by using more number of experimental data.

Experimental

Ethyl ether and tetrahydrofuran were purified from peroxides, dried and rectified in dry nitrogen gas atmsosphere. Benzene ('chemically pure' grade), n-hexane ('pure'grade), n-butyl bromide ('pure'grade) and bromobenzene ('pure'grade) were purified, dried and rectified.[2,3] Magnesium metal turnings (Schering-Kahlbaum)were used after sieved (fraction 0.5)

and washed with diluted HCl, with distilled water until the disappearence of chlorine-ion , with ethyl alcohol and rapidly dried at 100°C. Obtained glittering magnesium turnings were hold in the atmosphere of dry nitrogen gas.

Kinetics of the magnesiumorganic compound formation was followed by the reaction heat. An earlier[1,4] described thermographic method was used. The temperature in the reaction flask was measured by the thermistor MT-54. The thermograms were recorded by potentiometer E_z-8.

The effective rate constants were calculated by the three following methods.

(i) In accordance with the law of the first-order reaction and using the full extent of the kinetic curve, rate constants were calculated by Eq.(1)

$$k = \frac{2.3}{t} \lg \frac{\Delta T_o^{\infty}}{\Delta T_o^{\infty} - \Delta T_o} \quad sec^{-1} \qquad (1)$$

(ii) The first-order rate constants were determined from the thermal maximum of reaction. Since at this point the reaction rate is proportional to the rate of heat liberation which in turn is equal to the cooling rate,

$$\rho \Delta T_{max} = k \, (\Delta T_o^{\infty} - \Delta T_{omax})$$

we obtain

$$k = \frac{\rho \Delta T_{max}}{(\Delta T_o^{\infty} - \Delta T_{omax})} \quad sec^{-1} \qquad (2)$$

(iii) Based on the differential method[5]:

$$k = \frac{\Delta \left[\lg \frac{\Delta \Delta T_o}{\Delta t} \; 2.3 \right]}{\Delta t} \quad sec^{-1} \qquad (3)$$

In Eqs.(1),(2),(3) t denotes time in sec; ΔT_o^{∞} is the integral temperature difference between the reaction flask and the thermostat at the end of reaction, ΔT_o is the integral temperature difference at any time t; ΔT_{omax} is the integral temperature difference at the thermal maximum; ρ is

the cooling coefficient in sec^{-1}.

Rate constants calculated in this manner are equal to the sum of rate constants all the first-order reactions proceeding in parallel. The rate constant k_1 for magnesiumorganic compound formation may be calculated according to the formula:

$$k_1 = X_\infty \cdot k/100 \qquad (4)$$

where X_∞ denotes the yield of magnesiumorganic compound (in %).

Kinetic measurements were made under conditions eliminating the induction period[6,1], the yield of Grignard reagent was determined by the method of Gilman.[7]

All the kinetics measurements were taken at $20^\circ \pm 0.05$, the volume of solution was 40 ml, and if not given other value the weight of Mg was 1.5 g and the initial concentration of halide 0.2 N.

Rate constant k was calculated by formula (1) and k_1 by formula (4).

The results of measurements are presented in Tables 1 through 4.

The rate constant was independent of the initial concentration of halide (see Table 1).

T a b l e 1

Results of Kinetic Measurements at Various Initial Concentration of Halide in Ethernal Solutions

Halide	Initial concentration of halide, N	Yield of Grignard reagent	$k \cdot 10^2 sec^{-1}$	$k_1 \cdot 10^2 sec^{-1}$
$n\text{-}C_4H_9Br$	0.1	92	1.85	1.70
-"-	0.2	90	1.87	1.68
-"-	0.5	90	1.89	1.70
-"-	1.0	88	1.90	1.68
C_6H_5Br	0.2	98	1.04	1.02
-"-	0.48	98	1.06	1.05

In order to complete the earlier studies the dependence of reaction rate on the effective surface of magnesium(which had been taken proportional to the weight of magnesium) was investigated. The respective experimental data are represented in Table 2.

Table 2

Dependence of Rate Constants on the Weight of Magnesium

The weight of Mg(g)	Excess of Mg	Yield of Grignard reagent	$k.10^2$ sec^{-1}	$\frac{k.10^2}{g}$	$k_1.10^2$ sec^{-1}	$\frac{k_1.10^2}{g}$
Bromobenzene in tetrahydrofuran						
0.75	4.4	96	0.54	0.72	0.52	0.69
			0.52	0.69	0.50	0.66
1.5	8.8	98	1.13	0.75	1.11	0.74
3.0	17.6	97	2.06	0.68	2.00	0.66
			1.96	0.65	1.90	0.63
			1.98	0.66	1.94	0.65
4.5	26.4	98	2.90	0.65	2.85	0.63
			2.95	0.66	2.90	0.65
6.0	35.2	99	2.85		2.83	
			2.88		2.85	
9.0	52.8	98	2.85		2.79	
n-Butyl bromide in ethyl ether						
0.75	4.4	80	0.90	1.20	0.72	0.95
			0.97	1.30	0.77	1.02
1.50	8.8	90	1.87	1.25	1.68	1.12
3.0	17.6	92	3.60	1.20	3.30	1.10
4.5	26.4	91	4.95	1.10	4.50	1.10
			5.00	1.11	4.55	1.10
9.0	52.8	89	5.05		4.50	
10.5	61.5	90	4.95		4.27	

In addition the kinetics of n-butylmagnesium bromide formation in mixtures of ethyl ether with n-hexane or benzene was investigated. The results are represented in Tables 3 and 4.

Table 3

Rate Constants for the Reaction Between n-Butyl Bromide and Mg in Binary Mixtures of Ethyl Ether with Benzene

N_{DEE}	Yield of Grignard reagent	$k.10^2$ sec^{-1}	$k_1.10^2$ sec^{-1}	$\frac{k_1.10^2}{N_{DEE}}$
1	90	1.87	1.68	1.68
0.5	50	1.60	0.80	1.60
0.2	50	0.60	0.30	1.52
0.1	43	0.35	0.15	1.50

N_{DEE}=molar fraction of diethyl ether

Table 4

Rate Constants for the Reaction Between n-C_4HgBr and Mg in Binary Mixtures of Ethyl Ether with n-Hexane

N_{DEE}	Yield of Grignard reagent	$k.10^2$ sec^{-1}	$k_1.10^2$ sec^{-1}	$\frac{k.10^2}{N_{DEE}}$	$\frac{k_1.10^2}{N_{DEE}}$
1	90	1.87	1.68	1.87	1.68
0.5	84	1.00	0.84	2.00	1.68
0.25	88	0.44	0.39	1.76	1.56

N_{DEE} = molar fraction of diethyl ether.

Discussion

The results obtained, principally confirm the conclusion that the investigated reaction is of the third order.

It appeared that the rate constants k_1 (the magnesium-organic compound formation) are proportional to the weight of Mg up to the 26-fold excess of the latter. The further increase in the weight of Mg both in diethyl ether and in tetrahydrofuran did not influence the rate constant value.

Results of data processing by the least-squares method in terms of Eq.(5) are reported in Table 5,

$$k = a_0 + a_1 g \qquad (5)$$

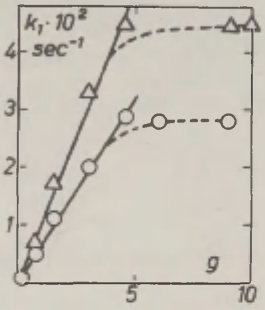


Fig. 1

Dependence of rate konstant k_1 on the weight of metallic magnesium. Δ, n-C_4HgBr in DEE; O, C_6H_5Br in THF

T a b l e 5

The Results of the Least-squares Data Processing in Terms of Eq.(5)

The system	a_0	a_1	R	SD	n
k					
C_6H_5Br in THF	0.095±0.041	0.632±0.014	0.998	0.055	8
n-C_4H_9Br in DEE	0.189±0.089	1.077±0.030	0.998	0.117	6
k_1					
C_6H_5Br in THF	0.080±0.041	0.622±0.014	0.998	0.055	8
n-C_4H_9Br in DEE	0.072±0.017	1.005±0.036	0.997	0.141	6

SD = standard deviation

n = number of experimental points

Our experimental data confirm, too, the independence of rate constants from the initial concentration of halide (see Table 1).

