

KINETIC STUDY OF ALKALINE HYDROLYSIS OF SUBSTITUTED PHENYL TOSYLATES. XXII. VARIATION OF ORTHO SUBSTITUENT EFFECT WITH SOLVENT

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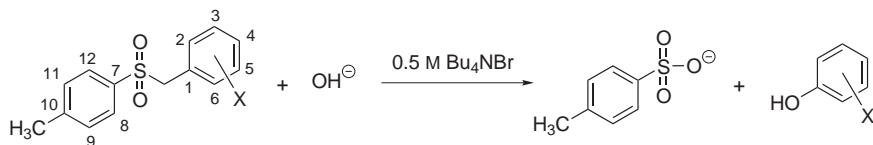
Dedicated to Professor Otto Exner on the occasion of his 80th birthday.

The second-order rate constants k ($\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$) for the alkaline hydrolysis of *meta*-, *para*-, and *ortho*-substituted phenyl tosylates $4\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{OC}_6\text{H}_4\text{-X}$ in aqueous 0.5 M Bu_4NBr have been measured spectrophotometrically in a wide temperature range. The $\log k$ values for *ortho*-substituted derivatives at various temperatures together with *meta*- and *para*-substituted derivatives were analyzed using the modified Fujita-Nishioka equation $\log k_{\text{m,p,ortho}} = c_0 + c_{1(\text{m,p,ortho})}\sigma^\circ + c_{2(\text{ortho})}\sigma_{\text{I}} + c_3(1/T) + c_{4(\text{m,p,ortho})}(1/T)\sigma^\circ + c_{5(\text{ortho})}(1/T)\sigma_{\text{I}}$. In order to study the dependence of substituent effects, especially ortho inductive and resonance terms on different solvent parameters, the following equation was used: $\Delta \log k_{\text{m,p,ortho}} = c_0 + c_{1(\text{m,p,ortho})}\sigma^\circ + c_{2(\text{ortho})}\sigma_{\text{I}} + c_3\Delta E + c_4\Delta Y + c_5\Delta P + c_{6(\text{m,p,ortho})}\Delta E\sigma^\circ + c_{7(\text{m,p,ortho})}\Delta Y\sigma^\circ + c_{8(\text{m,p,ortho})}\Delta P\sigma^\circ + c_{9(\text{ortho})}\Delta E\sigma_{\text{I}} + c_{10(\text{ortho})}\Delta Y\sigma_{\text{I}} + c_{11(\text{ortho})}\Delta P\sigma_{\text{I}}$. $\Delta \log k = \log k^{\text{X}} - \log k^{\text{H}}$, σ° and σ_{I} are the Taft polar and inductive substituent constants, E , Y and P , are the solvent electrophilicity, polarity and polarizability parameters, respectively. In data treatment $\Delta E = E_{\text{S}} - E_{\text{H}_2\text{O}}$, $\Delta Y = Y_{\text{S}} - Y_{\text{H}_2\text{O}}$, $\Delta P = P_{\text{S}} - P_{\text{H}_2\text{O}}$ were used. The solvent electrophilicity was found to be the main factor responsible for changes in the ortho, para, and meta polar substituent effects with medium. The variation of the ortho inductive term with the solvent electrophilicity E_{S} was found to be twice smaller than that for para substituents, while the ortho resonance term appeared to vary with solvent nearly similarly to that for para substituents. The ortho effect caused by the supplementary inductive effect from ortho position was found to disappear in a solvent whose electrophilic solvating power is comparable to pure DMSO ($E \approx 4$).

Keywords: Esters; Sulfonates; Phenyl tosylates; Alkaline hydrolysis; Substituent effects; Ortho effects; Solvent effects; Kinetics.

In previous papers, the dependence of the ortho, para, and meta substituent effects in the alkaline hydrolysis of substituted phenyl tosylates, $4\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{OC}_6\text{H}_4\text{-X}$, and benzoates, $\text{C}_6\text{H}_4\text{CO}_2\text{C}_6\text{H}_4\text{-X}$, in water, aqueous 2.25 M Bu_4NBr , 80% (v/v) DMSO and 5.3 M NaClO_4 (see lit.¹⁻³ and references therein) dependent on temperature was studied.

One purpose of the present work was to extend our study of substituent effects and to obtain more information about variation of the inductive and resonance effects of ortho substituents and polar effect of meta and para substituents with solvent and temperature in the transition from water to aqueous 0.5 M Bu_4NBr . The electrophilic solvating power of the latter is reduced compared to water and 5.3 M NaClO_4 , but higher than that of aqueous 2.25 M Bu_4NBr and 80% (v/v) DMSO. With that aim the second-order rate constants of the alkaline hydrolysis of *ortho*-, *meta*-, and *para*-substituted phenyl tosylates $4\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{OC}_6\text{H}_4\text{-X}$ ($\text{X} = \text{H}$, 4- NO_2 , 4-CN, 3- NO_2 , 3-Cl, 4-Cl, 2- NO_2 , 2-CN, 2-F, 2-Cl, 2- CH_3 , 2- OCH_3) in aqueous 0.5 M Bu_4NBr at various temperatures, were determined and analyzed (Scheme 1).



SCHEME 1

Another goal of the present work was to study the significance of different solvent parameters for the substituent effects, in particular ortho effects, in the alkaline hydrolysis of substituted phenyl tosylates, $4\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{OC}_6\text{H}_4\text{-X}$, on the basis of our earlier kinetic data for various media (water, aqueous 1 M Bu_4NBr , 2.25 M Bu_4NBr , 80% (v/v) DMSO, 5.3 M NaClO_4 , 4.8 M NaCl , 30% EtOH, 60% EtOH, 80% EtOH, lit.^{1,2,4} and references therein) and kinetic data for aqueous 0.5 M Bu_4NBr reported in this work.

The log k values for the alkaline hydrolysis of substituted phenyl tosylates in the case of meta and para substituents were found to be correlated with σ° constants. In water, the inductive influence from ortho position was found to be 1.5-fold stronger than that from para and meta position. In transition from water to aqueous 2.25 M Bu_4NBr and 80% aqueous DMSO media, the electrophilic solvating power of which is reduced compared with water, the polar effect of para and meta substituents was found to be enhanced by about 1.0 units of the ρ° scale (at 75 °C in water $\rho^\circ = 1.7$, in 2.25 M Bu_4NBr $\rho^\circ = 2.7$). In the alkaline hydrolysis of substituted phenyl benzoates the ρ° value changed nearly to the same extent when going from

water to aqueous 2.25 M Bu₄NBr (at 50 °C in water $\rho^\circ = 1.01$, in 2.25 M Bu₄NBr $\rho^\circ = 2.03$)³. The variation of the ortho inductive term with solvent and temperature appeared to be nearly half of that of para substituents. Due to the reduced variation of ortho inductive effect with solvent, compared to that of para substituents, a considerable decrease in the ortho effect (i.e. the difference $\log k_{\text{ortho}}^X - \log k_{\text{para}}^X$) caused by the inductive influence, has been observed while going from water to less electrophilic media (aqueous 2.25 M Bu₄NBr and 80% DMSO). The ortho, meta, and para polar substituent effects were found to decrease and the ortho effect was observed to increase when going from water to an inorganic salt solution like 5.3 M aqueous NaClO₄¹.

The variation of the substituent effects (ρ) with solvent properties has been studied mainly in the case of meta and para substituents. In the study of Koppel and Karelson⁵ the dependence of ρ values on the solvent parameters have been studied for acid dissociation of benzoic acids and phenols including the values for individual solvents and the gas phase, according to a special variant

$$A = A_0 + yY + eE \quad (1)$$

of the Koppel–Palm equation^{6,7}

$$A = A_0 + yY + pP + eE + bB + \delta E_s \quad (2)$$

In Eq. (2) A and A_0 are reactivities or physico-chemical properties in a given medium and in the gas phase (standard medium), respectively; Y is the polarity parameter of solvent as a function of dielectric permittivity ϵ , usually in the form $(\epsilon - 1)/(\epsilon + 2)$ or $(\epsilon - 1)/(2\epsilon + 1)$; P is the polarizability parameter of solvent as a function of refractive index n in the form $(n^2 - 1)/(n^2 + 2)$ or $(n^2 - 1)/(2n^2 + 1)$; E is the electrophilicity parameter based on $E_T(30)$ values⁶⁻⁸, corrected for the influence of solvent polarity Y and polarizability P ; B is the nucleophilicity parameter by Koppel and Paju⁹. The steric parameters E_s , constructed on the basis of isostericity principle¹⁰ take into account steric interactions of the solvent molecules with the solute.

When the variation of substituent effects on the dissociation of some Brønsted acids with solvent was considered⁵, solvent polarity was found to be the main influencing factor. The influence of electrophilicity was found to be somewhat less important, whereas the influence of polarizability and basicity were negligible. Later¹¹, in different reaction series (acid dissociation of benzoic acids, phenols, anilinium ions, pyridinium ions; alkaline

hydrolysis of esters and solvolysis of benzyl chlorides) the solvent electrophilicity was found to be the main factor that influences polar effects of substituents, while solvent polarity appeared to be considerably less important.

