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ALKYL AND ALKENYL ESTERS OF SULFONIC ACIDS. XXI

Kinetic Isotope Effects of Alkyl and Alkenyl Esters of Sulfonic Acid

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Hydrolysis kinetics of allyl-p-toluene sulfonate labeled with C^{14} or deuterated in α-position and also the hydrolysis kinetics of different alkyl and alkenyl sulfonates in H_2O and D_2O has been studied spectrophotometrically and conductometrically. The results obtained show that with solvolysis of structurally different compounds (esters of sulfonic acids, alkenyl halides) changes in the character of the transition state are just in different degree of covalency of a breaking bond. State of a substance in the solution depends on specific solvation power which results in the ionization of a solute. Depending on the substrate structure and solvent polarity the ionization of $C{-}O_{ester}$ bond can occur only, or formation of ion pairs and their separation into ions takes place.

Study of the reaction kinetics of alkenyl esters of substituted benzenesufonic acids has established that the hydrolysis reaction obeys the regularities of the first or second reaction order[1], depending on conditions of studies.

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To study in detail influence of structural factors, nucleophilicity of a reagent, and medium polarity on the reaction mechanism of alkyl and alkenyl sulfonates, the present work has studied the hydrolysis kinetics of allyl--p-toluene sulfonate labelled with C^{14} or deuterated in α-position and also the hydrolysis kinetics of different alkyl and alkenyl sulfonates in H_2O and D_2O.

As known from the literature [2,3] isotope effects in nucleophilic substitution reactions at aliphatic atom of hydrocarbon can assume different values , depending on the reaction mechanism, i.e. ratios $k_{C^{12}}/k_{C^{14}}$, k_H/k_D, and k_{H_2O}/k_{D_2O} can be both more and less than unity. Bender, Hoeg, and Buist[4,5] have proved that for a bimolecular substitution reaction between methyl iodide marked with C^{14} and different nucleophiles values of isotope effects, $k_{C^{12}}/k_{C^{14}}$, are within the limits from 1.07 to 1.15. In solvolysis reaction in non-aqueous media occuring via monomolecular mechanism for benzyl tosylates[6] and 2-phenyl ethyl tosylates[7-9] with deuterium in α-position of aliphatic carbon atom of ester alcohol component the isotope effect has the value of k_H/k_D equalled to 1.13-1.14. Seltzer proves that for the reaction proceeding via S_N1 mechanism introduction of deuterium in α-position to the reaction center slows down the reaction by about 10-12%.

Experimental

Esters are obtained according to Ref.11. Allyl-C^{14}-chloride, allyl-α-d^2-chloride, and D_2O were of 98% of isotope purity. Allyl-C^{14}-p-toluene sulfonate (b.p. 65-67°, $2\cdot10^{-3}$mm; d_4^{20}1.1767; n_4^{20}1.5206) and allyl-α-d^2-p-toluene sulfonate (b.p. 69-70°, $4\cdot10^{-3}$mm; d_4^{20}1.1783; n_4^{20}1.5204) were prepared from suitable allyl chloride and silver salt of p-toluenesulfonic acid. The solvents were purified by the known methods[12]. The kinetic experiments were carried out conductometrically(C)[13] and spectrophotometrically(S) on SF-16 spectrophotometer[14]. Neutral hydrolysis of alkyl and alkenyl benzene sulfonates was studied by the C and S methods parallelly, that of allylmethane sulfonate and allyl chloride by the C and T (titrimetric) methods. Alkaline hydrolysis of allyl-p-toluene sulfomate was studied by the C and T methods and that of allyl chloride by the T method. When using two techniques, the tables give averaged data. The concentration of esters is $1\cdot10^{-3}$ - $1\cdot10^{-5}$mol/l; alkali concentration is 0.02M. Analytical wave lengths were determined by maximum changes in the ester optical density on the given wave length with the conversion degree not less than 85-90%. Rate constants were calculated by the known first order equations. Mean value from 3-5 parallel runs was considered as a rate constant. The mean error was within 2%.

Results and Discussion

One can see from Table 1 that the isotope effect, $k_C12/k_C{}^{14}$, can assume different values depending on a solvent nature and reaction type. In neutral hydrolysis reactions $k_C{}^{12}/k_C{}^{14}$ dependes little on solvent nature, if compared with differences in rate constants. However, the general trend can be observed: with an increase in solvent polarity the k_C12/k_C14 value decreases as a rule. The numerical value of k_C12/k_C14 is the greatest for alkaline hydrolysis reaction, the value of k_C12/k_C14 for allyl chloride (ACh) being higher than for allyl-p-toluene sulfonate (ATS).

Injection of deuterium into α-position of allyl radical leads to opposite results (Table 2). Effects of α-deuteration increase with solvent polarity and decrease for alkaline hydrolysis, for ACh the isotope effect opposite in direction being observed. The opposite isotope effect was observed for some alkyl halides and Refs. 3, 15-21 present the causative factors of its origination. It is of the most interest to compare the results of isotope studies with the results of kinetic ones, viz., to trace the interrelation between the values of k_C12/k_C14, k_H/k_D, k_{H_2O}/k_{D_2O}, and k_{OH^-}/k.

Table 1

Isotope Kinetic Effect of α-Carbon Atom of C^{14}. X-$^{14}CH_2CH=CH_2$. ATS (30°) and ACh (50°)

X	Solvent	K_CI2, I/ sec	K_CI4, I/ sec	K_CI2/K_CI4	K_CI2/K_CI4, %
I	2	3	4	5	6
$4-CH_3C_6H_4SO_2O$	CH_3OH	$(I.65 \pm 0.02)\cdot IO^5$	$(I.55 \pm 0.02)\cdot IO^5$	I.06	6.I
		$(I.69 \pm 0.03)\cdot IO^5$	$(I.62 \pm 0.02)\cdot IO^5$	I.04	4.2
		$(I.67 \pm 0.02)\cdot IO^5$	$(I.60 \pm 0.03)\cdot IO^5$	I.04	4.2
	C_3H_7OH	$(5.47 \pm 0.I2)\cdot IO^6$	$(5.20 \pm 0.IO)\cdot IO^6$	I.05	5.0
		$(5.67 \pm 0.07)\cdot IO^6$	$(5.24 \pm 0.08)\cdot IO^6$	I.08	7.6
		$(5.57 \pm 0.09)\cdot IO^6$	$(5.22 \pm 0.09)\cdot IO^6$	I.06	6.3
	t - C_4H_9OH	$(I.72 \pm 0.02)\cdot IO^6$	$(I.58 \pm 0.03)\cdot IO^6$	I.09	8.2
		$(I.80 \pm 0.03)\cdot IO^6$	$(I.64 \pm 0.02)\cdot IO^6$	I.IO	8.9
		$(I.84 \pm 0.03)\cdot IO^6$	$(I.62 \pm 0.03)\cdot IO^6$	I.I3	I2.0
	90% CH_3OH-HOH	$(4.07 \pm 0.02)\cdot IO^5$	$(3.86 \pm 0.02)\cdot IO^5$	I.05	5.2
		$(4.I5 \pm 0.09)\cdot IO^5$	$(3.83 \pm 0.03)\cdot IO^5$	I.08	7.8
		$(4.II \pm 0.08)\cdot IO^5$	$(3.83 \pm 0.03)\cdot IO^5$	I.07	6.8
	70% CH_3OH-HOH	$(I.I9 \pm 0.02)\cdot IO^4$	$(I.06 \pm 0.0I)\cdot IO^4$	I.I2	II.0
		$(I.I5 \pm 0.0I)\cdot IO^4$	$(I.I4 \pm 0.02)\cdot IO^4$	I.0I	0.I
		$(I.I7 \pm 0.02)\cdot IO^4$	$(I.IO \pm 0.0I)\cdot IO^4$	I.06	6.0

Table 1 (continued)

I	2	3	4	5	6
4-$CH_3C_6H_4SO_2O$	50% CH_3OH-HOH	$(2.69\pm0.03)\cdot IO^{4}$	$(2.59\pm0.03)\cdot IO^{4}$	I.04	3.7
		$(2.75\pm0.04)\cdot IO^{4}$	$(2.58\pm0.02)\cdot IO^{4}$	I.06	6.2
		$(2.69\pm0.02)\cdot IO^{4}$	$(2.59\pm0.02)\cdot IO^{4}$	I.04	3.8
	30% OH_3OH-HOH	$(5.34\pm0.I2)\cdot IO^{4}$	$(5.08\pm0.09)\cdot IO^{4}$	I.05	4.9
		$(5.24\pm0.08)\cdot IO^{4}$	$(5.I8\pm0.II)\cdot IO^{4}$	I.0I	I.2
		$(5.42\pm0.07)\cdot IO^{4}$	$(5.I0\pm0.08)\cdot IO^{4}$	I.06	5.9
		$(5.36\pm0.09)\cdot IO^{4}$	$(5.I6\pm0.06)\cdot IO^{4}$	I.04	3.8
	HOH	$(I.36\pm0.03)\cdot IO^{3}$	$(I.30\pm0.02)\cdot IO^{3}$	I.04	4.5
		$(I.I6\pm0.02)\cdot IO^{3}$	$(I.I6\pm0.02)\cdot IO^{3}$	I.00	0.0
		$(I.26\pm0.04)\cdot IO^{3}$	$(I.20\pm0.02)\cdot IO^{3}$	I.05	3.4
	90% $(CH_3)_2CO$-HOH	$(I.I6+0.02)\cdot IO^{6}$	$(I.03\pm0.02)\cdot IO^{6}$	I.I2	II.2
		$(I.03\pm0.02)\cdot IO^{6}$	$(I.09\pm0.0I)\cdot IO^{6}$	0.94	4.2
		$(I.2I\pm0.02)\cdot IO^{6}$	$(I.I2\pm0.02)\cdot IO^{6}$	I.08	7.5
		$(I.I9\pm0.0I)\cdot IO^{6}$	$(I.06\pm0.02)\cdot IO^{6}$	I.I2	II.0
		$(I.2I\pm0.02)\cdot IO^{6}$	$(I.06\pm0.0I)\cdot IO^{6}$	I.I4	I2.4
	40% $(CH_3)_2CO$-HOH	$(9.95\pm0.I2)\cdot IO^{5}$	$(9.33\pm0.I7)\cdot IO^{5}$	I.07	6.3
		$(9.97\pm0.I7)\cdot IO^{5}$	$(9.3I\pm0.II)\cdot IO^{5}$	I.07	6.7

Table 1 (continued)

I	2	3	4	5	6
4-$CH_3C_6H_4SO_2O$	90% 4,4-$C_4H_8O_2$ - HOH	$(6.08\pm0.09)\cdot IO^7$ $(5.96\pm0.IO)\cdot IO^7$ $(6.02\pm0.08)\cdot IO^7$	$(5.64\pm0.I2)\cdot IO^7$ $(5.60\pm0.09)\cdot IO^7$ $(5.62\pm0.07)\cdot IO^7$	I.08 I.06 I.07	7.3 6.I 6.7
	40% 4,4-$C_4H_8O_2$ - HOH	$(I.68\pm0.02)\cdot IO^4$ $(I.78\pm0.02)\cdot IO^4$ $(I.73\pm0.03)\cdot IO^4$	$(I.55\pm0.03)\cdot IO^4$ $(I.67\pm0.02)\cdot IO^4$ $(I.6I\pm0.03)\cdot IO^4$	I.08 I.06 I.07	7.8 6.2 7.0
	0.02M KOH 90% CH_3OH-HOH	$(7.76\pm0.I2)\cdot IO^5$ $(7.72\pm0.09)\cdot IO^5$	$(6.93\pm0.IO)\cdot IO^5$ $(6.99\pm0.I2)\cdot IO^5$	I.II I.IO	IO.7 9.5
	0.02M KOH 30% CH_3OH-HOH	$(7.33\pm0.I4)\cdot IO^4$ $(7.32\pm0.I2)\cdot IO^4$	$(6.60\pm0.08)\cdot IO^4$ $(6.56\pm0.09)\cdot IO^4$	I.II I.I2	IO.0 IO.4
	0.02M KOH 40% $(CH_3)_2CO$-HOH	$(I.50\pm0.02)\cdot IO^4$ $(I.60\pm0.02)\cdot IO^4$ $(I.55\pm0.03)\cdot IO^4$	$(I.30\pm0.02)\cdot IO^4$ $(I.45\pm0.03)\cdot IO^4$ $(I.42\pm0.02)\cdot IO^4$	I.I5 I.IO I.IO	I3.4 IO.0 9.4
CI	C_2H_5OH	$(7.76\pm0.I2)\cdot IO^6$ $(7.75\pm0.I7)\cdot IO^6$	$(7.09\pm0.IO)\cdot IO^6$ $(7.II\pm0.08)\cdot IO^6$	I.09 I.09	8.7 8.3

Table 1 (continued)

I	2	3	4	5	6
IO	50% C_2H_5OH-HOH	$(I.72\pm0.03)\cdot I0^5$	$(I.62\pm0.02)\cdot I0^5$	I.06	5.9
		$(I.82\pm0.02)\cdot I0^5$	$(I.74\pm0.02)\cdot I0^5$	I.05	4.4
		$(I.80\pm0.03)\cdot I0^5$	$(I.68\pm0.03)\cdot I0^5$	I.07	6.7
	HOH	$(2.44\pm0.04)\cdot I0^5$	$(2.30\pm0.04)\cdot I0^5$	I.06	5.8
		$(2.46\pm0.03)\cdot I0^5$	$(2.36\pm0.05)\cdot I0^5$	I.04	4.I
	0.5M NaOEt C_2H_5OH	$(9.40\pm0.I7)\cdot I0^3$	$(8.20\pm0.I3)\cdot I0^3$	I.I4	I2.8
		$(9.50\pm0.I5)\cdot I0^3$	$(8.I0\pm0.I8)\cdot I0^3$	I.I7	I4.8
		$(9.48\pm0.I9)\cdot I0^3$	$(8.I5\pm0.09)\cdot I0^3$	I.I6	I4.I
	0.5M NaOH	$(I.40\pm0.03)\cdot I0^2$	$(I.20\pm0.02)\cdot I0^2$	I.I7	I4.3
		$(I.52\pm0.02)\cdot I0^2$	$(I.35\pm0.0I)\cdot I0^2$	I.I3	II.2
	50% C_2H_5OH-HOH	$(I.32\pm0.02)\cdot I0^2$	$(I.I5\pm0.02)\cdot I0^2$	I.I5	I2.8
		$(I.36\pm0.02)\cdot I0^2$	$(I.20\pm0.02)\cdot I0^2$	I.I3	II.8
		$(I.40\pm0.0I)\cdot I0^2$	$(I.I9\pm0.0I)\cdot I0^2$	I.I7	I5.0

The hydrolysis mechanism of allylbenzene sulfonates dependes on reaction conditions and experimentally determined reaction order is connected with the medium polarity and reagent nucleophilicity. Table 2 lists first order rate constant values obtained in the presence of 0.02M KOH and ratios of catalyzed (k_{OH}-) and non-catalyzed(k) hydrolysis rate constants. As follows from Table 2 the value of k_{OH}-/k for ATS and ACh depends largely on medium polarity and with its increase the ratio of k_{OH}-/k decreases which indicates that the reaction sensitivity to the reagent nucleophilicity decreases but in water the rate constant of ATS is independent of alkali additions. The dependence obtained shows that the reaction mechanism changes step by step from bimolecular to monomolecular with an increase in the medium polarity when passing from methanol to water.

As can be seen from Tables 1 and 2 the ratio of k_C12/k_C14 decreases with increase in the medium polarity and has the same direction as changes in the ratio of k_{OH}-/k. The ratio k_H/k_D has opposite direction relative to k_{OH}-/k. It appears that the value of isotope effect, k_C12/k_C14, of the order of 1.10-1.15 is characteristic of the reactions in which tendency to bond formation is much stronger than to bond breaking[4,5,22]. The value of k_H/k_D of the order of 1.10-1.15 (this corresponds to the deceleration of the reaction by 10-15%) is typical of the reactions tending to bond breaking[6,8,23].

Thus the analysis of isotope effects k_C12/k_C14 and k_H/k_D and the ratio k_{OH}-/k allows to conclude that the interaction between ATS or ACh and nucleophilic reagent depends on medium polarity. On the one hand, an increase in the reaction rate constant in the presence of OH^- ions (except water) acknowledges that hydrolysis of ATS and ACh in the media studied proceeds via bimolecular mechanism; on the other hand, the rate constant sensitivity to an increase in the reagent nucleophilicity decreases with an increase in the medium polarity.Hence, the hydrolysis of ATS and ACh in the media studied proceeds via bimolecular mechanism;

Table 2

α-Deuteration Effect on the Hydrolysis Rate Constant of Allyl-p-Toluene Sulfonate and Allyl Chloride. X-$CD_2CH=CH_2$

X	T°C	Solvent	K_H, 1/sec	$K_{Д}$, 1/sec	$K_H/K_{Д}$	K_{OH^-}, 1/sec	K_{OH^-}/K
I	2	3	4	5	6	7	8
4-$CH_3C_6H_4SO_2O$	50	CH_3OH	$(I.6I\pm0.02)\cdot IO^4$ $(I.70\pm0.03)\cdot IO^4$ $(I.69\pm0.02)\cdot IO^4$	$(I.55\pm0.02)\cdot IO^4$ $(I.65\pm0.03)\cdot IO^4$ $(I.63\pm0.02)\cdot IO^4$	I.04 I.03 I.04	$(5.26\pm0.08)\cdot IO^4$	3.25
	50	t -C_4H_9OH	$(I.0I\pm0.02)\cdot IO^5$ $(I.05\pm0.0I)\cdot IO^5$ $(0.97\pm0.0I)\cdot IO^5$	$(I.00\pm0.0I)\cdot IO^5$ $(I.02\pm0.0I)\cdot IO^5$ $(I.00\pm0.0I)\cdot IO^5$	I.0I I.03 0.97	$(3.I4\pm0.05)\cdot IO^4$	3I.I
	30	90% $(CH_3)_2CO$-HOH	$(I.I2\pm0.0I)\cdot IO^6$ $(I.20\pm0.02)\cdot IO^6$ $(I.I4\pm0.02)\cdot IO^6$	$(I.09\pm0.0I)\cdot IO^6$ $(I.I3\pm0.02)\cdot IO^6$ $(I.II\pm0.0I)\cdot IO^6$	I.03 I.06 I.03	$(2.32\pm0.04)\cdot IO^5$	20.0
	30	40% $(CH_3)_2CO$-HOH	$(9.96\pm0.I4)\cdot IO^5$ $(9.99\pm0.I7)\cdot IO^5$ $(9.92\pm0.09)\cdot IO^5$ $(9.9I\pm0.I5)\cdot IO^5$	$(9.40\pm0.I8)\cdot IO^5$ $(9.50\pm0.I2)\cdot IO^5$ $(9.48\pm0.I9)\cdot IO^5$ $(9.42\pm0.I4)\cdot IO^5$	I.06 I.05 I.05 I.05	$(I.70\pm0.02)\cdot IO^4$	I.7I

Table 2 (continued)

I	2	3	4	5	6	7	8
4-$CH_3C_6H_4SO_2O$	30	90% 4,4-$C_4H_8O_2$-HOH	$(5.96\pm0.09)\cdot\mathrm{I0}^{7}$ $(6.08\pm0.\mathrm{I0})\cdot\mathrm{I0}^{7}$ $(6.02\pm0.\mathrm{I2})\cdot\mathrm{I0}^{7}$	$(5.80\pm0.09)\cdot\mathrm{I0}^{7}$ $(5.92\pm0.\mathrm{I2})\cdot\mathrm{I0}^{7}$ $(5.86\pm0.07)\cdot\mathrm{I0}^{7}$	I.03 I.03 I.03	-	-
	30	40% 4,4-$C_4H_8O_2$-HOH	$(\mathrm{I}.70\pm0.03)\cdot\mathrm{I0}^{4}$ $(\mathrm{I}.76\pm0.02)\cdot\mathrm{I0}^{4}$ $(\mathrm{I}.73\pm0.03)\cdot\mathrm{I0}^{4}$	$(\mathrm{I}.63\pm0.02)\cdot\mathrm{I0}^{4}$ $(\mathrm{I}.67\pm0.03)\cdot\mathrm{I0}^{4}$ $(\mathrm{I}.59\pm0.03)\cdot\mathrm{I0}^{4}$	I.04 I.05 I.09	-	-
	40	90% CH_3OH-HOH	$(\mathrm{I}.\mathrm{I2}\pm0.0\mathrm{I})\cdot\mathrm{I0}^{4}$ $(\mathrm{I}.\mathrm{I2}\pm0.02)\cdot\mathrm{I0}^{4}$	$(\mathrm{I}.09\pm0.0\mathrm{I})\cdot\mathrm{I0}^{4}$ $(\mathrm{I}.\mathrm{I0}\pm0.0\mathrm{I})\cdot\mathrm{I0}^{4}$	I.03 I.02	$(2.70\pm0.04)\cdot\mathrm{I0}^{4}$	2.4I
	40	80% CH_3OH-HOH	$(\mathrm{I}.93\pm0.03)\cdot\mathrm{I0}^{4}$ $(\mathrm{I}.83\pm0.02)\cdot\mathrm{I0}^{4}$ $(2.03\pm0.03)\cdot\mathrm{I0}^{4}$	$(\mathrm{I}.87\pm0.03)\cdot\mathrm{I0}^{4}$ $(\mathrm{I}.78\pm0.02)\cdot\mathrm{I0}^{4}$ $(\mathrm{I}.96\pm0.03)\cdot\mathrm{I0}^{4}$	I.03 I.03 I.04	$(4.32\pm0.07)\cdot\mathrm{I0}^{4}$	2.24
	40	70% CH_3OH-HOH	$(3.02\pm0.05)\cdot\mathrm{I0}^{4}$ $(3.\mathrm{I2}\pm0.04)\cdot\mathrm{I0}^{4}$ $(3.09\pm0.06)\cdot\mathrm{I0}^{4}$	$(2.9\mathrm{I}\pm0.04)\cdot\mathrm{I0}^{4}$ $(3.06\pm0.05)\cdot\mathrm{I0}^{4}$ $(3.02\pm0.06)\cdot\mathrm{I0}^{4}$	I.04 I.02 I.02	$(6.26\pm0.\mathrm{II})\cdot\mathrm{I0}^{4}$	2.04
	40	60% CH_3OH-HOH	$(4.55\pm0.08)\cdot\mathrm{I0}^{4}$ $(4.50\pm0.07)\cdot\mathrm{I0}^{4}$ $(4.60\pm0.09)\cdot\mathrm{I0}^{4}$	$(4.35\pm0.06)\cdot\mathrm{I0}^{4}$ $(4.30\pm0.05)\cdot\mathrm{I0}^{4}$ $(4.40\pm0.08)\cdot\mathrm{I0}^{4}$	I.05 I.05 I.05	$(9.56\pm0.\mathrm{I9})\cdot\mathrm{I0}^{4}$	2.\mathrm{I0}