In Fig. 2 the dependence of rate constants of ethyl ether in mixtures with benzene or n-hexane is represented.

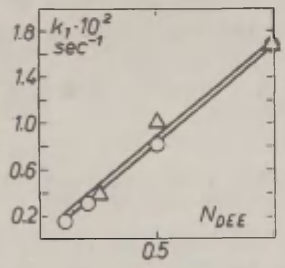


Fig. 2

Dependence of k_1 on the molar fraction of ethyl ether for the reaction between n-bytyl bromide and magnesium in binary mixtures of ethyl ether with benzene (o) or n-hexane (Δ).

In both the cases the proportionality between the values of k_1 and molar fraction of ethyl ether (N_{DEE}) was observed. Similar relation was observed for k in case of the mixture of ethyl ether with n-hexane.

The results of the data processing by the least-squares method according to the equation

$$k = b_0 + b_1 N_{DEE} \qquad (6)$$

are reported in Table 6.

Table 6

Results of the Least-squares Data Processing According to Eq.(6)

The system	b_0	b_1	R	SD	n
k					
DEE/n-hexane	0.050±0.081	1.882±0.123	0.997	0.066	3
k_1					
DEE/n-hexane	0.030±0.019	1.714±0.029	0.999	0.016	3
DEE/benzene	0.035±0.014	1.707±0.026	0.999	0.018	4

SD = standard deviation ; n = number of experimental points

In an approximation, good enough, the N_{DEE} value can be considered to be proportional to the molar concentration of ethyl ether in the binary mixtures. Therefore one can regard the proportionality between k_1 and N_{DEE} as a proof of the kinetical order equal to unity in respect of DEE.

Thus the supplementary experimental results once more confirmed that the summary kinetical order was equal to three and the expression of the reaction rate could be described by the following equation:

$$V = k_{III} S_{Mg} N_{DEE} [RHal] \qquad (7)$$

where

k_{III} denotes the 'real' third-order rate constant, S_{Mg} is the effective surface of Mg.

Equation (7) is not valid for the reaction in the induction period or in a great excess of magnesium. Earlier[1] we suggested a free-radical reaction mechanism from which could be concluded the above-mentioned result – the third order of the reaction

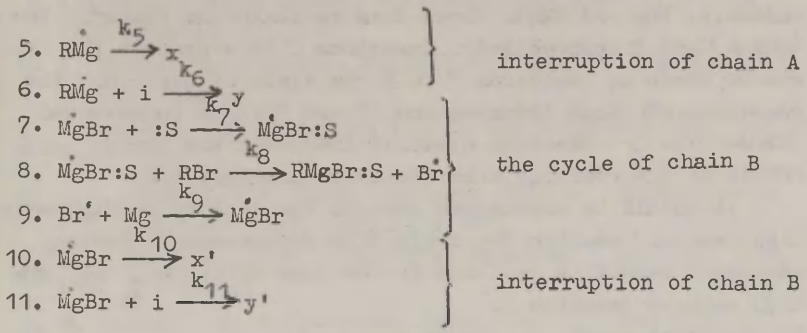
By the way, the first direct proof for the occurrence of free radicals in the Grignard reagent formation has recently been reported by Bodewitz, Blomberg and Bickelhaupt.[8,9]

In accordance with the suggested scheme of mechanism[1] in the first step of chain reaction there are generated two free radicals: $R\dot{M}g$ and $\dot{M}gBr$. Only the radical $R\dot{M}g$ was indicated to take part in the transfer reaction.

Now a more specified reaction scheme of two pathways in parallel is suggested, one involving $R\dot{M}g$ and another involving $\dot{M}gBr$.

Reaction Scheme

1. $RBr + Mg \xrightarrow{k_1} R\dot{M}g + \dot{M}gBr$ — initiation of the chain reaction
2. $R\dot{M}g + :S \xrightarrow{k_2} R\dot{M}g:S$
3. $R\dot{M}g:S + RBr \xrightarrow{k_3} RMgBr:S + R'$ — the cycle of chain A
4. $R' + Mg \xrightarrow{k_4} RMg$



where

S: denotes the basic solvent, i is the inhibitor which is responsible for the destruction of free radicals.

Taking into account the very high reactivity of free radicals one can consider their concentration stationary during the whole process. According to the steady state method one can deduce following expression for the reaction rate:

$$V = \left(\frac{k_2}{k_5 + k_6[i]} + \frac{k_7}{k_{10} + k_{11}[i]} \right) k_1 [RBr] [S:] S_{Mg} \qquad (8)$$

At higher concentrations of inhibitor i the inequolities $(k_5 + k_6[i]) \gg k_2$ and $(k_{10} + k_{11}[i]) \gg k_7$ become valid. It is obvious that during the induction period the reaction rate has a zero value. After the inhibitor has been consumed by virtue of reactions 6 and 11, it appears that $k_6[i] \approx k_{11}[i] \approx 0$, and one can express the rate of reaction in the following form:

$$V = \left(\frac{k_2}{k_5} + \frac{k_7}{k_{10}} \right) k_1 [RBr] [S:] S_{Mg} \qquad (9)$$

This equation is **indistinguishable from Eq. (7) since**

$$k_{III} = \left(\frac{k_2}{k_5} + \frac{k_7}{k_{10}} \right) k_1$$

Suggested scheme expresses a free-radical chain reaction with two chains, A and B, in parallel. Reaction 1 initiates both of the chains. The first step is the generation of free

radicals, $\dot{R}Mg$ and $\dot{M}gBr$. These free radicals can transfer the chains A and B respectively. Reactions 2 to 4 present the cycle of chain A, reactions 7 to 9 the cycle of chain B. The reactions of chain interruption (5 and 10) are represented schematically . Reaction 6 and 11 interrupt the chains as a result of the reaction with the chain terminator,i.

It should be emphasized that in the case of sufficiently high rate of reaction 10, cycle B is suppressed. Likewise, analogous result is in force in the case of cycle A at the high rate of reaction 5.
In the first case $k_{III} = \frac{k_2}{k_5} k_1$,
and in the second one $k_{III} = \frac{k_7}{k_{10}} k_1$.

The ratios of the rate constants for the transfer to those of the chain interruption, k_2/k_5 and k_7/k_{10}, express the chain length. The rate constant for the summary reaction, k_{III}, is equal to the product of the rate constant for the chain generation, k_1, with the sum of chain lengths, the product being characteristic of the non-branched chain reactions.

In the suggested scheme great importance was attributed to solvent: S . After the formation of free radicals they are drawn out of the surface by the solvent and reactive particles $\dot{R}Mg$:S and $\dot{M}gBr$:S can be formed. The complexes $\dot{R}Mg$:S and $\dot{M}gBr$:S easily react with alkyl halides but do not take part in reactions of chain interruption, i.e. $v_2=v_3$ and $v_7=v_8$. Moreover, the solvent maintains the formed Grignard reagent RMgBr:S in souble state.

If to assume tnat complexes $\dot{R}Mg$:S or $\dot{M}gBr$:S,too,would considerably take part in the chain interruption reactions the rate equation for Grignard reagent formation would have a complicated shape and the above-mentioned summary kinetical third order would turn out to be invalid.