The variation of the ortho substituent effects with solvent parameters and simultaneously with meta and para substituents is studied to an essentially lesser extent. In the alkaline hydrolysis of substituted phenyl tosylates⁴, 4-CH₃C₆H₄SO₂OC₆H₄-X, the ortho inductive term was found to increase with decreasing solvent electrophilicity properties more than twice less than the inductive term. In the alkaline hydrolysis of substituted phenyl tosylates, 4-CH₃C₆H₄SO₂OC₆H₄-X, the data for *ortho*-substituted derivatives simultaneously with *meta*- and *para*-substituted derivatives have been analyzed according to the modified Fujita and Nishioka¹² equation (3) including the data for various media (water, aqueous 80% DMSO, aqueous 5.3 M NaClO₄, 4.8 M NaCl, 1 M Bu₄NBr, 2.25 M Bu₄NBr and 30, 60, and 80% aqueous ethanol) at 75 °C.

$$\Delta \log k_{m,p,ortho} = c_0 + c_{1(m,p,ortho)}\sigma^\circ + c_{2(ortho)}\sigma_I + c_3\Delta E + c_{4(m,p,ortho)}\Delta E\sigma^\circ + c_{5(ortho)}\Delta E\sigma_I \quad (3)$$

In Eq. (3) $\Delta \log k = \log k^X - \log k^H$, the difference in solvent electrophilicities, $\Delta E = E_S - E_{H_2O}$, was used as parameter of the medium. In Eq. (3) the reaction constants c_1 and c_4 are common for ortho, meta, and para substituents but c_2 and c_5 refer only to ortho substituents. In Eq. (3) Fujita and Nishioka¹² assumed that $(\sigma^\circ)_{ortho} - (\sigma^\circ)_{para}$. The terms $c_{2(ortho)}\sigma_I$ and $c_{5(ortho)}\Delta E\sigma_I$ are a measure of the additional ortho inductive effect (compared to the para inductive effect) for water and the additional ortho inductive effect dependent on the ΔE parameter in the transition from pure water to binary aqueous solutions, respectively.

In the present work, the supplementary kinetic data were available for the study variation of substituent effects with solvent in the alkaline hydrolysis of substituted phenyl tosylates according to the multilinear relationship and, in addition to the solvent electrophilicity (E) scale, the solvent polarity (Y), and polarizability (P) scales were included.

EXPERIMENTAL

The preparation procedure and characteristics of the substituted phenyl tosylates and technique of kinetic measurements are described in lit.^{1,2,4} and references therein. 2-Cyano- and 4-cyanophenyl tosylates were synthesized by the reaction of tosyl chloride with the corre-

sponding cyanophenols in 1 M aqueous Na_2CO_3 solution¹³ and recrystallized from 60% aqueous ethanol. Both the phenyl tosylates were dried in a desiccator over P_2O_5 . The esters were identified by melting points and NMR spectroscopy chemical shifts (see Scheme 1). ^1H and proton-decoupled ^{13}C NMR spectra of compounds were measured in CDCl_3 at 300 K on a Bruker AC-200 spectrometer. The chemical shifts (δ , ppm) are referenced to an internal TMS (δ 0). Coupling constants (J) are given in Hz.

2-Cyanophenyl tosylate: m.p. 88–89 °C. ^1H NMR: 2.46 s, 3 H (CH_3); 7.34–7.68 m, 6 H (H-3, H-4, H-5, H-6, H-9, H-11); 7.72 d, 2 H, $^3J = 8.5$ (H-8, H-12). ^{13}C NMR: 21.77 (CH_3); 114.44 (CN); 150.38 (C-1); 107.91 (C-2); 138.77 (C-3); 127.36 (C-4); 134.26 (C-5); 123.81 (C-6); 146.36 (C-7); 128.84 (C-8, C-12); 130.10 (C-9, C-11); 131.80 (C-10).

4-Cyanophenyl tosylate: m.p. 90.4–90.9 °C. ^1H NMR: 2.46 s, 3 H (CH_3); 7.14 d, 2 H, $^3J = 9.0$ (H-2, H-6); 7.35 d, 2 H, $^3J = 8.5$ (H-9, H-11); 7.62 d, 2 H, $^3J = 9.0$ (H-3, H-5); 7.72 d, 2 H, $^3J = 8.5$ (H-8, H-12). ^{13}C NMR: 21.73 (CH_3); 117.00 (CN); 152.66 (C-1); 123.43 (C-2, C-6); 133.91 (C-3, C-5); 111.26 (C-4); 146.13 (C-7); 128.47 (C-8, C-12); 130.06 (C-9, C-11); 132.04 (C-10).

As the reagent, 0.0950 M tetrabutylammonium hydroxide was used. A carbon dioxide-free tetrabutylammonium hydroxide solution was prepared from 10% aqueous Bu_4NOH (Chemapol, reagent for polarography) by passing the hydroxide solution through an anion-exchange column (Amberlite IRA-400) in argon atmosphere. The salt, Bu_4NBr (pure grade, Reakhim, Moscow), was purified by triple recrystallization from acetone, precipitated with ether and dried in vacuum.

The kinetics was measured spectrophotometrically as described earlier¹. To avoid salt effect on kinetic measurements, a nearly constant alkali concentration was used. The pseudo-first-order rate constants, k_1 (s^{-1}), were determined using a least-squares computer program. The second-order rate constants k ($\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$) were calculated by dividing the pseudo-first-order rate constants k_1 (s^{-1}) by alkali concentration. The kinetic measurements were repeated more than three times for each derivative and the average values of the second-order rate constants k ($\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$) were calculated. The k values for substituted phenyl tosylates in aqueous 0.5 M Bu_4NBr , the number of measurements and the wavelength λ used in spectrophotometric kinetic measurements are given in Table I.

DATA PROCESSING

For study of the substituent effects on a single temperature, the $\log k$ values of the alkaline hydrolysis of substituted phenyl tosylates were treated according to the Taft equation (4), the modified Fujita and Nishioka¹² equation (5), and the Charton¹⁴ equation (6):

$T = \text{const.}$, X is not constant

$$\log k_{\text{m,p}} = \log k_0 + (\rho^\circ)_{\text{m,p}} \sigma^\circ \quad (4)$$

$$\log k_{\text{m,p,ortho}} = \log k_0 + (\rho^\circ)_{\text{m,p,ortho}} \sigma^\circ + c_{\text{I(ortho)}} \sigma_{\text{I}} \quad (5)$$

$$\log k_{\text{ortho}} = \log k_0 + (\rho^\circ_{\text{I}})_{\text{ortho}} \sigma_{\text{I}} + (\rho^\circ_{\text{R}})_{\text{ortho}} \sigma^\circ_{\text{R}} \quad (6)$$

TABLE I
The second-order rate constants k (in $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$) for alkaline hydrolysis of substituted phenyl tosylates, $4\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{OC}_6\text{H}_4\text{-X}$, in aqueous $0.5 \text{ M Bu}_4\text{NBr}$ at various temperatures^a

X	λ^b nm	T, °C	$10^2 k^c$ $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$	n^d	X	λ^b nm	T, °C	$10^2 k^c$ $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$	n^d
4-NO ₂	410	40	1.78 ± 0.01	3	2-NO ₂	430	40	2.89 ± 0.05	3
		50	3.75 ± 0.07	4			50	6.03 ± 0.01	3
		60	6.77 ± 0.19	3			60	9.80 ± 0.15	4
		75	20.1 ± 2.4	3			75	26.2 ± 0.8	7
4-CN	295	40	0.807 ± 0.035	4	2-CN	330	40	2.24 ± 0.02	3
		50	2.04 ± 0.01	4			50	4.49 ± 0.14	4
		60	4.20 ± 0.53	4			60	7.55 ± 0.19	4
		75	9.43 ± 0.33	3			75	21.6 ± 0.1	3
3-NO ₂	295	40	0.792 ± 0.039	3	2-F	290	40	0.131 ± 0.004	3
		50	1.95 ± 0.08	4			50	0.317 ± 0.006	3
		60	3.97 ± 0.21	3			60	0.557 ± 0.068	5
		75	10.7 ± 0.3	3			75	2.09 ± 0.10	4
3-Cl	295	40	0.104 ± 0.013	3	2-Cl	295	40	0.142 ± 0.001	3
		50	0.252 ± 0.012	6			50	0.294 ± 0.007	3
		60	0.621 ± 0.026	3			60	0.603 ± 0.037	4
		75	1.80 ± 0.20	3			75	2.07 ± 0.02	3
4-Cl	302	50	0.145 ± 0.007	3	2-CH ₃	290	50	0.00826 ± 0.00018	3
		60	0.334 ± 0.005	3			60	0.0178 ± 0.0005	3
		75	1.16 ± 0.02	3			75	0.0877 ± 0.0023	3
H	295	50	0.0224 ± 0.0005	3			80	0.131 ± 0.014	5
		60	0.0650 ± 0.0021	4	2-OCH ₃	295	50	0.0105 ± 0.0002	3
		75	0.208 ± 0.006	4			60	0.0294 ± 0.0059	3
		85	0.331 ± 0.003	3			75	0.120 ± 0.006	3
						80	0.165 ± 0.015	3	

^a Aqueous $0.0950 \text{ M Bu}_4\text{NOH}$ was used. ^b λ is the wavelength used in kinetic measurements. ^c k is the arithmetic mean value of the second-order rate constants with value of standard deviation of arithmetic mean. ^d n equals to the number of the remaining k values after exclusion of significantly deviating rate constants in the calculation of the arithmetic mean values.