Table 2 (continued)

I	2	3	4	5	6	7	8
$4\text{-}CH_3C_6H_4SO_2O$	40	50% CH_3OH-HOH	$(6.77\pm0.09)\cdot IO^4$ $(6.70\pm0.IO)\cdot IO^4$ $(6.82\pm0.09)\cdot IO^4$	$(6.40\pm0.08)\cdot IO^4$ $(6.35\pm0.09)\cdot IO^4$ $(6.42\pm0.IO)\cdot IO^4$	I.06 I.06 I.06	$(I.29\pm0.02)\cdot IO^3$	I.9I
	40	40% CH_3OH-HOH	$(9.9I\pm0.I7)\cdot IO^4$ $(9.72\pm0.09)\cdot IO^4$ $(I.0I\pm0.0I)\cdot IO^3$	$(9.27\pm0.I7)\cdot IO^4$ $(9.07\pm0.20)\cdot IO^4$ $(9.53\pm0.I6)\cdot IO^4$	I.07 I.07 I.07	$(I.7I\pm0.03)\cdot IO^3$	I.76
	40	30% CH_3OH-HOH	$(I.32\pm0.02)\cdot IO^3$ $(I.26\pm0.0I)\cdot IO^3$ $(I.4I\pm0.02)\cdot IO^3$	$(I.23\pm0.02)\cdot IO^3$ $(I.I6\pm0.0I)\cdot IO^3$ $(I.29\pm0.02)\cdot IO^3$	I.07 I.09 I.09	$(2.20\pm0.04)\cdot IO^3$	I.75
	40	20% CH_3OH-HOH	$(I.60\pm0.02)\cdot IO^3$ $(I.72\pm0.03)\cdot IO^3$ $(I.60\pm0.02)\cdot IO^3$	$(I.47\pm0.02)\cdot IO^3$ $(I.56\pm0.02)\cdot IO^3$ $(I.49\pm0.03)\cdot IO^3$	I.09 I.IO I.07	$(2.74\pm0.03)\cdot IO^3$	I.59
	40	IO% CH_3OH-HOH	$(2.06\pm0.02)\cdot IO^3$ $(2.02\pm0.03)\cdot IO^3$	$(I.89\pm0.02)\cdot IO^3$ $(I.77\pm0.02)\cdot IO^3$	I.09 I.I4	$(3.02\pm0.05)\cdot IO^3$	I.50
	40	HOH	$(3.56\pm0.06)\cdot IO^3$ $(3.50\pm0.04)\cdot IO^3$	$(3.05\pm0.05)\cdot IO^3$ $(2.92\pm0.04)\cdot IO^3$	I.I7 I.20	$(3.48\pm0.05)\cdot IO^3$	I.00
	50	0.02M KOH, C_2H_5OH	$(8.06\pm0.09)\cdot IO^3$ $(8.02\pm0.I6)\cdot IO^3$	$(8.0I\pm0.I2)\cdot IO^3$ $(7.82\pm0.I5)\cdot IO^3$	I.00 I.03	$(8.04\pm0.I2)\cdot IO^3$	I2.2

Table 2 (continued)

I	2	3	4	5	6	7	8
I0	50	C_2H_5OH	$(7.68\pm0.I4)\cdot I0^{6}$	$(7.94\pm0.09)\cdot I0^{6}$	0.97	$(9.40\pm0.08)\cdot I0^{3}$	I224
			$(7.82\pm0.09)\cdot I0^{6}$	$(8.02\pm0.I3)\cdot I0^{6}$	0.96	$(9.53\pm0.I0)\cdot I0^{4}$	I2I9
			$(7.78\pm0.I2)\cdot I0^{6}$	$(7.98\pm0.I8)\cdot I0^{6}$	0.97	$(9.45\pm0.07)\cdot I0^{3}$	I2I5
	50	50% C_2H_5OH-HOH	$(I.72\pm0.02)\cdot I0^{5}$	$(I.72\pm0.02)\cdot I0^{5}$	I.00	-	-
			$(I.80\pm0.03)\cdot I0^{5}$	$(I.78\pm0.0I)\cdot I0^{5}$	I.0I	-	-
			$(I.75\pm0.03)\cdot I0^{5}$	$(I.72\pm0.03)\cdot I0^{5}$	I.02	-	-
			$(I.82\pm0.04)\cdot I0^{5}$	$(I.80\pm0.02)\cdot I0^{5}$	I.0I	-	-
			$(I.80\pm0.02)\cdot I0^{5}$	$(I.83\pm0.02)\cdot I0^{5}$	0.98	-	-
	50	HOH	$(2.40\pm0.04)\cdot I0^{5}$	$(2.40\pm0.03)\cdot I0^{5}$	I.00	-	-
			$(2.48\pm0.08)\cdot I0^{5}$	$(2.44\pm0.04)\cdot I0^{5}$	I.02	-	-
			$(2.38\pm0.03)\cdot I0^{5}$	$(2.38\pm0.02)\cdot I0^{5}$	I.00	-	-
			$(2.52\pm0.04)\cdot I0^{5}$	$(2.46\pm0.03)\cdot I0^{5}$	I.02	-	-
	50	0.5 M C_2H_5ONa, C_2H_5OH	$(9.36\pm0.I8)\cdot I0^{3}$	$(9.72\pm0.I2)\cdot I0^{3}$	0.96	-	-
			$(9.55\pm0.I0)\cdot I0^{3}$	$(9.9I\pm0.I8)\cdot I0^{3}$	0.96	-	-
			$(9.47\pm0.I2)\cdot I0^{3}$	$(9.86\pm0.I9)\cdot I0^{3}$	0.96	-	-
			$(9.46\pm0.I3)\cdot I0^{3}$	$(9.79\pm0.20)\cdot I0^{3}$	0.97	-	-

however, depending on the medium polarity, covalent interaction between ester and nucleophile molecules is preceded by the C-O (ATS) or C-Cl (ACh) bond polarization. Covalent bond ionization can result both in the system where two oppositely charged ions are separated from each other and in the system where cation and anion are attracted electrostatically and form thus ion pairs[24-26]. The diagram of this two phase process can be represented as:

$$XC_6H_4SO_2OCH_2R \underset{k2}{\overset{k1}{\rightleftharpoons}} XC_6H_4SO_2O^{\delta-}\cdots{}^{\delta+}CH_2R \qquad (1)$$

$$XC_6H_4SO_2O^{\delta-}\cdots{}^{\delta+}CH_2R \xrightarrow[\text{slow}]{k3} XC_6H_4SO_2O^{-} + {}^{+}CH_2R \xrightarrow[\text{fast}]{+\ddot{N}} \text{products} \qquad (2)$$

or

$$XC_6H_4SO_2O^{\delta-}\cdots{}^{\delta+}CH_2R + \ddot{N} \xrightarrow[\text{slow}]{k3} \text{products} \qquad (3)$$

The effective rate constant is expressed by equation (4) where K_{eq} is an equilibrium constant and $\ddot{N}$ is a nucleophile

$$k_{eff} = \frac{k_1 \cdot k_3}{k_2} = K_{eq} \cdot k_3 \qquad (4)$$

Results of kinetic studies of ATS in H_2O and D_2O substantiate the formation of ion pairs during the solvolysis of ATS. One can see from Table 3 that the value of isotope effect, k_{H_2O}/k_{D_2O}, is surprisingly constant and corresponds to the deceleration of the reaction by 6-10% when passing to D_2O despite considerable changes in the rate constant depending on the structure of ester alcohol radical. Besides, in esters 4, 7-10, and 17-23 rate constant in water does not change in the presence of hydroxile ions which confirms the monomolecular reaction mechanism. Hence, absence of interrelation between changes in rate constants and values k_{H_2O}/k_{D_2O} shows that the ratio k_{H_2O}/k_{D_2O} characterizes mainly differences in the solvation of ester initial states.

Table 3

Hydrolysis Rate Constants of Esters of Sulfonic Acids in H_2O and D_2O. XSO_2Y

X	y	T°C	κ_{H_2O}, I/sec	$\kappa_{Д_2O}$, I/sec	$H_2O/Д_2O$	λ max, nm	№.№
I	2	3	4	5	6	7	8
C_6H_5	CH_3	60	$(5.60\pm0.IO)\cdot IO^4$ $(5.56\pm0.09)\cdot IO^4$ $(5.58\pm0.07)\cdot IO^4$	$(5.07\pm0.08)\cdot IO^4$ $(5.09\pm0.IO)\cdot IO^4$ $(4.99\pm0.06)\cdot IO^4$	I.IO I.09 I.II	265	I.
C_6H_5	C_2H_5	60	$(5.30\pm0.07)\cdot IO^4$ $(5.50\pm0.08).IO^4$ $(5.40\pm0.IO)\cdot IO^4$	$(4.84\pm0.05)\cdot IO^4$ $(4.99\pm0.IO)\cdot IO^4$ $(4.98\pm0.08)\cdot IO^4$	I.09 I.IO I.08	265	2.
C_6H_5	C_3H_7	60	$(2.02\pm0.04).IO^4$ $(2.08\pm0.02).IO^4$ $(2.08\pm0.03)\cdot IO^4$	$(I.82\pm0.02)\cdot IO^4$ $(I.90\pm0.03)\cdot IO^4$ $(I.92\pm0.0I)\cdot IO^4$	I.II I.09 I.08	262	3.
C_6H_5	$2\text{-}C_3H_7$	30	$(I.23\pm0.02)\cdot IO^3$ $(I.22\pm0.0I)\cdot IO^3$	$(I.I2\pm0.0I)\cdot IO^3$ $(I.II\pm0.02)\cdot IO^3$	I.IO I.IO	228	4.
C_6H_5	C_4H_9	60	$(2.35\pm0.04)\cdot IO^4$ $(2.49\pm0.05)\cdot IO^4$ $(2.42\pm0.03)\cdot IO^4$	$(2.23\pm0.03)\cdot IO^4$ $(2.33\pm0.04)\cdot IO^4$ $(2.3I\pm0.02)\cdot IO^4$	I.05 I.07 I.05	26I	5.

Table 3 (continued)

I	2	3	4	5	6	7	8
C_6H_5	C_5H_{II}	60	(3.90±0.06).IO^4 (3.86±0.05)·IO^4 (4.06±0.07)·IO^4	(3.50±0.06)·IO^4 (3.58±0.05)·IO^4 (3.57±0.07)·IO^4	I.II I.08 I.I4	265	6.
4-$CH_3C_6H_4$	CH_2=$CHCH_2$	40	(3.54±0.06)·IO^3 (3.56±0.05)·IO^3	(3.3I±0.06)·IO^3 (3.33±0.07)·IO^3	I.07 I.07	262	7.
4-$CH_3C_6H_4$	CH_3CH=$CHCH_2$	50	(5.65±0.I0)·IO^I (5.60±0.I2)·IO^I	(5.I0±0.08)·IO^I (5.08±0.I0)·IO^I	I.II I.I0	262	8.
4-$CH_3C_6H_4$	CH_2=$C(CH_3)CH_2$	50	(5.42±0.06)·IO^3 (5.54±0.09)·IO^3 (5.43±0.07)·IO^3	(4.98±0.08)·IO^3 (5.08±0.I0)·IO^3 (5.03±0.07)·IO^3	I.09 I.09 I.08	225	9.
4-$CH_3C_6H_4$	CH_2=$CH(CH_3)CH$	50	(4.I5±0.08)·IO^I (4.I9±0.06)·IO^I (4.I7±0.09)·IO^I	(3.75±0.08)·IO^I (3.79±0.06)·IO^I (3.77±0.05)·IO^I	I.II I.I0 I.II	225	IO.
4-$CH_3C_6H_4$	CH≡CCH_2	60	(2.70±0.04)·IO^4 (2.88±0.03)·IO^4 (2.79±0.05)·IO^4	(2.48±0.03)·IO^4 (2.58±0.05)·IO^4 (2.53±0.04)·IO^4	I.09 I.II I.I0	262	II.

Table 3 (continued)

I	2	3	4	5	6	7	8
$4\text{-}CH_3C_6H_4$	$C_6H_5CH_2CH_2CH_2$	60	$(I.52\pm0.02)\cdot I0^4$ $(I.56\pm0.03)\cdot I0^4$ $(I.54\pm0.02)\cdot I0^4$	$(I.40\pm0.03)\cdot I0^4$ $(I.44\pm0.0I)\cdot I0^4$ $(I.42\pm0.02)\cdot I0^4$	I.09 I.08 I.08	263	I2.
$4\text{-}CH_3C_6H_4$	$C_6H_5C{\equiv}CCH_2$	60	$(2.40\pm0.04)\cdot I0^3$ $(2.62\pm0.03)\cdot I0^3$ $(2.56\pm0.02)\cdot I0^3$	$(2.30\pm0.03)\cdot I0^3$ $(2.4I\pm0.04)\cdot I0^3$ $(2.37\pm0.03)\cdot I0^3$	I.04 I.08 I.08	263	I3.
$4\text{-}CH_3C_6H_4$	$(CH_3)_2CHCH_2$	60	$(4.78\pm0.08)\cdot I0^5$ $(4.79\pm0.I0)\cdot I0^5$	$(4.53\pm0.06)\cdot I0^5$ $(4.54\pm0.07)\cdot I0^5$	I.06 I.06	225	I4.
$4\text{-}CH_3C_6H_4$	$CH_3OCH_2CH_2$	60	$(I.57\pm0.02)\cdot I0^5$ $(I.60\pm0.03)\cdot I0^5$	$(I.46\pm0.03)\cdot I0^5$ $(I.50\pm0.02)\cdot I0^5$	I.07 I.07	229	I5.
$4\text{-}CH_3C_6H_4$	$CICH_2CH_2$	60	$(5.58\pm0.I0)\cdot I0^6$ $(5.40\pm0.09)\cdot I0^6$ $(5.52\pm0.08)\cdot I0^6$	$(5.38\pm0.I2)\cdot I0^6$ $(5.27\pm0.08)\cdot I0^6$ $(5.3I\pm0.09)\cdot I0^6$	I.04 I.02 I.04	262	I6.
CH_3	CH_3		$(2.I5\pm0.03)\cdot I0^4$ $(2.20\pm0.02)\cdot I0^4$ $(2.23\pm0.04)\cdot I0^4$ $(2.22\pm0.02)\cdot I0^4$	$(2.03\pm0.02)\cdot I0^4$ $(2.06\pm0.04)\cdot I0^4$ $(2.09\pm0.05)\cdot I0^4$ $(2.05\pm0.02)\cdot I0^4$	I.06 I.07 I.07 I.08	-	I7.

Table 3 (continued)

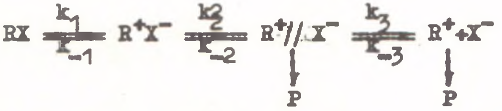
I	2	3	4	5	6	7	8
CH_3	C_2H_5	60	$(I.98\pm0.04)\cdot IO^4$ $(I.96\pm0.02)\cdot IO^4$	$(I.83\pm0.02)\cdot IO^4$ $(I.8I\pm0.0I)\cdot IO^4$	I.08 I.08	-	I8.
C_6H_5	$CH_2{=}CHCH_2$	20	$(6.30\pm0.I2)\cdot IO^4$ $(6.4I\pm0.09)\cdot IO^4$ $(6.22\pm0.08)\cdot IO^4$	$(5.80\pm0.I0)\cdot IO^4$ $(5.87\pm0.09)\cdot IO^4$ $(5.73\pm0.I0)\cdot IO^4$	I.09 I.09 I.09	265	I9.
$4\text{-}CH_3OC_6H_4$	$CH_2{=}CHCH_2$	20	$(2.82\pm0.04)\cdot IO^4$ $(2.87\pm0.02)\cdot IO^4$ $(2.92\pm0.03)\cdot IO^4$	$(2.60\pm0.03)\cdot IO^4$ $(2.58\pm0.04)\cdot IO^4$ $(2.74\pm0.03)\cdot IO^4$	I.08 I.II I.07	240	20.
$4\text{-}CIC_6H_4$	$CH_2{=}CHCH_2$	20	$(I.02\pm0.02)\cdot IO^3$ $(I.05\pm0.0I)\cdot IO^3$ $(I.02\pm0.0I)\cdot IO^3$	$(9.I5\pm0.I8)\cdot IO^4$ $(9.23\pm0.I3)\cdot IO^4$ $(9.22\pm0.I6)\cdot IO^4$	I.II I.I3 I.II	229	2I.
$4\text{-}BrC_6H_4$	$CH_2{=}CHCH_2$	20	$(I.03\pm0.0I)\cdot IO^3$ $(I.09\pm0.02)\cdot IO^3$ $(I.06\pm0.02)\cdot IO^3$	$(9.52\pm0.I8)\cdot IO^4$ $(9.58\pm0.09)\cdot IO^4$ $(9.55\pm0.I5)\cdot IO^4$	I.08 I.I3 I.II	234	22.
$4\text{-}NO_2C_6H_4$	$CH_2{=}CHCH_2$	20	$(3.25\pm0.06)\cdot IO^3$ $(3.34\pm0.03)\cdot IO^3$ $(3.28\pm0.05)\cdot IO^3$	$(2.82\pm0.03)\cdot IO^3$ $(2.94\pm0.05)\cdot IO^3$ $(2.79\pm0.04)\cdot IO^3$	I.I5 I.I4 I.I7	250	23.

Thus the obtained values of isotope effects k_C12/k_C14 and k_H/k_D and the ratio k_{OH^-}/k substantiate that, depending on medium polarity, the hydrolysis of ATS occurs via mono or bimolecular mechanism.

Comparison of k_{H_2O}/k_{D_2O}, k_{OH^-}/k and the ratios of rate constants of structurally different esters indicates that differences in the solvation of initial esters depending on the structure of an alcohol radical and substituent in sulfonic acid are insignificant. Introduction of electron-donating or electronegative substituents into benzenesulfonic acids has no marked activating or deactivating effect on k_{H_2O}/k_{D_2O}.

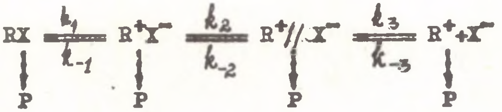
On the basis of the obtained results one may come to the conclusison that with solvolysis of structurally different compounds (esters of sulfonic acids, alkenyl halides) changes in the character of the transition state are just in a different degree of covalence of a breaking bond only. State of a substance in the solution depends on specific solvation power. This results in ionization of a solute and, depending on its structure and medium polarity, in formation of ion pairs and their separation into ions.

Proceeding from the above,the originally proposed by Winstein conception of ion pairs according to which a solvolytic product can be formed from solvent separated ion pair or carbonium ions (5) should be extended with allowance for possibility of participation of structurally different ion pairs in nucleophilic substitution reactions. In the modified form the Winstein scheme (6) should involve different mechanisms which can be realized in consiquence of changes in rate ratios in different steps whose formation and number depends in turn on a reacting substance structure and solvent (where P's are reaction products).



$$\begin{tikzcd}
RX \arrow[r, shift left, "k_1"] & R^+X^- \arrow[l, shift left, "k_{-1}"] \arrow[r, shift left, "k_2"] & R^+//X^- \arrow[l, shift left, "k_{-2}"] \arrow[r, shift left, "k_3"] \arrow[d] & R^+ + X^- \arrow[l, shift left, "k_{-3}"] \arrow[d] \\
 & & P & P
\end{tikzcd}$$

(5)



$$\begin{tikzcd}
RX \arrow[r, shift left, "k_1"] \arrow[d] & R^+X^- \arrow[l, shift left, "k_{-1}"] \arrow[r, shift left, "k_2"] \arrow[d] & R^+//X^- \arrow[l, shift left, "k_{-2}"] \arrow[r, shift left, "k_3"] \arrow[d] & R^+ + X^- \arrow[l, shift left, "k_{-3}"] \arrow[d] \\
P & P & P & P
\end{tikzcd}$$

(6)

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Indices of Modified Static Model for the Description of Aromatic Reactivity.

1. Polycyclic Arenes.

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New indices of the static model of aromatic reactivity are introduced. Correlation equations which include these indices describe the reactivity of alternant polycyclic arenes in electrophilic substitution better than the equation of the known localization approach and, unlike the latter, reflect also reagent nature and medium effects.

Previously one of us published the results of studying reactivity of some multinuclear hydrocarbons when sulfonating with sulfuric acid in nitrobenzene[1]. Peculiarity of these data involves an unusual redistribution of the relative aromatic reactivity with changes in the medium composition. Qualitatively these facts were interpreted on the basis of the hypothesis about the important role of substrate - reagent electrostatic interactions in the aromatic reactivity (AR). However, the recent work[3] consideres the same data exclusively from the viewpoint of specific solvation[4]. Not denying the significance of the latter we should like to note that the analysis[3] based on the comparison of sulfonation and detritiation reaction rates does not prove actually that non-specific solvation effects are insignificant (if they are common to the both compared reactions and close in intensity).

In this connection it is of interest to set a wider task than interpretation of these or those medium effects, namely to elucidate just how accurately the AR could be desribed within the framework of electrostatic model which should,in principle, take into account both medium effect (as dielectric continuum) and reagent chareacter. As known (see, e.g. Refs. 5-7) previous attempts of this kind have not given good enough results, probably due to oversimplification of the so called "static" AR model. The aim of the present work is to check the new model based on the consideration of dipole-dipole (-charged) interactions of substrate-reagent, using the index (correlation) approach.

According to the static AR model attack of a substrate by a charged (or polar) reagent can be described with changes in the effective electronegativity of the attacked carbon atom ($\Delta\alpha$)*, and changes in interaction of this atom with neighboring ones (whose contribution is the most significant with attack of a substrate by radical reagent when $\Delta\alpha =0$) can be taken into account by changes in resonance integrals of the corresponding bonds($\Delta\beta$).Then expanding π- electron energy in Taylor series by the power series of small quantities of $\Delta\alpha$ and $\Delta\beta$, taking into account properties of alternant symmetry, and confining oneself to the first non-zero expansion terms, one obtains a standard expression of the static AR model[6,7] for substrate energy changes under the action of an approaching reagent:

$$\Delta E = \frac{1}{2}\pi_{rr}(\Delta\alpha)^2 + \left(\sum_s P_{rs}\right)\Delta\beta \qquad (1)$$

---

* The $\Delta\alpha$ value can be identified with an electrostatic potential generated by an approaching reagent on the r<u>th</u> atom (see Ref. 6 and Appendix 1).