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KINETICS OF THE GRIGNARD REAGENT FORMATION. 2. EFFECT OF SOLVENT AND HALIDE ON THE ORGANOMAGNESIUM COMPOUND FORMATION

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The kinetics of the reaction between magnesium and a series of bromides in various basic solvents was investigated. It was found that in ethyl ether and in butyl ether the influence of alkyl group in RBr on the rate of the reaction was determined by steric effects. In tetrahydrofuran the reaction rate was practically independent of the structure of alkyl group.

Based on the suggested scheme of mechanism the influence of basic solvent on kinetics of organomagnesium compound formation is discussed. It is supposed that depending on the nature of media one of the possible two pathways of the chain transfer reactions predominates.

The kinetic data of organomagnesium compound formation have been published only in a few papers. The former studies on the kinetics of Grignard reagent formation have been made by Kilpatrick and Simons[1,2] (the reaction between etheral ethyl bromide and magnesium). Later on this reaction has been studied by Markow and Peschev[3] (the reaction between Mg and n-C_4H_9I in toluene). We have investigated the kinetics of Grignard reagent formation from CH_3Br, C_2H_5Br, n-C_3H_7Br, n-C_4H_9Br and tert-C_4H_9Br in ethyl ether, and in some cases in butyl ether and tetrahydrofuran.[4,5,11]

The other papers are dealing with kinetic studies of organomagnesium compound formation by adsorption of gaseous alkyl halides on films of sublimed magnesium.[6,7,8]

The results obtained by several authors are incomparable by virtue of different measurements conditions. The lacking of kinetic studies in various media, except some of our preceding papers,[5,11] should be pointed out.

In this study we continue the investigation of quantitative dependence of rate constants upon the structure of alkyl bromide and solvent.

Experimental

The halides ('pure'grade) were dried over heated calcium chloride and rectified. Ethyl ether, propyl ether, butyl ether and tetrahydrofuran were purified from peroxides, dried and fractionated under dry pure nitrogen gas.[9] Dimethoxymethane ('pure'grade) and triethylamine ('pure'grade) were treated with potassium hydroxide and then distilled from sodium metal.

Methyl bromide was prepared from methanol and HBr.[10] The gaseous methyl bromide was led through the Drechsel washer with liquid sodium hydroxide, conc. sulfuric acid and through the calcium chloride tube, and then collected into corresponding absolute solvent. For kinetic measurements an aliquot portion of that solution was added to the solution under study.

Magnesium metal turnings (Schering-Kahlbaum) were used after sieved (fraction 0,5)and purified as described earlier.[11]

Kinetics of the reaction was followed by the thermographic method.[12]

Kinetic measurements were made under conditions eliminating the induction period[2,4], the yield of Grignard reagent was determined by titration with acid. All the kinetics measurements were taken at $20^{\circ}\pm0.05$, the volume of solution was 40 ml, the weight of Mg was 1.5 g and the initial concentration of halide 0.2 n.

The first-order rate constants were calculated as described in a preceding paper.[11]

Table 1

Rate Constants of the Reaction Between Mg and Halide in Various Media

Halide	$k.10^2$ sec^{-1}			$k_1.10^2$ sec^{-1}		
	DEE	DBE	THF	DEE	DBE	THF
CH_3Br	2.07±0.08	1.41±0.13	1.80±0.07	2.07±0.08	1.41±0.13	1.80±0.07
C_2H_5Br	2.63±0.10	1.32±0.08	0.85±0.05	2.55±0.10	1.28±0.08	0.83±0.05
n-C_3H_7Br	2.11±0.08	1.30±0.07	0.91±0.09	1.94±0.08	1.07±0.07	0.86±0.09
iso-C_3H_7Br	1.38±0.08	0.93±0.12	0.90±0.08	1.10±0.08	0.69±0.12	0.72±0.08
n-C_4H_9Br	1.87±0.06	1.21±0.07	1.12±0.09	1.68±0.06	0.96±0.07	0.84±0.09
iso-C_4H_9Br	1.16±0.05	0.90±0.08	1.03±0.05	1.98±0.05	0.58±0.08	0.78±0.05
sec-C_4H_9Br	1.72±0.06	0.97±0.09	1.15±0.04	1.29±0.06	0.69±0.09	0.74±0.08
tert-C_4H_9Br	0.77±0.10	-	-	0.19±0.10	-	-
n-$C_5H_{11}Br$	1.77±0.09	-	-	1.57±0.09	-	-
$C_6H_5CH_2Br$	1.65±0.13	-	1.02±0.08	1.27±0.13	-	0.76±0.08
C_6H_5Br	1.04-0.05	-	1.13-0.09	1.02-0.05	-	1.11-0.09

k denotes the rate constant of summary reaction

k_1 denotes the rate constant of magnesium-organic compound formation

DEE=ethyl ether, DBE=butyl ether, THF=tetrahydrofuran

The results of measurements are presented in Tables 1 and 2.

Table 2

Rate Constants of the Reaction Between Mg and n-Butyl Bromide in Various Media

The medium	$k \cdot 10^2$ sec^{-1}		$k_1 \cdot 10^2$ sec^{-1}		The Yield of magnesiumorganic compounds
	by the first-order law	by the thermal maximum	by the first-order law	by the thermal maximum	
Propyl ether	1.30±0.08	1.30±0.10	1.07±0.08	1.07±0.10	82
Dimethoxy-methane	2.04±0.11	2.10±0.14	1.98±0.11	2.03±0.14	97
Triethyl-amine	0.46±0.10	0.49±0.15	0.36±0.10	0.38±0.15	78

Discussion

The results obtained show that the variation of the hydrocarbon substituent in bromide and the variation of solvent as well have a comparatively small influence on the summary reaction rate constant. However, the yield of Grignard compound depends on the structure of bromide and on the nature of solvent. The yields of Grignard reagents decrease with the increase in the branching of alkyl groups and with the decrease in the concentration of ethyl ether in binary mixtures with benzene or n-hexane .[11] It appeared that in these cases the magnesiumorganic compound was partially precipitated to the surface of metal and so it may have caused a decrease in the reaction rate and in the yield, too.

The change in the summary rate constants, k, was not greater than 0.5 log units, that for the magnesiumorganic compound formation, k_1, not greater than 1.1 log units. That was valid for the reactions in media of ethyl ether and in butyl ether. In tetrahydrofuran the rate constants were

practically independent of the structure of alkyl group of bromide.

It appeared that the logarithm of the rate constant k_1 for ethyl ether (DEE) linearily depended on the rate constant k_1 for butyl ether (DBE) the slope of the straight line being practically equal to unity (see Fig.1):

$\log k_1(DEE) = 0.238(\pm 0.019) + 0.991(\pm 0.133) \log k_1(DBE)$

$R = 0.957$, $SD = 0.048$ $n = 7$

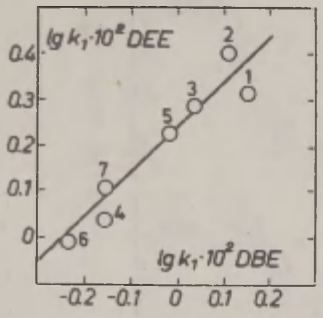

Fig. 1.

Dependence of $\log k_1$(DEE) on $\log k_1$(DBE)

1, CH_3; 2, C_2H_5; 3, n-C_3H_7; 4, iso-C_3H_7; 5, n-C_4H_9; 6, iso-C_4H_9; 7, sec-C_4H_9.

No such a result was obtained for the dependence between rate constant k_1 for THF, on the one hand, and k_1 for DEE and DBE, on the other hand. These data permit us to state that the Grignard reagent formation in DEE or DBE proceeds in one way but in THF another formation mechanism takes place.