The activation parameters $\log A$ and activation energy E values were calculated according to Eq. (7):

$T \neq \text{const.}$, X is constant

$$\log k = \log A - (E/2.3RT) . \quad (7)$$

To study the influence of the substituent effects dependent on temperature, the $\log k$ values were subjected to a regression analysis using Eq. (8):

$T \neq \text{const.}$, X is not constant

$$\begin{aligned} \log k_{\text{m,p,ortho}} = & c_0 + c_{1(\text{m,p,ortho})}\sigma^\circ + c_{2(\text{ortho})}\sigma_{\text{I}} + c_3(1/T) + \\ & + c_{4(\text{m,p,ortho})}(1/T)\sigma^\circ + c_{5(\text{ortho})}(1/T)\sigma_{\text{I}} . \end{aligned} \quad (8)$$

To study the influence of solvent effects on variation of substituent effects the $\Delta \log k = \log k^{\text{X}} - \log k^{\text{H}}$ values for *ortho*-, *meta*-, and *para*-substituted derivatives at 75 °C in various media were correlated with Eqs (9) and (10):

$$\begin{aligned} \Delta \log k_{\text{m,p,ortho}} = & c_0 + c_{1(\text{m,p,ortho})}\sigma^\circ + c_{2(\text{ortho})}\sigma_{\text{I}} + c_3\Delta E + c_4\Delta Y + \\ & + c_5\Delta P + c_{6(\text{m,p,ortho})}\Delta E\sigma^\circ + c_{7(\text{m,p,ortho})}\Delta Y\sigma^\circ + \\ & + c_{8(\text{m,p,ortho})}\Delta P\sigma^\circ + c_{9(\text{ortho})}\Delta E\sigma_{\text{I}} + c_{10(\text{ortho})}\Delta Y\sigma_{\text{I}} + \\ & + c_{11(\text{ortho})}\Delta P\sigma_{\text{I}} \end{aligned} \quad (9)$$

$$\begin{aligned} \Delta \log k_{\text{ortho}} = & a_0 + a_1\sigma_{\text{I}} + a_2\sigma_{\text{R}}^\circ + a_3\Delta E + a_4\Delta Y + \\ & + a_5\Delta P + a_6\Delta E\sigma_{\text{I}} + a_7\Delta Y\sigma_{\text{I}} + a_8\Delta P\sigma_{\text{I}} + \\ & + a_9\Delta E\sigma_{\text{R}}^\circ + a_{10}\Delta Y\sigma_{\text{R}}^\circ + a_{11}\Delta P\sigma_{\text{R}}^\circ . \end{aligned} \quad (10)$$

The inductive effect from the ortho position, different from that from the meta and para derivatives, was assumed^{12,15}. Similarly, in the case of ortho substituents, the variation of the inductive term with temperature and solvent parameters, different from that for meta and para derivatives, was assumed. As a measure of the ortho effect, the additional inductive term and the corresponding cross-terms for ortho substituents were included. For ortho substituents, the resonance term and its variation with temperature and solvent parameters were considered to be equal to those for para substituents.

Equations (4)–(6) and (9) include data at a single temperature, Eq. (8) at various temperatures. The data for *meta*- and *para*-substituted phenyl esters simultaneously with *ortho*-substituted esters were treated according to Eqs (5), (8), and (9). The data for only *ortho*-substituted derivatives were treated according to Eqs (6) and (10), and for *meta*- and *para*-substituted esters with Eqs (4), (8), and (9) to compare the susceptibilities obtained with those determined with the simultaneous use of data for *ortho*-, *meta*-, and *para*-substituted derivatives. In processing of data for *ortho*-substituted derivatives with Eqs (6) and (10), the log k value for the unsubstituted derivative ($X = H$) as standard was included besides the *ortho*-substituted derivatives.

The Taft polar σ° ^{16,17}, inductive σ_I ¹⁸ and resonance σ°_R ($\sigma^\circ_R = (\sigma^\circ)_{para} - \sigma_I$)¹⁹ scales were used in the data processing (Table II). In the data processing $(\sigma^\circ)_{ortho} = (\sigma^\circ)_{para}$ were used. The previous statistical data treatment^{1,4}

TABLE II

Substituent parameters used for correlation and values of log A and activation energy E (in kJ mol⁻¹) for alkaline hydrolysis of substituted phenyl tosylates, 4-CH₃C₆H₄SO₂OC₆H₄-X, in aqueous 0.5 M Bu₄NBr, calculated using Eq. (7)

X	σ° ^{16,17}	σ_I ¹⁸	σ°_R ¹⁹	log A	E , kJ mol ⁻¹	R	s	n
H	0	0	0	9.856 ± 0.470	83.44 ± 3.05	0.998	0.033	4
				9.486 ± 0.343	81.00 ± 2.18	0.999	0.034	5 ^a
4-NO ₂	0.81	-	-	8.617 ± 0.376	62.20 ± 2.36	0.998	0.029	4
4-CN	0.72	-	-	8.523 ± 0.685	63.40 ± 4.39	0.993	0.053	4
3-NO ₂	0.71	-	-	9.089 ± 0.321	66.96 ± 2.01	0.999	0.025	4
3-Cl	0.37	-	-	9.417 ± 0.270	74.30 ± 1.70	0.999	0.021	4
4-Cl	0.28	-	-	9.771 ± 0.236	78.06 ± 1.51	0.999	0.012	3
2-NO ₂	0.81	0.63	0.19	7.822 ± 0.419	56.10 ± 2.64	0.997	0.033	4
2-CN	0.72	0.58	0.11	8.005 ± 0.465	57.94 ± 2.93	0.996	0.036	4
2-Cl	0.28	0.47	-0.20	8.691 ± 0.531	69.34 ± 3.33	0.997	0.041	4
2-F	0.21	0.52	-0.35	8.842 ± 0.735	70.34 ± 4.64	0.994	0.057	4
2-CH ₃	-0.14	-0.05	-0.10	10.411 ± 0.790	89.91 ± 5.11	0.995	0.056	4
2-OCH ₃	-0.15	0.25	-0.41	10.289 ± 0.383	88.21 ± 2.49	0.999	0.027	4

^a The log $k = -4.001$ value calculated with Eq. (4) at 40 °C, was included in addition to the experimental log k values.

confirmed that there was no resonance in the case of 2-N(CH₃)₂ substituent and in the common data treatment the correction $\rho\sigma^{\circ}_R$ was added. In the case of *ortho*-substituted derivatives, the σ_1 scale was included for taking into consideration the additional inductive effect from *ortho* position. Mainly the following substituents were included: X = H, 4-NO₂, 3-NO₂, 4-CN, 4-Cl, 3-Cl, 4-NH₂, 3-NH₂, 4-N(CH₃)₂, 3-N(CH₃)₂, 4-CH₃, 3-CH₃, 4-OCH₃, 3-OCH₃, 2-NO₂, 2-CN, 2-F, 2-Cl, 2-CH₃, 2-OCH₃, 2-NH₂, 2-N(CH₃)₂.

In the data processing according to Eqs (4)–(8) the second-order rate constants k_2 of the alkaline hydrolysis of *ortho*-, *meta*-, and *para*-substituted phenyl tosylates in 0.5 M aqueous Bu₄NBr at various temperatures, reported in Table I, were used. In Eqs (9) and (10) the analogous data for the alkaline hydrolysis of *ortho*-, *meta*-, and *para*-substituted phenyl tosylates at 75 °C in pure water, aqueous 0.5 M Bu₄NBr (present work), 1 M Bu₄NBr, 2.25 M Bu₄NBr, 80% (v/v) DMSO, 5.3 M NaClO₄, and 4.8 M NaCl (lit.^{1,2,4} and references therein) were included. In Eq. (9) the values of ΔE , ΔY , and ΔP are the differences in electrophilicities, polarities and polarizabilities on going from pure water to the corresponding aqueous binary solution, $\Delta E = E_S - E_{H_2O}$, $\Delta Y = Y_S - Y_{H_2O}$, and $\Delta P = P_S - P_{H_2O}$, respectively. The standard medium, where ΔE , ΔY , and ΔP are equal to zero, is pure water and the standard substituent is X = H. The electrophilicity E values of Koppel and Palm^{8,20–22}, polarity Y calculated as function of dielectric permittivity ϵ in the form $(\epsilon - 1)/(\epsilon + 2)$ and the polarizability P as a function of refractive index n_D in the form $(n^2 - 1)/(n^2 + 2)$ were used.

The data processing was carried out using a multiple-parameter linear least-squares (LLSQ) procedure²³. The significantly deviating points were excluded using the Student criterion. The exclusion of the significantly deviating points was performed on different confidence level of the t -test²³. Results of the data treatment in the present work are given mainly on the confidence level 0.99.