Since with alternant hydrocarbons self-polarizabilities of atom-atom π_{rr} are closely correlated with free valences $F_r = \sqrt{3} - \sum P_{rs}$ (in the Hückel calculations they coinside even numerically[5]), one does not go usually beyond the correlations with π_{rr}.

Physical content of the first term of (I) is evident: that is energy of electrostatic interaction between a charge (dipole) of a reagent and the induced charge, $q_r = \pi_{rr} \cdot \Delta\alpha$ on the attacked carbon atom. It is, however, also evident that changes in the charge on the r$^{\underline{th}}$ atom lead inevitably to the generation of charges on other atoms of the aromatic system $q_i = \pi_{ir} \cdot \Delta\alpha$. As a result, an induced dipole appeares:

$$\sum_{i=1}^{n} \left(\pi_{ir} \vec{R}_i\right) \Delta\alpha \equiv \vec{k}_r \Delta\alpha \qquad (2)$$

Here $\vec{R}_i$ is a radius-vector of an i$^{\underline{th}}$ π-center in the arbitrary coordinate system. The induced dipole interacting with the reagent field makes an additional contribution to the energy. Really, more strict analysis (see Appendix 1) shows that the $\vec{K}_r$ value can be considered as a new quantrum-chemical index of the static AR model. This is a precondition for using the following correlation equation

$$\lg f_r = a\Delta\pi_{rr} + b\Delta k_r \qquad (3)$$

Here f_r is a partial rate factor; Δ symbolizes differences of the corresponding values for this and standard (benzene) substrates; $k_r = |\vec{K}_r|$. Equation (3) describes AR much better over one-parameter correlations of the $\lg f_r = a\Delta\pi_{rr}$ type[8].

Let us refine the model further, taking into account the reagent nature. Assuming that a reagent approaches along the line passing through the attacked atom and the center of the corresponding ring (sterically averaged attack axis) and that with a dipole reagent its molecule has time to take the most advantageous antiparallel orientation relative to an induced dipole , the corresponding correlation equation for the dipole reagent will have form (3) and for the ion reagent:

$$\lg f_r = a\Delta\pi_{rr} + b\Delta\varkappa_r \tag{4}$$

where $\varkappa_r = k_r\cdot\cos\theta$; θ is an angle between an induced dipole vector and an attack axis.

The content of the k_r and $\varkappa_r$ indices is analogous to that of the μ and λ parameters from Refs. 1 and 2, respectively; thus, the $\pi_{rr}\Delta\mu$ value (see Ref. 2 and Appendix) is closely related to the k_r value (within the framework of the corresponding approximations).

Discrepancy of predictions of the static and dynamic models known in the literature as an "intersection" case (see Ref. 5, p.325) is, probably, due to the fact that the static model neglects completely the reagent-substrate bond formation, i.e. partial charge transfer from the reagent to the substrate. The known approach of Nagakura[9] takes into account structures with charge transfer which results in the dependence of the calculated AR values on the substrate ionization potential (or its electron affinity in the nucleophilic substitution reactions). It is natural to assume that within the framework of the given model consideration of the substrate ionization potential (I_s) together with π_{rr} and k_r will improve its agreement with the experiment, the coefficient at I_s characterizing, probably, charge transfer and a new bond formation[*]. Thus,

$$\lg f_r = a\Delta\pi_{rr} + b\Delta k_r + c\Delta I_s$$

(or an analogous equation with $\varkappa_r$). Since the values of I_s are not known for all polycyclic substrates, this work uses in their place coefficients at β in the expression

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[*] Ref. 13 proves the necessity to take into account I_s in AR from other positions.

for the energy of the highest occupied orbital (M_m) which, as known, (cf. Ref. 5) are linearly correlated with I_s:

$$I_s = 5.978 + 3.229\, M_m \pm 0.1 \text{ (eV)}$$

(This correlation uses the values of I_s[10] obtained by the method of photoionization and spectrally; the M_m values are calculated by a simple method of HMO). The final form of the correlation equation for AR is:

$$\lg f_r = a\,\Delta \pi_{rr} + b\Delta\, k_r + c(-\Delta M_m) \qquad (5)$$

or

$$\lg f_r = a\Delta \pi_{rr} + b\Delta\, \varkappa_r + c(-\Delta M_m) \qquad (6)$$

To check equations (5) and (6) all the most representative reaction seires of electrophilic substitution in polycyclic arenes for as complete set of aromatic positions as possible are used (see notes k ÷ r for Table 2). From the correlations only positions burgened with strong steric hindrances (4-phenanthryl, I-triphenylyl) and also substrates fluorene, biphenylene, and fluoranthene are excluded. For fluorene calculation of quantum-chemical indices in π-electron approximation is hindered. Data on the reactivity of biphenylene, as known [11,12], do not keep within the common correlations (within the framework of the dynamic model), probably, due to considerable structural hindrance of the substrate. Fluoranthene is excluded from the correlations as belonging to non-alternant hydrocarbons for which, strictly speaking, simple relationships of the (5) and (6) type do not work.

Two S_N1 solvolytic series are included into the correlations. The reason is that removal of an anion in the limiting step of these reactions and development of a positive charge on the extracyclic carbon atom models exactly the situation of an electrophilic attack.

Table 1 lists quantum-chemical indices π_{rr}, k_r, and $\varkappa_r$ calculated in the bound version of the perturbation theory in the π-electron approximation of the LCAO MO SCF method. The parameters and correlation indices are presented in Table 2. It should be emphasized that this work uses the same parameters of π-electron hamiltonian as in the previous calculations of UV and NMR spectra, diamagnetic susceptibility, electric polarizabilities, and splitting constants in zero field of alternant hydrocarbons (see Ref. 14). A good agreement between calculated and experimental physico-chemical characteristics is a ground to believe that AR indices calculated in the same approximation will reflect correctly the chemical behavior of molecules studied.

The following points are important to consider the suggested model to be adequate:

1. New indices k_r or $\varkappa_r$ describe AR even better than traditional π_{rr} (cf. the values of r_{mq} and r_{nq} in Table 2). Only in detritiation and bromination series $r_{mq} \approx r_{nq}$.

2. Combined usage of indices π_{rr} and $k_r(\varkappa_r)$ is more effective than to use each of them separately[8].

3. Almost in all cases consideration of the term with I_s improves the correlation. Thus, the ratio of remainder variances for the correlations by two-parameter (without I_s) and three-parameter equations $F_{23} = S^2_{(2)}/S^2_{(3)}$ exceeds, as a rule, unity (Table 2). Though comparatively low values of F_{23} satisfy low reliability of the conclusion, it should be noted that in the correlations by (5) and (6), unlike the correlations by (3) and (4), points for benzene fall just to the regression hypersurface (see the column of free terms). The same refers to some other positions (pyrenyl-2, biphenylil-4, naphthyl-2).

On the whole, application of equations (5) and (6) for the AR correlation should be recognized as successful. Considerable mutual interdependence of indices (see columns r_{mn}, r_{mp}, and r_{np}) and small sample sizes with a great

Table 1

Quantum-Chemical Indices of Polycyclic Arenes

Position number	Substrate	r	$\overline{\pi}_{rr}$, eV^{-1}	k_r Å.eV^{-1}	$\varkappa_r$, Å.eV^{-1}	M_m^5
1.	Benzene		0.1201	0.1315	0.1315	1.000
2.	Bephenyl	3	0.1198	0.1286	0.1141	0.704
3.	Bephenyl	4	0.1223	0.1724	0.1724	
4.	Naphthalene	1	0.1283	0.1520	0.1518	0.618
5.	-"-	2	0.1207	0.1522	0.1417	
6.	Anthracene	1	0.1297	0.1600	0.1590	0.414
7.	-"-	2	0.1213	0.1702	0.1489	
8.	-"-	9	0.1433	0.1972	0.1972	
9.	Phenanthrene	1	0.1281	0.1470	0.1461	0.605
10.	-"-	2	0.1208	0.1536	0.1510	
11.	-"-	3	0.1218	0.1633	0.1542	
12.	-"-	9	0.1265	0.1782	0.1569	
13.	Pyrene	1	0.1324	0.2118	0.1899	0.445
14.	-"-	2	0.1198	0.1327	0.1327	
15.	-"-	4	0.1269	0.1771	0.1543	
16.	Perylene	3	0.1330	0.2391	0.2391	0.340
17.	Triphenylene	2	0.1216	0.1610	0.1593	0.67
18.	Chrysene	6	0.1287	0.1928	0.1754	0.52
19.	Fluoranthene*	1	0.1274	0.1598	0.1285	0.618
20.	-"-	2	0.1203	0.1425	0.1346	
21.	-"-	3	0.1314	0.1822	0.1822	
22.	-"-	7	0.1255	0.1132	0.1083	
23.	-"-	8	0.1218	0.1567	0.1561	

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* For bond length in the five-membered cycle 1.486 Å (β = -1.946 eV)

number of coefficients determined are unfavorable factors. This results in a high value of a standard error when estimating coefficients a,b, and c (see the corresponding columns in Table 2). By the same reason further estimates of the significance of the conclusions belong to the higher confidence level (20% unless otherwise noted).

It should be noted that theoretically predicted difference in the behavior of ion and molecular reagents is realized: reactions involving the former are described better by Eq. (6) and those with the latter by Eq. (5). This conclusion is significant for sulfonation and bromination series; in detritiation, solvolysis, and nitration series both equations give close results, but in no case significant differences in the opposite direction are present. Hardly could this occur by chance. Therefore further analysis for detritiation, solvolysis, and sulfonation series will be carried out on the basis of Eq. (6), and that for nitration and halogenation on the basis of (5).

With this application of Eqs. (5) and (6) to the reaction series all the correlations chosen are good. According to Table 3 they are even much better than the correlations within the framework of the localization approach with the use of indices L_r^{ω} [5].

Significant (on the level of 0.95) deviations of points from the regression hypersurface occur very seldom: position 3 of biphenyl in the detritiation series and position 2 of triphenylene in the nitration series[*].

Correlation equations (5) and (6) with the coefficients listed in Table 2 have failed to describe the reactivity of fluoranthene. In quantum-chemical calculations for these substrates variation of the geometry (interfragmentary bond length in the five-membered cycle) was from 1.400 to 1.537 Å. However, also this measure does not allow to decrease dis-

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[*] The same points get out of the correlation for sulfonation and chlorination, respectively, but with the confidence level of 0.90.

Table 2

Correlation of the Partial Rate Factor Logarithm for Electrophilic Substitution Reactions by Eqns. (5) and (6)

Reaction Series	Aromatic position[a]	N[b]	Equation	R[f]	S[h]	
Protodetritiation[k]	1-18	18	(5)	0.978	0.43	1
			(6)	0.979	0.43	2
Acetolysis of Arylmethyltosylates[l]	1,4,5,7,10-12,14,15	9	(5)	0.942	0.31	3
			(6)	0.948	0.30	4
Acetolysis of Arylmercuriperchlorates[m]	1,4-6,10-12	7	(5)	0.976	0.40	5
			(6)	0.975	0.41	6
Nitration $AcONO_2$[n]	1,3-5,9-13, 16-18	12	(5)	0.968	0.38	7
			(6)	0.968	0.38	8
Sulfonation 0.9 mol/kg H_2SO_4 in $PhNO_2$[o]	1-5,8-13	11	(5)	0.948	0.85	9
			(6)	0.975	0.60	10
Sulfonation 2,0 mol/kg H_2SO_4 in $PhNO_2$[p]	1-5,9-12	9	(5)	0.859	0.94	11
			(6)	0.940	0.62	12
Sulfonation 5.5 mol/kg H_2SO_4 in $PhNO_2$[p]	1-5,9-12	9	(5)	0.895	0.74	13
			(6)	0.957	0.48	14
Sulfonation 8,0 mol/kg H_2SO_4 in $PhNO_2$[p]	1-5,9-12	9	(5)	0.905	0.61	15
			(6)	0.961	0.40	16
Molecular bromination[q]	1,3-5,8,12, 13,18	8	(5)	0.997	0.40	17
			(6)	0.989	0.80	18
Molecular chlorination[r]	1-4,9,11-13, 17	9	(5)	0.957	0.95	19
			(6)	0.947	1.05	20

Table 2 (continued)

	a[c]	b[c]	c[c]	d[d]
1.	156 ± 24	23.3 ± 5.5	2.99 ± 0.87	0.06
2.	145 ± 25	24.0 ± 5.6	3.45 ± 0.83	0.06
3.	63.1±41.1	23.0 ± 9.1	1.44 ± 0.74	0.09
4.	42.7±43.1	45.3 ±16.4	1.65 ± 0.66	-0.06
5	170 ± 51	10.4 ±16.3	3,45 ± 1.46	-0.11
6	161 ± 58	18.9 ±40.8	3.26 ± 2.03	-0.09
7	74.2±39.7	7.34 ±7.12	4.82 ± 1.33	-0.05
8	78.3±39.0	6.03 ±6.72	5.06 ± 1.26	0.03
9	77.2±58.0	49.2 ±17.3	3.33 ± 2.86	-0.36
10	15.3±45.7	65.1 ±13.4	4.46 ± 1.85	-0.44
11	84.0±108	48.6 ±23.9	3.24 ± 3.20	-0.33
12	39.9±73.6	59.8 ±15.1	4.12 ± 1.97	-0.33
13	118 ± 85	44.0 ±18.8	2.38 ± 2.51	-0.26
14	81.2±56.9	51.6 ±11.7	3.27 ± 1.52	-0.27
15	140 ± 70	39.5 ±15.6	1.00 ± 2.09	-0.21
16	110 ± 47	45.1 ± 9.6	1.80 ± 1.26	-0.21
17	264 ± 31	48.7 ±10.9	5.76 ± 1.76	-0.15
18	233 ± 73	37.3 ± 26.6	9.04 ± 2.95	-0.37
19	231 ±117	48.4 ±19.8	3.30 ± 3.71	0.05
20	231 ±131	45.2 ±22.8	5.22 ± 3.83	-0.16

Table 2 (continued)

	r_{mn} e)	r_{mp} e)	r_{mq} e)	r_{np} e)	r_{nq} e)	r_{pq} e)	F h)	F_{23} i)
1	0.694	0.551	0.899	0.616	0.866	0.751	105	1.73
2	0.729	0.551	0.899	0.558	0.868	0.751	106	2.10
3	0.581	0.194	0.665	0.503	0.875	0.666	13.1	1.46
4	0.678	0.194	0.665	0.406	0.873	0.666	14,7	1.87
5	0.468	0.611	0.872	0.704	0.693	0.874	20.1	2.15
6	0.697	0.611	0.872	0.882	0.882	0.874	18.9	1.39
7	0.766	0.747	0.848	0.818	0.867	0.938	30.8	2.36
8	0.724	0.747	0.848	0.768	0.819	0.938	39.2	2.69
9	0.720	0.703	0.811	0.751	0.911	0.822	20.9	1.04
10	0.787	0.703	0.811	0.695	0.947	0.822	44.7	1.60
11	0.365	0.442	0.532	0.531	0.784	0.673	4,7	1.00
12	0.404	0.442	0.532	0.389	0.862	0.673	12.7	1.56
13	0.365	0.442	0.622	0.531	0.799	0.672	6.7	0.98
14	0.404	0.442	0.622	0.389	0.865	0.672	17.9	1.60
15	0.365	0.442	0.689	0.531	0.792	0.608	7.5	0.87
16	0.404	0.442	0.689	0.389	0.869	0.608	20.2	1.17
17	0.714	0.765	0.928	0.854	0.903	0.919	236	2.95
18	0.824	0.765	0.928	0.810	0.907	0.919	58.2	2.69
19	0.670	0.732	0.856	0.718	0.880	0.823	18.1	0.97
20	0.629	0.732	0.856	0.611	0.814	0.823	14.4	1.14

Notes to Table 2

a) Numbers refer to positions as listed in Table 1.
b) Volume of the sample. c) Standard errors of the coefficient estimates are given. d) Intercept. e) Pair correlation coefficients. Indices m,n,p, and q denote $\Delta\overline{\pi}_{rr}$, $\Delta k_r (\Delta\varkappa_r)$, $-\Delta(m_m)$ and lgf, respectively. f) Experimental correlation coefficient. g) Standard error. h) Fisher criterion concerned with the regression ($F = S^2_{regr.}/S^2_{rem.}$). i) ratio of remainder variances in the correlations by (3) or (4) and by (5) or (6). k). The data summarized in Refs. 11 and 15. System CF_3COOH(98.04%) - CCl_4(1.96%), 70°C. lgf's for triphenylene-2 are recalculated[16] from the other system and for anthracene from the deuterodeprotonation series[11]. Data on detritiation of 3- and 4-H^3-biphenyl are abstracted from Ref. 17, the lgf_3 (-0.22) value being calculated for the standard system, using the corresponding value for the $HClO_4-H_2O-CF_3COOH$ system (25°C) and the lgf_4 values for both systems. Recalculation is based on the assumption that the lgf_3/lgf_4 value is the same in both systems. l) In AcOH at 40°C[12]. m) In AcOH at 24.9°C[18]. n) In Ac_2O at 0°C[19,20]. o) Data from Ref. 1 added with the lgf values for anthracene-9 and pyrene-1 (6.68 and 6.39, respectively, O. Kachurin and L. Velichko, to be published). p) Ref. 1. q) 50% AcOH at 25°C. Relative rates for other substrates, except benzene, biphenyl, and naphthalene, are extrapolated from other media[21]. r) In AcOH at 25°C. Data on the rates and product compositions of chlorination of benzene, biphenyl, naphthalene, and phenanthrene are abstracted from Refs. 22-24. The lgf values for pyrene-1 and triphenylene-2 are given according to Ref. 25.

Table 3

Indices of the Correlations $\lg f = a\Delta L_r^{\omega} + b$ for Some Reaction Series

Reaction Series[a)]	a	b	r	S	F[b)]
Detritiation	8.60	0.56	0.960	0.56	1.70
Acetolysis of tosylates	6.19	0.36	0.864	0.42	1.96
Sulfonation (0.9 mol/kg of H_2SO_4)	9.22	0.42	0.927	0.88	2.15
Sulfonation (8.0 mol/kg of H_2SO_4)	7.70	0.04	0.880	0.61	2.33
Nitration	5.95	0.84	0.928	0.53	1.95
Chlorination	12.7	0.36	0.918	1.24	1.70

Notes: a) Aromatic positions are the same as in Table 2
b) Ratio of the remainder variance in this correlation to that in (5) or (6).

agreements between the calculated and experimental lg f values simultaneously in positions 1-3 and 7-8. This may be associated with the presence of π-electron charges in non-alternant hydrocarbons since within the framework of the static approach charges also are indices of the reactivity[5-7] and should be taken into account when estimating AR.

Application of multiparameter equations (5) and (6) allows, unlike the localization approach, to take effectively into account also factors not connected with a substrate structure (reagent nature and medium effects). In this connection it is of interest to note that the suggested model describes redistribution of the positional reactivity of polycyclic substrates on sulfonating in various media. For example, for rich and poor in solvent media (0.9 and 8.0 mol/kg of H_2SO_4, respectively) regression equations of the (6) type give two various orders for the relative reactivity of phenanthrene: $9 \gg 3 > 2 > 1$ and $9 \gg 1 > 3 > 2$. Though the first among them differs from the experimental one

($3 > 2 \geqslant 9 \geqslant 1$), but deviations of the calculated lg f values from the experimental ones are much less than when calculating within the localization approach. Disagreements between the experiment and calculation by (6) are the greatest here for position 9 and are caused evidently, by specific solvation effects[4] not taken into account by the suggested model.

Thus the developed approach describes on the whole reliably electrophilic substitution reactions in the series of alternant polycyclic arenes allowing to take into consideration the dependence of AR on the reagent nature and reaction medium.

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Quantum-chemical calculations were carried out using a "Minsk-22" computer by the program used in Ref. 8.

For all alternat hydrocarbons standard geometry (on the basis of regular haxagonals with a side of 1.400 Å) was assumed. With calculations for fluoranthene the geometry was varied - interfragmentary bond length in a five-membered cycle. The resonance intergral of this bond was calculated on the basis of the known relationship[14]:

$$\beta = -2.354 \exp. \left[-2.291 (R-1.400)\right] , \text{eV}$$

R is a bond length in Å.

Multiple regression analysis was carried out by the known program [26], using ES 1022 computer. The exclusion of significantly deviated points was not carried out.

Appendix

Let us consider the interaction of two reacting molecules which are so separated that a chemical bond formation between them could be neglected (corresponding overlap integrals and, hence, resonance integrals equal zero). Then the bond-matrix residual charge orders (Y) and also the Fock operator matrix have block structure relevant to substrate and reagent (e.g., $Y = \begin{vmatrix} Y_A & 0 \\ 0 & Y_B \end{vmatrix}$ and Hartree-Fock matrix equations are separated into two related equations for the corresponding blocks. For example, for block A:

$$[H_A + G_A(Y_A) + G_A(Y_B), Y_A]_- = 0; (Y_A)^2 = 1 \qquad (1)$$

Here $[\,,\,]_-$ denotes anticommutator, H_A is a matrix of one electron integrals of A molecular skeleton, Γ_{ps} are integrals of an interelectron interaction

$$[G_A(Y_A)]_{pq} = \Gamma_{pq}(Y_A)_{pq} - 2\delta_{pq} \sum_{s \in \{A\}} \Gamma_{ps}(Y_A)_{ss} \qquad (2)$$

$$[G_A(Y_B)]_{pq} = -2\delta_{pq} \sum_{s \in \{B\}} \Gamma_{ps}(Y_B)_{ss} \qquad (3)$$

As one can see from Eq. (1) changes in the electron distribution of an isolated A substrate under the action of reagent B are determined by the presence of matrix $G_A(Y_B)$ in (I). This matrix may be considered as a small perturbation, if A and B molecules are well spaced. Then in zero order of the perturbation theory (I) reduces to a standard Hartry-Fock equation for an isolated molecule. To find changes in the electron distribution of a substrate under the action of a reagent in the first order of the theory one should solve the following matrix equation

$$N_A Y_A^1 + Y_A^1 N_A - G_A(Y_A^1) + Y_A^\circ G_A(Y_A') Y_A^\circ = G_A(Y_B^\circ) - Y_A G_A(Y_B^\circ) Y_A \qquad (4)$$

where $N_A = [H_A + G_A(Y_A^\circ)]\, Y_A^\circ$

By virtue of linearity of Eq. (4) elements of the Y_A' matrix may be expressed via mutual atom-atom polarizabilities π_{ik} and atom-bond polarizabilities $\pi_{i,pq}$ of an isolated A molecule.