The relationship between rate constant and the inductive constant σ^* and the steric constant E_s^o, of alkyl groups of halides was investigated. The independence of logarithms of rate constants k and k_1 from σ^* constants was found.

The relationship between E_s^o for alkyl groups and logk or $\log k_1$ for various media are presented in Figs. 2 and 3.

A linear relationship between above-mentioned values for the cases of DEE and DBE can be seen. The results of the data processing (the point for R=sec-C_4H_9 not included) by the least-squares method according to the following equation

$$\log k = \log k_o + \delta E_s^o \qquad (1)$$

are presented in Table 3.

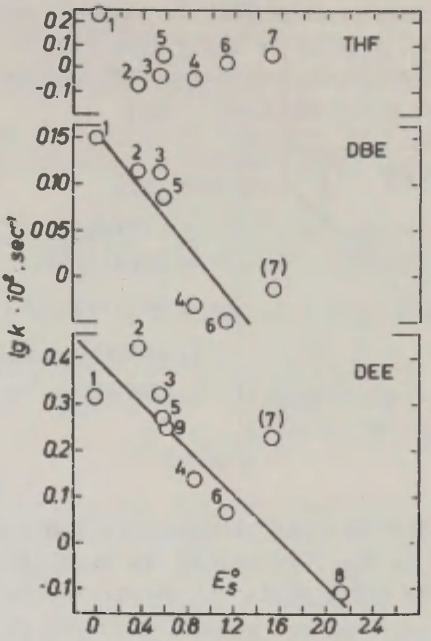

Fig. 2

Dependence of rate constant k on steric constant E_s° of alkyl group.

1, CH_3; 2, C_2H_5; 3, n-C_3H_7; 4, iso-C_3H_7; 5, n-C_4H_9; 6, isc-C_4H_9; 7, sec-C_4H_9; 8, tert-C_4H_9; 9, n-C_5H_{11}

DEE=ethyl ether, DBE=butyl ether, THF=tetrahydrofuran

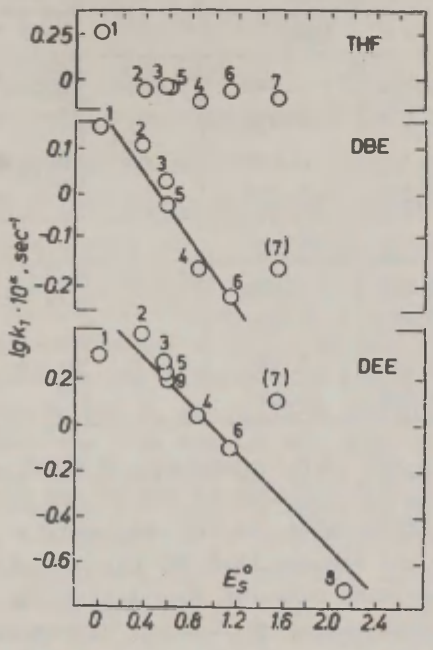

Fig. 3

Dependence of rate constant k_1 on steric constant E_s^o of alkyl group.

1, CH_3; 2, C_2H_5; 3, n-C_3H_7; 4, iso-C_3H_7; 5, n-C_4H_9; 6, iso-C_4H_9; 7, sec-C_4H_9; 8, tert-C_4H_9; 9, n-C_5H_{11}

DEE=ethyl ether, DBE=butyl ether, THF=tetrahydrofuran

Table 3

Results of the Least-squares Data Processing According to Eq.(1)

Solvent	$\log k_0$	σ	R	SD	n
	lgk				
DEE	0.398 ±0.036	0.246 ±0.036	0.937	0.064	8
DBE	0.173 ±0.026	0.191 ±0.039	0.924	0.035	6
	$\lg k_1$				
DEE	0.498 ±0.057	0.528 ±0.058	0.965	0.100	8
DBE	0.187 ±0.028	0.367 ±0.041	0.975	0.037	6

It appeared that the steric hindrance of alkyl group of the bromide decelerated the reaction in DEE or DBE but in the media of THF such a correlation was not obtained.

From literature one can see that THF was used for preparation of organomagnesium compound when latter did not form in DEE. It has been suggested that the effectiveness of THF is caused by its greater basicity as compared with that of DEE.[13]

Obtained experimental data testified the independence of rate constants from the structure of alkyl group of bromide in the medium of THF. This phenomenon may be interpreted according to the mechanism scheme suggested by us in a previous work.[11]

In accordance with this scheme for the transfer reaction two pathways, A and B, in parallel are considered, one (A) involving the radical RMg and another (B) involving radical MgBr.

The effective third-order rate constants of pathways A and B have been expressed as follows:

$$k_{III(A)}=k_1k_2/k_5 \quad \text{and} \quad k_{III(B)}=k_1k_7/k_{10}$$

involving rate constants of following elementary reactions:

1. $RBr + Mg \xrightarrow{k_1} \dot{R}Mg + Br\dot{M}g$
2. $\dot{R}Mg + S: \xrightarrow{k_2} \dot{R}Mg:S$
5. $\dot{R}Mg \xrightarrow{k_5}$ interruption of chain A
7. $\dot{M}gBr + S: \xrightarrow{k_7} \dot{M}gBr:S$
10. $\dot{M}gBr \xrightarrow{k_{10}}$ interruption of chain B

One can see that the values of k_7 and k_{10} are independent of the nature of alkyl group R in alkyl halide. If we assume the independence of k_1 from R the value of $k_{III(B)}$ must also be independent of R. At the same time the value of $k_{III(A)}$ depends on the structure of alkyl group so far as the rate constant k_2 and k_5 are related to the elementary reactions in which the free radical $\dot{R}Mg$ takes place.

Based on these results one can suppose that the pathway A predominates for the transfer reaction in DEE or DBE, but the pathway B in THF. If it is true, a quite specific mechanism of solvent effect on the reaction of Grignard reagent formation becomes evident.

To specify the rôle of solvent the rate constants of n-butylmagnesium bromide formation were measured also in propyl ether (DPE), in dimethoxymethane (DMM) and in triethylamine (TEA).

In Table 4 rate constants of n-butylmagnesium bromide formation in various solvents and the characteristics of solvents used are represented.

Comparing the rate constants from Table 4 with each other a very slight difference in their values appears, although the characteristics of used solvents are rather different.

Evidently, in the case of present reaction series the solvent must be regarded, above all, as a reagent, and not

Table 4

Rate Constants of the Reaction Between Mg and n-C_4H_9Br in Various Solvents and Solvent Constants

Solvent	$k.10^2$ sec^{-1}	$k_1.10^2$ sec^{-1}	B[a]	E_s[b]	D^{20}	n_D^{20}	μ
DEE	1.87	1.68	280	-2.4	4.335	1.3527	1.15
DPE	1.30	1.07	279	-2.5	3.39	1.3803	1.18
DBE	1.21	0.96	285	-2.8	3.06	1.3993	1.22
THF	1.12	1.09	282	-0.9	7.39	1.4076	1.87
DMM	2.04 1.02[c]	1.98 0.99[c]	223	-1.8	2.7	1.3530	-
TEA	0.46	0.36	650	-4.4	2.42	1.4040	0.77

[a] measure of the basicity: IR shift, $\Delta\nu_{OH}$ in C_6H_5OH at the complex formation with the base in CCl_4.[17]

[b] isosteric constants of solvent molecules.[18]

[c] taking into account the statistical correction of 0.5

as a medium. This point of view is unambigously supported by the fact that the reaction is of the first order in respect of solvent.[4,11]

Probably, in this case the reaction rate depends on the reaction centre of the solvent while the alkyl groups at the central atom excert no essential influence. The oxygen atom plays the role of the reaction centre in the molecules of solvent DEE, DPE, DBE, DMM and THF. Dimethoxymethane, DMM, is a bidentatic base. After corresponding statistic correction the obtained rate constant value for DMM is rather close to those calculated for other ethers.