The substituent parameters used in the correlations and the values of log A and activation energies, E (kJ mol⁻¹), for aqueous 0.5 M Bu₄NBr calculated with the Arrhenius equation (7), are listed in Table II. The results of the data treatment with Eqs (4)–(6) at various temperatures and those including various temperatures (Eq. (8)) are presented in Tables III and IV, respectively. The values of solvent characteristics used in data treatment are listed in Table V. The results of the data treatment with Eq. (9) are collected in Table VI. The dependence of $(\rho^{\circ})_{m,p}$ and $(\rho_1)_{ortho}$ on $(1/T)$ and on the solvent electrophilicity ΔE are shown in Figs 1 and 2.

DISCUSSION

Influence of Substituents and Temperature in aqueous 0.5 M Bu₄NBr

The alkaline hydrolysis of substituted phenyl tosylates, 4-CH₃C₆H₄SO₂OC₆H₄-X, is considered to proceed by bimolecular nucleophilic substitution mechanism S_N2³⁵⁻³⁷, which involves the attack of the negatively charged hydroxide ion on the sulfur atom. The acyl-oxygen bondbreaking has been proved. The positive ρ values for the alkaline hydrolysis of substituted phenyl tosylates indicate that electron-withdrawing groups stabilize the transition state by delocalization of the fractional negative charge in the transition complex. The electron-donating groups destabilize the transition state with negative charge or stabilize the ground state of esters by decreasing the fractional positive charge on the sulfur atom in esters of 4-methylbenzene-1-sulfonic acid.

For most substituted phenyl tosylates the transitions from pure water to aqueous 0.5 M Bu₄NBr solution result in a decrease in the rate constants of alkaline hydrolysis. The retardation was found to be lower for esters with

TABLE III

Results of the correlation with Eqs (4)–(6) for alkaline hydrolysis of substituted phenyl tosylates, 4-CH₃C₆H₄SO₂OC₆H₄-X, in aqueous 0.5 M Bu₄NBr at various temperatures^a

T °C	Equation	log k ₀	(ρ ^o) _{m,p(ortho)}	c _{I(ortho)} OR ρ _{I(ortho)}	(ρ ^o _R) _{ortho}	R	s ₀	n/n ₀
75	(4)	-2.645 ± 0.043	2.356 ± 0.076	-	-	0.997	0.07	6/6
	(5)	-2.635 ± 0.083	2.309 ± 0.084	0.543 ± 0.110	-	0.994	0.11	12/12
	(6)	-2.730 ± 0.106	-	3.041 ± 0.203	1.922 ± 0.252	0.991	0.13	7/7
60	(4)	-3.168 ± 0.019	2.489 ± 0.033	-	-	0.999	0.03	6/6
	(5)	-3.178 ± 0.048	2.482 ± 0.070	0.462 ± 0.094	-	0.996	0.09	12/12
	(6)	-3.240 ± 0.107	-	3.092 ± 0.206	2.188 ± 0.252	0.992	0.013	7/7
50	(4)	-3.624 ± 0.019	2.709 ± 0.034	-	-	0.999	0.024	6/6
	(5)	-3.640 ± 0.038	2.729 ± 0.055	0.495 ± 0.078	-	0.998	0.058	11/12
	(6)	-3.709 ± 0.130	-	3.491 ± 0.250	2.278 ± 0.307	0.990	0.14	7/7
40	(4)	-4.001 ± 0.089	2.712 ± 0.160	-	-	0.995	0.10	4/4
	(5)	-3.995 ± 0.079	2.694 ± 0.110	0.682 ± 0.140	-	0.993	0.118	10/10 ^b

^a c_{I(ortho)} is the susceptibility to the additional ortho inductive effect in Eq. (5). ^b The log k = -4.001 value for unsubstituted derivative calculated with Eq. (4) and the log k values for 2-OCH₃- and 2-CH₃-derivatives calculated with Eq. (7) (-4.386 and -4.584, respectively) were included in addition to the experimental log k values.

TABLE IV

Results of the correlation of kinetic data with Eq. (8) for alkaline hydrolysis of substituted phenyl tosylates in 0.5 M Bu₄NBr at various temperatures

Reaction constant	<i>meta</i> - and <i>para</i> -substituted derivatives	Weight	<i>ortho</i> -, <i>meta</i> - and <i>para</i> -substituted derivatives	Weight
c_0	9.778 ± 0.373		9.433 ± 0.575	
$c_{1(m,p,ortho)}$	-1.305 ± 0.416	0.75	-0.853 ± 0.973	0.82
$c_{2(ortho)}$	–		-1.128 ± 1.399	0.045
$c_3 \times 10^{-3}$	-4.317 ± 0.126	0.24	-4.210 ± 0.190	0.14
$c_{4(m,p,ortho)} \times 10^{-3}$	1.271 ± 0.373	0.044	1.122 ± 0.322	0.01
$c_{5(ortho)} \times 10^{-3}$	–		0.566 ± 0.464	0.01
n/n_0	23/23 ^a		49/49 ^a	
R	0.999		0.995	
s	0.037		0.098	
s_0	0.043		0.099	
t	0.999		0.999	

^a The log $k = -4.001$ value for unsubstituted derivative calculated with Eq. (4) at 40 °C was included in addition to the experimental log k values. ^b The log $k = -4.001$ value for unsubstituted derivative calculated with Eq. (4) at 40 °C and the log k values for 2-OCH₃-derivatives calculated with Eq. (7) (-4.386) were included in addition to the experimental log k values.

TABLE V

The values of electrophilicity E , dielectric permittivity ϵ , refractive index n_D , polarizability $P = (n^2 - 1)/(n^2 + 2)$, and polarity $Y = (\epsilon - 1)/(\epsilon + 2)$ at 25 °C for aqueous solutions

Medium	$E^{20-22,23}$	n_D^{20-23}	ϵ	P	Y	ΔE	ΔP	ΔY
Water	21.74	1.333	78.39 ²⁴	0.2057	0.9627	0	0	0
0.6 M Bu ₄ NBr ^a	16.53	1.363	61.2 ²⁵	0.2223	0.9525	-5.21	0.0166	-0.0102
1.0 M Bu ₄ NBr	13.77	1.383	50.5 ²⁵	0.2333	0.9429	-7.97	0.0276	-0.0198
2.25 M Bu ₄ NBr	8.11	1.447	60.29 ²⁶	0.2672	0.9518	-13.63	0.00615	-0.0109
5.3 M NaClO ₄	25.53 ^b	1.3719 ²⁸	32.4 ²⁷	0.2272	0.9128	3.79	0.0215	-0.0499
80% DMSO	7.93	1.455 ²⁹	63.8 ³⁰	0.2713	0.9544	-13.81	0.0656	-0.0083
4.8 M NaCl	22.34 ^b	1.3757 ³¹	43.33 ³²	0.2293	0.9338	0.60	0.0236	-0.0289
30% EtOH	16.67	1.3506 ³¹	63.6 ³⁴	0.2155	0.9543	-5.07	0.0098	-0.0084
60% EtOH	13.84	1.3626 ³¹	46.7 ³⁴	0.2221	0.9384	-8.30	0.0164	-0.0243
80% EtOH	12.83	1.3657 ³¹	34.7 ³⁴	0.2238	0.9183	-9.22	0.0181	-0.0444

^a In the case of aqueous 0.5 M Bu₄NBr solution the characteristics for 0.6 M Bu₄NBr were used as much as the concentration of Bu₄NOH was taken into account. ^b Determined for methanolic solution.

TABLE VI

Results of the correlation with Eqs (9) and (10) for kinetic data of alkaline hydrolysis of substituted phenyl tosylates, 4-CH₃C₆H₄SO₂OC₆H₄-X, in various media at 75 °C ^{a,b,c}. Solvent electrophilicity parameter, Δ*E*, was included

Reaction constant	Meta, para substituents Eq. (9)	Weight	Ortho, meta, para substituents Eq. (9)	Weight	Ortho substituents Eq. (10)	Weight
<i>c</i> ₀ (<i>a</i> ₀)	0.057 ± 0.039 0.052 ± 0.033 ^a		0.047 ± 0.027 0.045 ± 0.025 ^a		-0.019 ± 0.069 -0.037 ± 0.071 ^a	
<i>c</i> _{1(m,p,ortho)}	1.806 ± 0.062 1.818 ± 0.056 ^a	0.95 0.96	1.863 ± 0.015 1.806 ± 0.012 ^a	0.91 0.93	- -	
<i>c</i> _{2(ortho)}	- -		0.853 ± 0.005 0.832 ± 0.003 ^a	0.06 0.05	- -	
<i>a</i> _{1(ortho)}	- -		- -		2.772 ± 0.124 2.802 ± 0.017 ^a	0.63 0.64
<i>a</i> _{2(ortho)}	- -		- -		1.704 ± 0.131 1.710 ± 0.019 ^a	0.34 0.35
<i>c</i> ₃ (<i>a</i> ₃)	0.025 ± 0.0036 0.0033 ± 0.0001 ^a	0.04 0.03	0.0094 ± 0.0016 0.0051 ± 0.0022 ^a	0.002 0.002	0.0037 ± 0.0060 0.0053 ± 0.0066 ^a	0.001 0.004
<i>c</i> _{6(m,p,ortho)}	-0.656 ± 0.0077 -0.0698 ± 0.0069 ^a	0.003 0.004	-0.0699 ± 0.0046 -0.0856 ± 0.0042 ^a	0.03 0.015	- -	
<i>c</i> _{9(ortho)}	- -		0.0360 ± 0.0085 0.0480 ± 0.0070 ^a	0.001 0.001	- -	
<i>a</i> _{6(ortho)}	- -		- -		-0.0346 ± 0.0143 -0.0406 ± 0.0154 ^a	0.004 0.004
<i>a</i> _{9(ortho)}	- -		- -		-0.0751 ± 0.0151 -0.0747 ± 0.0163 ^a	0.014 0.011
<i>n/n</i> ₀	45/45 60/60 ^a		75/85 95/115 ^a		47/47 64/64 ^a	
<i>R</i>	0.990 0.992 ^a		0.995 0.996 ^a		0.989 0.987 ^a	
<i>s</i>	0.119 0.112 ^a		0.102 0.083 ^a		0.154 0.169 ^a	
<i>s</i> ₀	0.144 0.133 ^a		0.105 0.088 ^a		0.149 0.160 ^a	
<i>t</i>	0.999 0.999 ^a		0.95 0.95 ^a		0.999 0.999 ^a	