Thus, in order to find changes in the substrate energy under the action of a reagent in the first and second orders of the perturbation theory it is enough to know self- and mutual polarizabilities, charge distribution of isolated A and B molecules and their mutual arrangement. Thus, approximating in great distances $\Gamma_{ik} = 1/2R_{ik}$ one obtains for energy corrections.

$$\Delta E_A^1 = -\sum_{\substack{k\in\{A\}\\ s\in\{B\}}} \frac{q_k^A q_s^B}{R_{ks}} \tag{5}$$

$$\Delta E_A^2 = \frac{1}{2}\sum_{i,k\in\{A\}} \pi_{ik}^A \sum_{s,l\in\{B\}} \frac{q_s^B q_l^B}{R_{is} R_{kl}} \tag{6}$$

It should be noted, however, that when constructing AR models (with index approach) one usually disengages oneself from reagent nature and reaction coordinate which involves the usage of the corresponding approximations in (5) and (6). For example, restricting summation in formulae (5) and (6) to a maximum term corresponding to a substrate atom attacked by a reagent (r) and introducing the denotation

$$\Delta\alpha_B = -\sum_{s\in\{B\}} \frac{q_s^B}{R_r} \quad ^{*)}$$

one obtains standard expression of the static AR model:

$$E = q_r^A \Delta\alpha_B + \frac{1}{2}\pi_{rr}^A (\Delta\alpha_B)^2 + \dots \tag{7}$$

Other approximations are also possible. Thus, taking into account that

$$\sum_{i\in\{A\}} \tilde{\pi}_{ik} \sum_{s\in\{B\}} q_s^B / R_{is} = (Y_A^1) = \Delta q_k^A$$

is nome other than charge changes in molecule A under the action of reagent B, i.e. formulae (5) and (6) determine

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[*] From this definition one can see that $\Delta\alpha_B$ is just a potential generated by a reagent at the location of an attacked atom.

energy of an electrostatic interaction of substrate-reagent, one may carry out multipolar expansion in these formulae. Since in alternant hydrocarbons all $q_K^A \equiv 0$ one may confine oneself to the interaction of induced substrate dipole - reagent charge (or dipole). Then reagent induced substrate dipole will play the role of a reactivity index:

$$\vec{d}_A = \sum_{k\in\{A\}} \Delta q_k^A \vec{R}_k^A = \sum_{i,k\in\{A\}} \pi_{ik}^A R_k^A \sum_{s\in\{B\}} q_s^B / R_{si} \qquad (8)$$

Restricting the summation in the last expression also by the attacked center nearest to the reagent, one obtains more evident (abstracted from the reagent) dependence of $\vec{d}_A$ (and, hence of the interaction energy) on the character of a position and substrate type in the form of the approximate equality:

$$\vec{d}_A \approx \Big(\sum_{i\in\{A\}} \pi_{ri}^A R_i^A\Big)\Delta\alpha_B \equiv \vec{K}_r \Delta\alpha_B \qquad (9)$$

Difference of this approach from the traditional static model is in that the latter assumes that an approaching reagent induces a charge on the attacked atom and interacts with it, whereas this approach considers the interaction of an induced dipole on the substrate with a reagent charge (dipole). Thus, the dipole moment, $\vec{K}_r$, induced by the reference reagent ($\Delta\alpha_B = 1$) should be an AR index along with π_{rr}.

Since when deriving formulae (7) and (9) different approximations were used the linear combination of $\vec{K}_r$, with π_{rr} will evidently describe AR more completely than each of these indices separately. Another interpretation of the successful combined usage of the K_r and π_{rr} indices is also possible: consideration of changes in the resonance integrals of a carbon atom attacked by a reagent within the framework of the static approach leads to that free valences appear as AR indices, the valences, as noted, being closely correlated with π_{rr}.

With radical substitution, when a reagent offers neither a charge nor a significant dipole good correlations of AR with π_{rr} only are observed.

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ON KINETICS OF THE INTERACTION OF CERTAIN 2- AND 6- CHLOROPYRIMIDINES WITH SODIUM ALCOHOLATES

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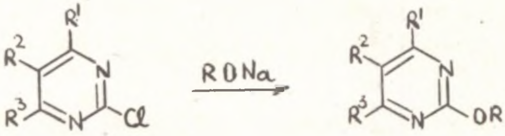
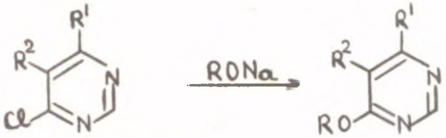
Rate constans for nucleophilic substitution of chlorine in a series of alkyl-substituted 2-and 6-chloropyrimidines with sodium ethylate and isopropilate at 20-60°C were determined, and activation energies calculated. It was found that alkyl-substituents diminish reactivity of 2-and 6-chloropyrimidines in reactions with alcoholates. These substituents manifest the greatest deactivating influence when being in the 5-th position of the pyrimidine ring.

In our previous investigations on a synthesis of biologically active compounds we have often used alkyl-substituted 2-and 6-chlorpyrimidines as starting materials[1-3]. In order to elucidate their comparative reactivity when interacting with nukleophilic reagents we have studied kinetics of the following reactions:



I-IV



V-VIII

$R = C_2H_5,\ (CH_3)_2CH$

We found only a very limited data on kinetics of interaction between chloropyrimidines and alcoholates in the previously published works. First work in which kinetics of this kind was described (for the reaction of 2-chloropyrimidine with sodium ethylate) was published in 1956 [4]. In more recent works rate constants for reactions of certain derivatives of 2-chloropyrimidine [5] and 6-chloropyrimidine [6] with sodium methylate in absolute methanol were determined.

Experimental

2-Chloropyrimidines (I-IV) were obtained by reduction of the corresponding 2,6-dichloropyrimidines with zinc dust[7-9].Compounds V-VIII were synthesized from 2-thiouracils.A mercapto group was eliminated by the action of Raney nickel [10]and a hydroxy-group was reduced by chlorine with the use of phosphorus oxychloride[7]. Structure and purity of the synthesized substances were proved by the elemental analysis and PMR spektrum data, obtained by the spectrometer B 4870 "Tesla"at the freguency of 80 MHz. For all substances mentioned above quantum-mechanical calculations were carried out using a method CNDO/2, as previously described [11]in the Institute of Physics of the Lithuanian Academy of Science.The electronic densities on atoms,bond orders, dipole moments, energy levels, and the total energy were calculated.

Kinetic Measurements

Solutions of chloropyrimidines and alcoholates were thermostated within 20 minutes and mixed. At appropriate intervals of time the concentration of chlorine ions in the reaction mixture was measured by mercurimetric titration. Measurements were carried out up to 25-60% of the reaction conversion at several temperatures in the range from 20 to 60°C. Rate constants were calculated using a second order kinetic equation.

For each chloropyrimidine 5 experiments at 3-4 various temperatures were carried out. The reaction rate constant was determined as an arithmetic mean of all the experimental constants at the given temperature.

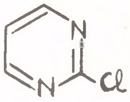
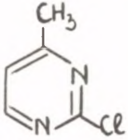
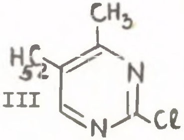
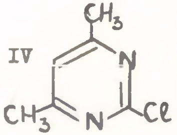
Results and Discussion

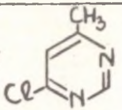
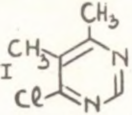
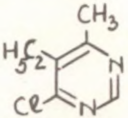
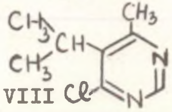
The results of kinetic investigations and certain data of quantum-chemical calculations are presented in the Table.

Alkyl-substituents in any position of the pyrimidine ring diminish the rate of the nucleophilic substitution of chlorine. The greatest diminishing effect is produced by alkyl-groups in the 5-th position. These effects are caused by electronic or solvation factors rather than by a steric hindrance (see, for example, compounds II, III and VII, VIII in the Table). No proper correlation exists between the reactivity of chloropyrimidines I-VIII and the charge distribution in their molecules, calculated using a CNDO/2 method.

It has been shown in Ref.5 that substituent effects on the reactivity of 2-chloropyrimidines are identical to those in the reactions involving sodium methylate and piperidine.It makes a ground to use our kinetic data for the evaluation of comparative activity of substituted chloropyrimidines in the reactions with aliphatic amines

Table

Formula	R = C_2H_5			R = $(CH_3)_2CH$			Electronic charges on atoms c		Dipole moment 𝒟
	Temper. °C	$k.10^4$ a	E_A b	Temper. °C	$k.10^4$	E_A	C_2	C_6	
I 	20	2.60±0.12[e]		20	2.46±0.01				
	30	5.50±0.04	14.4±0.6	30	6.31±0.05	15.0±0.5	0.297	0.144	[d] 4.619
	40	13.0±0.2		40	14.02±0.26				
II 	20	0.77±0.15		20	0.90±0.01				
	30	2.20±0.02	18.2±0.4	30	2.76±0.05	15.5±0,6	0.303	0.150	4.998
	40	7.40±0.29		40	5,01±0.04				
III 	20	0.072±0.003		30	0.29±0,00				
	40	0.58±0.01	18.7±1.3	40	0,74±0.00	15.6±0.7	0,292	0.128	5.241
	50	1.42±0.05		50	1.53±0.00				
	60	3.14±0.04		60	3.37±0.08				
IV 	30	0.56±0,01		30	0.73±0.01				
	40	1.32±0.05	18.9±0,9	40	1,65±0.04	16.0±0.8	0.308	0.192	5.352
	50	3.40±0.03		50	3.46±0.02				
	60	7.02±0.12		60	7.75±0.06				

Formula	R = C_2H_5			R =$(CH_3)CH$			Electronic charges on atoms		Dipole moment
	Temper. °C	k.10^4	E_A	Temper. °C	k.10^4	E_A	C_2	C_6	D
V 	20	4.70±0.14		20	2.86±0.05				
	30	12.0±0.07	13,9±	30	5.31±0.11	13.7±	0.243	0.311	3.966
	40	24.0±0.35	0.5	40	12.81±0.13	0.5			
VI 	30	1,80±0.01		30	1,16±0.02				
	40	4.40±0,02	16,7±	40	2,93±0.01	17.1±	0.196	0.233	2,977
	50	9,80±0.06	0,6	50	6,77±0.30	0.6			
VII 	30	0,88±0.02		30	0,74±0.00				
	40	1.90±0.02	17.4±	40	1.66±0,01	17.2±	0.198	0,230	2.621
	50	4,50±0.11	0.7	50	3.22±0.02	0,6			
VIII 	30	0,91±0.01		30	0,45±0.00				
	40	2.02±0,03	16.0±	40	1,00±0.01	15,0±	0.195	0.227	2.584
	50	4.48±0.01	0.8	50	2,01±0,03	0.8			
	60	9.22±0.18		60	3.97±0,01				

a Second order rate constants l/mol.sec)

b Activation energy (kcal/mol)

c Electronic charges on atoms and dipole moments, colculated using a CNDO/2 method

d Experimental value equals 3.58 D (in benzene, at 25°)[12]

e Standard deviations are reported.

which are widely used for synthesis of potential biologically active compounds.

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Study of Solvent Dependence of ρ^{o}.
1. Statistical Data Handling

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In order to check how the relationship $\rho^{o}_{js} - \rho^{o}_{jo}$ = const (j and s are indices of a reaction series and medium, respectively) works with different media we have treated the data available on 14 reaction series with a varied substituent: pKa of benzoic acids, phenols, anilinium ions, dimethylanilinium ions, thiophenols, pyridinium ions, conjugated acids of pyridine-N-oxides; lgk values for alkaline hydrolysis of ethyl benzoates, phenyl acetates, phenyl tosylates, phenyldimethylthiophosphinates and for solvolysis of benzyl chlorides and cumyl chlorides. The following solvents, besides water, were embraced: methanol, ethanol, 1-and 2-propanol, butanol, methyl-2-propanol, acetonitrile, nitromethane, DMF, DMSO, acetone and binary mixtures of water with methanol, ethanol, dioxane, DMSO, acetone and concentrated aqueous solutions of tetrabutylammonium bromide, and sodium perchlorate The total number of the series studied is 190.

When studying salt effects in the case of electroneutral substituents [1-13] we have found that the difference $\rho_{js}-\rho_{jo}$ remains constant.

$$\rho_{js} - \rho_{jo} = \mathrm{const} \qquad (1)$$

Indices j and s denote a reaction series and medium, respectively. As a standard medium water was chosen.

That means that in passing from water to a certain salt solution changes of ρ are independent of a reaction series studied.

In this connection a problem appears whether Eq. (1) can be applied for a wider set of solvents. With this purpose we have treated the data on different solvents, embracing 14 reaction series with a varied substituent (in all 190 series). The list of these reactions and solvents is given above.

The present work describes the tehnique of data treatment and gives the reaction series constants calculated (see the Table).

Statistic data handling was carried out on a "Nairi-2" computer, using the program of multiregression analysis with automatic choice of significant argument scales and exclusion (according to Student) of significantly deviating points (on the confidence level of 0.95).

The data were treated according to the following equations:

$$\lg k^X - \lg k_0 = \Delta \lg k^X = \rho\sigma^0 \qquad (2)$$

$$\Delta \lg k^X = \rho\sigma^0 + \rho_R^+\sigma_R^+ \qquad (3)$$

$$\Delta \lg k^X = \rho\sigma^0 + \rho_R^-\sigma_R^- \qquad (4)$$

$$\Delta \lg k^X = \rho\sigma^0 + \rho_R^-\sigma_R^- + \rho_R^+\sigma_R^+ \qquad (5)$$

Superscript X denotes substituent(s) in metha/para position of benzene ring.

The experimental value of lgk for unsubstituted derivative ($X=C_6H_5$) was used as a $\lg k_0$ value.

When calculating, the "recommended" values of σ^0 and also σ_R^+ and σ_R^- from the Tables[15] were used.

In carrying out this work the issues of the Tables[16,24,42,45,50] were used as a main source of the initial data. Besides, the data for some reaction series not embraced by this edition were also enlisted.

If some constants are essentially the same for the same compound, the corresponding arithmetic means were used. If disagreements between the data of different authors were more significant, the calculations used the series, each involving the data of the same author. If the agreement between the ρ°'s for the same reaction series estimated in terms of the data of different authors is bad, all the parallel values are listed in the Table. For example, for acidic dissociation of anilinium ions in ethanol, the Table presents the results of data treating of four parallel series.

Figs. 1-3 illustrate the plots of ρ° values for various processes vs. molar per cent (M%) of a solvent for methanol--water, ethanol-water, and DMSO-water systems. One can see that with binary mixtures the plot is roughly monotonous. For methanol-water and ethanol-water systems the plot of ρ° vs. M% of alcohol passes through the maximum. In DMSO--water system the plot may be looked upon as linear over the whole range beginning with pure water and ending with pure DMSO. For anilinium ions the analogous plot is curved.

The results of data handling on 190 reaction series are listed in the Table. Abbreviations from Ref. 16 are used to denote solvents.

In column n/n_0 the denominator reflects the total number of data subject to the regression treatment and the numerator equals a number of points remained after excluding significantly deviating points. Columns "s" and "r" present the total standard error and correlation coefficient, respectively. In column "Equation" the equation by which the data were treated is entered. Letter "A" added to the number of an equation (e.g., 2A) means that calculations were done by the equation whose left-hand side equals $\lg k^X$ and to the right-hand side the intercept ($\lg k_0$) is added.

Table

	Medium (M%)	ρ°	ρ_R^-	ρ_R^+	n/n_o	s	r	Eqn.	Source of data	Notes
1	2	3	4	5	6	7	8	9	10	11
	Acidic dissociation of m- and p- substituted benzoic acids 25°C									
1.	H_2O	-0.944±0.017	0	0	18/20	0.048	0.994	3	16	
2.	H_2O-MeOH(30.9)	-1.36 ±0.12	0	-	3/3	0.13	0.884	2	16	
3.	H_2O-MeOH(47,6)	-1.28 ±0.03	0	0	5/5	0.032	0.997	3	16	
4.	H_2O-MeOH(51.0)	-1.53 ±0.16	0	0	4/4	0.19	0.916	3	16	
5.	H_2O-MeOH(57,3)	-1.34 ±0.02	0	-0.12±0.03	6/6	0.25	0.998	3	16	
6.	H_2O-MeOH(64.1)	-1.55 ±0.16	0	0	4/4	0.19	0.920	3	16	
7.	H_2O-MeOH(80.1)	-1.49 ±0.19	0	0	4/4	0.22	0.885	3	16	
8.	MeOH	-1.39 ±0.05	0	-0.27±0.05	14/4	0.076	0.988	3	16	
9.	H_2O-EtOH(16.3)	-1.34 ±0.03	0	-0.15±0.05	11/12	0.041	0.995	3	16	
10.	H_2O-EtOH(17.1)	-1.57 ±0.06	0	-0.15±0.05	6/7	0.058	0.996	3	16	
11.	H_2O-EtOH(23.6)	-1.49 ±0.02	0	-0.13±0.02	20/23	0.039	0.997	3	16	
12.	H_2O-EtOH(27.3)	-1.39 ±0.08	0	-0.23±0.07	6/6	0.092	0.991	3	16	
13.	H_2O-EtOH(29.8)	-1.40 ±0.05	0	-	12/12	0.072	0.987	2	16	
14.	H_2O-EtOH(41.9)	-1.73 ±0.12	0	-0.33±0.11	8/8	0.14	0.985	3	16	
15.	H_2O-EtOH(48.1)	-1.52 ±0.04	0	-0.21±0.07	8/8	0.055	0.994	3	16	
16.	H_2O-EtOH(51.9)	-1.57 ±0.03	0	-0.21±0.04	8/8	0.036	0.998	3	16	

Table (continued)

1	2	3	4	5	6	7	8	9	10	11
17.	H_2O-EtOH(55.3)	-1.78±0.11	0	0	6/6	0.128	0.982	3	16	
18.	H_2O-EtOH(69.6)	-1.64±0.05	0	0	12/12	0.069	0.990	3	16	
19.	H_2O-EtOH(73.6)	-1.83±0.26	0	0	7/7	0.319	0.933	3	16	
20.	H_2O-EtOH(85.5)	-1.80±0.19	0	-	4/5	0.11	0.986	2	16	
21.	EtOH	-1.60±0.06	0	-0.26±0.10	14/14	0.086	0.984	3	16	
22.	PrOH	-1.62±0.04	0	-0.29±0.04	13/15	0.047	0.995	3	16	
23.	i-PrOH	-1.80±0.06	0	-	4/5	0.11	0.986	2	16	
24.	t-BuOH	-3.36±0.17	0	0	5/5	0.30	0.953	3	17	
		-3.88±0.16	0	-1.74±0.65	4/4	0.149	0.975	3	17	Without 3,5-$(NO_2)_2$ derivative
25.	$HOCH_2CH_2OH$	-1.34±0.03	0	-0.24±0.03	13/15	0.034	0.996	2	16	
26.	CH_3NO_2	-2.50±0.09	0	0	4/4	0.100	0.981	3	18	
		-1.78±0.19	0	-0.62±0.12	13/13	0.230	0.971	3	19	
27.	CH_3CN	-2.49±0.11	0	0	7/7	0.270	0.940	3	16	
28.	$HCN(CH_3)_2$	-2.32±0.09	0	0	7/7	0.200	0.968	3	16	
29.	H_2O-DMSO(5.88)	-1.15±0.04	0	-	3/3	0.071	0.988	2	20	
30.	H_2O-DMSO(9.7)	-1.20±0.04	0	0	5/5	0.067	0.994	3	20	
31.	H_2O-DMSO(12.0)	-1.31±0.03	0	-0.17±0.03	4/7	0.024	0.999	3	16	
32.	H_2O-DMSO(14.0)	-1.33±0.07	0	0	4/5	0.082	0.988	3	20	
33.	H_2O-DMSO(19.5)	-1.42±0.08	0	0	4/5	0.091	0.986	3	20	

Table (continued)

1	2	3	4	5	6	7	8	9	10	11
34.	H_2O-DMSO(20.2)	-1.31±0.03	0	-0.17±0.03	4/7	0.024	0.999	3	16	
35.	H_2O-DMSO(26.7)	-1.54±0.06	0	0	6/6	0.100	0.990	3	20	
36.	H_2O-DMSO(32.0)	-1.41±0.04	0	-0.36±0.04	6/7	0.035	0.998	3	16	
37.	H_2O-DMSO(35.5)	-1.65±0.05	0	0	5/6	0.093	0.994	3	20	
38.	H_2O-DMSO(48.6)	-1.88±0.05	0	0	6/6	0.096	0.995	3	20	
39.	H_2O-DMSO(59.0)	-1.82±0.05	0	0	6/6	0.055	0.996	3	16	
40.	H_2O-DMSO(59.4)	-2.00±0.07	0	0	6/6	0.13	0.992	3	20	
41.	H_2O-DMSO(70.0)	-2.10±0.06	0	0	6/6	0.11	0.994	3	20	
42.	H_2O-DMSO(82.8)	-1.97±0.01	0	-0.29±0.01	5/8	0.006	0.999	3	16	Para substituents only
43.	H_2O-DMSO(83.0)	-2.27±0.11	0	0	6/6	0.21	0.981	3	20	
44.	DMSO	-2.62±0.10	0	0	14/14	0.27	0.978	3	16	
45.	H_2O-D(5.03),30°C	-1.02±0.08	0	0	11/14	0.161	0.947	3	21	
46.	H_2O-D(6.87)	-1.20±0.03	0	-0.23±0.04	10/10	0.033	0.997	3	16	
47.	H_2O-D(12.4),30°C	-1.38±0.05	0	-0.18±0.07	11/11	0.090	0.990	3	21	
48.	H_2O-D(12.7)	-1.31±0.03	0	0	14/14	0.062	0.988	3	16	
49.	H_2O-D(13.6)	-1.33±0.02	0	-0.16±0.04	13/13	0.033	0.996	3	16	
50.	H_2O-D(20.0)	-1.39±0.04	0	0	14/14	0.081	0.984	3	16	
51.	H_2O-D(24.1),30°C	-1.31±0.07	0	-0.24±0.10	11/11	0.130	0.979	3	21	
52.	H_2O-D(33.9)	-1.49±0.03	0	0	14/14	0.071	0.988	3	16	
53.	H_2O-D(36.2)	-1.46±0.02	0	-0.19±0.03	11/12	0.025	0.999	3	16	