In the case of triethylamine the nitrogen atom acts as a reaction centre. In comparison with ethers the corresponding rate constant has a lower value. However, one should take into account that not only the basicity of the reaction centre determines the reaction rate, but also the occurrence of steric hindrances in the complex formation.

Rate constants measurements on the reaction between Mg and n-C_4H_9Br (see Table 4) were made under conditions of unchanged weight of magnesium. As so far as the investigated reaction had a kinetical order in respect of solvent, the obtained values for rate constants must be divided by the solvent concentration. Results of corresponding recalculation are presented in Table 5. No essential changes resulted from that recalculation because of the slight differences in molar volumes of used solvents. Moreover, the interspace of recalculated rate constant values for various solvents became more narrow.

Table 5

Recalculation of Rate Constants Considering the Kinetical Order in Respect of Solvent

Solvent	Concentration of solvent (C_s), M	$\frac{k.10^2 sec^{-1}}{C_s}$	$\frac{k_1.10^2 sec^{-1}}{C_s}$
DEE	9.62	0.194	0.174
DPE	7.85	0.166	0.138
DBE	5.92	0.205	0.163
DMM	8.15	0.125[a]	0.121[a]
THF	12.30	0.091	0.089
TEA	7.12	0.064	0.051

[a] taking into account the statistical correction of 0.5

One of the factors which influence the rate of reaction may be the solubility of corresponding magnesiumorganic compound. One can presume the higher is the solubility the easier the free radicals RMg and MgBr are drawn out of the surface by the solvent.

Unfortunately, only few data on solubility of magnesiumorganic compounds are available. In the paper of Hamelin[15] the solubility of ethylmagnesium bromide in various media is reported (see Table 6). From the papers of Ashby[16] and our experimental work it follows that the magnesiumorganic compounds

are practically insoluble in the triethylamine medium.

One can assume that the solubility of n-butylmagnesium bromide is similar to that of ethylmagnesium bromide.

Table 6

Solubility of Ethylmagnesium Bromide in Various Media

Solvent	Solubility n $= \frac{[EtMgBr]}{[solvent]}$
Benzene	i.s
Toluene	i.s
Anisole	0.03
iso-DPE	0.14
DEE	0.71
DBE	0.92
THF	0.12
Pyridine	0.00

Obviously the rate constant for the formation of butylmagnesium bromide decreases with the decreasing solubility of the organomagnesium compound.

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KINETICS OF THE GRIGNARD REAGENT FORMATION. 3. INVESTIGATION OF THE INDUCTION PERIOD

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The dependence of induction period on admixture of the ether peroxide or water was investigated. Empirical relationships between induction period and the contents of the above-mentioned inhibitors were established. The influence of solvent and alkyl group structure of alkyl bromide on the induction period is discussed.

Usually the reaction between metallic magnesium and alkyl or aryl halide does not start immediately but after the induction period. It is known that this period is greatly variable by the addition of activators or inhibitors. Among the activators that have been recommended iodine is used most frequently. A small amount of preformed Grignard reagent or magnesium halides reduces, too, the induction period. The various admixtures in solvents (moisture, peroxides, oxygen) are to be regarded as the most plausible inhibitors. A purely mechanical inhibition, conditioned by an oxide film on the metal, prevents, too, an effective contact between the ether-halide solution and the metal.

In this study the influence of peroxide and moisture on the induction period was dealt with.

Experimental

The peroxide-containing solutions were prepared as follows. A glass stoppered bottle was about 1/2 filled with absolute solvent and exposed to the light. During a month an auto-

oxidation of ethers had been effected. The quantitative determination of peroxide was carried out by the reduction method.[1] The nature of formed peroxide was not studied, their concentration was expressed in mequiv/l ether. For kinetic measurements an aliquot portion of that solution was added to the solution under study.

Ethyl ether, tetrahydrofuran, n-butyl bromide, bromobenzene and magnesium were purified as described earlier.[2,3]

The reaction kinetics was followed thermographically.[4,5,3] All the kinetics measurements were taken at $20^{\circ} \pm 0.05$, the volume of solution was 40 ml, the weight of magnesium was 1.5 g, and if not given any other value the concentration of halide was 0.2 n.

The thermograms processing results the S-shaped kinetic curves. Rate constants were calculated from the slope of the straight line in co-ordinates $\log \Delta\Delta T_o/\Delta t$ vs. t.[6]

In the cases of peroxide-containing solvents at a certain moment the reaction mixture became turbid and yellowish. Considerable coloration occurred in tetrahydrofuran. In a certain period the yellowish colour disappeared and a vigorous reaction started (see Fig. 1).

In Table 1, as an example, the analytical data (the amount of basic[7] and the total amount[8] of magnesium, and halide by Volhard) for the reaction mixture (in which the concentration of peroxide is equal to 10 mequiv/l) are represented. The reaction proceeds between Mg and $n\text{-}C_4H_9Br$.

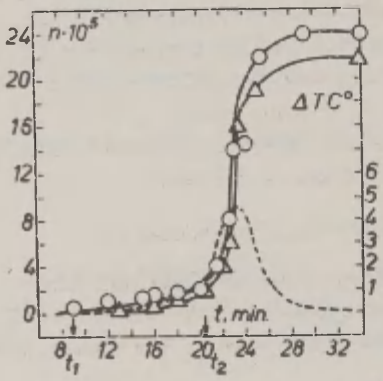

Fig. 1
The kinetic curve for accumulation of basic (△) and total (o) amount of magnesium and the reaction thermogram (dotted line). t_1 and t_2 denote the time of appearence and disappearence of yellowish colour

In Fig. 1 the obtained analytical data and the reaction thermogram are presented graphically. So far as the halogen concentration is close to the concentration of total amount of magnesium only the value of the latter is shown.

T a b l e 1

The Time-dependence of the Content of Reaction Mixture

Time min	The Amount of basic magnesium equiv. 10^5 (Acidimetry)	The total amount of magnesium equiv. 10^5 (Complexometry)	Halogen equiv. 10^5 (Argentometry)
5	0	0	0
9	0	0.4	0.4
11	0	-	0.6
12	-	1.0	-
13	0.1	-	-
14.5	-	1.2	-
15	-	1.2	1.0
15.5	-	-	1.2
16	0.55	1.5	1.5
18	1.0	1.7	1.8
20	-	2.0	-
20.5	1.90	-	2.8
21.5	-	4.0	4.0
22	4.0	-	4.0
22.5	6.0	8.0	12
23	-	14	-
23.5	15	-	17
24	-	14.6	-
25	19	-	22
29	-	24	24
34	21.8	24	24

For induction period we took the time-interval from the addition of halide to reaction mixture up to the primary rise of temperature.

The data on dependence of induction period (τ_i) and the 'yellow' period (τ_y) upon concentration of peroxide are presented in Tables 2 and 3

Table 2

Dependence of Induction and 'Yellow' Periods and Rate Constants on the Peroxide Concentration for the Reaction Between Mg and $n\text{-}C_4H_9Br$ in Ethyl Ether

Peroxide Concentration mequiv/l	τ_i min	τ_y min	$k \cdot 10^2$ sec^{-1}
1.2	3.8	1.25	1.87
2.5	4.4	2.25	1.74
3.7	5.0	3.20	1.65
5.0	6.0	4.2	1.80
7.5	7.4	6.0	1.80
10.0	9.0	7.2	1.62
11.0	11.1	8.5	1.58
12.5	13.8	9	1.79
13.7	25	10	1.79
16.2	-	-	-*

* the reaction did not start throughout two days.