^a The log *k* values for 30, 60, and 80% aqueous EtOH at 60 °C as well as for pure water, 0.6 M Bu₄NBr, 1.0 M Bu₄NBr, 2.25 M Bu₄NBr, 80% DMSO, 5.3 M NaClO₄, 4.8 M NaCl at 75 °C were included. ^b The program makes it possible to treat data in four different ways: 1. Exclusion of insignificant argument scales was performed before excluding considerably deviating points. 2. Exclusion of significantly deviating points was performed before excluding insignificant argument scales. Both ways of data treatment have two different modes of forming cross terms: (i) Cross terms can be formed from centered basic argument scales. (ii) Cross terms are formed from non-centered basic argument scales. When the values for insignificant scales are shown, the cross terms were formed from centered basic argument scales.

^c A table containing the results of the correlations with Eqs (9) and (10) for kinetic data of alkaline hydrolysis of substituted phenyl tosylates, 4-CH₃C₆H₄SO₂OC₆H₄-X, in various media at 75 °C when three solvent parameters, the solvent electrophilicity, Δ*E*, the solvent polarity, Δ*Y*, and the solvent polarizability, Δ*P*, were included, is available as supplementary material (Table SI).

electron-withdrawing substituents but higher in the case of electron-donating substituents. When going from water to aqueous 0.5 M Bu_4NBr for 4- NO_2 -substituted derivative no decrease in the rate of alkaline hydrolysis at 75 °C was detected but for the unsubstituted derivative the decrease in the log k value was found to be about 0.5 units compared with the corresponding values in water¹.

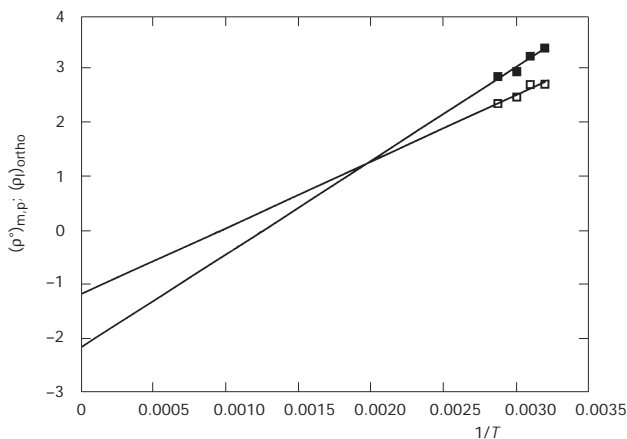


FIG. 1

Dependence of $(\rho^\circ)_{m,p}$ and $(\rho_1)_{ortho}$ on $(1/T)$ for the alkaline hydrolysis of substituted phenyl tosylates in 0.5 M aqueous Bu_4NBr : ■ ortho substituents, □ meta and para substituents

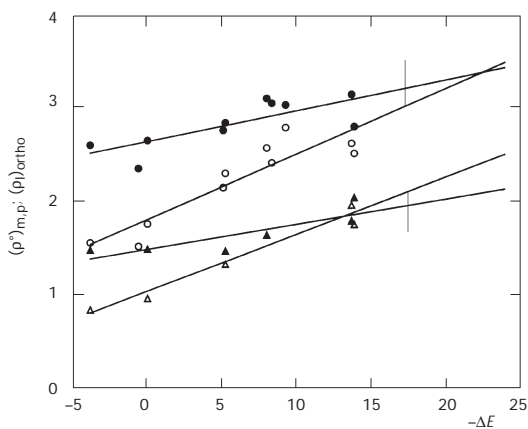


FIG. 2

Dependence of $(\rho^\circ)_{m,p}$ and $(\rho_1)_{ortho}$ on the solvent electrophilicity ΔE for the alkaline hydrolysis of substituted phenyl tosylates^{1,2,4} and benzoates³ in various media. Shaded circles and triangles denote *ortho*-substituted derivatives

Earlier the variation of the reaction rates due to the polar effect of substituents in the alkaline hydrolysis of *meta*- and *para*-substituted phenyl tosylates was described by σ° constants. In the case of *ortho* derivatives, the influence of substituents appeared to be well described when the complementary inductive scale was included. For the alkaline hydrolysis of substituted phenyl tosylates in water, the inductive effect from *ortho* position was found to exceed that from *para* position, but the resonance from *ortho* position appeared to be equal to that from *para* position.

In aqueous 0.5 M Bu₄NBr the log k values for *meta*- and *para*-substituted derivatives gave excellent correlation with σ° constants (Eq. (4), Table III) as was found earlier^{1,2,4} for water, aqueous 2.25 M Bu₄NBr, 5.3 M NaClO₄, 80% DMSO as well as for 30, 60, and 80% aqueous ethanol. When data for *ortho*-substituted derivatives were treated simultaneously with *meta* and *para* derivatives (Eq. (5)), the additional inductive σ_1 scale was included for *ortho* substituents. When only *ortho*-substituted derivatives were treated, the Charton equation (6) was used. The values of reaction constants for *ortho*-substituted derivatives (ρ_I)_{ortho}, and (ρ_R)_{ortho} calculated with Eq. (6) separately for *ortho*-substituted derivatives were approximately the same when calculated simultaneously with *ortho*-, *meta*-, and *para*-substituted derivatives: (ρ_I)_{ortho} = (ρ°)_{m,p,ortho} + $c_{1(\text{ortho})}$ and (ρ_R)_{ortho} = (ρ°)_{m,p,ortho} (see Table III).

The (ρ°)_{m,p} and (ρ_I)_{ortho} for 0.5 M Bu₄NBr at various temperatures ranged between 2.3–2.7 and 2.9–3.4, respectively. Earlier the (ρ°)_{m,p} and (ρ_I)_{ortho} for pure water were found in ranges 1.75–1.88 and 2.8–3.0⁴. In transition from pure water to aqueous 0.5 M Bu₄NBr the polar effect of *meta* and *para* substituents increased by ca. 0.5–0.6 units of (ρ°)_{m,p}. At the same time the change in the susceptibility to the *ortho* inductive effect, (ρ_I)_{ortho}, was essentially lower, in ranges 0.15–0.20 units of (ρ_I)_{ortho}. Earlier,³ on going from pure water to aqueous 2.25 M Bu₄NBr, the change in the (ρ°)_{m,p}, and (ρ_I)_{ortho} values in the alkaline hydrolysis of substituted phenyl tosylates as in the alkaline hydrolysis of phenyl benzoates occurred in ranges 0.9–1.1 and 0.4–0.5, respectively, though the susceptibilities to the polar influence of *ortho*, *meta*, and *para* substituents in water differed two-fold. The analysis of data for alkaline hydrolysis of phenyl tosylates in aqueous 0.5 M Bu₄NBr demonstrates once again that the *ortho* inductive term varies with solvent more than twice less compared with the *para* inductive term. In the case of alkaline hydrolysis of substituted phenyl tosylates, the *ortho* effect (i.e. $\log k_{\text{ortho}}^X - \log k_{\text{para}}^X$) of nearly 1.0 units of (ρ_I)_{ortho} in pure water diminishes to 0.6 units in 0.5 M Bu₄NBr and 0.45 units in 2.25 M Bu₄NBr. When

the inductive term of para substituents reaches the level of ortho substituents, the ortho effect caused by the induction effect disappears.

To study the variation of the ortho inductive and resonance effects as well as the meta and para polar effects with temperature, the kinetic data at various temperatures were processed according to Eq. (8) (Table IV) including the data simultaneously for *ortho*-, *meta*-, and *para*-substituted derivatives and separately for meta and para derivatives. When the data for *meta*- and *para*-substituted derivatives were processed with Eq. (8), the additional terms for ortho substituents were omitted.

Equation (8) is a multilinear relationships with cross terms. According to Palm and Istomin^{20,38} this kind of equations exhibit a remarkable property called isoparametricity. The phenomenon of isoparametrical relationship is possible if there are represented the cross terms in correlation equation. The isoparametrical point for temperature T is known as isokinetical (or iso-equilibrium) temperature. At isokinetical temperature all reactions of the series including various substituents should proceed with the same rate.