Table (continued)

1	2	3	4	5	6	7	8	9	10	11
54.	H_2O-D(45.9),30°C	-1.47±0.12	0	-0.40±0.13	11/11	0.161	0.963	3	21	
55.	H_2O-D(50.0)	-1.53±0.04	0	0	12/12	0.081	0.987	3	16	
56.	H_2O-An(2.66)	-1.07±0.02	0	-0.28±0.03	12/12	0.024	0.998	3	16	
57.	H_2O-An(7.57)	-1.15±0.02	0	0	12/12	0.033	0.995	3	16	
58.	An	-1.80±0.08	0	-	4/4	0.060	0.996	2	16,35	
59.	H_2O-$(C_4H_9)_4NBr$ (7.75 M)	-2.09±0.08	0	0	14/16	0.105	0.982	3	16,12	

Acidic dissociation of m- and p- substituted phenols, 25°C

Medium (M%)		ρ°	ρ_R^-	ρ_R^+	n/n_o	s	r	Eqn.	Source of data	Notes
1	2	3	4	5	6	7	8	9	10	11
60.	H_2O	-2.36±0.06	-2.08±0.22	0	26/31	0.143	0.991	4	16	
61.	H_2O-MeOH(19.1)	-2.50±0.03	-2.47±0.09	0	4/5	0.027	0.999	4	16	
62.	H_2O-MeOH(27.3)	-2.40±0.07	-2.74±0.13	0	4/4	0.022	0.999	4	16	
63.	H_2O-MeOH(30.9)	-2.43±0.11	- -	0	4/4	0.124	0.970	2	16	
64.	H_2O-MeOH(43.9)	-2.67±0.08	-2.19±0.25	0	3/3	0.074	0.999	4	16	
65.	H_2O-MeOH(62.3)	-2.64±0.13	-2.20±0.37	0	3/3	0.109	0.997	4	16	
66.	H_2O-MeOH(80.1)	-2.62±0.17	-1.89±0.50	0	3/3	0.148	0.994	4	16	
67.	MeOH	-2.80±0.23	-1.87±0.57	0	5/5	0.178	0.989	4	16	
68.	H_2O-EtOH(7.18)	-2.46±0.08	-	0	6/7	0.079	0.994	2	16	

Table (continued)

1	2	3	4	5	6	7	8	9	10	11
69.	H_2O-EtOH(11.7)	-2.60±0.16	-2.04±0.49	0	12/13	0.180	0.979	4	16	
70.	H_2O-EtOH(16.3)	-3.14±0.08	-2.20±0.22	0	9/11	0.076	0.998	4	16	
		-2.54±0.26	-2.69±0.57	0	10/11	0.196	0.981	4A	16	Without unsubstituted derivative
71.	H_2O-EtOH(22.8)	-2.66±0.13	-2.96±0.32	0	14/15	0.127	0.991	4	16	
72.	H_2O-EtOH(23.6)	-2.63±0.11	-2.47±0.31	0	10/10	0.121	0.994	4	16	
73.	H_2O-EtOH(29.8)	-3.22±0.06	-2.14±0.17	0	8/11	0.060	0.999	4	16	
		-2.79±0.28	-2.54±0.64	0	10/11	0.219	0.980	4A	16	Without unsubstituted derivative
74.	H_2O-EtOH(31.7)	-2.99±0.44	-2.64±0.81	0	5/5	0.248	0.984	4A	16	
75.	H_2O-EtOH(69.6)	-2.78±0.13	-2.49±0.37	0	10/11	0.130	0.993	4	16	Without unsubstituted derivative
		-2.94±0.18	-2.37±0.38	0	10/11	0.130	0.992	4A		
76.	H_2O-EtOH(85.5)	-3.17±0.22	-1.42±0.53	0	12/13	0.208	0.976	4	16	
		-2.98±0.20	0	0	13/13	0.143	0.971	4A	16	
77.	EtOH	-2.68±0.16	-2.34±0.47	0	11/11	0.166	0.985	4	16	
78.	i-PrOH	-3.07±0.12	-3.03±0.53	0	6/6	0.218	0.985	4	16	
79.	t-BuOH	-5.20±0.05	-4.79±0.23	0	6/6	0.097	0.999	4	17	

Table (continued)

1	2	3	4	5	6	7	8	9	10	11
80.	CH_3NO_2	-3.76±0.08	(3.76±0.08)	0	3/3	0.041	0.999	2A	18	For 4-NO_2 derivative $\sigma=\sigma^\circ+\sigma_R^-$ was used
81.	CH_3CN	-4.14±0.09	-5.27±0.36	0	8/11	0.173	0.998	4	22	
82.	$HCON(CH_3)_2$	-3.89±0.30	-	0	3/4	0.254	0.890	2	23	
83.	DMSO	-4.03±0.19	-4.61±0.68	0	9/10	0.373	0.989	4	22	
		-2.79±0.42	-2.59±1.00	0	9/10	0.388	0.942	4	16,48	
84.	H_2O-D(1.81)	-2.38±0.30	-	0	8/8	0.281	0.854	2	16	
85.	H_2O-D(5.03)	-2.70±0.40	0	0	7/8	0.543	0.727	4	21	
86.	H_2O-D(12.4)	-2.46±0.34	-3.16±1.10	0	8/8	0.422	0.927	4	21	
87.	H_2O-D(24.1)	-2.70±0.30	-2.54±1.10	0	8/8	0.424	0.948	4	21	
		-2.75±0.22	-3.01±0.56	0	3/3	0.176	0.987	4	16	
88.	H_2O-D(45.9)	-2.71±0.26	-3.66±0.92	0	8/8	0.355	0.961	4	21	
89.	An	-4,77±0.75	-4.77±0.75	0	8/8	0.316	0.986	4	16	
90.	H_2O-Bu_4NBr (7.75M)	-3.27±0.93	(-3,27±0.93	0	3/3	0.083	0.999	2A	12,16	For 4-NO_2 derivative $\sigma=\sigma^\circ+\sigma_R^-$ was used

Table (continued)

Acidic dissociation of m- and p-substituted anilinium ions, 25°C

1	2	3	4	5	6	7	8	9	10	11
91.	H_2O	-2.84±0.04	-2.80±0.11	-0.54±0.10	24/32	0.078	0.997	5	24	
92.	H_2O-MeOH(30.9)	-3.01±0.23	-	-3.30±1.01	3/3	0.180	0.992	3	24	
93.	MeOH	-3.58±0.32	-3.23±0.80	-0.89±0.23	11/11	0.175	0.994	5	24	
		-3.02			9/9	0.343	0.973		25,26	
94.	H_2O-EtOH(11.7)	-3.44	-	-	9/9	0.076	0.989	2	25,24	
95.	H_2O-EtOH(14.4)	-3.04±0.24	-	0	9/9	0.151	0.972	3A	27	
96.	H_2O-EtOH(17.1)	-3.31±0.16	-	0	4/4	0.098	0.992	3	24	
97.	H_2O-EtOH(23.6)	-3.76±0.08	-3.15±0.27	0	5/5	0.104	0.998	5	24,28	
98.	EtOH	-3,54			9/9	0.302	0.985		25,26	
		-3.89±0.06	-	0	9/11	0.031	0.999	3	27	
		-4.82±0.13	-	-1.56±0.35	7/7	0.12	0.997	5	24	
		-1.76±0.22	-1.50±0.83	0	7/8	0.211	0.894	5	29	
99.	CH_3NO_2	-4.01±0.10	-1.40±0.14	-1.55±0.28	11/12	0.120	0.997	5	24,30	
100.	CH_3CN	-4.02±0.15	-1.82±0.34	-1.42±0.12	11/12	0.140	0.997	5	24	
101.	H_2O-DMSO(5.88)	-3.09±0.11	-	0	4/5	0.102	0.985	3	20,31,32	
102.	H_2O-DMSO(9.67)	-3.20±0.26	-	0.67±0.30	6/6	0.239	0.970	3	20,31,32	
103.	H_2O-DMSO(14.0)	-3.37±0.12	-	0	5/5	0.104	0.986	3	20,31,32	
104.	H_2O-DMSO(19.5)	-3.47±0.28	-	0.65±0.32	6/6	0.257	0.969	3	20,31,32	
105.	H_2O-DMSO(2.67)	-3.60±0.44	-	0.69±0.39	6/6	0.307	0.960	3	20,31,32	
106.	H_2O-DMSO(35.0)	-3.72±0.05	-3.27±0.11	-0.68±0.06	7/7	0.034	0.999	5	38	
107.	H_2O-DMSO(35.5)	-3.77±0.25	-	-0.80±0.30	6/6	0.237	0.978	3	20,31,32	
108.	H_2O-DMSO(48.6)	-3.84±0.43	-	0	6/6	0.406	0.939	3	20,31,32	

Table (continued)

1	2	3	4	5	6	7	8	9	10	11
109.	H_2O-DMSO(59.4)	-4.09±0.44	0	0	6/6	0.414	0.940	3	20,31,32	
110.	H_2O-DMSO(70.0)	-4.09±0.30	-	-0.90±0.36	6/6	0.282	0.987	3	20,31,32	
111.	H_2O-DMSO(83.0)	-4.21±0.14	-	0.70±0.17	5/6	0.130	0.994	3	20,31,32	
112.	DMSO	-4.04±0.08	-3.02±0.19	-0.52±0.25	4/4	0.056	0.999	5	24,33,34	
113.	H_2O-D(4.86)	-3.14±0.25	-	0	3/3	0.193	0.981	3	24	
114.	H_2O-D(14.3)	-3.47±0.07	-	-0.60±0.07	4/4	0.057	0.999	3	24	
115.	H_2O-D(32.3)	-3.41±0.08	-	-0.91±0.08	4/4	0.060	0.999	3	24	
116.	H_2O-D(48.2)	-3.24±0.15	-	-1.19±0.15	4/4	0.118	0.997	3	24	
117	An	-2.74±0.17	-3.83±0.35	-1.11±0.10	13/13	0.124	0.997	13	36	
Acidic dissociation of m- and p- substituted thiophenols, 25°C										
118.	H_2O	-1.97±0.10	-	-0.80±0.24	10/10	0.095	0.990	4	24,37	
119.	H_2O-EtOH(22.3)	-2.71±0.09	-	-1.00±0.24	9/9	0.096	0.996	4	24	
120.	H_2O-EtOH(85.5)	-2.78±0.15		-1.40±0.41	8/8	0.108	0.989	4	24	
Acidic dissociation of m-and p-substituted N,N-dimethylanilinium ions, 25°C										
121.	H_2O	-3.35±0.09	-0.45±0.13	-3.64±0.26	9/9	0.101	0.998	5	24	
122.	H_2O-EtOH(23.5), 50°C	-3.64±0.19	-	-	7/7	0.194	0.973	2	24	
123.	H_2O-EtOH(48.1)	-3.62±0.34	-	-	7/7	0.348	0.898	2	24	

Table (continued)

1	2	3	4	5	6	7	8	9	10	11
124.	H_2O-D(14.8)	-4.27±0.13	0	-3.13±0.36	8/8	0.128	0.997	5	24	
125.	DMSO(35.0)	-4.00±0.08	0	-3.79±0.16	5/5	0.059	0.999	5	38	
	Acidic dissociation of 3- substituted pyridinium ions, 25°C									
126.	H_2O	-5.78±0.09	-	-	5/5	0.073	0.999	2	24	
127.	CH_3NO_2	-7.32±0.42	-	-	5/5	0.022	0.995	2	39	
	Acidic dissociation of 3- substituted conjugated acids of pyridine-N-oxides, 25°C									
128.	H_2O	-2.85±0.11	-	-	3/3	0.089	0.996	2	40,41	
129.	CH_3NO_2	-4.51±0.12	-	-	3/3	0.094	0.998	2	39	
	Alkaline hydrolysis of m- and p- substituted ethyl benzoates, 25°C									
130.	H_2O	1.52±0.06	0	0.40±0.05	9/9	0.076	0.994	3	42	
131.	H_2O-EtOH(23.6)	2.17±0.11	0	0.47±0.08	5/5	0.100	0.996	3	42	
132.	H_2O-EtOH(33.0)	2.32±0.05	0	0.47±0.03	4/4	0.041	0.999	3	42	
133.	H_2O-EtOH(55.3)	2.48±0.01	0	0.34±0.01	5/5	0.015	0.999	3	42	
134.	H_2O-EtOH(68.9)	2.45±0.05	0	0.53±0.04	9/9	0.054	0.999	3	42	
135.	H_2O-EtOH(73.8)	2.34±0.04	0	0.30±0.05	17/18	0.088	0.994	3	42	
136.	H_2O-D(8.31)	1.98±0.09	0	0.44±0.07	4/4	0.083	0.997	3	42	
137.	H_2O-D(12.4)	2.05±0.10	0	0.51±0.08	4/4	0.089	0.997	3	42	
138.	H_2O-D(17.4)	2.13±0.13	0	0.55±0.10	4/4	0.119	0.995	3	42	
139.	H_2O-D(24.1)	2.16±0.04	0	0.53±0.04	4/4	0.050	0.999	3	42	

Table (continued)

1	2	3	4	5	6	7	8	9	10	11
140.	H_2O-DMSO(32.0)	2.35±0.06	0	0.33±0.07	4/4	0.052	0.999	3	42	
141.	H_2O-DMSO(59.0)	2.61±0.12	0	0.64±0.05	3/3	0.040	0.998	3	42	
142.	H_2O-DMSO(82.8)	2.99±0.20	0	0.42±0.09	3/3	0.066	0.995	3	42	
143.	H_2O-An(10.3)	1.88±0.12	0	0.49±0.09	3/3	0.095	0.997	3	42	
144.	H_2O-An(15.1)	2.01±0.15	0	0.58±0.25	4/4	0.070	0.988	3	42	
145.	H_2O-An(20.9)	2.34±0.05	0	0.39±0.04	6/6	0.049	0.999	3	42	
146.	H_2O-An(28.3)	2.40±0.05	0	0.41±0.06	17/18	0.086	0.086	3	42	
Alkaline hydrolysis of m- and p- substituted phenyl acetates										
147.	H_2O 15°C	0.94±0.08	0	0	4/4	0.073	0.974	2	43	
148.	H_2O 25°C	1.04±0.05	0	0	8/8	0.065	0.982	2	43	
149.	H_2O 35°C	1.00±0.08	0	0	3/3	0.070	0.981	2	43	
150.	H_2O 55°C	1.09±0.23	0	0	3/3	0.199	0.843	2	43	
151.	H_2O-EtOH(23.6)15°C	1.44±0.08	0	0	3/3	0.070	0.992	2	43	
152.	H_2O-EtOH(25.6)25°C	1.52±0.06	0	0	6/6	0.074	0.991	2	43	
153.	H_2O-EtOH(23.6)35°C	1.42±0.09	0	0	3/3	0.079	0.989	2	43	
154.	H_2O-EtOH(23.6)55°C	1.40±0.04	0	0	3/3	0.031	0.999	2	43	
155.	H_2O-EtOH(73.6)15°C	1.88±0.08	0	0	3/3	0.067	0.996	2	43	
156.	H_2O-EtOH(73.6)25°C	1.94±0.08	0	0	3/3	0.066	0.996	2	43	
157.	H_2O-EtOH(73.6)35°C	1.85±0.14	0	0	3/3	0.125	0.986	2	43	
158.	H_2O-D(17.5),25°C	1.46±0.09	0	0	5/5	0.078	0.988	2	44	

Table (continued)

1	2	3	4	5	6	7	8	9	10	11
159.	H_2O-D(33.1),25°C	1.75±0.06	0	0	3/3	0.054	0.996	2	44	
160.	H_2O-D(45.9),25°C	1.82±0.07	0	0	3/3	0.063	0.996	2	44	
Alkaline hydrolysis of m- and p- substituted phenyl tosylates										
161.	H_2O, 60°C	1.81±0.05	0	0	12/12	0.066	0.996	2	45	
162.	H_2O, 75°C	1.65	0	0					45	Calculated in terms of the dependence of ρ on temperature
163.	H_2O-EtOH(11.7), 60°C	2.11±0.07	0	0	3/3	0.067	0.992	2	45	
164.	H_2O-EtOH(31.7), 60°C	2.45±0.06	0	0	6/6	0.072	0.998	2	45	
165.	H_2O-EtOH(55.3), 60°C	2.63±0.11	0	0	4/4	0.049	0.997	2A	45	
166.	H_2O-$NaClO_4$(5.3 M) 75°C	1.28±0.12	0	0	3/3	0.081	0.983	2A	46	
Alkaline hydrolysis of m- and p- substituted phenyl benzoates										
167.	H_2O-25°C	1.08±0.07	0	0	4/4	0.079	0.977	2	42	
168.	H_2O-50°C	0.973±0.040	0	0	4/4	0.046	0.991	2	42	

Table (continued)

1	2	3	4	5	6	7	8	9	10	11
169.	H_2O-$NaClO_4$(5.3 M) 50°C	0.32±0.24	0	0	3/3	0.174	0.930	2	7.47	
	Alkaline hydrolysis of m- and p- substituted phenyldimethylthiophosphinates									
170.	H_2O,15°C	1.34±0.15	0	0	3/3	0.128	0.973	2	49	
171.	H_2O,25°C	1.34±0.15	0	0	3/3	0.129	0.973	2	49	
172.	H_2O,55°C	1.29±0.07	0	0	3/3	0.018	0.993	2	49	
173.	H_2O-EtOH(23.6),15°C	1.96±0.01	0	0	3/3	0.006	0.999	2	49	
174.	H_2O-EtOH(23.6),25°C	1.87±0.13	0	0	3/3	0.116	0.987	2	49	
175.	H_2O-EtOH(23.6),55°C	1.79±0.09	0	0	3/3	0.077	0.993	2	49	
176.	H_2O-EtOH(73.6),25°C	2.20±0.11	0	0	3/3	0.097	0.993	2	49	
177.	H_2O-EtOH(73.6),55°C	2.17±0.10	0	0	3/3	0.091	0.993	2	49	
	Solvolysis of benzyl chlorides									
178.	H_2O,60°C	-2.04±0.12	0	-4.57±0.63	4/5	0.138	0.993	3	14	
179.	H_2O,50°C	-1.89±0.43	0	0	4/4	0.206	0.893	3	14	
180.	H_2O-EtOH(23.6),50°C	-1.66±0.07	0	-0.94±0.26	13/15	0.111	0.968	3	14	
181.	H_2O-An(19.7),60°C	-1.36±0.09	0	0	10/11	0.142	0.909	3	14	
182.	H_2O-(28.8),60°C	-1.20±0.20	0	-2.58±0.61	4/4	0.176	0.959	3	14	
183.	H_2O-An(63.2),50°C	-0.65±0.26	0	-1.76±0.86	4/4	0.249	0.800	3	14	
184.	H_2O-DMSO(21.0)60°C	-1.25±0.09	0	-2.14±0.35	3/3	0.075	0.993	3	14	

Table (continued)

1	2	3	4	5	6	7	8	9	10	11
185.	H_2O-DMSO(28.5 ,60°C	-1.07±0.12	0	-1.69±0.48	3/3	0.105	0.982	3	14	
186.	H_2O-DMSO(51.0), 60°C	-0.48±0.02	0	-1.51±0.02	3/3	0.002	0.999	3	14	
	Solvolysis of cumyl chlorides									
187.	MeOH, 25°C	-4.92±0.22	0	-4.41±1.48	8/9	0.273	0.975	3	14	
188.	EtOH, 25°C	-4.69±0.09	0	-4.81±0.21	7/8	0.061	0.998	3	14	
189.	i-PrOH 25°C	-4.59±0.18	0	-4.69±0.36	7/7	0.100	0.992	3	14	
190.	H_2O-An(68.9),25°C	-5.06±0.11	0	-4.88±0.43	13/15	0.119	0.994	3	14	

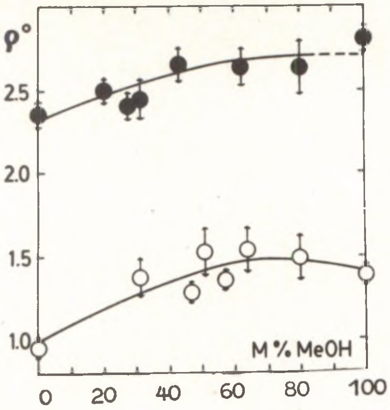

Fig.1

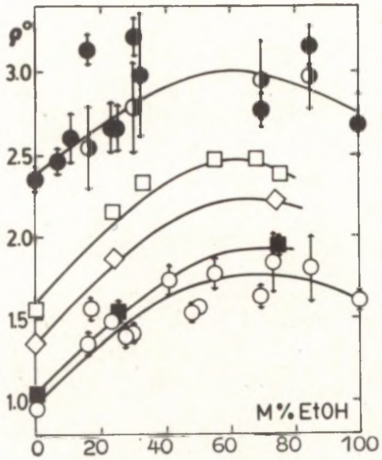

Fig.2

Figs. 1 and 2

Plot of ρ° vs. molar per cent (M%) of methanol (Fig.1) and M% of ethanol (Fig.2) for binary systems alcohol-water.

O, acidic dissociation of benzoic acids

●, acidic dissociation of phenols (◐, data treatment without unsubstituted derivative)

□, alkaline hydrolysis of ethyl benzoates

◇, alkaline hydrolysis of phenyldimethylthiophosphinates

■, alkaline hydrolysis of phenyl acetates

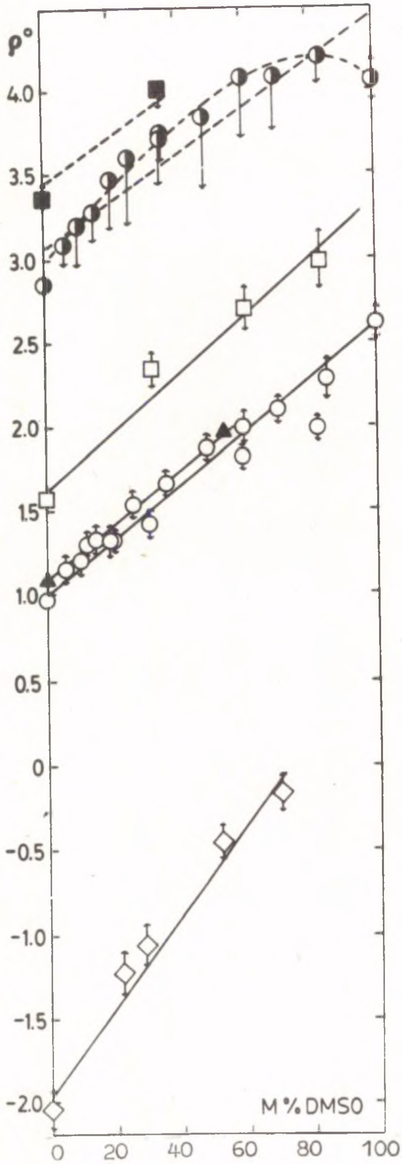

Fig. 3

Plot of ρ° vs. molar per cent (M%) of DMSO in DMSO-water system.