Table 3

Dependence of Induction and 'Yellow' Periods on the Peroxide Concentration in the Presence of Iodine for the Reaction Between Mg and $n\text{-}C_4H_9Br$ in Ethyl Ether

Peroxide Concentration mequiv/l	τ_i min	τ_y min	$k \cdot 10^2$ sec^{-1}
1.2	1.4	0.6	-
5.0	2.0	1.8	-
7.5	2.5	2.0	-
11.0	3.0	3.1	1.85
12.5	6.0	3.0	1.80
15.0	14	4.0	1.65
18.0	-	-	-*

* the reaction did not start throughout two days

Table 4

Dependence of Induction Period and Rate Constant on the Water Presence for the Reaction Between Mg and n-C_4H_9Br

The amount of water in DEE mol/l	Induction period min	$k \cdot 10^2$ sec^{-1}
$5.5 \cdot 10^{-3}$	12	0.90
$5.5 \cdot 10^{-3}$*	11.5	0.93
$11.0 \cdot 10^{-3}$	25	0.92
$15.4 \cdot 10^{-3}$	70	0.85
$15.4 \cdot 10^{-3}$*	68	0.90
$16.5 \cdot 10^{-3}$	220	0.87
$17.2 \cdot 10^{-3}$		-

* in the presence of iodine

Table 5

Dependence of Induction Period and Rate Constant on the Nature of Halide in DEE or THF

Halide	Initial Concentration of Halide mol/l	Induction period, min		$k.10^2$ sec^{-1}	
		DEE	THF	DEE	THF
C_2H_5Br	0.2	0.5	6.5	2.40	0.80
n- C_3H_7Br	0.2	0.5	8.2	1.82	0.81
n- C_4H_9Br	0.2	0.5	8.3	1.75	1.02
	1.0	0.5	-	-	-
	0.2*	0.25	-	1.79	-
iso- C_4H_9Br	0.2	1.1	8.0	1.10	0.98
sec- C_4H_9Br	0.2	1.3	7.8	1.41	0.99
tert-C_4H_9Br	0.2	45	-	0.79	-
C_6H_5Br	0.2	30	2.2	0.92	0.94

* in the presence of iodine

In the water presence all thermograms had a characteristic shape with two thermal maxima. When iodine was used the shape of thermograms was not changed. The amount of water in etheral solutions was determined by the Fischer method.[9] The results are represented in Table 4.

In Table 5 dependence of induction period and rate constant upon the nature of bromide in ethyl ether or tetrahydrofuran is presented.

Discussion

In some papers it has been pointed out that under similar conditions the induction period depends on the structure of alkyl group in alkyl halide and on the nature of halide atom.[10]

On the other hand, the fact that the induction period may be eliminated is of essential importance. If a known quantity of halide reacts to completion and after that a second portion is added, no induction period is observed.[11,4] Gzemski and Kilpatrick concluded that the induction period is conditioned by the need of cleansing the surface of metallic magnesium. In one of our papers[4] it has been shown that the change of reacted magnesium for a fresh weight of the latter practically does not influence the shape of kinetic curve and the reaction rate, too.

The absence of the induction period has also been shown by M^me^ Gault[12] who studied the organomagnesium compound formation by adsorption of gaseous alkyl halides on film of sublimed magnesium (in vacuo). From this follows that the induction period is not necessarily connected with the reaction mechanism, but may be caused by the action of removable factors. The above-mentioned facts and the S-shaped kinetical curves, too, permit us to suppose that the induction period is connected with the presence of inhibitor in the reaction mixture. The transfer reaction cannot take place before all the inhibitor has been reacted with free radicals generated by the initiation reaction of the chain.

The elimination of induction period results in the removal of the inhibitor.

In the case of the Grignard compound formation ether peroxides are known as mighty inhibitors. From our experimental data it is obvious that the induction period depends on the concentration of ether peroxides in the reaction mixture.

In the presence of peroxide the reaction mixture at a certain time coloured yellowish. Both the induction period and 'yellow' period depended on the peroxide concentration. That dependence is represented in Fig. 2.

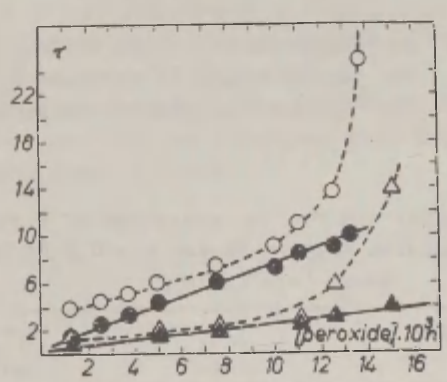

Fig. 2. Dependence of induction (τ_i) and 'yellow' (τ_y) periods upon concentration of peroxide (see Table 2, and 3). ○, τ_i; ●, τ_y; △, τ_i in the presence of iodine, ▲, τ_y in the presence of iodine.

In Fig. 3 (Table 6) the dependence of reciprocal of the induction period, $1/\tau_i$, on the peroxide concentration is presented.

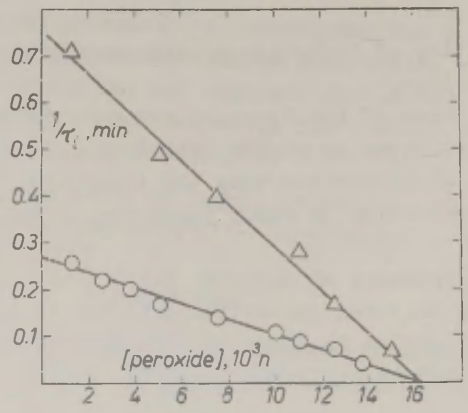

Fig. 3 Dependence of the value of $1/\tau_i$ upon the concentration of peroxide O, $1/\tau_i$; Δ, $1/\tau_i$ in the presence of iodine

T a b l e 6

The $1/\tau_i$ Values and the Concentration of Peroxide for the Reaction Between Mg and n - C_4H_9Br in Ethyl Ether (see Table 2)

Peroxide concentration mequiv/l	$1/\tau_i$ min^{-1}	$1/\tau_i$ a) min^{-1}
1.2	0.26	0.71
2.5	0.22	-
3.7	0.20	-
5.0	0.17	0.49
7.5	0.14	0.40
10.0	0.11	0.28
11.0	0.09	0.28
12.5	0.07	0.17
13.7	0.04	-
15.0	-	0.07

a) in the presence of iodine

In the reaction of magnesiumorganic compound formation the water (moisture) plays a role of inhibitor, too. The induction period much depends on the amount of water in reaction mixture and after reaching a critical concentration the reaction did not start at all. The critical concentration at which the induction period becomes infinity has been reported by M^me Meyer and M^me Shimodaira. In accordance with this work the critical concentration of water depends on the surface of magnesium, the concentration of halide and temperature.[13]

After induction period, at the same time of the primary rise of temperature, a white turbid is formed in the reaction mixture. As it has been shown in some papers [13,14] the composition of that precipitate corresponds to the formula of $MgBrOH \cdot 3H_2O$.

The data processing on the inhibitory influence of water in terms of that used for peroxides gave the similary result (see Table 7, Figs. 4 and 5).

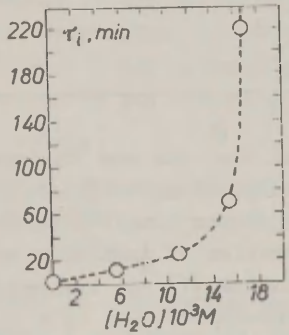

Fig. 4 Dependence of induction period (τ_i) on the water concentration in DEE for the reaction between Mg and n-C_4H_9Br

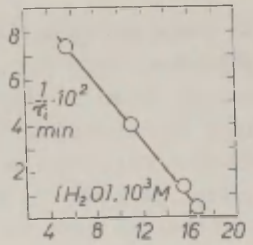

Fig. 5 Dependence of the $1/\tau_i$ value on the water concentration in ethyl ether

Table 7

Dependence of $1/\tau_i$ on the Water Presence in the Reaction Between Mg and n-C_4H_9Br in Ethyl Ether (see Table 4)

Concentration of water in DBE mol/l	$1/\tau_i \cdot 10^2$ min^{-1}
$5.5 \cdot 10^{-3}$	7.5
$11.0 \cdot 10^{-3}$	4.0
$15.4 \cdot 10^{-3}$	1.4
$16.5 \cdot 10^{-3}$	0.45

It appeared that one and the same relationship was valid for both the investigated inhibitors, peroxide and water, viz. an inverse proportionality between the induction period and the concentration of inhibitor was observed.