It follows from the results of the statistical data processing according to Eq. (8) (Table IV) that the $\log k$ values for the alkaline hydrolysis of substituted phenyl tosylates in 0.5 M Bu₄NBr could be correlated quite well with the modified Fujita and Nishioka equation (8). The constants c_0 and c_3 belong to unsubstituted derivatives and their values do not depend on substituents, including either the data only for *meta*- and *para*-substituted derivatives or the data set that can embrace the *ortho*-substituted derivatives as well. The reaction constant c_0 is nearly equal to the $\log A$ for unsubstituted derivative (for X = H, $\log A = 9.486$, Table II). In Eq. (8) the whole entropy term for *ortho*-substituted derivatives is expressed by the sum $c_0 + c_{1(m,p,ortho)}\sigma^\circ + c_{2(ortho)}\sigma_I$. The sensitivity of the entropy term to the inductive influence of ortho substituents $c_{I(ortho)}$ could be written as $c_{I(ortho)} = c_{1(m,p,ortho)} + c_{2(ortho)}$ while the sensitivity of the entropy term to resonance of ortho substituents $c_{R(ortho)}$ is considered to be the same as in the case of *para*-substituted derivatives, i.e. $c_{R(ortho)} = c_{1(m,p,ortho)}$. Similarly, the susceptibility of the ortho inductive effect to temperature variation in Eq. (8) is expressed as sum $c_{I(T)(ortho)} = c_{4(m,p,ortho)} + c_{5(ortho)}$.

For aqueous 0.5 M Bu₄NBr we found the $c_{I(ortho)} = -1.98$ and the values of $c_{1(m,p)}$ in the range from -0.85 to -1.31 (Table IV). For pure water¹ the values of $c_{I(ortho)}$ were in the range from -1.45 to -2.2 and $c_{1(m,p)} = 0$ (in aqueous 80% DMSO and 2.25 M Bu₄NBr $c_{1(m,p)} \approx -1.40$).

The polar effect of meta and para substituents, the inductive and resonance effects of ortho substituents were found to decrease with increasing temperature. In the case of meta and para substituents, the susceptibility of

the polar effect to the temperature variation of $c_{4(m,p)}$ was found to be in the range 1.12×10^3 – 1.27×10^3 (Table IV). When going from water to aqueous 0.5 M Bu_4NBr the dependence of the meta and para polar effects on temperature increased by ca. 0.6 units of $c_{4(m,p)}$ ($c_{4(m,p)}$ is ca. 0.6×10^3 in pure water¹). In aqueous 0.5 M Bu_4NBr the temperature dependence of the ortho inductive effect appeared to be slightly greater, $c_{1(T)(ortho)} = 1.7 \times 10^3$ ($= c_{4(m,p,ortho)} + c_{5(ortho)}$) (Table IV), than that for para substituents. The increase in the ortho inductive effect with temperature on going from pure water to aqueous 0.5 M Bu_4NBr is only 0.2×10^3 units of $c_{1(T)(ortho)}$ (in water $c_{1(T)(ortho)}$ was ca. 1.5×10^3). Consequently, the variation of the ortho inductive term with temperature was found to be about twice smaller than the polar effect of meta and para substituents. Similarly, in the alkaline hydrolysis of substituted phenyl tosylates and benzoates¹⁻³, in transition from pure water to aqueous 2.25 M Bu_4NBr and 80% DMSO, the variation of the ortho inductive term with temperature was found to be half that for para substituents, but by transfer from pure water to aqueous 5.3 M NaClO_4 the dependence of the ortho inductive influence on temperature was practically unchanged.

In transition from water to media, the electrophilic solvating power of which is reduced compared with water, the polar effect of substituents and the sensitivity to temperature variation was enhanced. In pure water the variation of the ortho inductive term with temperature was found to be more than twice larger than that for para substituents. Due to a reduced variation of the ortho temperature-dependent inductive term with solvent and temperature, compared to that of para substituents, a considerable decrease in the ortho effect (i.e. $\log k_{ortho}^X - \log k_{para}^X$), caused by an inductive influence, has been observed when going from water to less electrophilic media.

The variation of the reaction rates with the substituent and temperature in alkaline hydrolysis of substituted phenyl tosylates was well described by Eq. (8) (Table IV).

$$\begin{aligned}
 (\log k_{\text{calc}})_{m,p,ortho} &= 9.433 - (0.853\sigma^{\circ})_{m,p,ortho} - \\
 &- (1.128\sigma_{\text{I}})_{ortho} - 4.210(10^3/T) + \\
 &+ [1.122(10^3/T)\sigma^{\circ}]_{m,p,ortho} + [0.566(10^3/T)\sigma_{\text{I}}]_{ortho} \quad (11)
 \end{aligned}$$

$$R = 0.995, s = 0.098, s_0 = 0.099, n/n_0 = 49/49$$

The predicted $\log k_{\text{calc}}$ values calculated with Eq. (11) (Table IV) and the experimental $\log k_{\text{obs}}$ values (Table I) for *ortho*-, *meta*-, and *para*-substituted derivatives were compared.

$$(\log k_{\text{obs}})_{\text{m,p,ortho}} = -(0.013 \pm 0.035) + \\ + (0.993 \pm 0.015)(\log k_{\text{calc}})_{\text{m,p,ortho}} \quad (12)$$

$$R = 0.995, s = 0.093, s_0 = 0.102, n/n_0 = 47/47$$

In the alkaline hydrolysis of substituted phenyl tosylates the dependence for the polar effect of meta and para substituents as well as the ortho resonance term on temperature in water was an isoentropic relationship ($c_{1(\text{m,p})} = 0$)². We consider that in aqueous 0.5 M Bu₄NBr, similarly to pure water, the dependence of the ortho inductive term on temperature for tosylates reaction series corresponds to an isoparametric relationship, i.e. belongs to the isokinetic relationship as much the terms $c_{1(\text{ortho})}\sigma_{\text{I}}$ and $c_{1(\text{T})(\text{ortho})}(1/T)\sigma_{\text{I}}$ appeared to be different from zero ($c_{1(\text{ortho})} = -1.98$, $c_{1(\text{T})(\text{ortho})} = 1.7 \times 10^3$)^{20,38}. The dependence of the meta and para polar effect term on temperature in tosylates reaction series turned to the isokinetic relationship series when going from water to aqueous 0.5 M Bu₄NBr as factors $c_{1(\text{m,p})}\sigma^\circ$ and $c_{4(\text{m,p})}(1/T)\sigma^\circ$ appeared to be significant ($c_{1(\text{m,p})}$ is in the range from -0.85 to -1.31), $c_{4(\text{m,p})}$ is ca. 1.2×10^3) (Table IV).

For comparison, the models of an isoentropic, isoenthalpic, and isokinetic relationships were tested using special program developed by Exner³⁹. The $\log k$ values for the alkaline hydrolysis of substituted phenyl tosylates in aqueous 0.5 M Bu₄NBr were subjected to the statistical analysis separately for *ortho*-substituted derivatives, and *meta*- and *para*-substituted derivatives. So, in the case of ortho substituents as meta and para substituents, the isoenthalpic relationship was rejected and both the isoentropic and isokinetic relationships appeared to be accepted. According to the statistical criterions the isokinetic and isoentropic relationships could be considered as indistinguishable ones. Due to the relatively large deviations, the reactions constants $c_{1(\text{m,p})}$ and $c_{2(\text{ortho})}$ (Table IV) could be considered as indistinguishable from zero and the reaction series could be considered as isoentropic as well.

Assuming the isokinetic relationship for the alkaline hydrolysis of substituted phenyl tosylates in aqueous 0.5 M Bu₄NBr (Fig. 1), we calculated the isokinetic temperatures β for the ortho inductive effect³⁸: $\beta_{1(\text{ortho})} =$

$-c_{I(T)(ortho)}/c_{I(ortho)} = 852$ K, and for meta and para polar effect: $\beta_{m,p} = -c_{4(m,p)}/c_{1(m,p)} = 974$ K (Table IV). Approximately the same values for isokinetic temperatures β were found from the dependence of ρ on temperature $\rho_T = c_0 + c_1(1/T)^{40}$ (see Fig. 1): $\beta_{I(ortho)} = 802$ K [$\rho_{I(ortho)} = (-2.154 \pm 0.942) + (1.727 \pm 0.309)(10^3/T)$] and $\beta_{m,p} = 1066$ K [$\rho_{(m,p)} = (-1.144 \pm 0.844) + (1.220 \pm 0.276)(10^3/T)$]. The isokinetic temperature for the additional ortho inductive effect $\beta_{(ortho=para)} = -c_{5(ortho)}/(c_{2(ortho)}\sigma_I) = 566/1.128 = 502$ K. The same value for the additional ortho inductive effect $\beta_{(ortho=para)} = 500$ K was earlier found for the same reaction series in water¹. At isokinetic temperature $\beta_{(ortho=para)}$ the additional ortho inductive influence from ortho position disappears and the polar effect of ortho substituents become equal to that for para substituents.