○, acidic dissociation of benzoic acids.

◐, acidic dissociation of anilinium ions

■, acidic dissociation of N,N-dimethyl-anilinium ions

□, alkaline hydrolysis of ethyl benzoates

▲, alkaline hydrolysis of phenyl benzoates

◇, solvolysis of benzyl chlorides

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The Basicities of Acetanilide and 4-Cyanoacetanilide in Aqueous Solutions of Sulfuric and Perchloric Acids

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The basicity constants, K_{BH^+}, and solvation paramaters m^* of acetanilide and 4-cyanoacetanilide have been calculated from UV-spectrophotometric data in aqueous solutions of sulfuric and perchloric acids at 25°C. The excess acidity method has been used. No evidence has been found for ion-pairs ($BH^+ \cdot A^-$) formation in aqueous solutions.

Several studies have been concerned with the basicity of substituted acetanilides[I-5].

The position of protonation of acetanilides and other amides has been comprehensively discussed by Giffney and O'Connor[2]. One must conclude on present evidence, that acetanilides protonate predominantly on the carbonyl oxygen[2-6].

The pK_{BH^+} values of a number of acetanilides have previously been measured and quoted in the literature[I-4]. But there does not appear to be any previous measurement of the basicity constant of 4-cyanoacetanilide. On the other hand, the basicity constant of acetanilide itself has been measured in several papers[I-5] and its reported values are in the range (-I.38) ÷ (-I.74). This uncertainty in pK_{BH^+} value is due, at least in part, to the non-uniformity of methods, used for pK_{BH^+} calculations by different authors. Nevertheless, the uncertainty limits of pK_{BH^+} are not very broad. Unfortunately, the solvation parameter values for acetanilide, collected from references[I-4] exhibit a very poor internal agreement. Using the slope (n_A) of the plots of log I vs. H_A[7] as a parameter reflecting the solvation phenomena at the acetanilide protonation, the following situation is observed. In the UV spectrophotometric studies by O'Connor et al.[2] and de Lockerente et al.[I] carried out at the wavelength 238 nm, slopes n_A=I.09 ÷ I.I2 and n_A=I.I have been obtained, respectively. The same spectrophotometric method and the same wavelength were used by Hashmi and Johnson, who determined n_A=0.60[3]. They succeed in confirming this result by ^{I}H NMR measurements which give n_A=0.66. A similar value (0.67) for the slope n_A was obtained by Tamme and Haldna[4]. They measured the absorbance not as usually on the maximum at 238 nm but on the other peak which is found at I95-2I5 nm. The reason for such a large discrepancy in n_A values obtained in different papers is not clear.

All the previous measurements of acetanilides protonation have used aqueous sulfuric acid as a solvent. The aqueous solutions of perchloric acid have not been used for these purposes, bacause bases with $pK_{BH^+} > -3$ have, as a rule, very similar pK_{BH^+} values in $H_2O-H_2SO_4$ and $H_2O - HClO_4$ mixtures[8]. Nevertheless, there exists a point of view, that the ionized form of weak bases (BH^+) can be involved in the equilibrium[9]

$$BH^+ + A^- \rightleftharpoons BH^+ \cdot A^- , \qquad (I)$$

where A^- is an anion of a strong acid (SO_4^{2-}, HSO_4^- or ClC_4^- for instance). The protonation of acetanilides is probably a suitable case to study whether Eq.I is shifted to right or not. This is due to the fact that the positive charge in ionized amides is not remarkably delocalized and therefore the BH^+ - form is specially suited for ion pair formation (Eq. I). On the other hand, acetanilides are protonated to a considerable extent already in moderately concentrated sulfuric acid solutions where the sulfate-ion concentration is rather high. If the ion pair formation takes place at all, it should occur at the protonation of acetanilides in aqueous sulfuric acid solutions. It should be noted, that the ion pair formation (Eq.I) is less favored in perchloric acid solutions because of lower charge density on ClO_4^- over SO_4^{2-} . Thus, if the ion pairs $BH^+ \cdot SO_4^{2-}$ are being formed, there should be some differences in the protonation of acetanilides in H_2O - H_2SO_4 and in H_2O - $HClO_4$. That is the reason why we decided to study the protonation equilibria of acetanilides in both strong acid-water solutions.

Experimental

Materials. Sulfuric acid (chemically pure) was standardized by the density measurements. Perchloric acid (chemically pure), 58 % (w/w) was distilled under reduced pressure in order to prepare acid with higher concentration.The concentration of perchloric acid was standardized by the density measurements. Aqueous solutions of both acids were prepared by dilution with distilled water by weighing.

Acetanilide (pure) was recrystallized from distilled water and had m.p. 114.1°C.

4-cyanoacetanilide was synthesized from 4-cyanoaniline by acylation with glacial acetic acid. The product was recrystallized from water and sublimed at 3 mm Hg. The sample used had m.p. 203÷208°C.

Measurements of Absorption Spectra. A stock solution of the base was prepared by dissolving substrate (0.05÷0.I2 g) in weighted amounts of ethanol. At any acid concentration used two samples (20 cm^3) of acid solution were weighted.To the first of them a weighted amount (0.08÷0.07 g) of stock solution of base was added. For preparing the reference solution to the second portion of aqueous acid the same amount of ethanol as to the sample solution was added.The UV spectra were recorded on a "Specord" spectrophotometer with thermostated (25.0 ± 0.2°C) cells of I0.3 and I mm path lengths.

All the solutions of acetanilide were stable over a time period about 30 min. needed to record the spectra. But the solutions of 4-cyanoacetanilide were not stable over this period of time. Small changes were observed in their spectra recorded in 15 min. intervals. Four of such spectra were recorded in each case (with the time intervals I5 min.) and a linear extrapolation was used in order to obtain the absorbance values at the moment of adding the base.

Results and Discussion

For each base studied spectra (from I90 to 300 nm) were recorded in the strong acid-water mixtures used (see Figs. I and 2).

The sets of spectra measured in $H_2O - H_2SO_4$ and in $H_2O - HClO_4$ were similar to each other for both bases studied. For acetanilide there was no lateral shift in the short wave length absorption maximum (located at I98.5 nm). The same was the case for the peak at 240 nm in aqueous solutions of perchloric acid. But in $H_2O - H_2SO_4$ the absorption maximum at 240 nm in water shifts to 244 nm in 90 % (w/w). This shift was not observed by Giffney and O'Connor [2].

The position of absorption maximum of 4-cyanoacetanilide at 250 - 260 nm was found to be solvent dependent - see Fig. 2. In order to obtain the indicator ratio $I=[B]/[BH^+]$ values not interferred by lateral shifts the characteristic vector analysis (CVA)[II-I3] was used. The respective computer program (Y-3) based on the Simonds algorithm[II] was written in Fortran IV for the computer EC-I022. The maximum size of the data matrix for the program Y-3 is 60 x 60.

For the both weak bases studied a large number of spectral points were used(interval between adjasent points I or 2 nm). According to our experience the large number of points seems to be unavoidable if the second vector accounts

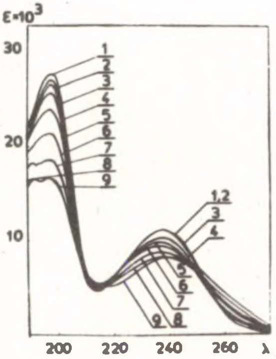

Fig.I. Spectra of acetanilide in H_2O-$HClO_4$ (+25°C): I-water;2-4.3%;3-I6.6%;4-25.7%;5-34.6%;6-44.9%;7-54.6%;8-66.4%;9-73.3% $HClO_4$.

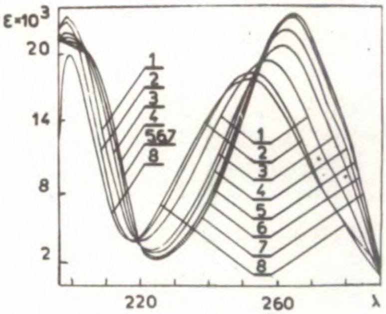

Fig.2. Spectra of 4-cyano-acetanilide in H_2O-$HClO_4$ (+25°C):5-water;6-7.I%;7-20.8%;4-33.8%;3-40.2%; I-49.I%;2-60.4%;8-73.I% $HClO_4$.

for a few % of the observed variability only. The parameters used for CVA calculations and % of the observed variability accounted by the resulting vectors are listed in Table I. The resulting from this treatment first and second characteristic vectors (CV) depend upon the wavelength as illustrated in Figs. 3 and 4.

The coefficients of the first and the second characteristic vector depend upon the w/w % of acid solutions as illustrated in Figs 5 and 6.

The shape of the first and second CV do not depend on the strong acid used - see Figs 3 ÷ 6. This can be taken as undirect evidence that no ion pair formation occurs

Table I

Parameters for CVA Calculations

Parameters	Acetanilide		4-Cyanoacetanilide	
	$H_2O-H_2SO_4$	$H_2O-HClO_4$	$H_2O-H_2SO_4$	$H_2O-HClO_4$
Number of wavelengths used(NV)	46	47	55	55
Number of acid solutions (NR)	28	26	26	I6
The % of the observed variability accounted for by the first vector and	94.8	9I.2	96.9	95.9
second vector	3.3	5.6	2.5	3.3

with BH^+ form of the weak bases studied.

The protonation behavior as a function of acid concentration is contained in the resulting coefficients of the first characteristic vector (see Figs 5 + 6) and these were used directly[I3] to obtain values of the indicator ratio:

$$I = \frac{[B]}{[BH^+]} = \frac{Y - Y_{BH^+}}{Y_B - Y} \quad , \qquad (2)$$

where Y is the value of the coefficient of the first CV for the given acid concentration.

Obtained in this way log I values are listed in Table 2. It should be noted, that in the case of the acetanilide in $H_2O-H_2SO_4$ no good plateau in Y values was observed in concentrated acid solutions. The same difficulty was encountered by Moody et al[5]. Therefore for Y_{BH^+} the Y value in 9I w/w % H_2SO_4 was taken and values $I < 1$ were not

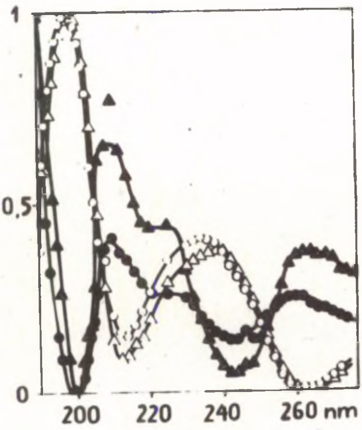

Fig.3. Acetanilide. In solutions $H_2O-H_2SO_4$:
-○- the first CV,
-●- the second CV.
In solutions $H_2O-HClO_4$:
-△- the first CV,
-▲- the second CV.

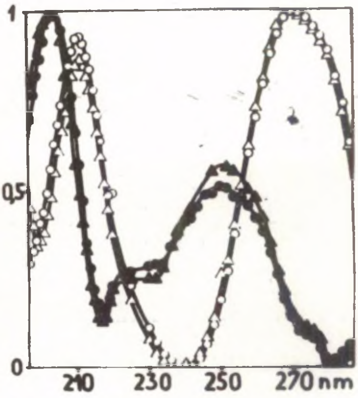

Fig.4. 4-Cyanoacetanilide.
In solutions $H_2O-H_2SO_4$:
-○- the first CV,
-●- the second CV.
In solutions $H_2O-HClO_4$:
-△- the first CV,
-▲- the second CV.

used as insufficiently reliable ones (see Table 2).

In all the cases studied the first CV accounts for some 9I ÷ 97 % of the observed variability (see Table I). The resulting coefficients of the second CV exhibit rather uniform smooth dependence upon the strong acid concentration for the both strong acids studied (see Figs.5 and 6). Till more experimental data are accumulated, we would postpone the discussion of this dependece.

The slopes obtained from plots of log I (Table 2) against H_A[7] are given in Table 3.

The slope $n_A = d(\log I)/dH_A$ for acetanilide is about 0.6 in both strong acid solutions used. This confirms the

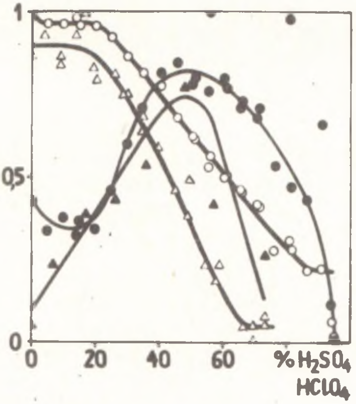

Fig.5. Acetanilide. In solutions $H_2O-H_2SO_4$:
-○- coefficients of the first CV,
-●- coefficients of the second CV.
In solutions $H_2O-HClO_4$:
-△- coefficients of the first CV,
-▲- coefficients of the second CV.

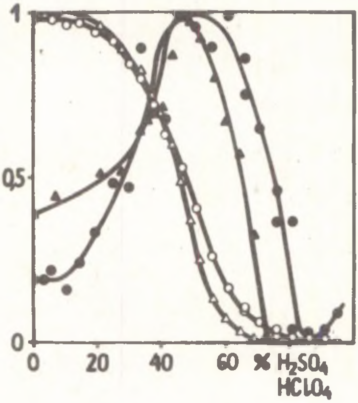

Fig.6. Cyanoacetanilide. In solutions $H_2O-H_2SO_4$:
-○- coefficients of the first CV,
-●- coefficients of the second CV.
In solutions $H_2O-HClO_4$:
-△- coefficients of the first CV,
-▲- coefficients of the second CV.

respective data of Hashmi, Johnson[3] and Tamme, Haldna[4]. But for 4-cyanoacetanilide n_A=0.9I ÷ 0.97, wich is close to n_A values obtained by Giffney and O'Connor[2] for a number of other substituted acetanilides.

The basicity constant (K_{BH^+}) and the solvation parameter (m^*) for the bases studied were evaluated by the excess acidity method[8]

$$-\log I - \log C_{H^+} = m^* X + pK_{BH^+} \qquad (3)$$

The obtained values of pK_{BH^+} and m^* are given in Table 4. The methods of Bunnett-Olsen[I4] and MCP[I5] were not used

Table 2

The Indicator Ratio $I=[B]/[BH^+]$ Values of Acetanilide and 4-Cyanoacetanilide at 25°C

Acetanilide				4-Cyanoacetanilide			
$H_2O - H_2SO_4$		$H_2O - HClO_4$		$H_2O - H_2SO_4$		$H_2O - HClO_4$	
% of acid	log I	% of acid	log I	% of acid	log I	% of acid	log I
20.3	I.055	I9.4	I.II6	24.8	I.053	33.8	0.657
25.I	0.905	25.7	0.829	29.9	0.759	37.7	0.479
30.2	0.734	28.5	0.7II	37.4	0.430	40.2	0.329
35.6	0.549	29.7	0.585	40.4	0.244	43.4	0.I54
40.5	0.436	34.6	0.4I9	45.8	0.065	46.0	-0.028
45.8	0.243	39.3	0.267	50.7	-0.I8I	49.I	-0.244
50.6	0.I27	44.9	0.022	56.0	-0.463	52.0	-0.483
56.3	0.04I	49.5	-0.I26	60.9	-0.695	60.4	-I.I70
		54.6	-0.384	65.8	-I.002		
		58.0	-0.5I3				

Table 3

The Slopes $n_A=d(\log I)/dH_A$

Base	n_A (a)	
	$H_2O - H_2SO_4$	$H_2O - HClO_4$
Acetanilide	0.57 ± 0.06	0.64 ± 0.09
4-Cyanoacetanilide	$0.9I \pm 0.03$	0.97 ± 0.02

(a) with confidence intervals for P=0.95.

because they have been found to give practically the same values of pK_{BH^+} and m^* as Eq. 3 if $pK_{BH^+} > -4$ and $m < I$[I6,I7]. It is apparent from Table 4 that the agreement between the pK_{BH^+} values of acetanilide determined in this investiga-

Table 4

Protonation Data for Acetanilide
and 4-Cyanoacetanilide at 25°C[a]

Base	$H_2O - H_2SO_4$	$H_2O - HClO_4$
Acetanilide		
pK_{BH^+}	-I.64 ± 0.07	-I.5I ± 0.08
m^*	0.23 ± 0.04	0.27 ± 0.04
4-Cyanoacetanilide		
pK_{BH^+}	-I.94 ± 0.07	-I.98 ± 0.04
m^*	0.49 ± 0.03	0.50 ± 0.02

(a)with confidence intervals for P=0.95

tion and previously (-I.4I) ÷ (-I.43) by Bunnett-Olsen method[2] is satsifactory. However, that is not the case for $m^* = I - \phi$ of acetanilide, because Giffney and O'Connor obtained $\phi = 0.I9 \div 0.25$ (i;e. $m^* = 0.75 \div 0.8I$).

The good agreement of pK_{BH^+} and m^* values in $H_2O - H_2SO_4$ and $H_2O-HClO_4$ for the both bases studied indicates that the ion-pairs $BH^+ \cdot A^-$ (Eq.I) are not formed in any detectable quantities.

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Synthesis and Properties of Arenesulfohydrazides of 2-Amino(arenesulfamido)-1,3,4-Tiadiazolyl-5-Sulfonyloxamine Acid

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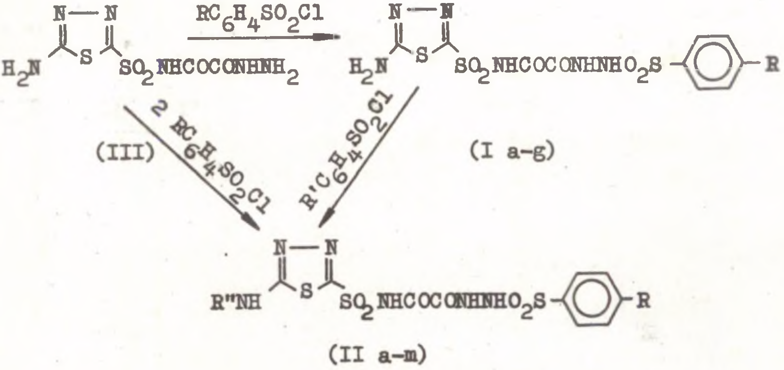
A series of arenesulfohydrazides of 2-amino-(arenesulfamido)-1,3,4-tiadiazolyl-5-sulfonyloxamine acids is synthesized. IR - spectra are taken and interpreted for them. Acidic ionization constants are studied potentiometrically in aqueous-dioxane mixtures. Correlation of the pK_a values of sulfohydrazide group with Hammett-Taft σ° constants is performed.

We have studied elsewhere[1] biological properties of N-tiadiazolylamides of arenesulfohydrazides of oxalic acid. They have been shown to possess hypoglycemic and diuretic action and display low toxicity.

In developing these studies it seems to be of interest to synthesize and study the properties of arenesulfohydrazides of 2-amino-1,3,4-tiadiazolyl-5-sulfonyloxamine acid (I,II).

These compounds were obtained via interaction of hydrazide of 2-amino-1,3,4-tiadiazolyl-5-sulfonyloxamine acid (III) with arenesulfochlorides in dry pyridine by the scheme:



Presence of two nucleophilic centers in hydrazide III favors the occurence of the reaction on hydrazide and amino groups. Hydrazide group is more nucleophilic and is the first to undergo the reaction which proceeds at room temperature for 8 hours to form compound I. Acylation of amino group to form compound II needs in heating for an hour.

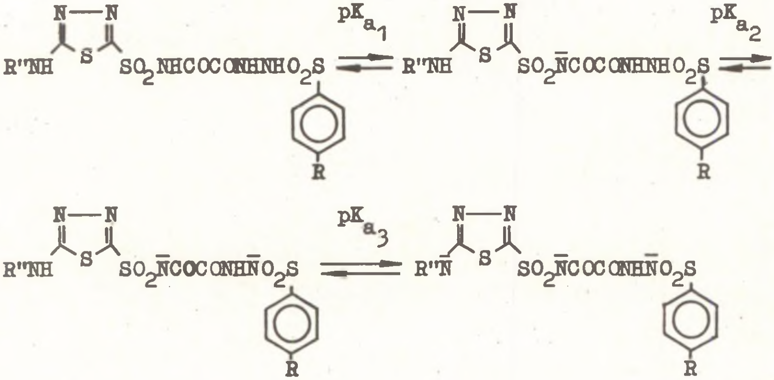
Synthesized compounds I and II are colorless or yellowish crystalline substances soluble in aqueous solutions of alkali, mineral acids, and organic solvents (Table 1).

The compounds obtained were identified by elemental analysis, IR-spectra, and thin layer chromatography.

In IR-spectra characteristic stretching oscillation bands of amide, carbonyl, and sulfonyl groups are observed. In the region of 1698-1680 cm^{-1} there is an intensive band characteristic of valence oscillation of CO group (1 amide band); II amide band caused by deformation oscillations of NH-group is at 1555-1518 cm^{-1}. Absorption bands characteristic of asymmetric and symmetric valent oscillations of sulfo group are observed in the region of 1367-1345 cm^{-1} and 1178-1162 cm^{-1}, respectively. At 3349-3040 cm^{-1} absorption bands of NH-group participating in the hydrogen bond can be found.

For all compounds in 60% aqueous dioxane acidic ionization constants characterizing sulfamide (pKa_1) and sulfohydrazide (pKa_2) groups were measured potentiometrically (Table 2).

Acid-base equilibria for the compounds studied can be represented as follows:



As one can see from the scheme the compounds studied have three centers of acidic ionization characterized by the pKa_1, pKa_2, and pKa_3 values.