In co-ordinates $1/\tau_i$ vs. concentration of inhibitor the straight line intersects the axis of concentration at the point which corresponds to infinity of the induction period.

The peroxide content in media, obviously, did not affect the kinetic of magnesiumorganic compound formation. Calculated rate constants are rather close to those calculated for the case of elimination of the induction period.

If the kinetical measurements were carried cut under conditions of the water presence, the obtained rate constants values were approximately twice less than for the elimination case. Moreover, in the water presence two thermal maxima in the thermograms were observed. That indicates the proceeding of two consecutive exothermic reactions. M^me Meyer et al.[13,14] investigating the inhibitory influence of water noticed that after induction period a reaction takes place in which part of the water reacts with magnesium and butyl bromide yielding a precipitation of $MgBrOH \cdot 3H_2O$ (the latter did not react with Grignard reagent). Only after that reaction the formation of Grignard reagent proceeds, the reagent instantly reacting with water. The latter process is the exothermic one.

From data represented in Table 5 it follows that in the case of ethyl ether the induction period essentially depends on the structure of halide (the induction period varied between 0.5 and 30÷45 min.), but in tetrahydrofuran any noticeable dependence was not observed (between 2.2 and 8.3 min).

According to the mechanism scheme suggested recently[3] a chain interruption as a result of the reaction between the free radicals and the chain terminator, i, is possible. If the transfer reaction follows the pathway A (see Ref.3) the interrupt of chain occures by the following reaction:

$$\dot{R}Mg + i \xrightarrow{k_6} y$$

In the case of pathway B (see ref. 3) the inhibitor, i, reacts with the free radical MgBr:

$$\dot{M}gBr + i \xrightarrow{k_{11}} y$$

We have suggested[15] that in ethyl ether medium for the transfer reaction the pathway A predominates, but in tetrahydrofuran the pathway B . Proceeding from the above-mentioned reaction equations one can suppose that in the first case the rate of reaction with inhibitor depends on the structure of the alkyl group, R, but in the second case the immediate influence of the alkyl group must be absent. Indeed, in the medium of tetrahydrofuran no essential dependence of induction period on the nature of R in bromide was observed.

Apparently, the substituent affects, dependent upon the solvent, in parallel both the rate of the Grignard reagent formation and the induction period. This phenomen can be interpreted in accordance with the suggested mechanism scheme involving two pathways in parallel.

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CORRELATION ANALYSIS OF THE STRUCTURE DEPENDENCE OF DIPOLE MOMENT IN THE VINYL ETHER SERIES

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The dipole moments (DM) of the CH_2=CHOR series (R = alkyl) have been correlated with σ^*, Δn and various steric constants using the equations of multiple and pair regressions. The best correlation was found to be the pair one with the Δn constant that was explained in terms of special short-ranged steric interaction affecting the π-component of DM.

Recently /1,2/ we have revealed a rather surprising dependence of the dipole moment (DM) of vinyl ethers, CH_2=CHOR (R = alkyl), on their radical structure. To explain this phenomenon, we were urged to introduce tentatively both the concept of the π-moment altering in a response to the coplanarity distortion, and the concept of a special skew polarisation of the double bond under the influence of an electric field orientated from the side at some angle to the double bond plane /2/. As a support of such assumptions the fairly close linear relationships between the DM values and steric or inductive constants of alkyl radicals have been mentioned therein. However, because the inductive (σ^*), hyperconjugative (Δn) and steric (E_s^o) constants of common alkyls are linearly related to each other, some uncertainties were left as to the real effect influencing the DM. A more distinct correlation analysis, with spreading the series of compounds studied, was desireable. It is just the work that was done and will be discussed below.

RESULTS

In Table 1 there are listed DM values (μ) determined by Gedestrand's method in octane at 25°C for 17 vinyl ethers; therein are also placed the σ^x, Δn and various steric constants of R, -0.12 being chosen as the σ^x value of C_5H_{11}-n/1/. The rest is explained in footnotes of Table 1 or conventionalized in earlier papers (cf Ref.6).

The dielectric constant of the solutions was measured with the "Tangens-2M" instrument on the 1.0 MHZ frequency, and the density of solutions was determined by hydrostatic weighing directly in the dielcometer, torsionic balance being used. Some of the μ values (Table 1) slightly differ from earlier reported ones /1,2/ - this is a result of remeasurement. Now the accuracy of the μ values is not worse than within $\pm$0.02 D.

The data of Table 1 have been treated by the least-squares method according to the following general correlation equation:

$$\mu = a_0 + a_1 \sigma^x + a_2 \Delta n + a_3 E_s \qquad (1)$$

to find the regression coefficients (a_i), their variances, the correlation coefficients (R or r) and general dispersion (standard deviation), S_0. All possible two-argument combinations and pair correlations ($\mu = b_0 + b_1 x_i$, where $x_i = \sigma^x, \Delta n, E_s^o$) were calculated, three types of E_s [$E_{s(R)}^o$, $E_{s(CH_2R)}^o$ and E_s^x /3/] for any equation being used.

Three choices (sets) of the μ values of Table 1 were subjected to the above procedure:

I : whole series (1-17)

II : compounds 1-10, 13-15, 17

III : compounds 1-10

Parameters of the best multi-argument regressions for these choices are put together in Table 2. Other combinations having worse indices (R and S_0) and the regression coefficients (a_i) of lesser accuracy have been omitted. The best pair correlations are represented in Table 3.

TABLE 1. The Dipole Moments of Vinyl Ethers and the Substituent Constants of Their Radicals (for footnotes p. t. o.)

№	R	μ., D	σ^x	Δ n	$E^o_{s(R)}$	$E^o_{s(CH_2R)}$	E^x_s (a
1	CH_3	1.11	0	3	0	-0.27	0
2	C_2H_5	1.19	- 0.10	2.4	- 0.27	-0.56	0.07
3	C_3H_7-n	1.19	- 0.115	2.4	- 0.56	-0.59	0.49
4	C_3H_7-i	1.48	- 0.19	1.8	- 0.85	-1.13	0.49
5	C_4H_9-n	1.20	- 0.13	2.4	- 0.59	-0.60	0.5 (i
6	C_4H_9-i	1.14	- 0.125	2.4	- 1.13	-0.60	1.05
7	C_4H_9-t	1.79	- 0.30	1.2	- 2.14	-1.94	3.60
8	C_5H_{11}-n	1.22	- 0.12	2.4	- 0.60	-0.60	0.5 (i
9	C_5H_{11}-t	1.84	- 0.315	1.2	- 3.0 (g	-2.5	4.15
10	C_6H_{11}-cyclo	1.64	- 0.26	1.8	- 1.19	-1.18	0.5 (i
11	$CH_2 = CH$	1.10	+ 0.59	1.8 (e	- 0.9 (j	-0.7	0.5 (i
12	C_6H_5	1.41	+ 0.60	1.8 (e	- 0.9 (j	-0.71	0.5 (i
13	$(CH_3)_3Si(CH_2)_2$ (b	1.20	- 0.16 (c	2.4	- 0.60 (i	-0.60 (i	0.5 (i
14	$(CH_3)_3Si(CH_2)_3$ (b	1.12	- 0.13 (c	2.4	- 0.60 (i	-0.60 (i	0.5 (i
15	$(C_2H_5)_3SiCH_2$ (b	1.26	- 0.32 (d	2.4 (f	- 2.0 (i	-2.0 (i	1.6 (i
16	$(C_2H_5)_3Si(CH_2)_2$ (b	1.31	- 0.17 (d	2.4	- 0.60 (i	-0.60 (i	0.5 (i
17	$(C_2H_5)_3Si(CH_2)_3$ (b	1.04	- 0.13 (d	2.4	- 0.60 (i	-0.60 (i	0.5 (i