The dependence of the activation energies E on the substituent effects in the alkaline hydrolysis of *meta*- and *para*-substituted as well as *ortho*-substituted phenyl tosylates is entirely caused by polar effects of substituents (Table II). In the alkaline hydrolysis of tosylates, the electron-withdrawing substituents stabilize the transition state by delocalization of the fractional negative charge in the transition complex, and, therefore, decrease the activation energy E . The electron-donating groups destabilize the transition state with negative charge or stabilize the ground state of esters by decreasing the fractional positive charge on the sulfur atom in esters of 4-methylbenzenesulfonic acid, so an increase in the activation energy could be observed. The influence of the ortho, meta, and para substituent polar effect on the activation energy is greater in aqueous 0.5 M Bu_4NBr compared with that in water. The activation energy for *ortho*-substituted derivatives in aqueous 0.5 M Bu_4NBr was found to be lower than those for *para*-substituted derivatives. However, in 0.5 M Bu_4NBr the decrease in the difference $E_{para}^X - E_{ortho}^X$ compared to that in pure water could be observed. While the change in the temperature-dependent ortho polar effect is essentially lower than that for para substituents on going from water to aqueous 0.5 M Bu_4NBr , for *ortho*-substituted derivatives the change in the activation energy is greater than that for *para*-substituted derivatives and comparable to that for unsubstituted derivatives. The activation energy E for the alkaline hydrolysis of substituted phenyl tosylates (Table II) appeared to increase for all substituents on going from water to aqueous 0.5 M Bu_4NBr . However, for esters with electron-donor substituents the increase in activation energies is greater than in the case of electron-withdrawing substituents. For instance, the change in activation energies on going from pure water to aqueous 0.5 M Bu_4NBr for unsubstituted derivative was ca.

11 kJ mol⁻¹, whereas for 4-NO₂ substituent ca. 2 kJ mol⁻¹. The changes in the activation energies for *ortho*-substituted derivatives were greater than that for *para*-substituted ones: for 2-NO₂ and 4-NO₂ substituents ca. 7 and 2 kJ mol⁻¹, respectively (Table II). In aqueous solutions, the activation energies for unsubstituted, 2-NO₂ and 4-NO₂ derivatives were found to be 70.55, 48.69, and 59.91 kJ mol⁻¹, respectively.

The log *A* values for *ortho* substituents in 0.5 M Bu₄NBr appeared to be smaller than those for *para* substituents due to the additional term $c_{2(\text{ortho})}\sigma_1$ (Table II).

Dependence of Substituent Effects on Solvent Parameters

In order to study the influence of solvent parameters on substituent effects in the alkaline hydrolysis of substituted phenyl tosylates, the $\Delta \log k$ values at 75 °C for various media (water, aqueous 0.5 M Bu₄NBr, 1 M Bu₄NBr, 2.25 M Bu₄NBr, 80% DMSO, 5.3 M NaClO₄, 4.8 M NaCl and 30, 60, and 80% EtOH) were subjected to the multilinear regression analysis according to Eqs (9) and (10) in two different ways: (i) only the solvent electrophilicity, ΔE , or (ii) all three solvent parameters, the solvent electrophilicity, ΔE , the solvent polarity, ΔY , and the solvent polarizability, ΔP , were included (Table VI). For comparison, the data treatment is shown separately for *meta*- and *para*-substituted derivatives (Eq. (9)) and *ortho*-substituted derivatives (Eq. (10)) as well as simultaneously for *ortho*-, *meta*-, and *para*-substituted derivatives (Eq. (9), Table VI).

The reaction constants c_0 , $c_{1(\text{m,p,ortho})}$, $c_{2(\text{ortho})}$, and $a_{1(\text{ortho})}$ and $a_{2(\text{ortho})}$ as intercepts and the values of characteristics of the substituent effects in pure water appeared to be rather constant values that do not depend significantly on the way used for data treatment; the data included either only for *meta*- and *para*-substituted derivatives or for *ortho*-substituted derivatives, or the data set can embrace the data simultaneously for *ortho*-, *meta*-, and *para*-substituted derivatives. The intercept values c_0 and a_0 in all cases did not exceed 0.1. The reaction constant $c_{1(\text{m,p,ortho})}$ is common for *ortho*-, *meta*-, and *para*-substituted derivatives. In the case of *meta* and *para* derivatives it shows the susceptibility to the polar effect of *meta* and *para* substituents in standard solution, pure water at 75 °C (Table VI). The values of $c_{1(\text{m,p,ortho})}$ found in different ways, appeared to vary in quite a narrow range, from 1.80 to 1.90. Earlier, the $(\rho^\circ)_{\text{m,p}}$ value for the alkaline hydrolysis of substituted phenyl tosylates in water at 75 °C was found to be in range 1.67–1.75^{1,4}. The reaction constants $c_{2(\text{ortho})}$, $a_{1(\text{ortho})}$, and $a_{2(\text{ortho})}$ are the characteristics of the inductive and resonance effects in pure water for

ortho substituents only. The reaction constant $c_{2(\text{ortho})}$ is the characteristic of the additional ortho inductive effect in pure water. The constants $a_{1(\text{ortho})}$ and $a_{2(\text{ortho})}$ are the total susceptibilities to the ortho inductive and resonance effects, respectively. The calculated susceptibility to the ortho inductive effect for water at 75 °C appeared to be a rather fixed value not depending on whether it could be calculated as sum of reaction constants $c_{1(\text{m,p,ortho})} + c_{2(\text{ortho})}$ for ortho, meta, and para derivatives in common data treatment or calculated with Eq. (10) as reaction constant $a_{1(\text{ortho})}$ for ortho derivatives only. In Table VI the sum of $c_{1(\text{m,p,ortho})} + c_{2(\text{ortho})}$ and the values of $a_{2(\text{ortho})}$ ranges between 2.65 and 2.80. Earlier⁴ the corresponding values of $(\rho_{\text{I}})_{\text{ortho}}$ for pure water at 75 °C were in the range 2.50–2.70. The value for the resonance constant $a_{2(\text{ortho})}$, calculated separately for ortho substituents, was nearly equal to the $c_{1(\text{m,p,ortho})}$ constant.

The solvent electrophilicity was the main factor responsible for the dependence of the substituent effects on medium as the contribution of cross terms containing the solvent electrophilicity ($c_{6(\text{m,p,ortho})}\Delta E\sigma^{\circ}$, $c_{9(\text{ortho})}\Delta E\sigma_{\text{I}}$, $a_{6(\text{ortho})}\Delta E\sigma_{\text{I}}$, $a_{9(\text{ortho})}\Delta E\sigma_{\text{R}}$) was significant when the $\Delta \log k$ values were processed according to Eqs (9) and (10) (Table VI). Therefore the variation of the meta, para polar effect, the ortho inductive and ortho resonance effects with solvent occurs mainly due to change in electrophilicity properties of the medium considered.

The cross term containing the solvent polarity $c_{7(\text{m,p,ortho})}\Delta Y\sigma^{\circ}$ was different from zero for the simultaneous data treatment with Eq. (9) for ortho, meta, and para derivatives. However, the contribution of solvent polarity on the polar effect of substituents could be considered as almost insignificant due to its very low relative weight. Besides, in the separate data treatment for meta, para, and ortho derivatives the term $c_{7(\text{m,p,ortho})}\Delta Y\sigma^{\circ}$ was excluded as insignificant. The term $c_{8(\text{m,p})}\Delta P\sigma^{\circ}$ was significant when the data for meta and para derivatives were processed with Eq. (9) and the data set involved 30, 60, and 80% aqueous EtOH at 60 °C as well. Due to very low weight of the polarizability term, $c_{8(\text{m,p})}\Delta P\sigma^{\circ}$, its effect could be considered as negligible.

The variation of the meta and para polar effect with the solvent electrophilicity was twice higher than that for the ortho inductive effect. The corresponding value for reaction constants $c_{6(\text{m,p})}$ was in the range from -0.065 to -0.087. In the case of ortho substituents, the susceptibility of the inductive effect to the solvent electrophilicity variation (i.e. in Eq. (9), the sum $c_{6(\text{m,p,ortho})} + c_{9(\text{ortho})}$ and $a_{6(\text{ortho})}$ in Eq. (10)) range from -0.3 to -0.04. Earlier⁴ nearly the same values for reaction constants $c_{6(\text{m,p})} = -0.065$ (constant

$c_{4(m,p,ortho)}$ in Eq. (3) and $a_{6(ortho)} = -0.026$ (difference $c_{4(m,p,ortho)} - c_{5(ortho)}$ in Eq. (3)) were found when the data for alkaline hydrolysis of substituted phenyl tosylates in a more narrow solvent range were studied. The ortho resonance effect was found to vary with the solvent electrophilicity nearly to the same extent as the polar effect of para substituents, $a_9 \approx c_{6(m,p,ortho)}$.