For all substances the first step involves ionization of 5-sulfamide fragment of a molecule (pKa_1) which is due to high electron-accepting power of sulfonyl and carbonyl groups besides the amide nitrogen. This assumption is also confirmed by the fact that the pKa_1 values change little under the action of electronic effects of substituents R_1 which is caused by a considerable distance between the reaction center and the latters.

The pKa_2 values of compounds I characterizing ionization of sulfohydrazide group depend markedly on substituent nature in the benzene ring of sulfohydrazide residue. This effect is estimated quantitatively by the Hammett-Taft equation.

Table 1

Arenesulfohydrazides of 2-Amino(arenesulfamido)-
-1,3,4-tiadiazolyl-5-sulfonyloxamine Acid (1,II)

Cpd.	Yield	B.p. °C	Found %		Gross-formula	Calculated	
			N	S		N	S
I a	97	204[*]	20.92	23.76	$C_{10}H_{10}N_6O_6S_3$	20.67	23.66
I b	94	214	20.00	22.77	$C_{11}H_{12}N_6O_6S_3$	19.98	22.87
I c	96	224-5	19.26	22.34	$C_{11}H_{12}N_6O_7S_3$	19.25	22.04
I d	90	248-9	20.78	20.78	$C_{12}H_{13}N_7O_7S_3$	21.15	20.75
I e	93	198-9	20.25	20.34	$C_{12}H_{13}N_7O_8S_3$	20.45	20.34
I f	92	214-5	17.60	20.00	$C_{10}H_9BrN_6O_6S_3$	17.31	19.82
I g	93	205	21.44	21.33	$C_{10}H_9N_7O_8S_3$	21.72	21.30
IIa	89	216-8	15.10	23.09	$C_{17}H_{16}N_6O_8S_4$	14.99	22.87
IIb	73	223-4	14.79	21.91	$C_{17}H_{16}N_6O_9S_4$	14.57	22.24
IIc	80	218-9	16.53	20.94	$C_{18}H_{17}N_7O_9S_4$	16.24	21.24
IId	70	220-1	13.71	20.78	$C_{16}H_{13}BrN_6O_8S_4$	13.43	20.50
IIe	62	225-7	16.71	21.62	$C_{16}H_{13}N_7O_{10}S_4$	16.60	21.71
IIf	92	244-5	15.27	23.73	$C_{16}H_{14}N_6O_8S_4$	15.37	23.46
IIg	87	212-3	14.84	22.02	$C_{18}H_{18}N_6O_8S_4$	14.62	22.31
IIh	85	204-5	14.16	21.04	$C_{18}H_{18}N_6O_{10}S_4$	13.87	21.17
IIi	85	225-6	16.77	19.26	$C_{20}H_{20}N_8O_{10}S_4$	16.98	19.44
IIj	84	214-5	15.90	18.73	$C_{20}H_{20}N_8O_{12}S_4$	16.20	18.54
IIk	90	282-4	13.54	20.61	$C_{16}H_{12}CI_2N_6O_8S_4$	13.65	20.83
IIl	71	208-9	12.05	18.24	$C_{16}H_{12}Br_2N_6O_8S_4$	11.93	18.24
IIm	85	216-7	17.81	20.36	$C_{16}H_{12}N_8O_{12}S_4$	17.63	20.17

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[*] all compounds are crystallized from the mixture of DMF, ethanol, and water;
all substances melt with decomposition.

$$pKa_2 = (9.11 \pm 0.09) - (1.69 \pm 0.23)\sigma^{\circ} \quad (r=0.999;\ S=0.05)$$

σ° values are taken from Ref. 2.

Table 2

pKa_1, pKa_2, and R_f Values for Arenesulfohydrazides of 2-Amino(arenesulfamido)-1,3,4-tiadiazolyl-5--sulfonyloxamine Acid (I,II)

Cpd.	R	R"	pKa in 60% aqueous dioxane		R_f
			pKa1	pKa2	
I a*	H	H	6.08	9.08	0.48
I b	CH_3	H	6.18	9.20	0.53
I c	CH_3O	H	6.25	9.42	0.54
I d	CH_3CONH	H	6.39	9.50	0.67
I e	CH_3OCONH	H	6.44	9.54	0.58
I f	Br	H	5.81	8.59	0.70
I g	NO_2	H	5.84	7.93	0.61
II a	H	$H_3CC_6H_4SO_2$	7.12	-	0.72
II b	H	$H_3COC_6H_4SO_2$	7.43	-	0.64
II c	H	$H_3CCONHC_6H_4SO_2$	7.06	-	0.51
II d	H	$BrC_6H_4SO_2$	7.23	-	0.62
II e	H	$NO_2C_6H_4SO_2$	7.04	-	0.82
II f	H	$C_6H_4SO_2$	6.17	-	0.69
II g	CH_3	$CH_3C_6H_4SO_2$	5.63	-	0.47
II h	CH_3O	$CH_3OC_6H_4SO_2$	5.68	-	0.52
II i	CH_3CONH	$CH_3CONHC_6H_4SO_2$	5.68	-	0.63
II j	CH_3OCONH	$CH_3OCONHC_6H_4SO_2$	5.75	-	0.43
II k	CI	$CIC_6H_4SO_2$	5.90	-	0.60
II l	Br	$BrC_6H_4SO_2$	5.93	-	0.55
II m	NO_2	$NO_2C_6H_4SO_2$	5.52	-	0.72

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* Numbers of the compounds are the same as listed in Table 1.

pK_{a_2} and pK_{a_3} values of sulfohydrazides II turned out to be close to each other and under these conditions of titration their separate estimation has proved to be a failure.

Experimental

IR-spectra were taken on a UR-20 spectrophotometer in tablets of KBr (with 0.5%); thin layer chromatography was done on Silufol plates in the acetic acid-n-butanol-water (10:40:1) system.

Ionization constants were determined by potentiometric titration at 25°C in 60% aqueous dioxane on a pH-340 apparatus, using glass and silver chloride electrodes. Hydrogen function of the glass electrode was checked in standard buffer aqueous solutions and also in buffer solutions in 60% aqueous dioxane[3]. The slope of a straight line in the coordinates of EMF-pH of buffer solutions was 0.057 in both cases. For comparison acetic acid ionization constants in water and 60% aqueous dioxane were determined. The experimental pK_a values of acetic acid are close to the literature ones: 4.76 in water and 7.51 in aqueous dioxane[4]. pK_a values were obtained as pH in the halfneutralization point. Measuring error of pK_a was within 0.1 un.

Arenesulfohydrazides of 2-Amino 1,3,4-tiadiazolyl-5--sulfonyloxamine Acid (1).

0.01 mole of arenesulfochloride was added to 0.01 mole of hydrazide of 2-amino-1,3,4-tiadiazolyl-5-sulfonyloxamine acid III in 15 ml of dry pyridine and left for 8 hours. The excess of pyridine was distilled off under a water-jet pump vacuum; the mixture was cooled, poured into 50 ml of water, and acidified with HCl 1:1 up to pH=5. The residue was filtered out, washed with water and dried.

Arenesulfohydrazides of 2-Arenesulfamido-1,3,4-tiadiazolyl-5-sulfonyloxamine Acids (II). 0.01 mole of arenesulfohydrazide of 2-amino-1,3,4-tiadiazolyl-5-sulfonyloxamine acid I and 0.01 mole (in the case of hydrazide III 0.02 mole) of arenesulfochloride was boiled for an hour and cooled.

Further procedure is the same as described above.

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Study of Solvent Dependence of ρ^o
2. Results and Discussion

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On the basis of 190 values of ρ^o belonging to 14 reaction series with a variable substituent the observance of the relationship

$$\rho^o_{js} - \rho^o_{jo} = \text{const} \qquad (1)$$

is checked for different organic solvents.

General statistical verification of the condition (1) was carried out according to the equation:

$$\rho^o_{js} = -\rho^o_{oo} + (\rho^o_{os} \pm \rho^o_{jo}) \qquad (2)$$

Indices j and s denote reaction and medium respectively. As a standard reaction (j=o) acidic dissociation of benzoic acids at 25°C was used; as a standard solvent (s=o) water was chosen.

Equation (1) is proved to work within the range of ρ^o_{js} from -5.35 to 7.32.

The present work was undertaken to check whether the relationship

$$\rho^o_{js} - \rho^o_{jo} = \text{const} \ (1)$$

well reflecting the medium effects in concentrated aqueous solutions of different salts[1,2] could be generalised for medium effects caused by the variation of solvent (j and s are indices of a reaction series and solvent respectively). With this purpose the data available on different solvents and referring to 14 reaction series with a variable substituent have been treated. Our previous communication[3] lists the results of the corresponding statistical data treatment for 190 reaction series in all.

Equation (1) may be rewritten as:

$$\rho^{\circ}_{js} - \rho^{\circ}_{jo} = \rho^{\circ}_{os} - \rho^{\circ}_{oo} = \text{const} \qquad (2)$$

$$\rho^{\circ}_{js} = -\rho^{\circ}_{oo} + (\rho^{\circ}_{os} + \rho^{\circ}_{oj}) \qquad (3)$$

$$\rho^{\circ}_{js} = (\rho^{\circ}_{os} - \rho^{\circ}_{oo}) + \rho^{\circ}_{oj} \quad \text{s=const} \qquad (4)$$

$$\rho^{\circ}_{js} = (\rho^{\circ}_{jo} - \rho^{\circ}_{oo}) + \rho^{\circ}_{os} \quad \text{j=const} \qquad (5)$$

$$\rho^{\circ}_{oo} = (\rho^{\circ}_{os} + \rho^{\circ}_{oj}) - \rho^{\circ}_{js} \qquad (6)$$

where ρ°_{oo} is constant ρ° for standard reaction in standard medium;

ρ°_{os} is constant ρ° for standard reaction in medium s;

ρ°_{jo} is constant ρ° for the considered reaction in standard medium.

The present work has chosen acidic dissociation of benzoic acids at 25°C as a standard reaction and water as a standard medium.

Eq. (3) is convenient for the general statistic verification of the observance of condition (1) since the linearity should be observed in the plot of ρ°_{js} vs. $(\rho^{\circ}_{os} + \rho^{\circ}_{jo})$ with slope 1 and intercept equalled to $-\rho^{\circ}_{oo}$ ($\rho^{\circ}_{oo} = 0.944 \pm 0.017$ and refers to a reference reaction in standard medium: pK_a H_2O for substituted benzoic acids).

In order to extend the data sampling in the coordinates of Eq. (3) ρ°_{js} values referring to different temperatures were treated, which is not strict enough. In so doing for each j ρ°_{jo} refers to the same temperature as ρ°_{js} and for ρ°_{os} the value for 25°C was used. (In the case of ρ°_{oo} temperature dependence is essentially absent[4]).

Observance of relationship (1) was also checked via comparing the ρ°_{oo} values by Eq. (6) with the experimental value. Table 1 presents the calculated ρ°_{oo} values for 105 reaction series. Deviation for the calculated ρ°_{oo} value is found according to the equation

$$s = \sqrt{s^2_{\rho^{\circ}_{js}} + s^2_{\rho^{\circ}_{jo}} + s^2_{\rho^{\circ}_{os}}}$$

For linear relationship (3) (Fig.1) slope and intercept are found. For initial sample of 117 ρ°_{js} values for 105 combinations of j and s indices (in same cases several alternative ρ°_{js} values related to the data sets reported by different authors were used) the linear regression is characterized by the following parameters:

$\rho^{\circ}_{oo} = 0.91 \pm 0.066$ slope $= 0.992 \pm 0.018$

$r = 0.979$ $s = 0.366$

After excluding (according to Student test on the confidence level of 0.95) 12 significantly deviating points for the final sampling of 105 ρ°_{js} values for 100 combinations of j and s the following result was obtained:

$\rho^{\circ}_{oo} = 0.930 \pm 0.035$ slope $= 0.992 \pm 0.010$

$r = 0.994$ $s = 0.186$

Ratio of the standard deviation s to the data dispersion equals 0.0939. Initial number embraced media (besides water) is 54; after excluding the points (the data for acetone are excluded) it is 53.

Among 12 significantly deviating ρ°_{js} values are, mainly, those alternative to other values taken into account. Among non-alternative values the following ρ°_{js} were excluded:

ρ°_{js} = 4.77 for acidic dissociation of phenols in acetone; ρ°_{js} = 2.74 for acidic dissociation of anilinium ions in acetone; ρ°_{js} = -0.48 for solvolysis of benzyl chlorides in aqueous DMSO (51 M%); ρ°_{js} = 4.27 for acidic dissociation of dimethyl anilinium ions in aqueous dioxane (14.8 M%); ρ°_{js} = 4.04 for acidic dissociation of anilinium ions in DMSO.

Among alternative values the following ρ°_{js} were excluded:

ρ°_{js} = 1.76; ρ°_{js} = 4.82; and ρ°_{js} = 3.89 for acidic dissociation of anilinium ions in ethanol; ρ°_{js} = 2.79 for acidic dissociation of phenols in DMSO. The ρ°_{js} values for acidic dissociation of phenols, pyridinium ions and conjugated acids of pyridine-N-oxides in nitromethane were also excluded, if the ρ°_{os} values equalled to 1.78 were used as ρ°_{os} (for acidic dissociation of benzoic acids in $MeNO_2$) instead of 2.50.

The results obtained evidence in favor of the observance of relationship (1). If that is so, linearities (4) and (5) should also work for separate reactions and media.

The results of treatment the ρ°_{js} values by Equs. (4) and (5) are listed in Tables 2 and 3 (Figs. 2 and 3). Relationship (4) works satisfactorily for 9 series of 11, and relationship (5) for 5 series of 7. Four cases when Equs. (4) and (5) do not work can be either due to shortcomings of model (1) or to the unreliability of the corresponding experimental data.

If in some cases model (1) is insufficient for adequate description of medium effects on ρ° values, with statistical treatment in the coordinates of Eq. (3) such points do not influence essentially the total positive result.

According to the data available there are no reasons to believe that at least one of such deviations is established with reliability. It does not follow, however, that it is not necessary to obtain some additional, more accurate experimental data in suspect cases. This is concerning especially, with reactions in acetone.

It is known [4,5,6] that

$$\rho^* = \frac{\alpha^*}{2.3\ RT} \left(\sigma^*_Y - \sigma^*_Z \right) \qquad (6)$$

Y denotes a reaction center of initial state and Z denotes final or activated state for any reaction series where substituents are directly bound with a reaction center. α^* is a universal constant of inductive interaction. Providing that initial and final (or activated) states differ in charge type only (i.e. $Z = Y\pm$) and assuming that constant σ^* for the neutral substituent is essentially independent of a solvent one obtains the following equation:

$$\rho^*_{js} - \rho^*_{j(H_2O)} = \frac{\alpha^*}{2.3\ RT} \left(\sigma^*_{y\pm(H_2O)} - \sigma^*_{y\pm(S)} \right) \qquad (7)$$

The inductive interaction universal constant α^* being independent of a solvent [6-8] and assuming that

$$\rho^*_{js} - \rho^*_{j(H_2O)} = \rho^\circ_{js} - \rho^\circ_{j(H_2O)} = \text{const} \qquad (9)$$

one obtains

$$\sigma^*_{y\pm(H_2O)} - \sigma^*_{y\pm(S)} = \text{const.} \qquad (10)$$

Thus when passing from water to any other solvent σ^* constants for all charged substituents should change by the same constant. Using the literature data one can verify just how this conclusion is realized for substituents CO_2^- and O^- when passing from water to DMSO. According to the literature data for CO_2^- group in water $\sigma^* = 0.75$[6], 0.71[6], and 0.93[7] (with electrostatic correction) and in DMSO $\sigma^*_{CO_2^-} = -0.09$[7]. Hence,

$$\sigma^*_{CO_2^-(H_2O)} - \sigma^*_{CO_2^-(DMSO)} = 0.80 \div 1.02$$

In water $\sigma^*_{O^-}$ =0.38[6] or 0[6] and for DMSO $\sigma^*_{O^-}$ = -1.09[8]:

$$\sigma^*_{O^-(H_2O)} - \sigma^*_{O^-(DMSO)} = 0.71 \div = 1.09$$

Assuming that when passing from water to DMSO changes in the ρ^* value equal $\rho^o_{os} - \rho^o_{oo}$ = 1.68 (for acidic dissociation of benzoic acids) and α^* =2.62[7,8] , the following calculated value is obtained for $\Delta\sigma^*_{y\pm}$:

$$\Delta\sigma^*_{y\pm} = \frac{2.3RT}{\alpha^*}(\rho^o_{os} - \rho^o_{oo}) = 0.87$$

It follows from these data that when passing from water to DMSO the $\sigma^*_{y\pm}$ values for substituents CO_2^- and O^- decrease actually by the same value which is essentially the same as the calculated value.

When studying salt effects the following equations were found to work [1,2]:

$$\lg k^x_{js} - \lg k^x_{jo} = \Delta \lg k^x_{js} = a_{js} \lg k^x_{jo} + b_{js} \qquad (11)$$

$$\lg k^x_{js} = (a_{js} + 1) \lg k^x_{jo} + b_{js} \qquad (12)$$

$$\Delta \lg k^x_{js} = a_{js}\rho_{jo}{}^x + a_{js} \lg k_o{}^o + b_{js} \qquad (13)$$

$$\lg k^x_{js} = (a_{js} + 1)\ \rho_{jo}{}^x + (a_{js} + 1) \lg k_o{}^o + b_{js} \qquad (14)$$

On the other hand,

$$\Delta \lg k^x_{js} = (\rho_{js} - \rho_{jo})\sigma^x + (\lg k^o_{js} - \lg k^o_{jo}) \qquad (15)$$

and

$$\lg k^x_{js} = \frac{\rho_{js}}{\rho_{jo}} \lg k^x_{jo} + \lg k^o_{js} - \frac{\rho_{js}}{\rho_{jo}} \lg k^o_{jo} \qquad (16)$$

Table 1

Medium	ρ^o_{js}	ρ^o_{os}	ρ^o_{oo}, calc.	Notes
Acidic dissociation of m- and p-substituted phenols, 25°C				
1. H_2O	-2.36±0.06			$\rho^o_{js} = \rho^o_{jo}$
2. H_2O-MeOH(19,1)	-2.50±0.03	-1.20	-1.06	a)
3. H_2O-MeOH(27.3)	-2.40±0.07	-1.36±0.12	-1.32±0.18	ρ^o_{os} for H_2O-MeOH(30.9)
4. H_2O-MeOH(30.9)	-2.43±0.11	-1.36±0.12	-1.27±0.22	
5. H_2O-MeOH(43.9)	-2.67±0.08	-1.28±0.03	-0.97±0.10	ρ^o_{os} for H_2O-MeOH(47,6)
6. H_2O-MeOH(62.3)	-2.64±0.13	-1.55±0.16	-1.27±0.22	ρ^o_{os} for H_2O-MeOH(64.1)
	-2.64±0.13	-1.34±0.02	-1.06±0.15	ρ^o_{os} for H_2O-MeOH(57.3)
7. H_2O-MeOH(80.1)	-2.62±0.17	-1.49±0.19	-1.23±0.26	
8. MeOH	-2.80±0.23	-1.39±0.05	-0.95±0.24	
9. H_2O-EtOH(7.18)	-2.46±0.08	-1.10	-1.00	a)
10. H_2O-EtOH(11.7)	-2.60±0.16	-1.34±0.03	-1.10±0.17	ρ^o_{os} for H_2O-EtOH(16.3)
11. H_2O-EtOH(16.3)	-3.14±0.08	-1.34±0.03	-0.56±0.11	
	-2.54±0.26	-1.34±0.03	-1.16±0.27	b)
12. H_2O-EtOH(22.8)	-2.66±0.13	-1.49±0.02	-1.19±0.15	ρ^o_{os} for H_2O-EtOH(23.6)
13. H_2O-EtOH(23.6)	-2.63±0.11	-1.49±0.02	-1.22±0.13	
14. H_2O-EtOH(29.8)	-3.22±0.06	-1.40±0.05	-0.54±0.10	
	-2.79±0.28	-1.40±0.05	-0.97±0.29	b)
15. H_2O-EtOH(31.7)	-2.99±0.44	-1.40±0.05	-0.77±0.45	

Table 1 (continued)

Medium	ρ°_{js}	ρ°_{os}	ρ°_{oo}, calc.	Notes
16. H_2O-EtOH(69.6)	-2.78±0.13	-1.64±0.05	-1.22±0.15	
	-2.94±0.18	-1.64±0.05	-1.06±0.20	b)
17. H_2O-EtOH(85.5)	-3.17±0.22	-1.80±0.19	-0.99±0.30	
	-2.98±0.20	-1.80±0.19	-1.08±0.28	b)
18. EtOH	-2.68±0.16	-1.60±0.06	-1.28±0.18	
19. i-PrOH	-3.07±0.12	-1.80±0.06	-1.09±0.18	
20. t-BuOH	-5.20±0.05	-3.36±0.17	-0.52±0.19	
		-3.88±0.16	-1.04±0.18	Without 3.5$(NO_2)_2$derivative
21. CH_3NO_2	-3.76±0.08	-2.50±0.09	-1.10±0.13	
		-1.78±0.19	-0.38±0.21	
22. CH_3CN	-4.14±0.09	-2.49±0.11	-0.71±0.15	
23. $HCON(CH_3)_2$	-3.89±0.30	-2.32±0.09	-0.79±0.32	
24. DMSO	-4.03±0.19	-2.62±0.10	-0.95±0.22	
	-2.79±0.42	-2.62±0.10	-2.19±0.44	
25. H_2O-D(1.81)	-2.38±0.30	-1.02±0.08	-1.00±0.32	ρ°_{os} for H_2O-D(5.03)
26. H_2O-D(5.03)	-2.70±0.40	-1.02±0.08	-0.68±0.41	
27. H_2O-D(12.4)	-2.46±0.34	-1.38±0.05	-1.28±0.32	

Table 1 (continued)