DISCUSSION

The data of Table 2 show that the multi-argument regressions of I and III choices are not worthwhile to discuss in detail because of their both low indices (especially for choice I) and uncertainties of the regression coefficients. The only two points perhaps deserving attention here are the following: (a) hyperconjugative terms in eqs. for whole series are significant (using Student's criterion) and (b) all terms of eqs. become statistically unreliable on going to the most limited series III, that prove to be a consequence of mutual linear relationships between arguments for this set. The correlations of choice II are more informative. First, some of them (lines 5–8 from above) represent closer relationships than any other of Table 2. Second, the hyperconjugative terms are still more significant in all eqs. of this set than in these of the whole series. Third, from the comparison of the figures in lines 5–8 one may conclude that a relationship of DM on structure parameters is to be expressed as follows:

$$\mu = 2.49 + 0.37(\pm 0.16)\,\sigma^{*} - 0.53(\pm 0.04)\,\Delta n \qquad (2)$$
$$R = 0.959,\ S_0 = 0.08$$

Footnotes for Table 1:
[a] From the work of Fellous et.al /3/; [b] synthesized by N.N. Vlasova and I.I. Tsykhanskaya; [c] calculated after Zhdanov /4/; [d] calculated after Yegorochkin /5/; [e] assumed that the C=C bond takes part in the hyperconjugation like two C-C bonds; [f] assumed that the Si-C bond hyperconjugates like the C-C bond; [g] approximation based on the E_s^o values of C_4H_9-t and $(C_2H_5)_3C$; [i] approximation based on the structure analogy; [j] assumed as for C_3H_7-i.

TABLE 2. Parameters of the Best Multi-argument Regressions for Various Choices

Choice	Combination of arguments	a_0	a_1	a_2	a_3	R	S_0
I	σ^x, Δn, $E^o_{s(R)}$	2.20	−0.18 ±0.12	−0.43 ±0.11	−0.01 ±0.07	0.860	0.13
	σ^x, Δn, $E^o_{s(CH_2R)}$	2.06	−0.14 ±0.13	−0.38 ±0.11	−0.05 ±0.09	0.864	0.12
	σ^x, Δn, E^x_s	2.11	−0.16 ±0.14	−0.398 ±0.11	0.02 ±0.05	0.862	0.12
	σ^x, Δn	2.22	−0.20 ±0.13	−0.45 ±0.07	-	0.860	0.12
II	σ^x, Δn, $E^o_{s(R)}$	2.40	0.45 ±0.16	−0.48 ±0.06	−0.05 ±0.04	0.963	0.07
	σ^x, Δn, $E^o_{s(CH_2R)}$	2.26	0.46 ±0.15	−0.44 ±0.06	−0.10 ±0.05	0.969	0.07
	σ^x, Δn, E^x_s	2.44	0.38 ±0.16	−0.50 ±0.07	0.01 ±0.03	0.960	0.09
	σ^x, Δn	2.49	0.37 ±0.16	−0.53 ±0.04	-	0.959	0.08
	Δn, $E^o_{s(R)}$	2.26	-	−0.50 ±0.08	−0.007 ±0.05	0.942	0.14
	Δn, $E^o_{s(CH_2R)}$	2.17	-	−0.48 ±0.10	−0.04 ±0.06	0.943	0.15
	Δn, E^x_s	2.29	-	−052 ±0.09	−0.002 ±0.04	0.942	0.17
III	σ^x, Δn, $E^o_{s(CH_2R)}$	1.09	−1.16 ±1.17	−0.05 ±0.23	−0.18 ±0.10	0.972	0.08
	σ^x, $E^o_{s(R)}$	0.93	−2.27 ±0.60	-	−0.03 ±0.06	0.954	0.13
	σ^x, $E^o_{s(CH_2R)}$	0.93	−1.28 ±0.59	-	−0.19 ±0.07	0.972	0.14

Though the inductive term here is hardly reliable, this equation will be further of help to justify some pair correlations.

There is a need to explain why regressions of choice I are more scattery. This seems to originate from rough approximations of some substituent constants for compounds 11-17, especially for the three last members of the series (had the purity of silicon-containing ethers 13-17 been put out of question).

Now come to pair correlations (Table 3). It is seen that the $\mu - \Delta n$ dependence again has some preference to all others. Though the correlations of choice III are of nearly an equal validity, the $\mu - \Delta n$ preference follows from its domination in choice II. This is also fully supported by multi-argument correlation results, in particular by Eq.(2).

TABLE 3. Parameters of the Best Pair Correlations for Various Choices

Choice	Argument	b_o	b_1	r	s_o^2	s_b^2
I	$E_s^o(CH_2R)$	1.04	-0.29	0.742	0.03	0.005
II	Δn	2.38	-0.49	0.942	0.008	0.002
	$E_s^o(CH_2R)$	1.10	-0.31	0.790	0.03	0.005
III	σ^*	0.93	-2.70	0.952	0.008	0.093
	Δn	2.36	-0.47	0.959	0.007	0.002
	$E_s^o(CH_2R)$	1.00	-0.38	0.954	0.008	0.002

Therefore, the DM - structure dependence of this series is described best as follows:

$$\mu = 2.36 - 0.47\ \Delta n \qquad (3)$$

$$r = 0.96,\ s_o^2 = 0.007,\ s_b^2 = 0.002$$

We are far from thinking to take it as an evidence

for real conjugative ground of DM changing. One could attempt to invoke here our earlier idea of the acceptor hyperconjugation for the case of the lone-pair electron elements having α-hydrogen /1,6/:

$$-\ddot{Z}-\overset{|}{\underset{|}{C}}-H \longleftrightarrow -\overset{\oplus}{Z}=\overset{|}{\underset{|}{C}},\ \overset{\ominus}{H} \qquad (4)$$

However, it is not easy to understand in these terms why DM of vinyl ethers depends considerably on temperature /7/, if this dependence has not a usual conformational (i.e. steric) cause. The concept of acceptor hyperconjugation fails also to explain without additional assumptions the charge increase on the β-vinylic carbon, monitored by NMR ^{13}C spectra /8/, with increasing Δn. All this says why we are close to consider the eq. (3) as of steric rather than of electronic nature[x].

Indeed, the Δn value as a proper measure of the alkyl branching should be a good intrinsic constant, say, of first order, for steric strains created by alkyls in their surroundings irrespective to any disturbance from outside. Perhaps it would be reasonable to separate the steric effect to two different interactions - short- and long-ranged ones with Δn and E_s constants. In this line, the eq. (3) could be easily interpreted as a result of the π-moment variation due to short-ranged steric interaction near the C_{sp^2} - O bond.

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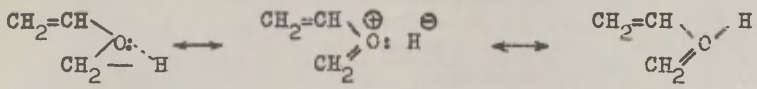
x/ The alternative approach represented by interaction (4) could survive, however, if we take it as making the oxygen more sp^2 and, despite some positive charge on this atom, forming better conditions for π-p overlapping:



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