It follows from Table VI that in the medium considered the total substituent effect for alkaline hydrolysis of substituted phenyl tosylates could be expressed by Eqs (13) and (14).

$$\begin{aligned} \Delta \log k_{m,p,ortho} = \log k^X - \log k^H = & 0.045 + 0.0051\Delta E + \\ & + (1.806\sigma^\circ)_{m,p,ortho} + (0.832\sigma_I)_{ortho} - (0.0856\Delta E\sigma^\circ)_{m,p,ortho} + \\ & + (0.0480\Delta E\sigma_I)_{ortho} \end{aligned} \quad (13)$$

$$R = 0.996, s = 0.083, s_0 = 0.088, n/n_0 = 95/115$$

$$\begin{aligned} \Delta \log k_{ortho} = \log k^X - \log k^H = & -0.037 + 0.0053\Delta E + \\ & + 2.802\sigma_I + 1.710\sigma^\circ_R - 0.0406\Delta E\sigma_I - 0.0747\Delta E\sigma^\circ_R \end{aligned} \quad (14)$$

$$R = 0.987, s = 0.169, s_0 = 0.160, n/n_0 = 64/64$$

The excellent fit between the experimental $\log k$ values (Table I and lit.^{1,2,4}) and predicted $\log k$ values ($\log k_{calc}$), calculated with Eq. (13) or (14), was found.

$$(\log k_{obs})_{m,p,ortho} = -(0.021 \pm 0.011) + (1.010 \pm 0.010)(\log k_{calc})_{m,p,ortho} \quad (15)$$

$$R = 0.995, s = 0.096, s_0 = 0.101, n/n_0 = 102/115$$

$$(\log k_{obs})_{ortho} = (0.034 \pm 0.014) + (0.971 \pm 0.013) (\log k_{calc})_{ortho} \quad (16)$$

$$R = 0.996, s = 0.088, s_0 = 0.090, n/n_0 = 49/64$$

In the alkaline hydrolysis of substituted phenyl tosylates, the induction factor from ortho position, 1.5-fold higher than that from para position in water, varies twice less than the polar effect from para position with changing solvent. When the inductive effect of para substituents reaches the level of ortho substituents, the additional inductive influence from ortho position disappears. From Eq. (13) could be calculated the value of the solvent electrophilicity, in which the ortho effect caused by the additional inductive effect from ortho position becomes zero.

$$(0.832\sigma_I)_{\text{ortho}} + (0.0480\Delta E\sigma_I)_{\text{ortho}} = 0 \quad (17)$$

$$\Delta E[(\rho_I)_{\text{ortho}} = (\rho_I)_{\text{m,p}}] = -0.832/0.048 = 17.3 \text{ and } E[(\rho_I)_{\text{ortho}} = (\rho_I)_{\text{m,p}}] = 4.4$$

Consequently, in alkaline hydrolysis of substituted phenyl tosylates, the polar effects of ortho and para substituents become equal in solvent with electrophilic solvating power nearly the same as that of pure DMSO ($E = 3.2$)⁸.

In Fig. 2 the dependence of the $\rho_{I(\text{ortho})}$ and $(\rho^\circ)_{\text{m,p}}$ values on ΔE values is shown. One can see that in alkaline hydrolysis of substituted phenyl tosylates the variation of the polar effect of meta and para substituents, and the ortho inductive effect with the solvent electrophilicity is nearly the same as in alkaline hydrolysis of substituted phenyl benzoates³ though the ratio of the susceptibilities to polar effect of substituents in water differed two-fold. Due to equal variation in substituent effects when passing from water to another solvent in the two reaction series considered, the same difference in polar substituent effects (including the additional ortho induction effect) found for water appears in other media. But the $\Delta E[(\rho_I)_{\text{ortho}} = (\rho_I)_{\text{m,p}}]$ value for the alkaline hydrolysis of substituted phenyl benzoates is nearly twice smaller (ca. 9–10) and corresponds approximately to aqueous 70% ethanol or 1 M Bu_4NBr (Table V).

As the media in the present work, pure water, aqueous organic salt solutions (0.5 M Bu_4NBr , 1.0 M Bu_4NBr , 2.25 M Bu_4NBr), aqueous inorganic salt solutions (5.3 M NaClO_4 , 4.8 M NaCl), and aqueous binary solutions (80% DMSO, 30% EtOH, 60% EtOH, 80% EtOH) were used. In transition from water to aqueous solutions of organic salts (0.5 M Bu_4NBr , 1.0 M Bu_4NBr , 2.25 M Bu_4NBr) and solutions in 80% DMSO and aqueous EtOH the electrophilic solvating power of which is reduced compared with water, the polar effects of ortho, meta, and para substituents were found to increase. On the other hand, the polar effect of ortho, meta, and para substituents

TABLE SI

Results of the correlation with Eqs (9) and (10) for kinetic data of alkaline hydrolysis of substituted phenyl tosylates, $4\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{OC}_6\text{H}_4\text{-X}$, in various media at 75 °C^a. Solvent electrophilicity, ΔE , polarity, ΔY , and polarizability, ΔP , parameters were included^b

Reaction constant	Meta, para substituents Eq. (9)	Weight	Ortho, meta, para substituents Eq. (9)	Weight	Ortho substituents Eq. (10)	Weight
c_0	0.057 ± 0.039 0.014 ± 0.035^a		0.051 ± 0.032 0.058 ± 0.026^a		0.015 ± 0.046 -0.042 ± 0.058^a	
$c_{1(m,p,ortho)}$	1.806 ± 0.062 1.905 ± 0.049^a	0.96 0.95	1.900 ± 0.040 1.899 ± 0.037^a	0.92 0.95	-	
$c_{2(ortho)}$	-		0.821 ± 0.067 0.824 ± 0.055^a	0.06 0.06	-	
$a_{1(ortho)}$	-		-		2.767 ± 0.073 2.763 ± 0.086^a	0.55 0.60
$a_{2(ortho)}$	-		-		1.816 ± 0.080 1.710 ± 0.019^a	0.29 0.25
c_3	0.0025 ± 0.0036 0.0062 ± 0.0028^a	0.04 0.03	0.0093 ± 0.0016 0.0021 ± 0.0021^a	0.002 0.002	0 0	
c_5	1.565 ± 0.589^a	0.005	0		-	
$c_{6(m,p,ortho)}$	-0.0656 ± 0.0077 -0.0736 ± 0.0067^a	0.003 0.003	-0.0672 ± 0.0048 -0.0762 ± 0.0045^a	0.018 0.006	-	
$c_{7(m,p,ortho)}$	-		1.00 ± 0.30 1.10 ± 0.30^a	0.001 0.001	-	
$c_{8(m,p,ortho)}$	-4.96 ± 1.86^a	0.002	-		-	
$c_{9(ortho)}$	-		0.0329 ± 0.0081 0.0451 ± 0.0067^a	0.002 0.005	-	
$a_{6(ortho)}$	-		-		-0.0298 ± 0.0075 -0.0423 ± 0.0088^a	0.027 0.005
$a_{9(ortho)}$	-		-		-0.0887 ± 0.0081 -0.0880 ± 0.0104^a	0.012 0.010
n/n_0	45/45 $52/60^a$		79/85 $93/115^a$		42/47 $59/64^a$	
R	0.990 0.995^a		0.995 0.996^a		0.996 0.992^a	
s	0.116 0.078^a		0.099 0.080^a		0.096 0.129^a	
s_0	0.141 0.098^a		0.102 0.086^a		0.094 0.128^a	
t	0.999 0.95^a		0.95 0.95^a		0.97 0.97^a	

^a The log k values for 30, 60, and 80% aqueous EtOH at 60 °C as well as for pure water, 0.6 M Bu₄NBr, 1.0 M Bu₄NBr, 2.25 M Bu₄NBr, 80% DMSO, 5.3 M NaClO₄, 4.8 M NaCl at 75 °C were included. ^b The program makes it possible to treat data in four different ways: 1. Exclusion of insignificant argument scales was performed before excluding considerably deviating points. 2. Exclusion of significantly deviating points was performed before excluding insignificant argument scales. Both ways of data treatment have two different modes of forming cross terms: (i) Cross terms can be formed from centered basic argument scales. (ii) Cross terms are formed from non-centered basic argument scales. When the values for insignificant scales are shown, the cross terms were formed from centered basic argument scales. When three different solvent parameters were included, exclusion of insignificant argument scales was performed before excluding considerably deviating points.

decreased in transition from water to inorganic salt solutions (5.3 M NaClO₄, 4.8 M NaCl) whose electrophilic solvating power is higher from that of water (Table V).

In organic salt solutions and 80% DMSO, the transition state of the nucleophilic substitution reaction S_N2 involving and negative charge could be considered as rather weakly electrophilically solvated which leads to essentially increased ρ values compared with pure water. In concentrated aqueous organic salt solutions similarly those in 80% DMSO, very few active water molecules are assumed to be able to form hydrogen bond and the large Bu₄N⁺ ions are not able to complex to the partially negatively charged phenolic oxygen in the transition state as small cations M⁺ do. In inorganic salt solutions, the complexation of small M⁺ cations to negatively charged transition state should decrease the polar effect of substituents in contrast with water.

SUPPLEMENTARY MATERIAL

Table SI containing the results of the correlations with Eqs (9) and (10) for kinetic data of alkaline hydrolysis of substituted phenyl tosylates, 4-CH₃C₆H₄SO₂OC₆H₄-X, in various media at 75 °C when three solvent parameters, the solvent electrophilicity, ΔE , the solvent polarity, ΔY , and the solvent polarizability, ΔP , were included, is available as supplementary material.

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