Medium	ρ°_{js}	ρ°_{os}	ρ°_{oo}, calc.	Notes
28. H_2O-D(24.1)	-2.70±0.31	-1.31±0.07	-0.97±0.33	
	-2.75±0.22	-1.31±0.07	-0.42±0.24	
29. H_2O-D(45.9)	-2.71±0.26	-1.47±0.12	-1.12±0.30	
30. An	-4.77±0.75	-1.80±0.08	0.61±0.75	
31. $H_2O-(n-C_4H_9)_4NBr$ (7.75 M)	-3.27±0.09	-2.09±0.08	-1.18±0.13	
Acidic dissociation of m- and p- substituted anilinium ions, 25°C				
32. H_2O	-2.84±0.04			$\rho^{\circ}_{js} = \rho^{\circ}_{jo}$
33. H_2O-MeOH(30.9)	-3.01±0.23	-1.36±0.12	-1.19±0.27	
34. MeOH	-3.58±0.32	-1.39±0.05	-0.65±0.33	
	-3.02	-1.39±0.05	-1.21	
35. H_2O-EtOH(11.7)	-3.44	-1.34±0.03	-0.74	ρ°_{os} for H_2O-EtOH (16.3)
36. H_2O-EtOH(14.4)	-3.04±0.24	-1.34±0.03	-1.14±0.25	
37. H_2O-EtOH(17.1)	-3.31±0.16	-1.57±0.06	-1.10±0.18	
38. H_2O-EtOH(23.6)	-3.60	-1.49±0.02	-0.73	
39. EtOH	-3.54	-1.60±0.06	-0.90	
	-3.89±0.06	-1.60±0.06	-0.55±0.09	
	-4.82±0.13	-1.60±0.06	0.38±0.14	
	-1.76±0.22	-1.60±0.06	-2.68±0.23	

Table 1 (continued)

Medium	ρ^o_{Js}	ρ^o_{os}	ρ^o_{oo},calc.	Notes
40. CH_3NO_2	-4.01±0.10	-2.50±0.09	-1.33±0.14	
		-1.78±0.19	-0.60±0.22	
41. CH_3CN	-4.02±0.15	-2.49±0.11	-1.31±0.22	
42. H_2O-DMSO(5.88)	-3.09±0.11	-1.15±0.04	-0.90±0.12	
43. H_2O-DMSO(9.67	-3.20±0.26	-1.20±0.04	-0.84±0.27	
44. H_2O-DMSO(14.0)	-3.37±0.12	-1.33±0.07	-0.80±0.15	
45. H_2O-DMSO(14.5)	-3.47±0.28	-1.42±0.08	-0.79±0.30	
46. H_2O-DMSO(26.7)	-3.60±0.44	-1.54±0.06	-0.78±0.45	
47. H_2O-DMSO(35.0)	-3.74±0.05	-1.65±0.05	-0.75±0.08	ρ^o_{os} for H_2O-DMSO(35.5)
48. H_2O-DMSO(35.5)	-3.77±0.25	-1.65±0.05	-0.72±0.25	
49. H_2O-DMSO(48.6)	-3.84±0.43	-1.88±0.05	-0.88±0.46	
50. H_2O-DMSO(59.4)	-4.09±0.30	-2.00±0.07	-0.75±0.31	
51. H_2O-DMSO(70.0)	-4.09±0.44	-2.10±0.06	-0.85±0.45	
52. H_2O-DMSO	-4.21±0.14	-2.27±0.11	-0.90±0.18	
53. DMSO	-4.04±0.08	-2.62±0.10	-1.42±0.13	
54. H_2O-D(4.86)	-3.14±0.25	-1.02±0.08	-0.72±0.27	ρ^o_{os} for H_2O-D(5.03)
55. H_2O-D(14.3)	-3.47±0.07	-1.33±0.02	-0.70±0.08	ρ^o_{os} for H_2O-D(13.6)
56. H_2O-D(32.3)	-3.41±0.08	-1.49±0.03	-0.92±0.09	ρ^o_{os} for H_2O-D(33.9)
57. H_2O-D(48.2)	-3.24±0.15	-1.53±0.04	-1.12±0.17	ρ^o_{os} for H_2O-D(50.0)

Table 1 (continued)

Medium	ρ°_{js}	ρ°_{os}	ρ°_{oo}, calc.	Notes
58. An	-2.74±0.17	-1.80±0.08	-1.90±0.21	
Acidic dissociation of m- and p-substituted thiophenols				
59. H_2O	-1.97±0.10			$\rho^{\circ}_{js} = \rho^{\circ}_{jo}$
60. H_2O-EtOH(22.3),22°C	-2.71±0.09	-1.49±0.02	-0.75±0.10	
61. H_2O-EtOH(85.5)	-2.78±0.15	-1.80±0.19	-0.99±0.28	
Acidic dissociation of m- and p-substituted N,N-dimethylanilinium ions, 25°C				
62. H_2O	-3.35±0.09			$\rho^{\circ}_{js} = \rho^{\circ}_{jo}$
63. H_2O-EtOH(23.5),50°C	-3.64±0.19	-1.49±0.02	-1.20±0.21	
64. H_2O-EtOH(48.1),	-3.62±0.34	-1.52±0.04	-1.25±0.35	
65. H_2O-D(14.8)	-4.27±0.13	-1.36±0.03	-0.47±0.16	
66. H_2O-DMSO(35.0)	-4.00±0.08	-1.65±0.05	-1.00±0.13	ρ°_{os} for H_2O-DMSO(35.5)
Acidic dissociation of 3-substituted pyridinium icns,25°C				
67. H_2O	-5.78±0.09			$\rho^{\circ}_{js} = \rho^{\circ}_{jo}$
68. CH_3NO_2	-7.32±0.42	-2.50±0.09	-0.96±0.44	
		-1.78±0.19	-0.34±0.47	

Table 1 (continued)

Medium	ρ°_{js}	ρ°_{os}	ρ°_{oo}, calc.	Notes
Acidic dissociation of 3-substituted conjugated acids of pyridine-N-Oxides, 25 °C				
69. H_2O	−2.85±0,11			$\rho^{\circ}_{js} = \rho^{\circ}_{jo}$
70. CH_3NO_2	−4.51±0.12	−2.50±0.09	−0.84±0.19	
		−1.78±0.19	−0.12±0.25	
Alkaline hydrolysis of m- and p- substituted ethyl benzoates, 25 °C				
71. H_2O	1.52±0.06			$\rho^{\circ}_{js} = \rho^{\circ}_{jo}$
72. H_2O-EtOH(23.6)	2.17±0.11	1.49±0.02	0.84±0.13	
73. H_2O-EtOH(33.0)	2.32±0.05	1.57±0.13	0.87±0.15	ρ°_{os} =(1.40+1.73)/2
74. H_2O-EtOH(55.3)	2.48±0.01	1.78±0.11	0.82±0.13	
75. H_2O-EtOH(68.9)	2.45±0.05	1.64±0.05	0.68±0.09	
		1.80±0.28	0.87±0.29	
76. H_2O-EtOH(73.8)	2.34±0.04	1.83±0.26	1.01±0.27	
77. H_2O-D(8.31)	1.98±0.09	1.29±0.06	0.83±0.12	ρ°_{os} =(1.20+1.38)/2
78. H_2O-D(12.4)	2.05±0.10	1.38±0.05	0.85±0.13	ρ°_{os} for H_2O-D(20.0)
79. H_2O-D(17.4)	2.13±0.13	1.39±0.04	0.78±0.14	
80. H_2O-D(24,1),35 °C	2.16±0.04	1.31±0.07	0.67±0.10	
81. H_2O-DMSO(32)	2.35±0.06	1.41±0.04	0.58±0.09	ρ°_{os} for H_2O-DMSO (35.5)
		1.65±0.05	0.82±0.10	

Table 1 (continued)

Medium	ρ°_{js}	ρ°_{os}	ρ°_{oo}, calc.	Notes
82. H_2O-DMSO(59.0)	2.61±0.12	1.82±0.05	0.73±0.18	
		2.00±0.07	0.91±0.18	ρ°_{os} for H_2O-DMSO (59.4)
83. H_2O-DMSO(82.8)	2.99±0.20	1.97±0.01	0.50±0.21	
		2.27±0.11	0.80±0.24	ρ°_{os} for H_2O-DMSO (83.0)
Alkaline hydrolysis of m- and p-substituted phenyl acetates				
84. H_2O ,15°C	0.94±0.08			$\rho^{\circ}_{js} = \rho^{\circ}_{jo}$ 15°C
85. H_2O ,25°C	1.04±0.05			$\rho^{\circ}_{js} = \rho^{\circ}_{jo}$ 25°C
86. H_2O ,35°C	1.00±0.08			$\rho^{\circ}_{js} = \rho^{\circ}_{jo}$ 35°C
87. H_2O ,55°C	1.09±0.23			$\rho^{\circ}_{js} = \rho^{\circ}_{jo}$ 55°C
88. H_2O-EtOH(23.6) 15°C	1.44±0.08	1.49±0.02	0.99±0.11	ρ°_{so} at 25°C
89. H_2O-EtOH(23.6),25°C	1.52±0.06	1.49±0.02	1.01±0.10	ρ°_{os} at 25°C
90. H_2O-EtOH(23.6),35°C	1.42±0.09	1.49±0.02	1.07±0.12	ρ°_{os} at 25°C
91. H_2O-EtOH(23.6),55°C	1.40±0.04	1.49±0.02	1.18±0.23	ρ°_{os} at 25°C
92. H_2O-EtOH(73.6),15°C	1.88±0.08	1.83±0.26	0.89±0.28	ρ°_{os} at 25°C
93. H_2O-EtOH(73.6),25°C	1.94±0.08	1.83±0.26	0.92±0.28	ρ°_{os} at 25°C
94. H_2O-EtOH(73.6),35°C	1.85±0.14	1.83±0.26	0.98±0.30	ρ°_{os} at 25°C
95. H_2O-D(17.5),25°C	1.46±0.09	1.36±0.03	0.94±0.11	
96. H_2O-D(33.1),25°C	1.75±0.06	1.49±0.03	0.78±0.08	

Table 1 (continued)

Medium	ρ°_{js}	ρ°_{os}	ρ°_{oo}, calc.	Notes
97. H_2O-D(45.9), 25°C	1.82±0.07	1.47±0.12	0.69±0.15	
Alkaline hydrolysis of m- and p-substituted phenyl tosylates				
98. H_2O, 60°C	1.81±0.05			$\rho^\circ_{js} = \rho^\circ_{jo}$ at 60°C
99. H_2O, 75°C	1.65±0.05			$\rho^\circ_{js} = \rho^\circ_{jo}$ at 75°C
100. H_2O-EtOH(11.7), 60°C	2.11±0.07	1.34±0.03	1.04±0.08	ρ°_{os} for H_2O-EtOH(16.3)
101. H_2O-EtOH(31.7), 60°C	2.45±0.06	1.40±0.05	0.76±0.09	ρ°_{os} for H_2O-EtOH(29.8)
		1.59±0.13	0.93±0.15	ρ°_{os} = (1.40+1.73)/2
102. H_2O-EtOH(55.3), 60°C	2.63±0.11	1.78±0.11	0.94±0.16	
103. H_2O-$NaClO_4$(5.3M), 75°C	1.28±0.12	0.32±0.24	0.69±0.27	ρ°_{os} for alkaline hydrolysis of phenyl benzoates
Alkaline hydrolysis of m- and p-substituted phenyl benzoates				
104. H_2O, 25°C	1.08±0.07			$\rho^\circ_{js} = \rho^\circ_{jo}$ at 25°C
105. H_2O, 50°C	0.973±0.040			$\rho^\circ_{js} = \rho^\circ_{jo}$ at 50°C
106. H_2O-$NaClO_4$(5.3M)	0.32±0.24	0.57	1.22	ρ°_{os} Found on the basis of the data on alkaline hydrolysis of tosylates

Table 1 (continued)

	Medium	ρ°_{js}	ρ°_{os}	ρ°_{oo},calc.	Notes
	Alkaline hydrolysis of m- and p- substituted phenyldimethyl thiophosphinates				
107.	H_2O,15°C	1.34±0.15			$\rho^\circ_{js} = \rho^\circ_{jo}$ at 15°C
108.	H_2O,25°C	1.34±0.15			$\rho^\circ_{js} = \rho^\circ_{jo}$ at 25°C
109.	H_2O,55°C	1.29±0.07			$\rho^\circ_{js} = \rho^\circ_{jo}$ at 55°C
110.	H_2O-EtOH(23.6),15°C	1.96±0.01	1.49±0.02	0.87±0.15	ρ°_{os} at 25°C
111.	H_2O-EtOH(23.6),25°C	1.87±0.13	1.49±0.02	0.96±0.20	
112.	H_2O-EtOH(23.6),55°C	1.79±0.09	1.49±0.02	0.99±0.18	ρ°_{os} at 25°C
113.	H_2O-EtOH(73.1),25°C	2.20±0.11	1.83±0.26	0.97±0.32	
114.	H_2O-EtOH(73.6),55°C	2.17±0.10	1.83±0.26	0.95±0.29	ρ°_{os} at 25°C
	Solvolysis of m- and p- substituted benzyl chlorides				
115.	H_2O,60°C	-2.04±0.12			$\rho^\circ_{js} = \rho^\circ_{jo}$ at 60°C
116.	H_2O,50°C	-1.89±0.43			$\rho^\circ_{js} = \rho^\circ_{jo}$ at 50°C
117.	H_2O-EtOH(23,6),50°C	-1.66±0.07	1.49±0.02	1.26±0.44	ρ°_{os} at 25°C
118.	H_2O-An(19,7),60°C	-1.36±0.09	1.76	1.08	ρ°_{os} at 25°C,cld. ρ°_{os} (see c/)
119.	H_2O-An(28,8),60°C	-1.20±0.20	1.82	0.98	ρ°_{os} at 25°C,cld. ρ°_{os} (see d/)

Table 1 (continued)

Medium(M%) Temperature °C	ρ^o_{js}	ρ^o_{os}	ρ^o_{oo}, calc.	Notes
120. H_2O-DMSO(21.0),60°C	-1.25±0.09	1.37±0.03	0.58±0.15	ρ^o_{os} at 25°C, = (1.42±1.31)/2
121. H_2O-DMSO(28.5),60°C	-1.07±0.12	1.54±0.06	0.57±0.18	ρ^o_{os} at 25°C, for H_2O-DMSO(26.7)
122. H_2O-DMSO(51.0),60°C	-0.48±0.02	1.88±0.05	0.32±0.13	ρ^o_{os} at 25°C,for H_2O--DMSO(48.6)
Solvolysis of m- and p- substituted cumyl chlorides				
123. H_2O	-5.35±0.11			$\rho^o_{jo} = \rho^o_{js}$(EtOH)-0.66
124. MeOH,25°C	-4.92±0.22	1.39±0.05	0.96±0.25	
125. EtOH,25°C	-4,69±0.09	1.60±0.06	0.94±0.16	
126. i-PrOH 25°C	-4.59±0.18	1.80±0.06	1.04±0.22	

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a) ρ^o_{os} is estimated in terms of the dependence of ρ^o_{os} on M% of ethanol for water - ethanol system

b) ρ^o_{js} is found on data handling without unsubstituted derivative

c) ρ^o_{os} is calculated on the basis of ρ^o_{js} for alkaline hydrolysis of ethyl benzoates

$$\rho^o_{os} = \rho^o_{oo} + (\rho^o_{js} - \rho^o_{jo}) = 0.94 + (2.34 - 1.52) = 1.76$$

d) ρ^o_{os} is calculated on the basis of ρ^o_{js} for alkaline hydrolysis of ethyl benzoates

$$\rho^o_{os} = \rho^o_{oo} + (\rho^o_{js} - \rho^o_{jo}) = 0.94 + (2.40 - 1.52) = 1.82$$

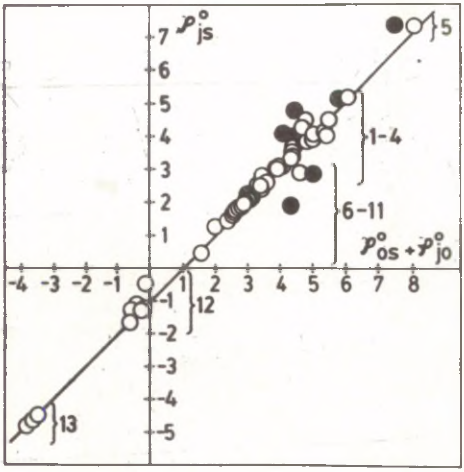

Fig. 1. Plot of ρ°_{js} vs. $(\rho^{\circ}_{os} + \rho^{\circ}_{js})$

●-Significantly deviating alternative values

1-4. — acidic dissociation of phenols, anilinium ions, N,N-dimethylanilinium ions,conjugated acids of pyridine-N--oxides.

5. — acidic dissociation of pyridinium ions

6. — acidic dissociation of thiophenols

7-11. — alkaline hydrolysis of ethyl benzoates, phenyl-tosylates, phenyl acetates, phenyldimethylthiophosphinates

12-13. — solvolysis of benzyl chlorides and cumyl chlorides

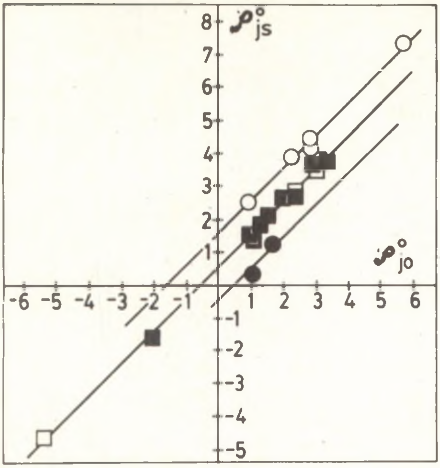

Fig.2. Plot of ρ^{o}_{js} vs. ρ^{o}_{jo} (s=const.s=o refers to water)

□ - EtOH

■ - H_2O-EtOH(23,6M%)

○ - $MeNO_2$

● - H_2O-$NaClO_4$ (5,3M)

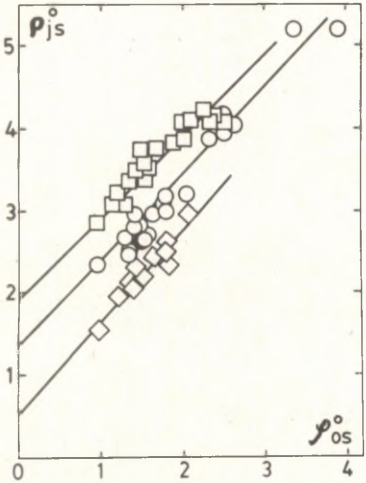

Fig. 3. Plot of ρ^{o}_{js} vs. (j=const.,j=0 refers to acidic dissociation of benzoic acids).

□ -acidic dissociation of anilinium ions

○ -acidic dissociation of phenols

◇ -alkaline hydrolysis of ethyl benzoates

Table 2

Results of Treatment of ρ^o_{js} Values by Eq. (4)

$$\rho^o_{js} = (\rho^o_{os} - \rho^o_{oo}) + \varkappa \cdot \rho^o_{jo} \quad , \; s = \text{const.}$$

Medium s=const.*	$(\rho^o_{os} - \rho^o_{oo})$ by Eq.(4)	$(\rho^o_{os} - \rho^o_{oo})$**	Slope $\varkappa$	r	s	n_j/n^o_j
1. MeOH	0.445±0.018	0.45	1.003±0.025	0.998	0.177	5/5
2. H_2O-EtOH(23,6)	0.415±0.052	0.55	1.050±0.039	0.991	0.170	12/13
3. H_2O-EtOH(73,6)	1.128±0.033	0.89	0.778±0.025	0.996	0.032	8/9
4. EtOH	0.587±0.004	0.66	0.985±0.022	0.999	0.146	4/4
5. i-PrOH	0,776±0.007	0.88	1.000±0.001	0.999	0.062	3/3
6. CH_3NO_2	1.608±0.037	1.56	0.992±0.012	0.999	0.043	4/5
7. CH_3CN	1.735±0.336	1.55	0.886±0.164	0.952	0.229	3/3
8. H_2O-DMSO(35,0)	0.779±0.120	0.71	1.000±0.055	0.994	0.108	4/4
9. H_2O-DMSO(70)	1.167±0.054	1.14	1.035±0.030	0.999	0.042	3/3
10. DMSO	1.919±0.231	1.68	0.803±0.113	0.972	0.158	3/3
11. H_2O-D(24,0)	0.272±0.092	0.37	1.071±0.043	0.997	0.061	4/5

---

* index s=0 refers to water

** index j=0 refers to acidic dissociation of benzoic acids

index ρ^o_{oo} = 0.944±0.017

Table 3

Results of Treatment of ρ°_{js} Values by Eq. (5)

$$\rho^\circ_{js} = (\rho^\circ_{jo} - \rho^\circ_{oo}) + \varkappa \cdot \rho^\circ_{os}\,, \quad j = \text{const}$$

Reaction j*	$(\rho^\circ_{jo}-\rho^\circ_{oo})$ by Eq.(5)	$(\rho^\circ_{jo}-\rho^\circ_{oo})$**	Slope $\varkappa$	r	s	n_s/n°_s
1. Acidic dissociation of phenols	1.150±0.088	1.42	1.061±0.050	0.978	0.144	21/24
2. Acidic dissociation of anilinium ions	2.319±0.139	1.90	0.748±0.085	0.873	0.191	24/24
3. Alkaline hydrolysis of ethyl benzoates	0.791±0.131	0.58	0.954±0.084	0.952	0.110	13/13
4. Alkaline hydrolysis of phenyl acetates	0.118±0.263	0.10	1.035±0.182	0.930	0.116	5/5
5. Alkaline hydrolysis of phenyldimethylphosphinates	0.431±0.001	0.40	0.966±0.001	0.999	0.001	3/3
6. Solvolysis of benzyl chlorides(60 °C)	-3.241±0.117 -2.735±0.651	-2.98 -2.98	1.459±0.082 0.960±0.493	0.993 0.697	0.056 0.232	4/5 4/4 ***
7. Solvolysis of cumyl chlorides	-6.022±0.158	-6.29	0.807±0.009	0.978	0.028	3/3

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*Index j=0 refers to acidic dissociation of benzoic acids

**Inex s=0 refers to water

***Point for solution H_2O -DMSO(51.0) is excluded

From relationships (13) and (15) it follows that:

$$a_{js} \cdot \rho_{jo} = \rho_{js} - \rho_{jo} \tag{17}$$

If $\rho_{js} - \rho_{jo}$ = const, a_{js} is inversely proportional to ρ_{jo} [1,2]. From relationships (12) and (16) it follows that the slopes of the plots of $\lg k^x_{js}$ vs. $\lg k^x_{jo}$

$$a_{js} + 1 = \frac{\rho_{js}}{\rho_{jo}} \tag{18}$$

are not constant neither within the same reaction series, nor within the same solvent (a_{js} depends both on a reaction series and on a solvent). Thus the conclusion can be made that the cases of apparent constancy of the value (18) established within relatively narrow limits of changes of ρ_{js} do not reflect the true picture.

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